CHEMICAL REVIEWS

THE ENTANGLEMENT CONCEPT IN POLYMER SYSTEMS

ROGER S. PORTER AND JULIAN F. JOHNSON

Chevron Research Company, Richmond, California   94802

Contents

I. Introduction

In sufficiently dilute solutions polymer chains are disengaged, separated, and behave as individual hydrodynamic units (79). In solutions of polymers of sufficiently high molecular weight and concentration, however, the effect of neighboring molecules cannot be described in the same simple terms of local frictional forces. Rheological properties reveal a strong rigidity and the appearance of long relaxation times, apparently caused by the requirement of coordinated flow through chain entanglements. The effects observed are an abrupt increase in viscosity dependence on molecular weight and the onset of a rubbery region. The precise nature of entanglements is not yet known.

Terminology employed to describe this phenomenon has varied. Thus the rubbery or entanglement region is referred to as the pseudoequilibrium rubbery plateau zone and the "box" distribution region in the nomenclatures established by Ferry (35) and by Tobolsky (141). Literature terminology referring to polymer entanglements, couplings, and temporary cross-linked or network systems generally refer to the phenomenon which is reviewed here (101). The entanglement terminology has become widely employed in this special sense and in this context does not apply to short-range intermolecular interactions. Material such as explanation of deviations from limiting behavior for individual polymer molecules in dilute solutions which are observed through the second virial coefficient and the Huggins constant, as determined from viscosity and osmotic pressure measurements, are not entanglements in the sense of this review (53). Entanglements

have been used in still another context to describe polymer solution behavior at moderate concentrations where polymer properties are reported independent of solvent type.

A minimum polymer molecular weight, dependent on concentration, is necessary to produce the characteristic rheological effects attributed to entanglements in polymer solutions. Similarly, such effects are present in bulk polymers only above some minimum molecular weight. Polymer chain spacings between entanglements are considered proportional to the minimum molecular weight for the rubbery plateau and related effects. Like glass transition temperatures, characteristic entanglement spacings represent a general feature of amorphous polymer systems. The widespread presence of entanglement effects indicates that they are not due to chemical or structural inhomogeneities. Polymer composition, *e.g.*, polarity and perhaps tacticity, can lead, however, to alteration in the frequency and strength of entanglements.

A. SCOPE OF THE REVIEW

Mark and Tobolsky first mentioned entanglements and the computation of entanglement spacings (76a). There have been no previous comprehensive reviews. Monographs citing experimental details and derivations are available (21, 35).

The methods for observation of entanglement characteristics and spacings are described. These include viscoelastic experiments, low shear viscometry, non-Newtonian flow measurements, and relaxation times determined by nuclear magnetic resonance.

By analogy with rubber elasticity, entanglement effects have been considered theoretically in terms of temporary cross-linked polymers. Other theories exist based on chain slippage, breakage, reformation of entanglements, etc. The review covers the conclusions of the theories and empirical correlations. This review appraises, but does not resolve, the interrelation of the two generally used methods for evaluating entanglement spacings. These are the composition (molecular weight and concentration) of the polymer system for the abrupt change in rheology and the theory of rubber elasticity using the properties of the pseudoequilibrium rubbery plateau.

Entanglement spacing determinations by the various experimental techniques are tabulated for about 40 different polymer compositions. The variation of entanglement conditions with polymer composition, concentration, solvent, and temperature are evaluated. The influence of such variables on entanglement spacing are used to estimate possible heats of entanglement.

B. NOTATION

a	Root-mean-square end-to-end distance per square root of number of monomer units
a_t	Shift factor for relaxation time ratio at two temperatures
c	Used as subscript to denote characteristic entanglement conditions
d	Sample or solution density
f	Segmental friction factor
g	Square of the ratio of the radius of gyration for equivalent molecular weight branched to linear polymers
k	Boltzmann's constant
m	Chain atoms per monomeric unit
n	Number of moles of network chains per unit volume
r_0	Radius of equivalent sphere
r^2	Mean-square end-to-end distance
t	Time
w	Frequency
$w(G''_m)$	Frequency for G''_m
$w(J''_m)$	Frequency for J''_m
A	A constant
A_0	Avogadro's number
C	Polymer concentration
C_0	Characteristic polymer entanglement concentration
D	Tensile compliance
$D(t)$	Tensile creep compliance
E	Young's (tensile) modulus
E_2	Rubbery modulus of stress relaxation
F	Tensile force per cross-sectional area
G	Shear modulus
G_t	Shear relaxation modulus
G_{10sec}	Ten-second shear relaxation modulus
G'	Shear storage modulus
G''	Shear loss modulus
G''_m	Maximum shear loss modulus
G_e	Pseudoequilibrium modulus
H	Shear relaxation spectrum
J	Shear compliance
$J(t)$	Shear creep compliance
J'	Shear storage compliance
J''	Shear loss compliance
J''_m	Maximum shear loss compliance
J_e	Pseudoequilibrium or steady-state shear compliance
K	Constant for a particular polymer and temperature
L_0	Translational friction coefficient per monomer unit
L	Length
L_s	Stretched length
L_u	Unstretched length
M	Molecular weight
M_n	Number-average molecular weight
M_v	Viscosity-average molecular weight
M_w	Weight-average molecular weight
M_z	Z-average molecular weight
M_{z+1}	$(Z+1)$-average molecular weight
M_0	Molecular weight per monomer unit
M_c	Characteristic entanglement molecular weight
M_e	Molecular weight between entanglements
N	Number of chain atoms per molecule
N_c	Characteristic entanglement chain length in atoms
N_e	Chain length in atoms between entanglements
Q	Flow activation heat
Q_0	Flow activation heat independent of entanglements
Q_1	Flow activation heat for polymer
Q_s	Flow activation heat for solution or solvent
Q_r	Flow activation heat at constant shear rate
R	Gas constant
S	Slippage factor
S_0^2	Unperturbed mean-square radius of gyration
T	Absolute temperature
T_g	Glass transition temperature

T_1 N.m.r. longitudinal relaxation time
T_2 N.m.r. transverse relaxation time
V Polymer volume fraction
V_a Volume per chain atom
V_0 Critical volume fraction of spheres
W Polymer weight fraction
X_c Entanglement constant
Z Degree of polymerization
δ Phase angle between stress and strain
η Viscosity
η' Dynamic viscosity
η_0 Low shear Newtonian viscosity
η_a Apparent steady-state viscosity
η_b Viscosity of a branched polymer
η_l Viscosity of a linear polymer of the same molecular
      weight for η_b of a branched polymer
τ Relaxation time
Δ Logarithmic decrement across plateau zone
ΔE Energy to form an entanglement
ΔE^* Flow activation energy

II. Methods for Observation of Entanglement Characteristics and Spacing

A. LOW SHEAR VISCOMETRY

Low shear viscosity measurements can be the most definitive method for determining characteristic entanglement spacings provided polymer systems are well defined (49, 77). Only simple equipment to measure high values of low shear Newtonian viscosity is required. A variety of viscometers, including capillaries, can give this information from measurements at sufficiently low stresses to ensure Newtonian flow. Low shear Newtonian viscosities can also be derived from various viscoelastic measurements.

The characteristic and minimum chain length composition for entanglement, N_c, is commonly observed as an abrupt increase in power dependence of low shear viscosity on polymer molecular weight. The Newtonian viscosity, η_0, for many different amorphous polymers in bulk and at fixed diluent concentration is observed to increase sharply to a constant 3.4 ± 0.1 power dependence on M_w as M_c is exceeded (see, for example, Figure 1). The 3.4 function is commonly independent of temperature, as flow activation energy generally does not vary with molecular weight in the entanglement region.

The abrupt change or break in viscosity dependence on molecular weight, expressed as chain length, N_c, is illustrated in Figure 1 with data on four polymers as compiled by Fox (45). The characteristic value of the entanglement composition, N_c, for each polymer will be discussed later. Below the break in Figure 1 the slope varies with molecular weight, temperature, and diluent concentration approaching a theoretical limit of 1.0 at higher temperatures and lower concentrations (16, 48). These effects arise because free volume, which influences viscosity, changes significantly with composition below the break (98). This effect of volume has been empirically incorporated in Figure 1 to give the theoretical
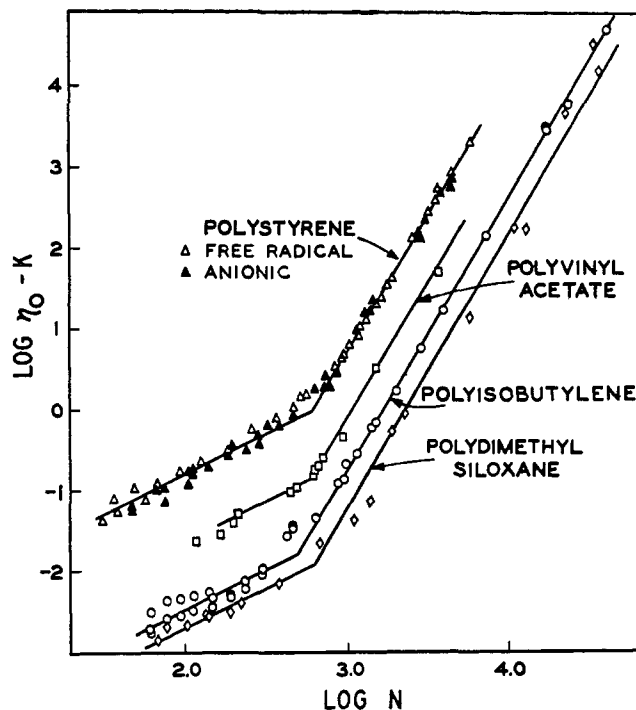

Figure 1.—Reduced viscosity vs. polymer chain length.

slope of 1.0 by using a constant, K, for each polymer (45). By similar approaches, Fox and, independently, other workers have corrected flow data to conditions of isofree volume. Below the break, fractions and blends are reported to fall on a single line with theoretical slope 1.0 using M_w (15, 16). Above the break in the entanglement region viscosity also depends on M_w (49, 75). This has been shown (98) for polyvinyl acetate with distributions, M_w/M_n, which varied from 34 to nearly 1. It had been previously reported that M_z should be used for samples with $M_w/M_n > 2$ (21a).

It has been suggested that at molecular weight $>5/2 M_c$ the 3.4 slope is exceeded (108). This type of deviation has been reported for several polymers, including polyvinyl acetate at higher molecular weights than shown in Figure 1 (98, 108, 143). A partial explanation may be that polymer chain branching is known to induce an increased dependence of η_0 on M_w. This has been reported for branched (low-density) polyethylene (90, 114) and for branched polybutadiene (70) and has been suggested for polyvinyl acetate (98). The effect of variations in the frequency and length of chain branches has not been fully evaluated. The hypothesis that branched polymers universally have lower viscosities than a linear polymer of equivalent M_w has been questioned (70).

A break has also been observed in plots of log η_0 vs. log C, polymer concentration (5, 101, 102). This has been reported for polyvinyl chloride, polyvinyl alcohol, and polystyrene (see, for example, Figure 2). The critical concentration at the break has been equated to the entanglement composition. In certain cases
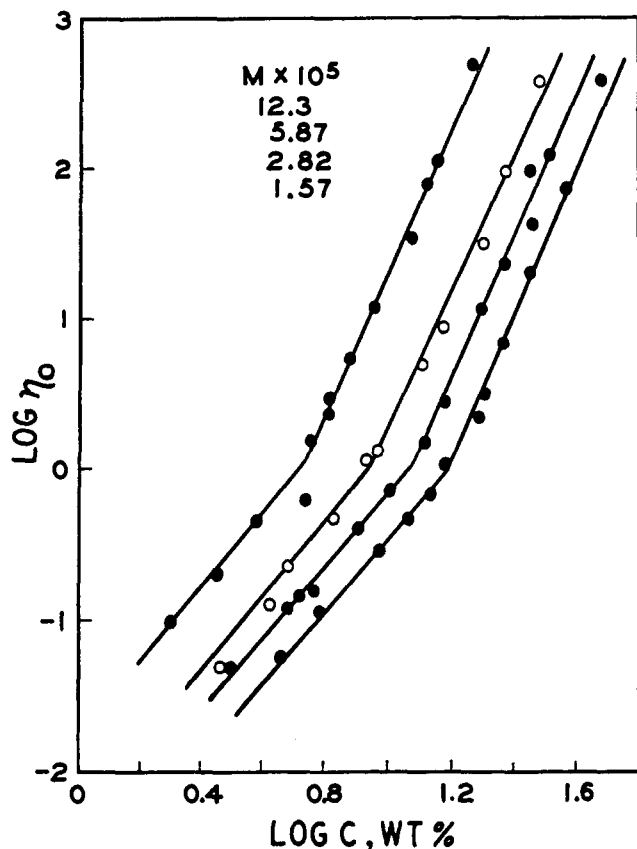
Figure 2.—Viscosity vs. concentration of polystyrene in toluene, 40°.

Figure 3.—N.m.r. relaxation times vs. number-average molecular weight.

equivalent entanglement compositions have been developed by η_0-M_w and η_0-C correlations. For some of these same and additional polymers, however, other workers (8) have reported that the η_0-C correlation does not reveal a sharp break.

