30. D.S.Tsiklis, Dokl.Akad.Nauk SSSR, 101, 129 (1955).
31. D.S.Tsiklis and S.M.Khodeeva, Inzh.-Fiz.Zhur., 1, 62 (1958).
32. D.S.Tsiklis and V.Ya.Maslennikova, Dokl.Akad.Nauk SSSR, 161, 645 (1965).
33. D.S.Tsiklis and V.M.Prokhorov, Zhur.Fiz.Khim., 40, 2335 (1966) [Russ.J.Phys.Chem., 1257 (1966)].
34. D.S.Tsiklis and V.M.Prokhorov, Dokl.Akad.Nauk SSSR, in the press.
35. D.S.Tsiklis, V.Ya.Maslennikova, and N.P.Goryunova, Zhur.Fiz.Khim., in the press.
36. V.Ya.Maslennikova, N.P.Goryunova, and D.S.Tsiklis, Dokl.Akad.Nauk SSSR, in the press.
37. A.E.Jones, Thesis, Ohio State University, 1964.
38. I.F.Connoly, J.Chem.Eng.Data, 11, 13 (1966).
39. I.R.Krichevskii and N.E.Khazanova, Zhur.Fiz.Khim., 13, 1690 (1939).
40. R.Wiebe and V.Gaddy, J.Amer.Chem.Soc., 59, 1984 (1937).
41. D.J.Korteweg, Wiener Ber., 98, 1154 (1889); Arch.Neerl., 24, 295 (1891).
42. D.S.Tsiklis and A.A.Zhukhovitskii, Trudy Gos.Nauch.--Issled.i Proekt.Inst.Azoitnoi Prom., No. 8, 7 (1957).
43. V.K.Semenchenko, Zhur.Fiz.Khim., 26, 1337 (1952).
44. D.S.Tsiklis and Yu.N.Vasil'ev, Zhur.Fiz.Khim., 37, 1355 (1963) [Russ.J.Phys.Chem., 720 (1963)].
45. H.Kamerlingh-Onnes, Proc.Sect.Sci.Roy.Acad., Amsterdam, 9, 459 (1906).
46. A.Michels, E.Dumoulin, and J.J.Dijk, Physica, 27, 866 (1961).
47. M.Randall and B.Sosnik, J.Amer.Chem.Soc., 50, 967 (1928).
48. G.Schneider, Ber.Bunsenges.phys.Chem., 70, 497 (1966).
49. W.Shottky, U.Ulich, and C.Wagner, "Thermodynamik", Berlin, 1929.
50. B.F.Dodge, "Chemical Engineering Thermodynamics", McGraw-Hill (Translated into Russian), Inostr.Lit., Moscow, 1950.
51. J.H.Hildebrand and P.L.Scott, "The Solubility of Non-electrolytes", 3rd Edn., New York, 1950.
52. I.Zernike, "Chemical Phase Theory", Antwerp, 1955.
53. P.W.Bridgman, "Recent Work in the Field of High Pressures", Rev.Mod.Phys., 18, 1 (1946) (Translated and supplemented by L.F.Vereshchagina), Inostr.Lit., Moscow, 1948.
54. V.Yu.Urbakh, Zhur.Fiz.Khim., 32, 1163 (1958).
55. I.N.Ostrovskii, Zhur.Fiz.Khim., 37, 942 (1963) [Russ.J.Phys.Chem., 501 (1963)].
56. I.R.Krichevskii and D.S.Tsiklis, Zhur.Fiz.Khim., 32, 1407 (1958); 37, 945 (1963) [Russ.J.Phys.Chem., 503 (1963)]:
57. J.D.van der Waals and P.Kohnstamm, "Lehbuch der Thermostatik" (Translated into Russian), ONTI, Moscow, 1936.
58. S.D.Haman, "Physico-Chemical Effects of Pressure", Butterworth, London, 1957.
59. J.S.Rowlinson, "Liquids and Liquid Mixtures", Butterworth, London, 1959.
60. A.V.Rakovskii, foreword to Ref.57.
61. D.S.Tsiklis, A.I.Kulikova, and A.N.Kofman, Zhur.Fiz.Khim., 37, 1613 (1963) [Russ.J.Phys.Chem., 867 (1963)].
62. A.Kreglewski, Bull.Acad.polon.Sci., Classe III, 5, 662 (1957).
63. K.Schäfer, "Statistische Theorie der Materie", Gottingen, 1960, Vol. I.
64. J.van Dranen, J.Chem.Phys., 20, 1175 (1952).
65. M.I.Temkin, Zhur.Fiz.Khim., 33, 2040 (1959) [Russ.J.Phys.Chem., 275 (1959)].
66. L.A.Rott, Zhur.Fiz.Khim., 36, 2235 (1962); 38, 528 (1964); [Russ.J.Phys.Chem., 1205 (1962); 286 (1964)]; Dokl.Akad.Nauk SSSR, 160, 1140 (1965).
67. R.D.Dunlap and J.H.Simons, J.Chem.Phys., 18, 335 (1950).
68. V.N.Mal'nev and S.I.Pekar, Zhur.Eksper.Teor.Fiz., 51, 1811 (1966).

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NEWTONIAN VISCOSITY OF CONCENTRATED SOLUTIONS OF POLYMERS

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The factors which influence the irreversible flow of high-molecular compounds and of their concentrated solutions have attracted increasing attention in recent years because of their relevance to current problems in the technology of polymer fabrication. However, the study of viscoelastic properties in polymers is important not only as a route to formulating the scientific foundations of technology: it can also provide valuable information on the nature and on the rates of conformational changes in macromolecules and also on their mutual arrangement (i.e. on the structure of the polymer and of its solution[1]).

Studies of the rheological properties of concentrated solutions of polymers began in the 1930's, when it was shown[2-4] that the anomalous flow of polymer solutions (and of the polymers themselves) arises from the interplay of elastic (reversible) deformations and viscous (irreversible) flow. It was subsequently shown[5] that relaxation phenomena are associated with the elastic deformations. Thus, concentrated polymer solutions give rise to a viscoelastic system: to investigate these solutions we must separate reversible from irreversible deformations, and also examine the rate of shear as a function of stress over a wide range of these parameters.

For polymer solutions of intermediate concentration this function gives, when plotted on logarithmic coordinates, a characteristic S-shaped curve with linear lower and upper sections at 45° to the horizontal axis[6] (Fig. 1).

Over these sections of the plot (i.e. in the regions of small or large shear rates or stresses) the viscosity coefficient is constant and the flow is Newtonian. The viscosities corresponding to the two linear sections are usually termed the maximum and the minimum Newtonian viscosity. It should be noted that with very concentrated solutions of high polymers, and with melts, the upper linear section (Fig. 1) is not observed: hence, most of the published values for the maximum Newtonian viscosity have been measured at insufficiently high stresses and shear rates. However, in many systems the viscosity depends on the applied shear stress even under these conditions, as can most clearly be seen by plotting the logarithm of the viscosity against the logarithm of the stress[7]. In this case the Newtonian viscosity is obtained by extrapolation to zero stress or to zero shear rate.

Low stresses cannot break down the structures present in melts or in solutions: hence, the Newtonian viscosity at low shear rates describes the flow of the solution without any disturbance of its structure. In this sense, studies of the Newtonian viscosity of polymer solutions are a very

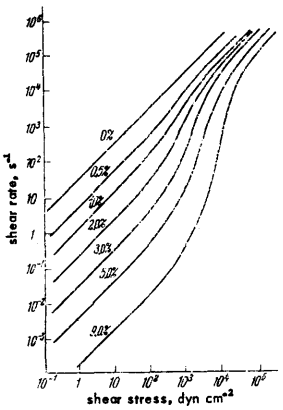


Fig. 1. Flow curves for solutions of polyisobutylene in decalin[6]. The numbers by the curves denote solution concentration.

important method of characterising their structure, particularly since direct structural examination of the solution (e.g. by electron microscopy) presents serious difficulty. At the same time, an extensive investigation by Vinogradov and coworkers[8,9] has shown that the maximum Newtonian viscosity has a fundamental significance, since it can be used as a normalising factor for a number of rheological characteristics.