The entanglement composition has been calculated in two different ways from low shear Newtonian viscosity data as a function of C at constant M. The entanglement composition has been taken as the break, if it is prominent, or from the minimum concentration for a constant and high power dependence of viscosity on C. A high and constant power dependence of η_0 on C at constant M is a general feature of the entanglement region for amorphous polymers. This power dependence is quite generally in the region of 5 to 6, and limited theoretical substantiation has been developed (22, 101, 102).

Flow activation energy, ΔE^*, or heat, Q, can become independent of polymer concentration at concentrations above the characteristic entanglement composition (63). This means that the constant and high power dependence of η_0 on C is independent of temperature just as the 3.4 power dependence of η_0 on M_w is not dependent on the temperature. Use of the two variables M and C have also been combined for predicting the characteristic entanglement composition from low shear viscometry (63, 75). It occurs where
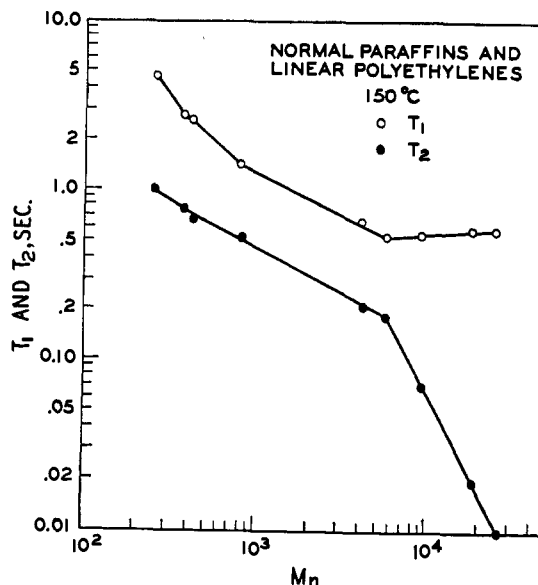
ΔE^* or Q becomes independent of composition, which is equivalent to the minimum product for constant power dependence of η_0 on M_w and C. In other cases only a marked change in concentration dependence of ΔE^* has been observed at the characteristic entanglement composition (5).

B. NUCLEAR MAGNETIC RESONANCE

Relaxation times measured by nuclear magnetic resonance, n.m.r., are related to rheological properties. Such measurements which involve decay times for longitudinal and transverse proton magnetization are generally made by the transient, spin–echo technique (85, 86, 123, 124, 136). Longitudinal or spin–spin relaxation time, T_1, has been found to follow an exponential decay law over a molecular weight range for a variety of amorphous polymers. Transverse relaxation can also be characterized by a single time, T_2, for molecular weights below M_c. Above M_c, however, transverse relaxation becomes nonexponential in a way which can be used to describe molecular weight distribution. The range for nonexponential decay, which can be represented as multiple T_2's, has been found to correspond to the entanglement region for polydimethylsiloxane and for polyisobutylene (124). Formerly, nonexponential decay for polyethylenes was less satisfactorily interpreted in terms of T_2's for two-phase systems (85). It has been reported that nonexponential transverse relaxation occurs below M_c for certain polydimethylsiloxanes (123, 124).

The entanglement molecular weight, M_c, is more strikingly observed in n.m.r. data by the abrupt change in T_2 as a function of molecular weight. Such data are shown in Figure 3, as developed by McCall, Douglass, and Anderson, using normal paraffins and frac-

tions of linear polyethylene (86). The T_2's were chosen so as to give the correct values in the exponential range (86). An abrupt change or break at M_c has also been found in T_2 values obtained on polydimethylsiloxane and on polyisobutylene (123, 124, 136). Entanglement conditions and characteristics have been elucidated by n.m.r. for only a few polymers and only by proton resonance. N.m.r. studies with polyethylene and polydimethylsiloxane have been of unique advantage because they possess protons but of a single type. N.m.r. can provide, through relaxation times, the characteristics, composition, and spacings for entanglements. The only report on solutions indicates that polymer in proton-free solvents behaves in much the same manner as pure polymer except that relaxation times are larger (86).

The relaxation times, T_1 and T_2 (see Figure 3), are purportedly governed by different mechanisms. The slow process, which dominates T_2, appears closely related to the motions which govern low shear Newtonian flow. This is suggested by the fact that the plot of T_2 vs. M_n, shown in Figure 3, is strikingly similar to correlations of η_0 vs. M_n. This implies that n.m.r. T_2 times can be used to determine both M and M_c. This is similar to the method of low shear viscometry with which n.m.r. relaxation times should be compared, since n.m.r. does not involve the application of mechanical stress.

C. VISCOELASTICITY

Viscoelastic properties of low molecular weight compounds are well understood (31, 35). More complex behavior and interpretation are involved in viscoelastic behavior of polymer systems incorporating entanglements. Manifestation of entanglements in terms of the rubbery plateau zone, as in correlations (a) through (d) below, has been observed experimentally by several techniques. Examples include shear and tensile creep measurements as a function of time (97) and torsional crystal and transducer shear measurements made as a function of frequency (40, 72, 72a). At polymer concentrations and molecular weights at and above the characteristic entanglement composition, viscoelastic measurements indicate a leveling out or intermediate, rubberlike region of low slope in experimental curves of: (a) shear relaxation modulus vs. time; (b) shear creep compliance vs. time; (c) shear storage modulus vs. frequency; (d) shear storage compliance vs. frequency.

The relaxation spectrum, H, is relatively flat where compliances have a low slope. The entanglement composition corresponds to the minimum concentration and molecular weight for the appearance of the plateau in moduli and compliances. The width and the height of this rubbery plateau are related to the number of entanglements per molecule. The shape of the relaxation spectrum and definition of the plateau zone de-
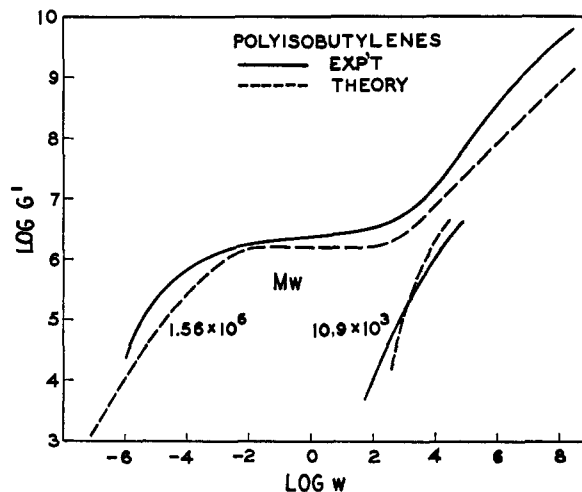

Figure 4.—Complex dynamic shear modulus vs. frequency, 25°.

pend on polymer molecular weight distribution (50a, 99).

Figure 4 shows the appearance of entanglements in terms of shear modulus as obtained from viscoelastic data on two well-defined amorphous polymers. Data on the higher molecular weight polyisobutylene in Figure 4 were obtained from dynamic measurements and from stress relaxation (38, 142). The results have been correlated in terms of G' as a function of frequency (80). The high molecular weight polyisobutylene in Figure 4, in contrast to the low polymer, exhibits the broad, quasi-equilibrium rubbery plateau region. This indicates that the characteristics of entanglement for polyisobutylene obviously set in at molecular weights above 10^4 and well below 10^5, as judged by the absence and extent of the plateau in two curves. The dashed lines are values developed from theory proposed in the original paper (38).

An approximate value of M_e may be calculated from the pseudoequilibrium shear modulus at the inflection in the stress relaxation curve or from the curve for the shear storage modulus, G', as a function of frequency, using the theories of rubber elasticity

$$M_e = \frac{dRT}{G}$$ (Eq. 1)

where G = shear modulus, G_{tsec}, or G'; d = density; T = absolute temperature; R = gas constant.

An increase in temperature is generally similar to an increase in time or a decrease in frequency in its effect on modulus or compliance. Thus, an equivalent viscoelastic measure of entanglement spacings has been derived by Tobolsky and Takahashi from torsional (shear) modulus measurements at a fixed time, 10 sec., as a function of temperature (145). For comparison with 10-sec. stress relaxation moduli, E_2, measured in extension, G_{10sec} has been multiplied by three. E_2 is then the value of $3G_{10sec}$ selected at the point in the
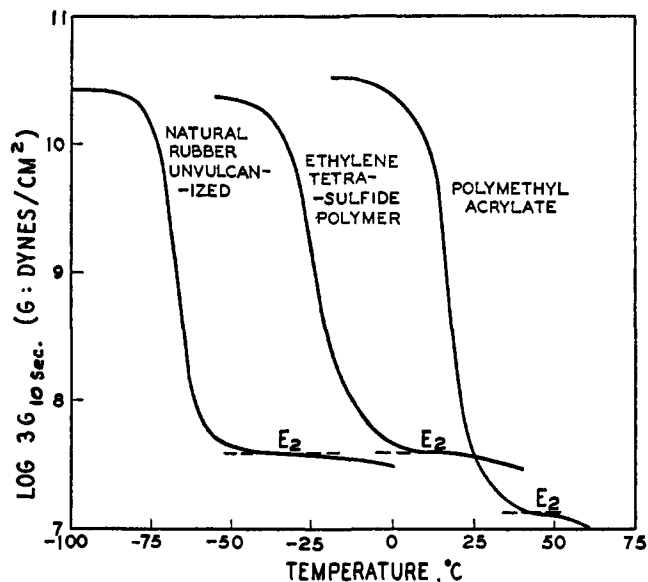
Figure 5.—Torsional shear modulus vs. temperature.

Figure 7.—Calculation of entanglement spacing from relaxation spectrum.

rubbery plateau region where the slope of log $3G_{10sec}$ vs. temperature is a minimum (see, for example, Figure 5). For moduli below 10^9 dynes/cm.^{2}, $E = 3G$, with deviations depending on Poisson's ratio. Figure 5 illustrates definition of E in this region, called E_2 by Tobolsky, as obtained from plots of log $3G_{10sec}$ vs. temperature for various polymers. Tobolsky has calculated M_e from the equation

$$M_e = 3dRT/E_2 \qquad \text{(Eq. 2)}$$

The appearance of entanglements in terms of compliance is excellently illustrated by the data on narrow fractions and blends of polyvinyl acetate (97, 98). The molecular weight dependence of shear creep is shown in the reduced variable treatment in Figure 6. This reduction, using a shift factor a_t, superimposes data on a particular system over a range of temperatures. At
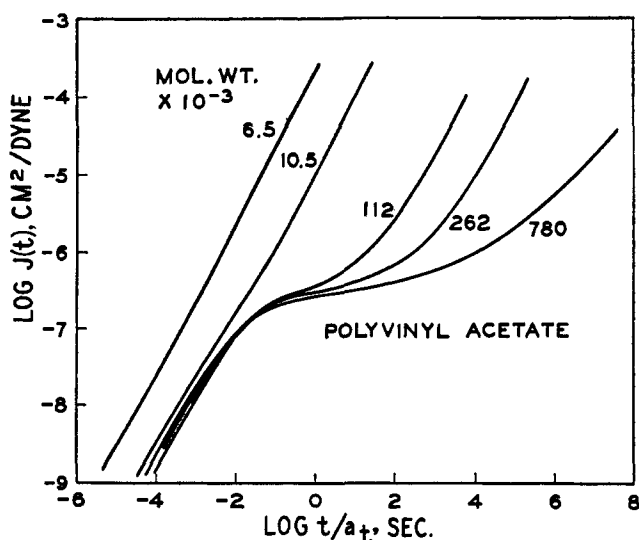
molecular weights below M_c, the compliance shows no deviation from simple behavior. At molecular weights above M_c (see Figure 6) the rubbery plateau appears prominently and increases up to five to six decades of time for the highest fraction. The displacement in Figure 6 at short times for low molecular weights can be treated quantitatively as a change in free volume, per se, changes in T_g with M. T_g becomes independent of M near M_c. The compliance at long times may be somewhat uncertain, although the relative curve positions are believed to be quite precise (97, 98). Measurements on blends of polyvinyl acetate fractions indicate that the plateau zone appears above a characteristic M_w and that the steady-state compliance is proportional to $(M_{z+1})(M_z)/M_w$ (98). A similar result for the effect of distribution on compliance has been derived by Bueche (16).

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

$$M_e = dRTJ \qquad \text{(Eq. 3)}$$

where J = shear compliance, J', or $J(t)$.

Entanglement spacing can also be calculated from the shape of the relaxation spectrum for a single sharp fraction of high molecular weight. Maxima in relaxation spectra give a comparative picture for the degree of entanglement, when reduced to corresponding states. A semiquantitative measure of entanglement is indicated by the logarithmic decrement, Δ, across the rubbery plateau zone, measured at constant H between slopes of $-1/2$ drawn in the so-called transitional and terminal zones for relaxation time, τ (see, for example, Figure 7 (35b)). It follows from the theory for monodispersed polymer developed by Ferry that

$$\Delta = 2.4 \log (M/2M_e) \qquad \text{(Eq. 4)}$$

Bueche also has given equations for calculating M_e from the shape of the plateau zone (21b). These methods

Figure 6.—Shear creep compliance vs. time reduced, 75°.

require only a single polymer. The precision of M_e, calculated from these equations, however, is of the order of $\pm 20\%$.

Marvin has developed more sophisticated equations for calculating M_e from maxima in shear loss modulus and compliance, G'' and J'', respectively. This approach may be considered an extension of Ferry and Bueche methods. Equation 5 gives an approximation, based on the theory of Marvin (81), for N_e using the minimum in the loss tangent, $J''/J' = \tan \delta_{min}$ (64)

$$\tan \delta_{min} = 1.02(M/N_eM_0)^{-0.80} \quad \text{(Eq. 5)}$$

where M is the molecular weight and M_0 is the molecular weight per monomer unit. N_e has subsequently been arbitrarily doubled. This is a modification of an earlier equation (126). This equation holds strictly for a monodispersed polymer, and dispersion will lead to higher values (64, 81).

Entanglement spacings may also be calculated from the maximum in loss compliance, J''_m, by the theory of Marvin. The following equation has been given by Richards, Mancke, and Ferry (125).

$$M_e = dRTJ''_m/0.42 \quad \text{(Eq. 6)}$$

In the Marvin theory, the quantity M_e appears as $M_c/2$ which is identified with the average molecular weight between the junction points of an equivalent network (107). A version of Eq. 6 could also be used to calculate M_e from G''_m as has been reported earlier using only a different constant in the equation (35e).

These several techniques generally provide consistent values of M_e, when expressed in weight average. As will be discussed later, the theoretical approach must be considered as tentative; the effects of molecular weight distribution and the distribution of entanglement chain lengths have not been adequately developed (35, 143).

D. HIGH SHEAR VISCOMETRY

The long relaxation times, caused by entanglements, lead to the easy observation of shear orientation and anisotropic flow which appear as deviations from simple Newtonian flow. The onset and magnitude of non-Newtonian flow, a temporary viscosity loss due to shear, can be used as an independent determination of entanglement spacing and composition. For a variety of amorphous polymers it has been found that the entanglement composition is a necessary and sufficient condition for the observation of prominent non-Newtonian flow (116, 119).

Capillary and rotational viscometer measurements indicate that 10- to 100-fold temporary viscosity losses due to shear occur abruptly at polymer molecular weights and concentrations above the characteristic entanglement composition. A generalized correlation of these results, showing this break in rheological be-
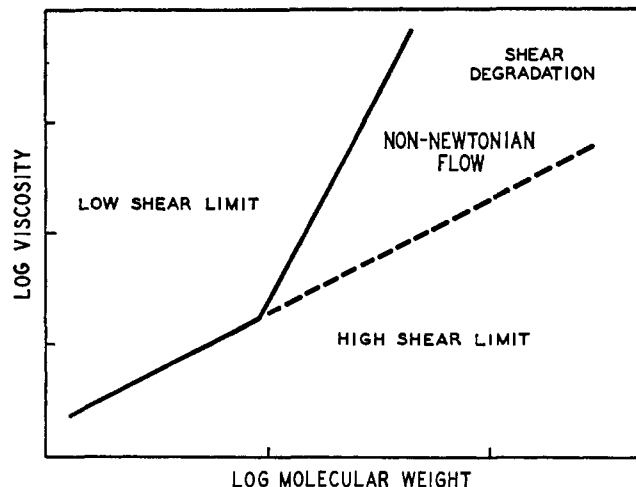
Figure 8.—Shear viscosities for systems of flexible, linear polymers.

havior, is shown in Figure 8. Steady-state high shear measurements on many different polymer systems with compositions below the break in Figure 8 indicate that viscosity is entirely Newtonian or independent of shear as shear stresses and rates approach 10^6 dynes/cm.^{2} and 10^6 sec.$^{-1}$, respectively. This indicates that the slope in Figure 8 below the break at the entanglement composition is independent of shear. Conversely, above the break the slope is independent of temperature but depends markedly on shear.

Non-Newtonian flow can be used to elucidate the entanglement composition as illustrated in Figure 9.
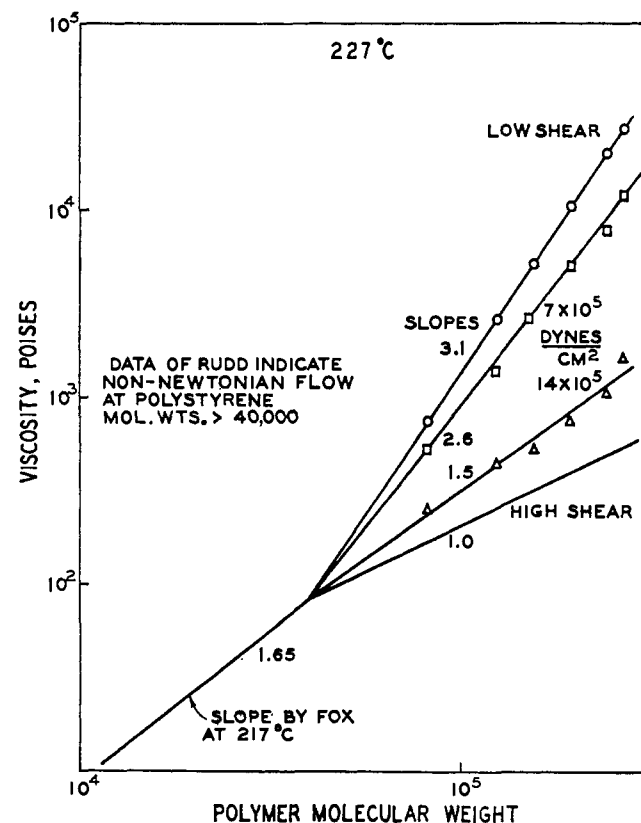
Figure 9.—Shear viscosities for polystyrene.
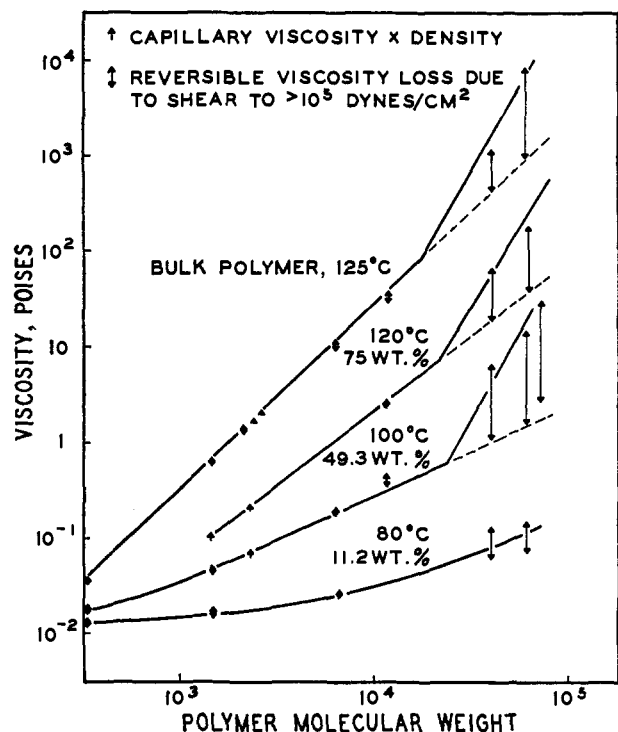
Figure 10.—Shear dependence of viscosity for polyisobutylenes in cetane.

Figure 11.—Dynamic viscosity as a function of frequency polyisobutylene in decalin.

Viscosities were measured in capillaries on a molecular weight series of narrow distribution polystyrenes. Correlations at constant stress (see Figure 9) are remarkably linear, as indicated by least-squares regression correlation coefficients of >0.98 (118). Slopes for log viscosity vs. log M decrease from 3.1 to 1.5 with increasing shear, with the lower limit not yet approached. Several independent sets of shear data on polystyrene (9, 127, 128) indicate a common intercept for the characteristic entanglement composition at M_c. The intercept is independent of shear (118, 128) and corresponds, with good precision, to the M_c for polystyrene elucidated by other techniques. The entanglement composition has been determined for a limited number of other cases by this intersection at a common M_c using a series of power law functions with exponents which decrease with increasing shear (115, 117, 120, 122, 133). Observations reporting an apparent change in M_c with shear are likely the result of a regular change in distribution with molecular weight which reportedly exists for the polyethylenes studied (131, 133).

Figure 10 shows the change of viscosity with molecular weight at a series of constant concentrations. The onset of the entanglement region is clearly indicated at the higher polyisobutylene concentrations and molecular weights by the prominent and coincident onset of both the 3.4 correlation and non-Newtonian flow. Figure 10 shows that limiting high shear viscosities coincide closely with an extension of data from lower molecular weights which are below the characteristic

entanglement composition. Such an extension of limiting high and low shear viscosities represents an ideal way of elucidating entanglement composition. However, stresses are generally unattainable for developing the high shear limit for high molecular weight bulk polymers. Polymer shear degradation is also a restrictive problem. Apparent steady-state and dynamic viscosities, η_a and η', for polymer systems are known to differ significantly at high and nominally equivalent shear rates. However, each η_a and η' (a) shows the same general dependence on shear variables, (b) yields to reduced variable treatment, and (c) shows the same general deviation with change of polymer molecular weight and distribution. Thus, η' vs. frequency can be used just as η_a vs. shear to elucidate the characteristic entanglement composition.

Figure 11 indicates dynamic viscosity as a function of concentration for a polyisobutylene, M_w 1.06 $\times$ 10⁶, in decalin at 25° (120). Correlations have been developed at a series of constant frequencies. Low shear data show a high, >5th power dependence of η_0 on V, polymer volume fraction, consistent with entanglement region. Convergence of constant frequency correlations at a common concentration indicates an entanglement composition, $(M_w V)_c$, of 19,000 in close accord with a value of 17,000 for undiluted polyisobutylene.

Correlations at constant steady-state shear rate for the same system as in Figure 11 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 non-Newtonian flow, is the same for all solutions.

For solutions of polymers of several types, including polystyrene, entanglement compositions have been defined by non-Newtonian flow. This has been accomplished by correlations at constant shear, both

shear rate or frequency and shear stress (6, 7, 26c, 118, 120, 128). It appears that correlations at constant shear stress give more consistent values for entanglement composition (6, 14a, 60, 118, 128) perhaps because stress involves apparent viscosity which will depend on, and compensate for, differences in molecular weight distribution among test polymers. Most importantly, constant shear stress correlations are consistent with reduced variables for non-Newtonian flow.

At constant shear rate, flow activation heat, Q_r, or energy varies with shear only for non-Newtonian conditions. Compositional conditions for finding a difference in Q_r at high and low shear thus represents a successful and alternate method of defining entanglement compositions from non-Newtonian flow (135).

III. THEORY

The prominent and important polymer properties attributed to entanglements have led to a myriad of theoretical interpretations. Although the mathematical approaches are varied, most theories incorporating entanglements involve mechanical and electrical analogies. They lead to conclusions which, in general, are in agreement with established empirical correlations. No single theory has been reported, however, which interrelates all of the observed empirical correlations which appear to be attributable to the same general phenomenon (35c, 116, 141a). The most widely applied theory is that of rubber elasticity.

A. RUBBER ELASTICITY

The equations of rubber elasticity have been derived by several approaches (76b, 141a). A basic form is

$$F = nRT[(L_s/L_u)^2 - (L_u/L_s)] \qquad \text{(Eq. 7)}$$

where F = tensile force per cross-sectional area on a sample of stretched length, L_s; L_u = unstretched sample length; n = number of moles of network chains per unit volume; R = gas constant; and T = absolute temperature.

A quantity M_e, the M_n of network chains, is commonly introduced in place of n in Eq. 7

$$M_e = \frac{d}{n} \qquad \text{(Eq. 8)}$$

where d = sample density.

For evaluation of M_e in terms of Young's modulus, E, Eq. 7 is further modified by Eq. 9 for the isothermal Young's modulus at any portion of the stress–strain curve.

$$E = L(\partial F/\partial L)_T \qquad \text{(Eq. 9)}$$

If measurements are carried out at small strain $(L \approx L_s \approx L_u)$, M_e may be calculated by incorporation of Eq. 8 and 9 into Eq. 7 as given in Eq. 10 (141a).

$$M_e = 3dRT/E \qquad \text{(Eq. 10)}$$

The same type of theoretical treatment also yields Eq. 11 for M_e in terms of shear modulus, G, in an ideal rubber network (81).

$$M_e = dRT/G \qquad \text{(Eq. 11)}$$

A correction factor, of disputed magnitude, is required for modulus measurements made on samples with molecular weights approaching M_e (141a).

Flory made a thorough evaluation of rubber elasticity (43, 44) and introduced a term into the theory of permanent cross links which provided agreement with experiment and was suggested to arise from entanglements of chain molecules between network points which behave effectively as cross links. Tobolsky further concluded from stretching a high molecular weight polyisobutylene, that some portion of the chain structure, perhaps entanglements, acted as fixed points and that at least instantaneously the conditions for the kinetic theory of elasticity are valid (76b). Tobolsky has also developed an independent derivation of the kinetic theory of rubber elasticity which leads to entanglement spacings on the assumption that all conformations of a polymer chain have equal energy. This assumption appears to be valid for many types of polymer chains (141a). Tobolsky has pointed out, however, that certain polymer chains show a marked tendency to favor extended conformations; whereas, others show a tendency to favor folded conformations. Deviations from "ideal" behavior might be observed on these grounds. Indeed, a motion different from conventional entanglements has been postulated as a possible explanation for nuclear magnetic relaxation data (86). This possibility, though unverified, would involve the motion of a fold along a single polymer chain.