Studies of the maximum Newtonian viscosity indicate that the flow mechanism of polymers and of their concentrated solutions is a general one. Hence it may be desirable to review briefly the main experimental and theoretical advances in the study of the viscosity of these polymers. Recent progress in this field is due mainly to the work of Kargin, Rebinder, Slominskii, Bartenev, Vinogradov, Trapeznikov, Ferry, Flory, Fox, Bueche, and others.

By generalising the large fund of experimental results obtained in recent years, two fundamental empirical relations have been derived, which relate the viscosity coefficient of a polymer (η) to the molecular weight (M)[10,11] and to temperature[12] respectively. Thus, for a large number of quite different polymers the plot of $\log\eta = f(\log M)$ consists of two intersecting straight lines whose point of intersection corresponds to a critical value of the molecular weight, M_c. Polymers for which $M > M_c$ obey the equation

$$\log\eta = 3.4\log Z + C, \qquad (1)$$

where Z is the degree of polymerisation and C is a constant. The second universal relation, known as the Williams, Landel, and Ferry (WLF) equation[12], states that the temperature dependence of the viscosity of polymeric substances can also be described by a universal empirical equation:

$$\log a_T = \log\frac{\eta_T \rho_S T_S}{\eta_S \rho_T T} = -\frac{C_1^0 (T - T_S)}{C_2^0 + T - T_S}, \qquad (2)$$

where η_T and ρ_T are the viscosity and the density of the polymer at the given temperature T, whilst η_S and ρ_S are the viscosity and the density of the polymer at the standard temperature T_S (reference temperature), chosen so as to make the plots of $\log a_T = f(T - T_S)$ for the different polymers coincide; C_1^0 and C_2^0 are coefficients dependent on the nature of the polymer and on the reference temperature. For polyisobutylene $T_S = 243°K$, $C_1^0 = 8.86$, and $C_2^0 = 101.6$. For other systems these coefficients are retained and the reference temperature is varied.

Eqn. (2) is applicable over the temperature range from the glass transition temperature T_g to $T_g + 100°$. Under these conditions the ratio $\rho_S T_S/\rho_T T$ is close to unity. Hence $\log a_T \simeq \log \eta_T/\eta_S$.

If the reference temperature is defined as the glass transition temperature of the experimental material, Eqn. (2) becomes universally applicable to polymers and low-molecular glass-forming liquids:

$$\log a_T = \log\frac{\eta}{\eta_g} = -\frac{17.44\,(T - T_g)}{51.6 + T - T_g}, \qquad (3)$$

where η_g is the viscosity at the glass transition temperature.

The glass point is the most convenient reference temperature because it can be determined for each polymer by an independent method, but measurements of viscosity and other mechanical properties are difficult to make in the neighbourhood of T_g. A temperature approximately 50° higher than the glass point is therefore commonly used: $T_S = T_g + 50°$.

Eqn. (2) is a particular case of the temperature dependence of any viscoelastic property, and demonstrates the principle of temperature–time superposition first formulated for polymers by Aleksandrov and Lazurkin[5]. Essentially, the principle states that temperature and the time of application (frequency) of a force play identical roles because the deformation shows a relaxation behaviour. Therefore, plots of the property against temperature can be mutually superimposed by shifting them along the temperature axis. This means that the ratio of the relaxation times (τ_r) at two temperatures is a constant:

$$\frac{(\tau_r)_T}{(\tau_r)_{T_S}} = a_T = \frac{\eta_1 \rho_S T_S}{\eta_S \rho T}.$$

Thus, the Newtonian viscosity is directly related to the relaxation time of the system.

Eqns. (1) and (2) can also be derived theoretically, starting from the fundamental postulates of the theory of the viscous flow of liquids and polymers.

Since liquids occupy a position intermediate between gases and solids, the liquid state has been treated from the point of view of both these states. At the turn of the century liquids were discussed by analogy with gases. X-Ray diffraction studies of simple liquids revealed the existence of ordered regions and gave rise to the hypothesis of a quasi-crystalline liquid structure. In reality, the liquid state is qualitatively different from the others, and can be described by means of the radial density distribution function[13].

Contemporary statistical theories of the liquid state are of two kinds: (a) the more accurate and more complicated theories based on studies of molecular distribution functions, and (b) the less accurate but simpler "lattice" theories or "free volume" theories, based on the concept of a quasi-crystalline liquid structure.

The idea of "free volume" in a liquid is not entirely unequivocal. Thus, in the statistical theory of liquids this term denotes a complex integral which can be evaluated to give a "mean" volume within which the "average" molecule is able to move freely at a given temperature. This "free volume" does not actually exist in a liquid: it is a fictitious

quantity which appears in statistical calculations as a result of the particular method of approximation used[13]. Yet, a number of workers have attempted to ascribe a physical significance to this term. Most of them interpret liquid free volume as empty regions between molecules, i.e. as voids or "holes" of molecular (monomer) dimensions arising from irregularities in packing[1]. Frenkel'[14] showed by thermodynamic arguments that molecular voids (vacancies) can exist also in real crystals. However, the free volume in crystals is different in nature from the free volume in liquids. Crystal free volume is due to asymmetry in the vibrations of the particles, and its distribution among the particles is continuous (Fig. 2*a*). This is the so-called vibrational volume. Liquid free volume consists of two parts: 1) a continuous part, also associated with the vibrations of the particles in the liquid, and 2) a discrete part, due to voids (Fig. 2*b*). The latter enables the particles to undergo continuous place exchange, i.e. the "holes" in a liquid are fluctuating entities[14,15].

The free volume of a substance is difficult to measure. Most commonly, the free volume v_f of a liquid or a crystal is determined as the difference between the specific volume of the material at the given temperature (v_{sp}) and at the absolute zero (v_0), the latter being obtained by extrapolating to $T \to 0$ the linear plot of $v_{sp} = f(T)$ (Fig. 3):

$$v_f = v_{SP} - v_0. \tag{4}$$

As the free volume increases, the specific volume of the liquid also increases: the major contribution to the thermal expansion coefficient of a liquid is the increase of free volume with increase of temperature.

The internal friction of liquids depends on the free volume, since relative movement of the molecules is made possible by the presence of free space between the molecules. This relation was first pointed out by Bachinskii[16], who proposed the equation

$$\eta = \frac{C}{v - w}, \tag{5}$$

where v is the specific volume of the liquid and w is the arithmetic mean of the volumes of 1 g of the liquid at the given temperature and at the freezing point. The difference $v - w$ was termed the "free" volume. If we write Eqn. (5) in the form

$$v = w + \frac{C}{\eta} \tag{6}$$

it is obvious that the plot of $v = f(1/\eta)$ at any given temperature should be a straight line not passing through the origin: this was confirmed for 66 different liquids. Associated liquids do not obey Eqn. (6).

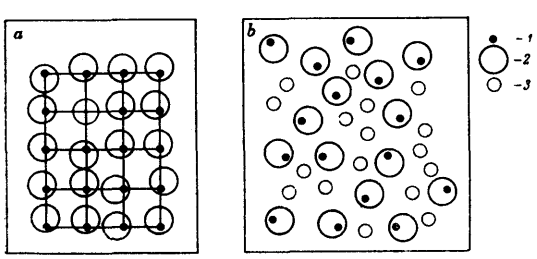


Fig. 2. Schematic representation of free volume[15]: (*a*) crystal; (*b*) liquid; 1) molecules, 2) vibrational volume of molecules, 3) "holes".