Many theories, frequently related to the model of rubber elasticity, have been developed to explain the abrupt change in viscosity dependence at a characteristic polymer concentration and molecular weight. Merker employed a model similar to that proposed by Furukawa for a network of pseudo cross links, the separation and recombination of which take place continually to maintain an equilibrium number of links. The apparent molecular weight resulting from entanglements is related to the total molecular weight of the free molecule (51, 89). Viscosity data, with and without entanglements, are satisfactorily fit by this mathematical procedure which predicts a region of rapid increase in network formation for systems approaching the characteristic entanglement composition.

Takemura considered the vibrational modes of a network of polymer molecules in a viscous medium (139). He was able to qualitatively predict relaxation spectra and an abrupt change from $\eta \propto M^{1/4}$, in dilute solution and at low M, to $\eta \propto M^3$ in bulk polymer systems. Sobue and Murakami have evaluated visco-

elastic properties of polymers in the vicinity of M_c employing the "box"-type curve of Tobolsky in the rubbery region (137). Hayashi has shown that a system consisting of temporary cross links (based on a modified Rouse model) is equivalent to a parallel combination of generalized three-dimensional Maxwell models. The relaxation spectrum predicted by Hayashi (57–61) is of the "box"-type and steady flow viscosity predicted to be $\eta \propto M^{3.3-3.4}$, alternatively, $M^{3.5}$.

A variety of network theories have also been advanced for explaining the shear dependence of viscosity for concentrated polymer systems. None of these, however, unless modified for minimum entanglement compositions, are adequate for general interpretation of established, empirical correlations (116). Lodge (74) has provided a qualitative theoretical treatment by concluding that flow of network aggregates occurs through the destruction and rebuilding of network points and that behavior should be Newtonian at low stress. Hayashi has also developed a mathematical formulation for the effect of shear on a temporary network, i.e., entangled system (58). Merker (89) suggests that the effect of shear, leading to non-Newtonian flow, can be incorporated into his network model of pseudo cross links.

Intuitively, if the number or importance of imagined polymer entanglements is reduced by shear, then limiting high shear viscosities should increase with molecular weight in a way similar to that for unentangled molecules. Indeed, it has been shown from available data (122) that limiting high shear viscosities for entangled systems are most accurately predicted by applying viscosity–molecular weight correlations for similar systems but with compositions (lower concentrations and molecular weight) below the entanglement point (75a).

B. VISCOSITY

Eyring, Ree, and Hirai have developed a theory from rate processes based on the concept of random walk of connected segments (33). This treatment leads to functions for low and high molecular weight which combine abruptly at M_c and change dependence from $\eta \propto M^{4/3}$ to $\eta \propto M^{10/3}$. This approach has not been generally utilized, and the theory does not consider the significance of changes in free volume with molecular weight. Fujita has extensively evaluated the free volume aspects of concentrated polymer systems and evolved a theory predicting $\eta \propto M^{3.4}$ (50, 140). This theory does not, however, interpret the observed long relaxation times in the rubbery region.

Chikahisa has presented a statistical mechanical theory of steady viscosity in bulk polymers (25, 26, 26a). This approach is based on the Born–Green theory of liquids and involves an assumption that frictional forces due to entanglements are proportional to the covolume occupied in common by two polymer molecules. Chikahisa thus derives a two-term equation which predicts $\eta \propto M$ and $\eta \propto M^3$ at low and high molecular weight, respectively, and a rather abrupt change between the two dependences at M_c. Aspects of this theory are equivalent to an approach of Bueche.

Bueche has given the foundation and considerable development to a valuable and essentially independent theory of viscosity for concentrated polymer systems (15, 17, 21c, 21A), which involves the Debye model of a free-draining molecule. The following expression is derived for viscosity, η

$$\eta = \frac{r^2 N d A_0 f}{36M} \qquad \text{(Eq. 12)}$$

where r^2 = average square end-to-end chain distance; N = number of chain atoms per molecule, d = polymer density, A_0 = Avogadro's number, M = molecular weight, and f = segmental friction factor.

The segmental friction factor is defined as the force needed to pull a molecule through solvent with unit velocity. This friction factor has been considered a complex term dependent on molecular weight (21A). The term "r^2/M" can be obtained from measurement of polymer coil dimensions in a poor solvent since this is generally considered the limiting value in concentrated systems.

Strong support for the form of Eq. 12 has been given by Fox and others in explaining the viscosity of polymer systems with concentrations and molecular weights below the characteristic entanglement composition. This theory predicts correctly that viscosity should depend on the first power of molecular weight in the limit. The limit is approached on polymer dilution and at higher temperatures, per se, increasingly higher than T_g (21c). Data corrected to constant free volume, or the equivalent, corrected for changes in T_g with composition, also yield $\eta \propto M$.

The quite different behavior which is encountered at M_c and above is postulated, according to Bueche, to result from one polymer chain being entangled with another. By analogy with the slippage of smooth ropes, flow velocity is expected to be reduced by a slippage factor, $S \le 0.5$, which is a measure of first-order coupling.

Thus, in the entanglement region the same general form of Eq. 12 applies but with a viscosity dependence on molecular weight which depends chiefly in the Bueche theory on the choice of S. From this approach a dependence of $\eta \propto M^{2.5}$ was originally derived (81). To achieve agreement with empirical correlations, S has been stated variously as 0.1–0.5 (15), 0.3–0.4 (17), and 0.2–0.3 (21c). A circulation term has also been introduced to alter this theory to give $\eta \propto M_w^{3.5}$, in agreement with empirical correlations.

More recently Bueche has further revised his theory to incorporate the effect of branching. It is found that

the viscosity, η_b, of a branched polymer is related to the η_1 of a similar linear polymer of identical molecular weight by Eq. 13 (20, 21A), if the chains are entangled.

$$\eta_b/\eta_1 = g^{7/2} \qquad \text{(Eq. 13)}$$

For nonentangled chains the ratio is merely equal to g, which is the square of the ratio of the radius of gyration of the branched molecule to that of the linear. The significance of this addition to theory is that M_c is predicted to occur at a factor of g smaller for linear polymers than for those which are branched.

Ferry has given an excellent summary and comparison of various theories. Entanglement effects are not incorporated in the basic models for these theories, although Bueche has introduced this feature as described above. Ferry, Landel, and Williams have also modified the Rouse theory for inclusion of entanglement effects (38). In this case an abrupt increase in the average segmental friction coefficient to a new value is introduced for conditions at and above the characteristic entanglement composition. The magnitude of the increase in friction coefficient depends on the degree of entanglement, viz., polymer concentration and molecular weight. Introduction of this admittedly artificial shift factor, in terms of friction coefficient, can, by proper choice of entanglement composition, provide a semiquantitative fit to the plateau region of the viscoelastic spectrum (38). This explanation of the plateau zone has been also handled semiquantitatively by alternate terminology and mathematics by Tobolsky and by use of "box" and "wedge" relaxation distribution models. The Tobolsky, Bueche, and Ferry modifications are essentially mathematical statements of experimental behavior and are not derived in a truly a priori fashion (141a).

C. MARVIN MODEL

The more elaborate mathematical Marvin model for viscoelastic behavior involves a ladder network which corresponds to the Bueche calculation of an entanglement network. This hypothetical model can be expressed as equivalent mechanical and electrical networks and utilizes the empirical 3.4 power dependence of viscosity on molecular weight rather than the 3.5 power derived by Bueche (82, 83). The resultant elaborate equations have been extensively stated (35c, 81, 83). Computer techniques have been utilized for solution. Ferry has published tables for the numerical evaluation of the Marvin model which predict both maxima and minima for G'' and J'' in the plateau zone. Not only are G''_m and J''_m predicted, but their position on the frequency scale, w, is also predicted. An approximate evaluation indicates

$$G''_m \simeq 0.32 dRT/M_e \qquad \text{(Eq. 14)}$$

$$w(G''_m) \simeq (95kT/a^2L_0Z^2)(M_e/M)^{1/2} \qquad \text{(Eq. 15)}$$

where L_0 = translational friction coefficient per monomer unit, k = Boltzmann's constant, a = root-mean-square end-to-end distance per square root of number of monomer units, Z = degree of polymerization. Thus G'' height is proportional to the number of network strands per unit volume, and the frequency is proportional to $M_e^{1/2}$. J'' is likewise approximated

$$J''_m \simeq 0.32M_e/dRT \qquad \text{(Eq. 16)}$$

$$w(J''_m) \simeq 48 \, M_0^2kT/a^2L_0M_e^2 \qquad \text{(Eq. 17)}$$

where M_0 = molecular weight per monomer unit. Thus, the height of J''_m is inversely proportional to the density of network strands, and the frequency is directly proportional to the square of that density. Other similar numerical constants have been suggested (35e) and subsequently used in Eq. 16, which should be compared with Eq. 6.

It is important to note that these methods of computation of entanglement spacings from viscoelastic behavior are independent of the theory of permanent cross-linked systems.

For viscoelastic data on poly-n-butyl methacrylate solutions in ethyl phthalate, entanglement spacings calculated from J_e, pseudoequilibrium network compliance, agree with the values calculated from Marvin theory and J''_m (94). The agreement, it is suggested, indicates that the Andrade network and the network responsible for J' are identical—a circumstance which is not always true (111). The values calculated from $w(J''_m)$ are somewhat higher, as is usual (35c). In a subsequent paper the two sets of values derived from J'' by the theory of Marvin were arbitrarily doubled for comparison with entanglement spacings calculated by other methods (45). The more commonly used forms of the equations used to calculate entanglement chain lengths are cited earlier in section IIC.

D. COMPOSITION DEPENDENCE

1. Polymer Coil Dimension

Bueche suggested in 1957 a relation between dimensions of polymer chains and entanglement chain length (18). Fox and Allen have also shown that viscosity in the entanglement region may be related to $(\bar{S}_0^2)^{3.4}$ where $\bar{S}_0^2$ is the unperturbed mean-square radius of gyration (45). Tobolsky has also reported from an evaluation of four polymers that maximum relaxation time, proportional to η, depends on $(\bar{S}_0^2)^{3.4}$ for the entanglement region. Maximum relaxation times were compared in corresponding states, i.e., at corresponding values of $T - T_g$ (141a).

Using the basic equations of Bueche, Fox has been able to deduce an expression for the characteristic polymer entanglement molecular weight

$$X_c = \frac{\bar{S}_0^2}{V_s}V \qquad \text{(Eq. 18)}$$

where X_0 is a constant, V_a the volume per chain atom, and V the polymer volume fraction. A value for X_0 of 4.7×10^{-15} has been chosen by Fox to obtain a consistent correlation for characteristic entanglement compositions for bulk polystyrene, polyvinyl acetate, polyisobutylene, and polydimethylsiloxane. The M_c values used for these polymers were obtained from relatively precise viscosity measurements as a function of chain length and temperature. These entanglement compositions have been modified and are considerably lower, however, than previously reported results. The correlation of Fox for predicting entanglement composition is, nonetheless, remarkably good, to $\pm 10\%$. The entanglement chain length for polymethyl methacrylate represents the only serious discrepancy for bulk polymer. However, some apparently excellent viscosity data by Kraus on polybutadienes indicate that the ratio of coil dimensions of linear and branched polymers change with molecular weight. This represents a deviation from the above concepts, particularly as the branched dimensions appear to exceed that for the linear equivalent polybutadiene at high molecular weight (69, 69a, 70).

2. Pendant Group Volume

The characteristic entanglement molecular weight has also been interpreted in terms of polymer chain composition and the composition and volume of groups appended to the chain. For vinylidene polymers M_c has been equated to the molar volume of short, nonpolar pendant groups (121). Pendant group volumes were calculated from the values of LeBas as cited by Glasstone (54). The volumes used are X and Y in the vinylidene polymer unit

$$
\begin{bmatrix}
& H & X & \\
-& C & C & - \\
& H & Y &
\end{bmatrix}
$$
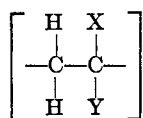
The regular increase of M_c with size of pendant groups is likely due to decreased chain flexibility caused by steric hindrance of pendant groups. The fact that polymer dimensions at θ conditions are considerably larger than their calculated free rotation dimensions indicates that steric hindrance is of decided importance (21c).

It has been suggested that the low M_c for a polycarbonate is due to its stiffness and polarity (11). The general conclusion for data on other polymers would suggest that if these two factors prevail, polarity is dominant over chain stiffness. Long as well as short pendant groups contribute to increasing M_c. The effect of long groups, however, is not basically a chain-stiffening effect but rather a plasticizing effect as indicated by a decrease in T_g with length of pendant group for the series poly(n-alkyl methacrylates) and for poly-

1-olefins. Indeed for a series of four different methacrylate polymers, n-butyl to n-dodecyl, M_c can be considered dependent on density alone, i.e., the density of the polymer backbone. That is, M_c is the same whether the backbone for these polymers is "diluted" by solvent or by side groups on the backbone.

The molar volume of pendant groups is also related to intramolecular hindrance to polymer chain rotation (84). This pendant volume correlation is also comparable to the polymer coil dimension concept of Fox for correlating characteristic entanglement chain lengths. In both correlations polymethyl methacrylate is the only notable deviation (45, 121).

The conclusions presented here concerning the dependence of entanglement chain length on polymer composition and coil dimensions are at variance with earlier conclusions necessarily based on less information. It has been supposed and widely quoted that nonpolar and polar polymers exhibit an N_c range of 600–1400 (1000) and 200–400, respectively (49, 95, 108).

3. Other Factors

Variations in stereoregularity, at least for polypropylene and polystyrene, have little influence on T_g, specific heat, and enthalpy (27). It may, therefore, be of minor influence on M_c with the possible exception of poly(n-alkyl methacrylates). Since heats of entanglement are small to zero for many common cases, cohesive energy density will perhaps be incidental to inherent chain stiffness in determining M_c. However, cohesive energy density increases generally with the size of pendant groups. It would seem, however, that cohesive energy density will play a role in addition to chain stiffness in determining flow activation energy with its formal relationship to heat of vaporization and intermolecular forces.

The weak polarity of ester side groups is indicated by the fact that spacing for polyvinyl acetate appears determined predominantly by steric effects (121). Ester groups are only weakly polar, and their inclusion as polymer segments leads to behavior similar to chain methylenes. Indeed, Fox has shown that linear polyesters of several different compositions have essentially the same M_c (49). This value, M_c about 290, is equivalent to the spacing for linear polyethylene. This suggests that the groups

$$
\begin{bmatrix}
-C-O- \\
\parallel \\
O
\end{bmatrix}
\quad \text{and} \quad
\begin{bmatrix}
& H & H & \\
-& C & C & - \\
& H & H &
\end{bmatrix}
$$
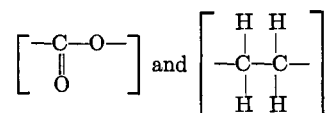
have the same effect in terms of chain flexibility and steric hindrance. This result is in striking agreement with conclusions developed by Bondi for low molecular weight compounds. Esters were found to have essentially the same viscosities and flow activation energies as equistructure hydrocarbons (13).

Entanglement spacing also appears related to other polymer properties which are influenced by chain flexibility. For nonpolar polymers, spacing increases generally with T_g and with activation energy for viscous flow. For polymers with polar pendant groups, the situation is quite different. Although their glass transition temperatures are generally high, entanglement spacings are generally quite low: polyvinyl alcohol $\sim$200–240; polyacrylic acid $\sim$130 (14); polyacrylonitrile and in a 90:10 copolymer with methyl methacrylate perhaps as low as 50 (121). These effects are likely the result of polymer–polymer interactions induced through polarity and hydrogen bonding.

B. CONCENTRATION DEPENDENCE

Characteristic entanglement compositions have been developed from abrupt changes in slope in plots of log η vs. log V, as well as vs. log M. It is proposed that $MV_c = M_cV$, although such abrupt changes in viscosity data as a function of concentration have not been generally reported. The hypothesis of a V_c as well as an M_c appears to be justified by the magnitudes and changes in power dependences of η on M and V at V_c. For a number of polar and nonpolar polymers, it has been shown experimentally that the characteristic entanglement composition at $(MV)_c$ is essentially constant over a range of concentrations and molecular weights for a particular polymer (39, 145a). This is in accord with both the theory of Bueche and the absence of entanglement heats. However, the general conditions for critical entanglement compositions in solution are not as yet fully defined. For example, a different dependence, substantiated by a packed spheres model, has been indicated by Onogi (102) and also developed independently by Cornet (26d). Extensive viscosity data on 5–15 wt. % solutions of polyvinyl alcohol, polyvinyl chloride, and polystyrene reportedly indicate a characteristic entanglement composition at a constant product of $(M^{1/2}W)_c$. Asai has reported corroborative data on solutions of polyvinyl chloride and polymethyl methylacrylate (4, 5). Entanglement compositions for these systems, in terms of $(MV)_c$, are, however, in reasonable accord with results reported by others. Moreover, at least for polystyrene, in terms of $(M^{1/2}W)_c$, results differ from the entanglement conditions published for bulk polymer and for other solutions.

In the equivalent sphere model of Onogi, the effects of entanglements are proposed to occur at a critical volume fraction of such spheres. Equation 19 was developed

$$CdN^{1/2} = 300V_0M_0/8\pi x^3 A_0 \qquad \text{(Eq. 19)}$$

where C = polymer concentration, weight per cent; d = solution density; A_0 = Avogadro's number; V_0 = critical volume fraction of spheres; M_0 = molecular

weight of monomer unit; and $x = r_0/N^{1/2}$ where r_0 = radius of equivalent sphere and N = polymer chain length.

Assuming a volume fraction of spheres $V_0 = 1.0$ ($V_0 = 0.524$ for cubical packing of spheres), Onogi has reported that a computation of coil dimensions, using his equivalent sphere model, agrees well with unperturbed dimensions evaluated from intrinsic viscosity data in a poor (θ) solvent.

It is important to point out that the dependence of entanglements on polymer concentration, which Onogi developed by theory and experiments, differs from other theories and experiments, principally that of Bueche and Fox. The entanglement dependence suggested by Onogi is not interpretable as a heat of entanglement.

A principal support for the square root dependence comes from curvature in Figure 9 for polystyrene viscosity data (102) at different concentrations. A change in the value at only the highest concentration is necessary to change curvature to linear and thus dependence from $N^{1/2}$ to N^1. Indeed such a change is quantitatively justified by a more satisfactory and higher value for entanglement transition as predicted from an improvement in the upper slope leading to the composition shown by Figure 8 (102). This change is further supported since it leads to an M_c for bulk polystyrene entirely in accord with other measurements. The computations based on the sphere model are inherently correct, but existing data do not appear to lead to its support as a basic postulate in explaining the viscosity of concentrated systems of amorphous polymer.

The packed sphere model of Onogi is qualitatively consistent with concepts of Maron (78, 79). Using solution data on several polymers and the Ree–Eyring theory for shear dependence of viscosity, Maron concluded that in concentrated solutions, rather than entangled, polymer chains curl upon themselves and compact to a small mass independent of solvent type.

IV. APPARENT HEATS OF ENTANGLEMENT

Flow activation heat, Q, as well as viscosity, has been considered due to two separable factors for concentrated systems of amorphous polymer (62, 63). One factor is entanglements, and another the increase of T' with increasing polymer concentration. According to Hirai, at high concentration

$$Q = 2\Delta E + Q_0 \qquad \text{(Eq. 20)}$$

where

$$Q = R[d \ln \eta/d(1/T)] \qquad \text{(Eq. 21)}$$

In Eq. 20, ΔE is the energy to form an entanglement. Q_0 is an activation term for a vitrified solution without entanglements and represented by the equations

$$(Q_s/Q_0)^{1/2} = 1 - AW \qquad \text{(Eq. 22)}$$

$$A = 1 - (Q_s/Q_1)^{1/2} \qquad \text{(Eq. 23)}$$

where W is weight fraction of a polymer, A is a constant for the system, and Q_1 and Q_s are activation heats of viscosity for the polymer and solvent (called solution (63)), respectively. Since Q_1 is usually much larger than Q_s, A is always near unity. Values for A, Q_s, and ΔE are given in Table I, essentially as reported by Hirai who cites the sources of the original data. In general, activation heats attributed to entanglements are small, <5 kcal. (62, 63).

TABLE I

ENERGY OF ENTANGLEMENTS AND RELATED TERMS
AFTER HIRAI (62, 63)

Polymer	Solvent	Q_s, kcal.	ΔE, kcal.	A
Polystyrene	Ethylbenzene	2.30	0.00	0.86
Polystyrene	Isopropylbenzene	2.60	0.35	0.98
Polystyrene	Xylene	2.00	0.50	1.02
Polystyrene	Dibenzyl ether	2.10	0.85	0.75
Polystyrene	Diethylbenzene	2.00	0.50	1.00
Polyvinyl chloride	Tricresyl phosphate	5.0	1.5	0.80
Polymethyl methacrylate	Ethyl phthalate	6.50	0.0	1.00
Polyisobutylene	Xylene	2.0	0.3	0.85

From shear creep compliance data on concentrated systems of polyisobutylene in cetane, a formal heat of dissociation of entanglement coupling points has been calculated. It is reported to vary with concentration and to reach a maximum of 1.8 kcal./mole at 68 wt. % polyisobutylene, calculated at 25° (100).

Heats of entanglement have also been postulated on the basis of M_e calculated from viscoelastic measurements (94). Spacings for poly-n-butyl methacrylate in ethyl phthalate are found to increase with temperature in a way which can be formally ascribed, in terms of van't Hoff equation, to a heat of entanglement or association of 2.1 kcal. (94, 130). This heat of entanglement is independent of concentration corresponding to entanglement spacings which decrease with an increase in concentration. A value of 2.8 as the power of concentration (94) is given in place of 2.3 and 2.6 cited earlier (35d). From these extensive viscoelastic studies of poly-n-butyl methacrylate an abnormally high dependence of viscosity on polymer concentration, ~14.4 power, is also reported, consistent with a heat of entanglement (94). This unexpected behavior is supported by related observations on undiluted poly-n-butyl methacrylate and on other alkyl methacrylates. Both the poly-n-hexyl and -n-butyl are reported to have a heat of entanglement dissociation of 2.27 kcal./mole; poly-n-octyl methacrylate, a value of 1.6 kcal./mole (12). The fundamental reason for this effect is unknown, although sequences of tactic order have been suggested to explain the concomitant effects of unusual temperature effects (heat of entanglement) and the unusually rapid increase in entanglement spacings with dilution (35d). The formal heat of entanglement implies that an equilibrium exists between existing and po-

tential entanglement sites, with the concentration of the latter in excess and essentially constant (12). It may be relevant that, unlike other polymers, for example, polystyrene, differences in tactic order in methacrylate polymers lead to large differences in glass transition temperature (134). These same effects, whatever their nature, may also be responsible for the divergence of values published for polymethyl methacrylate in bulk and in ethyl phthalate solvent (94).

The properties ascribed to alkyl methacrylates are inconsistent with the dependence of entanglements and viscosities reported for several other polymers (93). However, the general nature of temperature dependence is not clearly defined, although the variation of M_e with temperature, if it occurs, is not large (21a). In only a few cases have entanglement conditions for polymer solutions been related to those for bulk polymer—principally polystyrene and polyisobutylene. For these data $(NV)_c$ is a constant. The definitive study, viscosity measurements as a function of polymer concentration in a very good and a very poor solvent have not yet been reported.

Certain studies on polyvinyl alcohol solutions have revealed a constant product of $(NV)_c$ at the entanglement point which is considered normal (108). However, the same data have been interpreted to give a heat of entanglement based on the fact that $(NV)_c$ increases from 200 to 240 for temperatures from 30 to 80°. The viscosity η_c at $(NV)_c$ has been plotted vs. $1/T$. The activation energy calculated from the slope of this plot is reportedly independent of polymer concentration and equal to 2.3 kcal. over the flow activation heat for the solvent, water (108). This agrees with the value of 2.5 kcal. obtained by Hirai from the dependence of flow activation heat on reduced concentration (62).

In other cases, the dependence may be $(N^xV)_c$ or $(NV^x)_c$ where x is a fractional power. Both of these forms have been used to explain deviations from a constant $(NV)_c$. Such deviations can be interpreted in terms of a heat of entanglement or association which should really depend on polymer solvent but be insensitive to concentration.

Another type of abnormal behavior has been observed for polyethylene oxide (152). Although the temperature dependence is normal (no temperature dependence for M_e), independent viscosity (118) and viscoelasticity tests (152) indicate that entanglement coupling may be unduly strong as indicated by an unusually high power of dependence of viscosity on molecular weight, >3.4.

Entanglement conditions have been related to polymer concentration and coil dimensions by Fox and Allen (45). By this concept $(NV)_c$ is expected to increase 5–30%/100°, consistent with an apparent heat of association of about 0.1–1.0 kcal./mole. For the limited

data available of sufficient definition, *e.g.*, on polyethylene, polyisobutylene, polydimethylsiloxane, polystyrene, polyvinyl acetate, and importantly on polymethyl methacrylate, the temperature coefficient of $(NV)_c$ does not significantly exceed values derived from changes in coil dimensions.

V. REPORTED ENTANGLEMENT SPACINGS

A. GENERAL

The most reliable and definitive entanglement compositions are derived independently from the break in measurements as a function of molecular weight, and sometimes, concentration in each of the following observations: onset of the rubbery plateau in viscoelastic behavior, the abrupt change in transverse relaxation times measured by n.m.r., the change in low shear viscosity dependence, and the onset of non-Newtonian flow. *Asterisks have been placed in the tables opposite the entanglement length for each polymer which is considered most reliable or closest to a selected average of published results.* In some cases such a choice is impossible. Most entanglement chain lengths are given in chain atoms; the most probable values are also given in discussion in terms of molecular weight. Significant figures in the tables are generally greater than precision because values are interconverted between round numbers of chain length and molecular weight. Polymers with unusual compositions are reported only by molecular weight. For common polymers, Table II may be used to convert molecular weight to number of chain atoms.