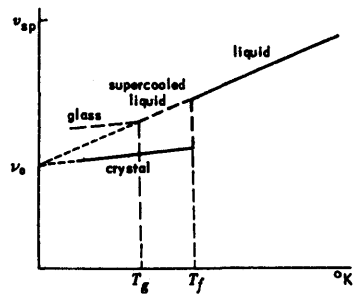


Fig. 3. $v-T$ diagram for a substance in the condensed phase.[15]

More recently, Doolittle[17] proposed another empirical equation for the viscosity of a liquid:

$$\ln \eta = \ln A + B\frac{v_0}{v_f}, \tag{7}$$

where v_0 and v_f are the occupied and the free volume respectively.

Eqn. (7) may be written in the form

$$\eta = A\, e^{Bv_0/v_f}. \tag{8}$$

It is interesting to note that the temperature does not appear explicitly in Eqns. (5) and (7). This is one of the most fundamental aspects of the modern theory of viscous flow, which is treated as a process made up of the activated jumps of individual elementary units of flow from one equilibrium position to another. The jumping frequency is controlled by the height of a potential barrier, and is denoted by the symbol I.

The activation theory of liquid flow, proposed by Frenkel'[14] and developed by Eyring and others[18], leads to the following expression for the temperature dependence of viscosity:

$$\eta = \frac{N_A h}{V} e^{\Delta G_{visc}/RT}, \tag{9}$$

where V is the molar volume of the liquid, ΔG_{visc} is the free energy of activation of the viscous flow of one mole of molecules passing from one equilibrium position to another. If we write $\Delta G_{visc} = \Delta H_{visc} - T\Delta S_{visc}$, Eqn. (9) takes the form

$$\eta = \frac{N_A h}{V} e^{\frac{-\Delta S_{visc}}{R}} e^{\frac{\Delta H_{visc}}{RT}} \tag{10}$$

The plot of $\log \eta = f(1/T)$ is thus a straight line whose slope is a measure of the quantity ΔH_{visc}, the heat of activation of the viscous flow. This quantity is determined by the temperature coefficient of viscosity. ΔS_{visc} is the entropy of activation of the viscous flow.

Experimental observations have shown that Eqns. (9) and (10) apply only over a narrow range of temperatures. Over a wider temperature interval the plot of $\log \eta = f(1/T)$ is curvilinear, and Kobeko suggests that the curvature of this plot is a characteristic of the liquid state[19]. From plots of this type one calculates the so-called apparent heat of activation of viscous flow:

$$\Delta H_{visc} = \frac{d \ln \eta}{R\, d\,(1/T)}, \tag{11}$$

which is itself a function of temperature. It can be shown theoretically that the heat of activation of viscous flow is

related to the temperature coefficient of the molecular jumping frequency I and also to the temperature coefficient of the free volume [20]:

$$\Delta H_{visc} = -R\left[\frac{\partial \ln I}{\partial (1/T)}\right]_{v_f} - R\left(\frac{\partial \ln I}{\partial v_f}\right)\left[\frac{\partial v_f}{\partial (1/T)}\right]. \quad (12)$$

Thus, the decrease of liquid viscosity with increase of temperature stems from two distinct causes: 1) the increase in jumping frequency and 2) the increase in free volume.

All these conclusions of the theory of the viscous flow of liquids are used in discussions of polymer flow. It is assumed that the elementary unit of flow is a portion (or segment) of the polymer chain rather than the entire chain. Chain segments are interconnected by valence bonds, and they interact with the segments of neighbouring chains, so that their motions are not mutually independent. The viscosity of the polymer is given as the product of two quantities: a function of the chain length $F(Z)$ and the reciprocal of the jumping frequency I:

$$\eta = \frac{F(Z)}{I}. \quad (13)$$

The form of the function $F(Z)$ is the same for all polymers: it allows for the interaction between units, and is independent of temperature. The jumping frequency depends both on temperature and on the local disposition of the units (i.e. on the free volume). The greater the free volume, the greater are the specific volume and the jumping frequency I, and the lower is the viscosity of the liquid or polymer [20].

Free volume considerations have proved very fruitful in bringing about an understanding of the viscous flow of polymers. Thus, it became clear that the quantity a_T in the WLF Eqn. (2) is related to the free volume of the polymer, and that the equation itself can be deduced theoretically from Doolittle's equation [1,12]. The expression obtained is indistinguishable from the WLF equation if the fractional free volume at the glass point is taken as $f = 0.025$, and the thermal expansion coefficient as $\alpha = 4.8 \times 10^{-4}$ deg^{-1}.