TABLE II

WEIGHT PER CHAIN UNIT FOR SOME COMMON POLYMERS

Polymer	Wt./unit
Polyethylene	14
Polypropylene	21
Polyisobutylene	28
Hevea—natural rubber	17
Polystyrene	52
Polyvinyl acetate	43
Polyacrylic acid	36
Polymethyl methacrylate	50
Poly-*n*-butyl methacrylate	71
Polyvinyl alcohol	22
Polyethylene oxide	14.7
Polycarbonate of Bisphenol A (4-Hydroxyphenyl)-2,2'-propane polycarbonate}	21.2
Polydimethylsiloxane	37

* Approximate molecular weight may be obtained from chain length by multiplication using tabulated values. For example, for polymethyl methacrylate with an N_e of 74 (Table III) an M_e of 3700 is calculated, 74 × 50.

Entanglement compositions have been widely reported from calculations based on the theory of rubber elasticity (145). Calculations which yield M_e or N_e, the molecular weight or chain atoms between entangle-

ments, are based on the height, width, and position of compliances and shear moduli. These values are by theory and rough empiricism related to $M_e = M_c/2$, M_c or N_c corresponding to the molecular weight or number of chain atoms for the characteristic break in the rheological measurement described above. Bueche has assumed this factor of two for polymethyl methacrylate, as have others (81, 119). In accord with the entanglement concept, the composition, M_c for bulk polymer, corresponds to polymer molecular weight for twice the length, M_e, needed to make a loop or entanglement. In previous summaries M_c and M_e have been compared directly without a factor of two (45, 77). A rationalization can be given in terms of gelation theory. By derivation M_e for molecular weight between entanglements should be number average. However, using the theory of rubber elasticity, M_e is proportional to compliance, which is empirically shown to depend on the higher moments M_w and M_z. Viscosity at the break is also known to depend on M_w.

There are some wide discrepancies not explained by a factor of two, between entanglement spacings calculated by the two basic methods. The unusual situation for polymethyl methacrylate and the spread of values for polyethylene are examples. Entanglement spacings calculated directly from the theory of rubber elasticity lack precision, to the extent of sometimes being considered unreliable. From present data there is no convincing relationship between M_c and M_e.

Schreiber, Rudin, and Bagley (133a) emphasize that a difference in the manifestation of entanglements may exist in elastic and viscous components. Viscosity and elasticity of polymer melts reported respond differently to changes in extrusion conditions and to thermal and shear history. The "die transit" or solution treatment of a polymer reportedly changes the degree of chain entanglement sufficiently to affect elasticity but not polymer viscosity.

Two sets of entanglement compositions have been calculated by Eyring for each of several polymer systems (33). Only one value for silicone, M_c 29,600, is tabulated here. One set of values was derived from the intersection of slopes of four-thirds and ten-thirds on plots of log η *vs.* log M. These values are no more definitive than direct measurements, and the procedure has not generally been accepted.

Fox and Allen have stated that entanglement spacings for several polymers have been defined to ±10%. They feel that their more recently reported and lower values for polystyrene, silicone, polyvinyl acetate, and polyisobutylene are of more theoretical significance (1, 45). For these polymers, two alternative ways of treating low molecular weight–viscosity data agree to ±10% in predicting M_c. Nonetheless, values derived predominantly from high molecular weight data should not be affected by such adjustments. Moreover, en-

tanglement compositions, obtained directly from measurement and without free-volume or other corrections, should agree with the abundance of values tabulated, which are considerably higher than values recalculated by Fox and Allen for the four polymers.

Values cited from loss compliance are only from the maximum, J''_m. Entanglement spacings derived from the frequency of the maximum are apparently quite erratic and subject to considerable uncertainty, at least for about the eight polymers evaluated in this way (35c, 77). The M_e calculated from the frequency of the maximum is generally 50% higher than that from J''_m. This has been considered intuitively reasonable since the latter should yield something like a number average by analogy with cross-linked networks; whereas, the former should give some kind of higher average. Values from J''_m have been doubled for comparison in terms of $(MV)_c$ (77). In this compilation characteristic entanglement compositions are not doubled and are given as $(MV)_e$, in accord with the theory of Marvin (107). Values derived from the width of the relaxation plateau in H are generally low, perhaps because of lack of definition of the spectrum at long times (35c). The possible distribution of entanglement spacings has in no way, as yet, been evaluated. The distribution may perhaps be represented by a probability distribution function just as permanent entanglements or cross links (76a, b).

Entanglement compositions for solutions are listed in Table III in terms of N times polymer volume fraction V. Where necessary, concentrations in other units are converted to approximate values of V. Molecular weights, converted to N, are generally M_v and M_w. Discrepancies exist in the literature covering molecular weight moments and temperature of measurement for citations of the same data. These differences are not resolved here and are simply cited as in the respective reference. In many cases differences are insignificant. Entanglement spacings originally reported in terms of degree of polymerization have been converted to chain atoms per entanglement length. The oldest reference citations generally give the original data; the more recent contain new interpretations and the calculation of entanglement composition. Although polymer density should likely be incorporated in or cited with N and M, this is not warranted by the general imprecision of measurements.

Brief comments on reported data follow with a tabulation of entanglement spacings and pertinent data on the method of measurement.

B. POLYETHYLENE

Schreiber and Bagley (132) have provided several entanglement spacings for linear polyethylene. Newtonian flow measurements on crude fractions of linear polyethylene and on normal paraffins gave values of 250 and 364 for N_c depending on whether a 3.4 or higher slope was used to correlate viscosities at high molecular weight. Schreiber, Bagley, and West (133) followed with the single, most definitive study on linear polyethylenes, which indicated an M_c of 4000 or an N_c of 286* for data on fractions. An equivalent value of 275 has been developed by Fox from viscosity data correlated from several sources (30, 31, 110, 146). Using most of these same data, a lower and approximate N_c of 143 had been reported earlier (114) and frequently cited (86, 118, 119). Busse and Longworth (22) suggest an N_c of about 300, which is governed by M_v.

Corroborating n.m.r. values of N_c, 410–680, or M_c, 5800–9600, i.e., about 7000, are less satisfactory than a later n.m.r. value of 5000–6000 (86).

Limited data available on branched polyethylenes indicate that they exhibit a low M_c, similar to that for linear polyethylene. Within the precision of present data on polyethylenes, no definitive relation can be established between the degree of branching and M_c (114, 118, 119).

C. POLYISOBUTYLENE

The first suggestion of an entanglement chain length was proposed by Tobolsky and Mark for polyisobutylene (76a, b). A recent N_c from bulk polymer (45), 460, was developed from the same data which was formerly interpreted to give published equivalent values of 608* (77) and 610 (49). The 607 or 608 are considered an M_c of 17,000 derived by the two methods (119). Powles (124) gives a slightly higher value, log M_c 4.29, which is supposedly a citation of earlier data. Yin, Lovell, and Ferry (152) indicated the rough range of values, 250–500, reported for N_e.

Trager, Dreval, and Trayanova (145a) have reported an $(NV)_c$ for solutions which is qualitatively consistent with values for bulk polymer. An $(NV)_c$ of 1400 differing from other results is based on insufficient data and should not be weighed heavily (49, 66). These same data have been used to give another approximate value cited by Ōyanagi (108).

Entanglement spacing have been developed from loss tangent (tan δ) for a polyisobutylene, M_v 1.5 × 10⁶, at concentrations from bulk down to a V of 0.64 in cetane. This set of values confirms the constancy of $(NV)_c$ but provides an abnormally large value, ∼2100, which may be due to the method of calculation and the breadth of the polymer molecular weight distribution (126). Indeed spacings from tan δ were arbitrarily doubled over an earlier expression (64). Published values without the factor of two are given in Table III.

D. HEVEA—NATURAL RUBBER

Although numerous measurements have been reported on *Hevea* or natural rubber, the entanglement spacing for this polymer is not as yet established.

TABLE III

REPORTED ENTANGLEMENT SPACINGS

Entanglement length N_e	Ref.	Measurement	Method	Polymer system	Temp., °C
			Linear Polyethylene		
N_e					
275	45	η vs. M_w	Newtonian flow	Bulk linear fractions and n-paraffins	140
~143	86, 114, 118, 119	η vs. M_w	Newtonian flow	Bulk linear fractions and n-paraffins	150
364, 250	132	η vs. M_w	Newtonian flow	Bulk linear fractions and n-paraffins	190
286*	133	η vs. M_w	Newtonian flow	Bulk linear fractions	190
~300	22	η vs. M_w	Newtonian flow	n-Alkanes; whole, linear polymer plus paraffin wax	150
~290	133	η vs. M_w	Non-Newtonian flow	Bulk linear fractions	190
<642	118	η vs. M_v	Non-Newtonian flow	Bulk whole polymer	150
357 ~ 429	86	T_2 vs. M_n	N.m.r.—spin echo	Bulk fractions and n-paraffins	150
410–680 (~500)	85, 119, 124	Multiple T_2's	N.m.r.—spin echo	Bulk linear fractions	120–200
N_e					
310	145	E_2 inflection	E vs. temp.	Bulk whole polymer	. . .
			Branched Polyethylene		
N_e					
171	114, 118, 119				
150–180 (~164)	114, 116 (32)	η vs. M_v	Newtonian flow	Bulk, whole, branched polymer and n-paraffins	110–160
290	116, 133				
286 (236)	114, 118, 119 (114, 132)	η vs. M_v	Non-Newtonian flow	Bulk, whole, branched polymer	110 (190)
263–593 (393)	114, 133				
			Polyisobutylene Bulk Polymer		
N_e					
460	45	η vs. M_w	Newtonian flow	Fractions	25–217
608*	34, 35c, 38, 47, 77, 116, 118, 121	η vs. M_v	Newtonian flow	Fractions	(30)–217
610	45, 117	η vs. M_v	Newtonian flow	Fractions	9–217
571 (~600)	117, 133	η vs. M_v	Newtonian flow	Whole polymer	135
607	115, 118, 119	η vs. M_v	Newtonian flow	Fractions	100–135
607	115, 118, 119	η vs. M_v	Non-Newtonian flow	Whole polymer	110–135
~1430	136	T_2 vs. M_v	N.m.r.—spin echo	Whole polymer	200 ± 5
N_e					
240	3, 45, 77	E inflection	Stress relaxation	Whole polymer	30, reduced
320	23, 77	E inflection	Stress relaxation	Whole polymer	25, reduced
292 (~286)	2, 76a, b, 141b, 145	E_2 inflection	E vs. temp.	. . .	. . .
296	29	E_2 inflection	E vs. temp.	Whole polymer	. . .
479	38, 121	Height G_e	Viscoelasticity	Whole polymer	25
440	35c, 36, 41	G inflection	Transducer method	N.B.S. bulk whole polymer	90 (−45 + 100)
320	41, 77	J' inflection	Transducer method	N.B.S. bulk whole polymer	90 (−45 + 100)
250	35c, 36, 41, 45, 77	J''_m	Transducer method	N.B.S. bulk whole polymer	50
			Polyisobutylene Solutions		
$(NV)_e$					
~1400	49, 66	η vs. M_v	Newtonian flow	Whole polymer 0.05–0.20 g./cc. in xylene and decalin	25
571*	117–120	η vs. M_v	Newtonian flow	Whole polymer 75 wt. % in cetane	135
571 (607)	29 (117)	η vs. M_v	Non-Newtonian flow	Whole polymer and rough fraction 49.3 wt. %, cetane and tetralin	135
571, 500	117, 121	η vs. M_v	Non-Newtonian flow	Whole bulk polymer and rough fraction 49.3 wt. % cetane	100–135
750	29, 120, 121	η vs. C	Non-Newtonian flow	M_w for N.B.S. whole polymer in decalin	25

TABLE III (Continued)

Entanglement length	Ref.	Measurement	Method	Polymer system	Temp., °C.
679	29, 120, 121	η vs. C	Viscoelasticity	M_w for N.B.S. whole polymer in decalin	25
1045	126	Tan δ	Viscoelasticity	1.00 V } for the M_v of a	15–45
1045		Tan δ	Viscoelasticity	0.91 V whole polymer in	25, reduced
1045		Tan δ	Viscoelasticity	0.85 V } cetane	
1094		Tan δ	Viscoelasticity	0.80 V	
996		Tan δ	Viscoelasticity	0.64 V	

Hevea-Natural Rubber

N_e					
296*	35c, 39, 45, 77, 153	G' inflection	Viscoelasticity	Bulk rough fraction	−30
120	39, 45, 77, 109	G' inflection	Viscoelasticity	Bulk rough fraction	−30
400	35c, 39, 77, 109	G' inflection	Viscoelasticity	Bulk rough fraction	−30
136	35c, 39, 45, 77, 109	J''_m	Viscoelasticity	Bulk rough fraction	−50
168	145	E_2 inflection	E vs. temp.	Bulk polymer	~−30
(500), 480, ~539	(35c), 19, 21, 45	$J(t)$ inflection	Creep compliance	Bulk whole polymer	10, reduced
250	19	$J(t)$ inflection	Creep compliance	Bulk whole GRS rubber	10, reduced