Bueche [21,22] also used free volume considerations, and proposed that the resistance to flow of a polymer arises from: (1) friction of the segments of the polymer chain as it moves relatively to its neighbours; (2) interaction between the segments joined by primary valence bonds into a long chain; (3) interlocking of the chains with formation of a network structure. If the chain consists of N monomer units and ζ_0 is the molecular (monomeric) friction factor, related to I (the number of jumps of the unit) and to δ (the average change in the position of its centre of gravity) by the expression

$$\zeta_0 = \frac{6kT}{I\delta^2}; \quad (14)$$

the viscosity coefficient is given by

$$\eta = FN\zeta_0, \quad (15)$$

where the proportionality coefficient F depends on the molecular weight of the polymer.

When $M > M_c$ (see p. 362)

$$\eta = k'M\rho\zeta_0; \quad (16)$$

when $M < M_c$

$$\eta = kM^{3.5}\rho^4\zeta_0 \quad (17)$$

where ρ is the density of the polymer, k' and k are constants.

I. CONCENTRATED SOLUTIONS OF POLYMERS

The term concentrated usually denotes solutions in which the solute molecules can interact with each other. In polymer solutions interactions of this type give rise to a steep increase in viscosity as compared with the viscosity of the pure solvent. Ferry [1] proposed that polymer solutions should be called concentrated if their relative viscosity is of the order of 100 or more. The lower concentration limit of the polymer can vary from 1% (for unusually long, rigid chains) to 10% (for flexible polymers of low molecular weight). The upper limit is the undiluted polymer.

Studies over a wide range of concentration, temperature, polymer chain length, and solvent type can lead to significant advances in establishing the relationships which govern the viscosity of concentrated polymer solutions.

1. Effect of Concentration

Up to the year 1960 our understanding of the isothermal concentration dependence of the viscosity of polymer solutions was limited, because most of the data then available related to a narrow concentration range. Thus, owing to experimental difficulties, most of the workers studied the viscosity of polymer solutions in the concentration range up to 0.2 [23-46] or 0.5 [47-52] weight fraction of the polymer.

Far fewer papers have dealt with the viscosity of solutions over the whole or most of the concentration range [53-58], but in recent years such papers have appeared in increasing numbers [60-69].

The viscosity of a solution varies with concentration as shown by the curves of Fig. 4. For solutions of polymers of fairly high molecular weight, and at low concentrations of the polymer, the curve is convex towards the ordinate axis. On further increasing the concentration the viscosity increases more slowly. A steeper rise sets in again when very concentrated polymer solutions are held near the glass point of the polymer. This effect is due to the rapid decrease of the relative free volume [70].

There have been repeated attempts to establish analytically the relation between the viscosity and the concentration of the solution. Thus, Flory [54] studied the viscosity

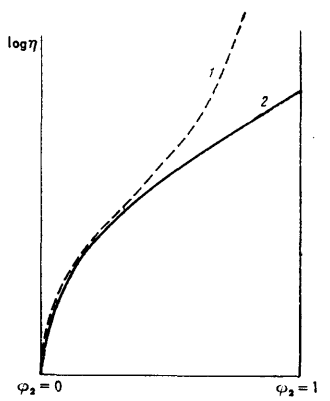


Fig. 4. Variation of solution viscosity with concentration:
1) solutions of glassy polymers; 2) solutions of elastic polymers.