Bulk Polystyrene

N_e					
~769	60, 118, 119, 120, 123, 127	η vs. M_v	Non-Newtonian flow	Fractions	227
>385	133	η vs. M_w	Non-Newtonian flow	Fractions and whole polymer	200
600	45	η vs. M_w	Newtonian flow	Linear fractions	160–217
630	1	η vs. M_w	Newtonian flow	Linear fractions	155–217
720, 730, 731	34, 35c, 48, 49, 77, 118, 119, 120, 149	η vs. M_v	Newtonian flow	Linear fractions	217, 130–217
~962	47, 75	η vs. M_n	Newtonian flow	Linear fractions	217
673*	50, 149	η vs. M_v	Newtonian flow	Fractions	217, and reduced
N_e					
610	1, 45, 77	E inflection	Viscoelasticity	Whole polymer	100
320	1, 45, 77	E inflection	Viscoelasticity	Fractions	110
371 (385)	145 (141b)	E_2 inflection	E vs. temp.	Whole polymer	...
192	35c, 144	Width H plateau	Viscoelasticity	Narrow and broad distribution polymers	115
660	35c, 144	G inflection	Viscoelasticity	Bulk narrow and broad distribution polymers	115

Polystyrene Solutions

$(NV)_e$					
635, 731, 769	68, 120	η vs. M_v and C	Newtonian flow	15, 20 wt. % whole polymer in toluene	30
857*	45	η vs. M_v	Newtonian flow	C_v, 50 and 75 vol. % fractions in dibenzyl ether	218
~1000	49	η vs. M_v	Newtonian flow	Fractions in 14–44 wt. % in diethylbenzene	30–100
660	37, 108	η vs. C	Newtonian flow	M_w whole polymer, 0.16–0.62 g./cc. in decalin and xylene	25
1005, 693, 516, 371	103–105	η vs. M_v	Newtonian flow	4.24 } vol. % M_v 6.13 whole polymer 9.52 in toluene 12.29	40
~750	60, 106	η vs. M_v	Newtonian flow	15 wt. % (~13 vol. %) whole polymer in toluene	30
654, 769	120	η vs. M_v	Non-Newtonian flow	15–20 wt. % in toluene fractions and whole polymer	30

Polydimethylsiloxane

N_e					
630	45	η vs. M_w	Newtonian flow	Bulk fractions and whole polymer	25
~950 (~811)	34, 49, 77 (86)	η vs. M_w	Newtonian flow	Bulk fractions and whole polymer	25
800	33	η vs. M_w	Newtonian flow	Bulk fractions and whole polymer	25
1100	10, 147	η vs. M_v	Newtonian flow	Bulk fractions and whole polymer	40

TABLE III (Continued)

Entanglement length	Ref.	Measurement	Method	Polymer system	Temp., °C.
811, 800	24, 89	η vs. M_w	Newtonian flow	Bulk whole polymer	25
784* (811)	7, 105, 119 (86)	η vs. M_v	Newtonian flow	Bulk whole polymer	25
784 (~800)	7, 114, 116, 118, 119 (133)	η vs. M_v	Non-Newtonian flow	Bulk whole polymer	25
700–1700	119, 123, 124	T_2 vs. M_v	N.m.r.—spin echo	Bulk whole polymer	25
~1000					
~1351	86	T_2 vs. M_n	N.m.r.—spin echo	Bulk fractions	22

N_e

320	45, 77	J' inflection	Viscoelasticity	Bulk whole polymer	25

Polyvinyl Acetate

N_c

570*	45, 92	η vs. M_w	Newtonian flow	Bulk linear fractions	120–160
528	35c, 92				100
(340), 240	(35c), 45, 77, 150	η vs. M_v	Newtonian flow	Bulk linear fractions	160
512	98	η vs. M_w	Newtonian flow	Bulk fractions at isofree volume	40

N_e

680, 480	35c, 77, 85	J''_m	Viscoelasticity	Bulk fractions	90
172	35c, 96	Width H plateau	Stress relaxation	M_w of bulk rough fractions	45–60 75, reduced
400, 338	35c, 45, 77, 151	G inflection	Viscoelasticity	Bulk fractions	50

Bulk Polymethyl Methacrylate

N_e

74	45, 77, 87	E inflection	Stress relaxation	Whole polymer	135
124	145	E_2 inflection	E vs. temp.	Whole polymer	...
204	12a, 35c	$G(t)$ inflection	Stress relaxation	Whole polymer	60–125
172	16, 35c	$J(t)$ inflection	Tensile creep	Fraction	110–140
88, ~90	16, 21, 45, 77	D inflection	Tensile creep	Fraction	140

N_c

>4080 < 7300	16	M_v for plateau	Tensile creep	Fractions	111
>3000	87	M_v for plateau	Stress relaxation	Whole polymer	50–125
~10,000	138	η vs. M_w	Stress relaxation	Whole polymer	170
200	14a	η vs. M_v	Non-Newtonian flow	Whole polymer	260

Polymethyl Methacrylate Solutions

$(NV)_c$

210 (~208)	16, 34, 45, 50, 91, 108, 138 (21, 49)	η vs. M_v	Newtonian flow	25 wt. % fractions in ethyl phthalate	60
70–180	5	η vs. C	Newtonian flow	Whole polymer in cyclohexane	30

Copolymers of Methyl Methacrylate and n-Butyl Methacrylate

53	146a	Retardation max.	Tortional creep	Whole random polymer MMA/BMA	91–123, reduced
55		Retardation max.	Tortional creep	90:10	88–113.5, reduced
72		Retardation max.	Tortional creep	70:30	69–98, reduced
83		Retardation max.	Tortional creep	50:50	58–81, reduced
91		Retardation max.	Tortional creep	30:70	34–60, reduced
90		Retardation max.	Tortional creep	0:100	5–38, reduced

Higher Alkyl Methacrylate Polymers

1. Poly-n-butyl methacrylate

$(NV)_e$

184		12, 35c, 45, 77	J''_m	Viscoelasticity	Bulk fraction	125
114		145	E_2 inflection	E vs. temp.	Bulk polymer	...
858	840	94	J''_m $J(t)$	Dynamic mechanical plus creep	30 ⎫ wt. % polymer	0, reduced
520	716				40.3 ⎪ in ethyl	
294	394				50 ⎬ phthalate	
184	230				60 ⎭	
184		12, 35c	J''_m	Viscoelasticity	Bulk polymer	100, reduced

TABLE III (*Continued*)

Entanglement length N_e	Ref.	Measurement	Method	Polymer system	Temp., °C.
2. Poly-*n*-hexyl methacrylate					
360	12, 35c, 45, 77	J''_m	Viscoelasticity	Bulk fractions	105
3. Poly-*n*-octyl methacrylate					
660	12, 28, 35, 77	J''_m	Viscoelasticity	Bulk fractions	90
500	12, 35c	Width H plateau	Viscoelasticity	Bulk fractions	90
~480	12, 71	Width H plateau	Viscoelasticity	Bulk fractions	54–140
~600	12	G' inflection	Viscoelasticity	Bulk fractions	100, reduced
4. Poly-*n*-dodecyl methacrylate					
1300	35c, 71	Width H plateau	Dynamic mechanical plus creep	Bulk fractions	−40 to +45 25, reduced
5. Poly-*n*-docosyl methacrylate					
2500	35c, 77, 129	J''_m	Viscoelasticity	Bulk whole polymer	60
Polyalkyl Acrylates					
1. Polymethyl acrylate					
200	35c, 77, 151	J''_m	Viscoelasticity	Bulk fractions	80
165	145	E_2 inflection	E vs. temp.	Bulk polymer	45
2. Polybutyl acrylate					
238	145	E_2 inflection	E vs. temp.	Bulk polymer	...
Polyesters					
1. Poly(decamethylene sebacate)					
290	42, 45 (49)	η vs. M_w	Newtonian flow	Bulk whole polymer	109 (80–200)
2. Poly(decamethylene adipate)					
280	34, 42, 45 (49)	η vs. M_w	Newtonian flow	Bulk whole polymer	109 (80–200)
3. Poly(decamethylene succinate)					
290	42, 49	η vs. M_w	Newtonian flow	Bulk whole polymer	80–200
4. Poly(diethylene adipate)					
290	42, 49	η vs. M_w	Newtonian flow	Bulk whole polymer	0–200
5. Poly(ω-hydroxy undecanoate)					
<326	8, 49	η vs. M_w	Newtonian flow	Bulk whole polymer	90
6. Poly(neopentyl succinate)					
810	52	η vs. M_w	Newtonian flow	Bulk whole polymer	>25 < 200
Polyethers					
1. Polyoxypropylene glycol					
364, 400, 414	45, 56	η vs. M_v	Newtonian flow	Bulk fractions	25
2. Polyethylene oxide					
~682	118, 119	η vs. M_v	Newtonian flow	Bulk whole polymer	100, 135
~682	118, 119	η vs. M_v	Non-Newtonian flow	Bulk whole polymer	100, 135
~211, 205, 200	77, 119, 152	Tan δ, J''_m	Viscoelasticity	Bulk whole polymer	65–120 100, reduced

TABLE III (*Continued*)

Entanglement length	Ref.	Measurement	Method	Polymer system	Temp., °C.
			Polyamides		
		1. Linear poly(ϵ-caprolactam)sebacic acid			
N_e					
324	34, 45, 49	η vs. M_n	Newtonian flow	Bulk whole polymer	253
		2. Tetra-chain poly(ϵ-caprolactam)sebacic acid			
N_e					
390	34, 45, 49	η vs. M_n	Newtonian flow	Bulk whole polymer	253
		3. Octa-chain poly(ϵ-caprolactam)sebacic acid			
N_e					
550	34, 45, 49	η vs. M_n	Newtonian flow	Bulk whole polymer	253
			Halogen Polymers		
		1. Polyvinyl chloride			
$(NV)_e$					
220, 221, 192, 191, 170, 169, 152, 153	4, 104	η vs. C	Newtonian flow	6.62, 6.67 vol. % M_w whole polymer in cyclohexanone	30
N_e					
132	145	E_2 inflection	E vs. temp.	Bulk polymer	...
			Other Polar Polymers		
		1. Polyvinyl alcohol			
$(NV)_e$					
200	108	η vs. C	Newtonian flow	M_w whole polymer	30
240	108	η vs. M_w	Newtonian flow	1–25 wt. % in water	80
218	108	η vs. M_w			30–80
188	108	η vs. M_w			30
~114	62, 91	η vs. M_v	Newtonian flow	2.9 wt. % whole polymer in water	30
147	102, 105	η vs. C	Newtonian flow	11.5 ⎫	40
195	102, 105	η vs. C	Newtonian flow	8.84 ⎪ vol. %	
340	102, 105	η vs. C	Newtonian flow	7.49 ⎬ M_v whole	
281	102, 105	η vs. C	Newtonian flow	6.75 ⎪ polymer in water	
270	102, 105	η vs. C	Newtonian flow	6.38 ⎭	
245, 130–280	103	η vs. C	Newtonian flow	M_v whole polymer 8.7 wt. % in water	30–40
		2. Polyacrylic acid			
$(NV)_e$					
130	14	η vs. M_v	Non-Newtonian flow	Whole polymer, 0.20 g./ml. in water	20
<830	67	η vs. M_v	Newtonian flow	Whole polymer, 0.20 g./ml. in water	20
			Other Hydrocarbon Polymers		
		1. *cis*-Polybutadiene			
N_c					
~414	39, 55, 69	η vs. M_w	Newtonian flow	Narrow, linear, bulk: 0.1 vinyl; 0.4 *cis*; 0.5 *trans* 1,4	27–107
N_e					
~222	39	$D(t)$ plateau	Tensile creep	Narrow, linear, bulk: 0.1 vinyl; 0.4 *cis*; 0.5 *trans* 1,4	−38 to +27
464	145	E_2 inflection	E vs. temp.	Bulk polymer	...
		2. Polyisoprene			
$(NV)_c$					
824	39	η vs. M_v	Newtonian flow	Narrow distribution polymer 1.82, 3.64, and 14.56 g./100 cc. of decane	25–75
		3. (Atactic) polypropylene			
N_e					
164	145	E_2 inflection	E vs. temp.	Bulk polymer	...

TABLE III (Continued)

Entanglement length N_c	Ref.	Measurement	Method	Polymer system	Temp., °C.
<4300	113	η vs. M_v	Newtonian flow	Bulk whole polymer	204

4. Poly(ethylene–propylene)

N_e					
89	145	E_2 inflection	E vs. temp.	Bulk whole copolymer 2:1	...
31	125	J''_m	Transducer	Bulk whole Copolymer 16:84	−35 to +45
56		J''_m	Transducer	Copolymer 56:44	+25, reduced
43	125	J' inflection	Transducer	Copolymer 70:30	25
70	32	$D(t)$ plateau	Tensile creep	Bulk whole Nordel Terpolymer 53: <47	0, reduced

5. Styrene–butadiene vulcanizate, SBR

N_e					
170	32, 96	$D(t)$ plateau	Tensile creep	Bulk whole copolymer	0, reduced

6. Butyl rubber, soft vulcanized

N_e					
~236	76a, b	E_2 inflection	E vs. temp.	Bulk whole copolymer	...

Additional Polymers

1. Cellulose tributyrate

$(MV)_c$					
~17,000		ΔE^* vs. $M_v V$	Newtonian flow	Fractions to 41 wt. % in 1,2,3-trichloropropane	−5 to +50
~20,000 (24,000 ± 6000)	73, 108	η vs. $M_v V$	Newtonian flow	1,2,3-trichloropropane	25
5000	62, 73	η vs. $M_v V$	Newtonian flow	Fractions to 41 wt. % in 1,2,3-trichloropropane	25

2. Cellulose trinitrate

$(MV)_e$					
~8200	108, 112	ΔE^* vs. C	Newtonian flow	Rough fraction, 2.0–18.2 wt. % in isophorone	35

3. Ethylene tetrasulfide polymer

N_e					
116	145	E_2 inflection	E vs. temp.	Bulk polymer	10

4. Polycarbonate of Bisphenol A, (4-hydroxyphenyl)-2,2'-propane polycarbonate or Lexan or Merlon

N_e					
<613	11	η vs. M_w	Newtonian flow	Bulk fractions and whole polymer	260–316
N_e					
113	88	E_2 inflection	Stress relaxation	Bulk whole polymer	...

This is because measurements have all been made by viscoelastic techniques and on a single polymer of generally ill-defined distribution. The rough range of values, N_e 130–500, depending on technique, has been reported (152). Certain data appear to exhibit two distinct pseudoequilibrium moduli, providing N_e values of 120 and 400 (76a, b). An $(MV)_c$ of 824 has been reported for a synthetic polyisoprene (39).

An N_e of 296* or an M_e ~5000 presumably revised from 4 × 159 and derived from the same data has been reported (77). The factor of four has been included to convert degree of polymerization to chain atoms for this polymer. The N_e values ~539, 500, and 480 (21, 35c, 77) are all based on the same data (19) and should not be weighed individually. Bueche reports that the molecular weight between entanglements is about 9000 or N_e ~539 presumably based on his earlier data (19).

The true N_e for Hevea or natural rubber may be near 300, although present data are far from conclusive. No values have been reported for solutions of Hevea rubber.

E. POLYSTYRENE

The earliest value of Fox and Flory (46, 47, 75), N_c ~962, is considered less accurate than the consistent set of values, N_c 720–731 (35c, 77, 118–120), which is essentially based on the same data (48). Williams has corrected these data (48) for the free-volume change with molecular weight, which occurs only at M <15,000 (149). The sharp break in low shear viscosity at isofree volume occurs at an N_c of 693* or an M_c of 35,000 (50,

149), substantially in agreement with the values from uncorrected data. This result differs significantly, however, from the values for M_c of 31,200 derived by Fox and Allen also for isofree volume conditions (45). The lower value of 600 for N_c is based on data which gave 730 and on new data (1) which alone provided a value of 630. Without definitive reference for method or system, Bueche has suggested about 400 chain atoms between entanglements (19). Yin, Lovell, and Ferry have indicated the rough range 200–600, reported for M_e, depending on technique (152). Several sets of solution data (45, 68, 120) are consistent with the N_c of bulk polymer in units of $(NV)_c$. Onogi claims that for solutions the entanglement composition depends on $(WN^{1/2})_c$ as determined by abrupt changes in viscosity-concentration correlations. Entanglement compositions are noted down to at least a V of 0.04. For the related polymer, poly-α-methylstyrene, at least one entanglement spacing has been calculated. An $(MV)_c$ of about 44,000 has been obtained for 12.5 wt. % polymer in toluene (26d).

F. POLYDIMETHYLSILOXANE

An N_c of 630 for bulk polydimethylsiloxanes has been reported (45) calculated from other data (10, 147). Earlier, Fox and Loshaek (49) reported $\sim$950 based on the same data and also data by Hunter, Warrick, Hyde, and Currie (65). Values cited in ref. 7, 33, 49, 77, 114, and 147 are all based on the same and interrelated data (10, 65, 147). A higher N_c of 1100 has also been reported using part of these same data (10, 147).

Bagley and West have published a value for M_c of 29,000 or N_c of 784* (7). An estimated average from non-Newtonian data at several shear rates is also near 29,000. This value has been widely quoted and is likely near the most probable value. At low rates of shear, however, an N_c as high as 1020 was reported (7).

Entanglement spacings for bulk polymer have been developed essentially from Newtonian flow with fragmentary data by other techniques. No values have been reported for solutions of polydimethylsiloxane.

G. POLYVINYL ACETATE

Fox and Allen (45) have recently reported an N_c of 570*, or M_c of 22,500, considered to be more satisfactory than 680 previously derived (77) from the same data (92). The lower value is also in accord with a recent and definitive value of N_c 512 or M_c 22,000 (98). Two divergent values, 480 and 680, have been calculated and reported (35c, 77) from the same data for the J''_m (150).

H. POLYMETHYL METHACRYLATE

At least three different values for N_e (74 (14), 124 (145), and 204 (35c)) have been derived for polymethyl methacrylate using viscoelastic data reported by Tobol-

sky, et al. (12a, 67, 145). Likewise, an array of values, 88–172 (16, 21, 35c, 45, 77, 128), have been developed for N_e using the same data obtained on bulk fractions at 110–140°. These values, all calculated from the theory of rubber elasticity, are all relatively low. Evaluation of the original data for most of these calculated values indicates that onset of the creep plateau, Figures 5 and 8 (16), actually occurs at an M_c of above 2.04×10^4 and below 3.6×10^5 or N_c 4080–7300. Marvin (81), in discussing the data of McLoughlin and Tobolsky (87), also points out a rubbery plateau is observable in the stress relaxation curve for an undiluted polymethyl methacrylate, M 3.6×10^6, yet is not apparent in the Young's modulus–time curve for a lower molecular weight polymer, M 1.5×10^5. Marvin goes on to point out that the chains in this polymer, N 3000, are "so short that any entanglements present do not persist long enough to be noticed in this fashion." These values are magnitudes higher than those calculated not from the onset but from the height of the plateaus, indicating a gross difference, at least for this polymer, between the entanglement spacings evaluated by rubber elasticity and by the break in rheological behavior.

The N_c for the onset of the plateau is in general accord with an N_c $\sim$10,000 reported for the break in a plot of apparent viscosity vs. M_w (138). These results suggest that for this polymer at least the N_c for the onset of the viscoelastic plateau agrees with the N_c for the break in the plot of log η vs. log M_w. On the other hand, these values exceed grossly, $\sim$10 times, the M_e derived from the theory of rubber elasticity.

One of two sets of solution data (4, 16) providing entanglement spacings has been widely reported, $(NV)_c = 200$–210. Measurements have been given at 60° (16), reported 30–60° (138), and suggested to apply over a range of temperatures. The concept of a constant $(NV)_c$ is substantiated or violated depending on whether comparison is made with the high or low set of values reported for bulk polymer. It is unclear whether the unusual breadth of deviation of values for this polymer is associated with its tendency to absorb water (87). The influence of tacticity is also not resolved and may be particularly important for polymethyl methacrylate, for which T_g and amorphous density are known to be strongly influenced by relative ratios of syndio- and isotactic placement.

I. HIGHER ALKYL METHACRYLATE POLYMERS

The M_e has been reported for a series of methyl methacrylate and n-butyl methacrylate copolymers (146a). A regular increase of M_e with n-butyl methacrylate content is observed.

In the case of solution data of poly-n-butyl methacrylate it is important to note that $(NV)_e$'s calculated from creep compliance and the theory of rubber elas-

ticity agree with values derived by Ferry from the maximum in J'' by the theory of Marvin (94). The agreement does not involve the factor of two times values from J'' which has been used elsewhere by Ferry and co-authors (77), which should give an M_c. Values tabulated here from J''_m are reported as M_e and $(MV)_e$, and are therefore not doubled.

Only data on n-octyl and on n-butyl methacrylates seem to indicate that the N_e from breadth of H and from $J(t)$ inflection agree better with values from J''_m rather than twice these (77). This is also true for corresponding data for E_2 inflection and J''_m on polymethyl acrylate.

In poly-n-dodecyl methacrylate, and related esters, it is of interest to note that side groups comprise by far the major part of molecular volume (71).

J. POLYESTERS

Entanglement chain length has been reported for a compositional series of linear polyesters (49). Two of these values have been recited (45) with the specification of 109° rather than the originally cited range 80–200°. All these values have been derived from the same data, nominally based on end-group determinations (49), which provide M_n. From known distributions of the polymers M_n has been converted to M_w with which rheological data are more generally correlated (42).

Using the two techniques, Newtonian and non-Newtonian flow, Garfield, Petrie, and Vanas (52) have found a considerably higher N_c based on the M_w of a polyester containing pendant groups, polyneopentyl succinate. The values for all linear polyesters are remarkably similar. No entanglement chain lengths have yet been developed for solutions of polyesters.

K. POLYETHERS

Commonly used nomenclature for polyethers is followed in the text. Various terminologies have been suggested which include polyolefin glycol (119), polyoxyolefin glycol (45, 56), and polyolefin oxide (77).

The smallest value, N_e 200, was estimated for polyethylene oxide from two sets of agreeing viscoelastic calculations (77, 152). This value was deemed normal but relatively small (118, 152). It has been doubled to the nearest thousand molecular weight (M_c 6000, N_c 409) (119) for a comparison with the molecular weight at the break in Newtonian and non-Newtonian correlations, N_c ~682 (118). The reference for polyoxypropylene glycol indicates in the text and in a figure M_c values of 8000 and 7000, respectively (56). These bracket (N_c 414, 364) an N_c also cited in the text (56) and recited (45).

L. POLYAMIDES

Entanglement chain lengths for poly(ϵ-caprolactam), $i.e.$, poly(ϵ-caproamide), have been given (45, 49).

Data on structurally related tetra- and octa-chain derivatives have been published (49).

Characteristics of non-Newtonian flow for the linear polyamides, polycaprolactam, and hexamethylene adipamide polymers, suggest an N_c of considerably higher value (121, 148), near 1000, than that reported from Newtonian flow.

M. HALOGEN POLYMERS

Essentially the same entanglement compositions, slightly modified, have been reported twice for a concentration series of polyvinyl chloride in cyclohexanone (4, 104). Compositions obtained from a break in η vs. C plots are said to be more constant in terms of $(N^{1/2}W)_c$ rather than $(NV)_c$. Newtonian-flow solution viscosities represent the only values for polyvinyl chloride; conversely, the only entanglement spacing reported for Teflon was obtained by stress relaxation measurements on bulk polymer (145).

N. OTHER POLAR POLYMERS

Entanglement properties of polar polymers, of necessity, have generally been studied only in solution. Copolymers of acrylonitrile and methyl methacrylate (90:10), at 10 wt. % in aqueous solutions of 48 wt. % NaCNS, indicate an $(MV)_c$ of 7500 by low shear viscometry (26b). Entanglement spacings for polyvinyl alcohol have been determined predominantly from the break in log η–log C plots and also from the break in η–M correlations. Consistent values have been obtained by the two approaches. Spacings are also reported to remain constant in terms NV from 1–25 wt. % in water (108) and to be consistent with a corrected result, $(NV)_c$ 188, for a 36% solution in water (62, 108). It has been reported that spacings increase markedly with temperature for polyvinyl alcohol in water (108).

Onogi and co-workers (101, 103–105) have provided considerable additional viscosity data on aqueous solutions of polyvinyl alcohol. The original data and interpretation have been republished (104, 105, 146). All entanglement compositions were determined from the break in viscosity–concentration plots. The entanglement composition reportedly varies with concentration from 130 to 280 (103) in terms of $(NV)_c$, although the values are generally consistent with results of other workers. It is reported that $(N^{1/2}W)_c$ provides a more constant correlation for entanglement composition (103–105).

O. OTHER HYDROCARBON POLYMERS

Entanglement spacings for polybutadienes have been measured by several techniques (55, 69, 69a, 145). Data on the same linear, narrow distribution polybutadiene series provided an N_c and N_e of about 414 and 222 using the measurements of Newtonian flow and longitudinal creep compliance, respectively.

Entanglement spacings for ethylene–propylene (E–P) rubbers, as measured for several copolymer ratios (125, 145), are surprisingly small. The coupling may be facilitated by some degree of local order. For the highest E–P ratio, 70:30, it has also been suggested that a spacing may be determined by small or incipient crystallites (125).

Dudek and Bueche have reported entanglement compositions for an E–P terpolymer vulcanizate (32). This polymer, Dupont Nordel, is 53% ethylene and contains a nonconjugated diene. N_e was obtained from tensile creep measurements performed at nine temperatures and reduced to 0°. The same procedure was used for SBR, a styrene–butadiene vulcanizate of unspecified monomer ratio (77).

P. ADDITIONAL POLYMERS

It has been reported that viscosity depends on $M_w^{3.4}$ for the polycarbonate of Bisphenol A. This correlation was not, however, carried to a low enough M for deviation; so only an upper limit—M_c 1300 or N_c 613—can be developed (11). A relatively short entanglement spacing, 113, has been reported from viscoelastic measurements (88).

Entanglement chain lengths for cellulose derivatives are not well defined. A range of values M_c 5000–20,000 has been developed (73). It is believed that the tributyrate is more flexible than vinyl polymer chains and the trinitrate derivative yet more so. This may be related to the stronger tendency for cellulose derivatives to entangle (112).

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