of solutions of poly(decamethylene adipate) over the entire composition range from pure solvent to the pure polymer, and showed that above 0.1 weight fraction of the polymer the viscosity varies with concentration according to the equation

$$\log\eta = A + B\omega_2^{1/2} \quad (18)$$

where ω_2 is the weight fraction of dissolved polymer, and A and B are constants. Eqn. (18) can be obtained from the equation relating the viscosity of a polymer melt to its molecular weight[71] by treating the solvent molecules as short polymer chains. Hence it was concluded that the mechanism of flow of concentrated polymer solutions is analogous to that of the polymers themselves: in the flow of concentrated solutions also the polymeric chains move as a result of the motion of their individual segments. Eqn. (18) was confirmed experimentally by the work of Spencer and Williams[47] on the viscosity of polystyrene solutions in the concentration range between 0 and 0.5, and also by an investigation[25] of the viscosity of butadiene–styrene rubber solutions in the concentration range between 0.10 and 0.19 weight fraction of the polymer. It was not confirmed, however, over a wider range of concentrations[48-51] for solutions of poly(vinyl acetate), polyisobutylene, and polystyrene.

Attempts were made to apply to the flow of concentrated polymer solutions the equation derived by Martin for the flow of dilute solutions of polymers[26,47]:

$$\log\frac{\eta_{sp}}{C} = \log[\eta] + K[\eta]C \quad (19)$$

where C is the concentration, $[\eta]$ is the characteristic viscosity, and K is a constant.

It follows from the reported measurements that Eqn. (19) satisfactorily describes the experimental results of the authors only if the concentration does not exceed 0.12 weight fraction of the polymer.

All the equations given above are empirical. There are now a number of theoretical equations for the concentration dependence of the viscosity of polymer solutions, derived on the basis of the fundamental concepts discussed above and on the assumption that dilution decreases the relaxation times of the system and the monomer friction coefficients.

In a solution, each monomer unit of a polymer chain is surrounded both by the units of neighbouring chains and by solvent molecules, the latter being able to move much more readily than the former. Hence, introducing small molecules whose motion (unlike that of the segments of molecular chains) immediately produces irreversible structural changes is enough to raise the fluidity, i.e. to lower the viscosity of the system[72].

The theoretical interpretation of the dilution of a polymer system is usually that the decrease in viscosity stems from the increase in free volume brought about by the introduction of the solvent. The following arguments are generally used: (1) the free volume of the solvent is greater than that of the polymer; (2) the volume of the solution is an additive function of the volumes of the components; (3) the free volume of the solution is the sum of the free volumes of the components:

$$v = v_1 + v_2 \quad (20)$$

where v, v_1, and v_2 are the volumes of the solution, the solvent, and the polymer respectively, and

$$v_f = (v_f)_1 + (v_f)_2 \quad (21)$$

where v_f, $(v_f)_2$ are the mean free volumes of the solution and the polymer (at the same temperature), and $(v_f)_1$ is the newly formed free volume resulting from the addition of solvent. Two attempts to derive the concentration dependence of the viscosity of polymer solutions have been reported. The first is due to Fujita and Kishimoto[73], who assumed that $(v_f)_1$ increases when the volume of solvent is increased, but is also a function of concentration and of temperature. If $(v_f)_1$ is assumed to be a function of temperature only, Eqn. (21) takes the form

$$v_f = (v_f)_2 + \gamma(T)v_1, \quad (22)$$

where $\gamma(T)$ is a function which characterises the particular polymer–solvent system.

Dividing Eqn. (22) by Eqn. (20) we obtain an expression for the relative free volume of the solution:

$$f = \frac{v_f}{v} = \frac{(v_f)_2}{v_2} + \left[\gamma(T) - \frac{(v_f)_2}{v_2}\right]\varphi_1, \quad (23)$$

where φ_1 is the volume fraction of solvent in the solution.

The ratio $(v_f)_2/v_2$ is the relative free volume of the polymer at temperature T, and it can be expressed in the form $f(T, 0)$ at $\varphi_1 = 0$ if the free volume of the solution is described by the function $f(T, \varphi_1)$. Eqn. (23) can then be written

$$f(T, \varphi_1) = f(T, 0) + \beta'(T)\varphi_1, \quad (24)$$

where

$$\beta'(T) = \gamma(T) - f(T, 0). \quad (25)$$

Using Eqns. (7) and (8) for T = const, the authors arrive at an expression of the form

$$-\frac{1}{\ln a_C} = f(T, \varphi_1^*) + \frac{f(T, \varphi_1^*)}{\beta'(T)}\cdot\frac{1}{\varphi_1 - \varphi_1^*} \quad (26)$$

$$a_C = \frac{\eta(T, \varphi_1)(1 - \varphi_1^*)}{\eta(T, \varphi_1^*)(1 - \varphi_1)}, \quad (26a)$$

where $\eta(T, \varphi_1)$ and $\eta(T, \varphi_1^*)$ are the viscosity coefficients of solutions for which the volume fractions of the first component are φ_1 and φ_1^* (chosen as a standard solution), $f(T, \varphi_1^*)$ is the free volume of the solution of standard concentration, and $\beta'(T)$ is a function which can be calculated from Eqn. (25).

It follows from Eqn. (26) that the plot of $\frac{1}{\ln a_C} = f\left(\frac{1}{\varphi_1 - \varphi_1^*}\right)$ should be a straight line whose slope is a measure of $\beta'(T)$ and whose intercept on the ordinate axis gives the value of $f(T, \varphi_1^*)$. The standard state can be defined as a solution of any arbitrary concentration, or the pure polymer.

The authors tested their equation with the following systems: polystyrene–diethylbenzene[56], polystyrene–dibenzyl ether[20], polystyrene–decalin[51], poly(methyl methacrylate)–diethyl phthalate[58], and poly(methyl acrylate)–diethyl phthalate[66].

Eqn. (26) holds for very concentrated solutions, and departures from linearity are observed when $\varphi_1 > 0.5$. The slope of the straight line increases with temperature, i.e. the quantity $\beta'(T)$ varies, and therefore also $\gamma(T)$, which (as was to be expected) has different values for different systems. The function $f(T, 0)$, i.e. the relative free volume of the polymer itself, calculated from the intercept of the straight line on the ordinate axis, is constant for a given polymer. Its temperature dependence can be approximated by two straight lines intersecting at the glass point of the polymer. Quantities calculated from Eqn. (26) for the polystyrene–ethylbenzene[65] and polyisobutylene–toluene[64]

systems are plotted in Fig. 5. Minor departures from linearity can be observed for the first system at $\varphi_1 > 0.5$, whereas for the second system Eqn. (26) is obeyed over practically the whole of the concentration range.

The second attempt to derive a theoretical equation for the concentration dependence of the viscosity of a polymer solution is due to Kelley and Bueche[74], and is based on similar premises. The authors express the relative free volume of the polymer and of the solution at a given temperature T in the form

$$v_{f_2}/v_2 = 0.025 + 4.8 \times 10^{-4}(T - T_g). \quad (27)$$

and

$$v_{f_1}/v_1 = 0.025 + \alpha_S(T - T'_g) \quad (27a)$$

where 0.025 is the relative free volume of the material at T_g; 4.8×10^{-4} deg^{-1} is the temperature coefficient of the relative free volume of the polymer (see p. 364); α_S is the temperature coefficient of the relative free volume of the solvent, which for liquids is of the order of 10^{-3} deg^{-1}, T_g and T'_g are the glass points of the polymer and the solvent respectively. Assuming additivity of the free volumes, the following expression is obtained for the relative free volume of the solution:

$$v_f/v = \varphi_2[0.025 + 4.8 \times 10^{-4}(T - T_g)] + (1 - \varphi_2)[0.025 + \alpha_S(T - T'_g)]. \quad (28)$$

Using Eqns. (8) and (17) the authors arrive at an expression for the viscosity of the solution:

$$\log \eta/B = 4 \log \rho[\varphi_2[0.025 + 4.8 \times 10^{-4}(T - T_g)] + (1 - \varphi_2)[0.025 + \alpha_S(T - T'_g)]]^{-4}, \quad (29)$$

where ρ is the density or concentration by weight of the polymer in solution, φ_1 and φ_2 are the volume fractions of the solvent and of the polymer, η is the viscosity of the solution, and B is a parameter which includes the molecular weight of the polymer.

The authors tested the validity of Eqn. (29) on the following systems: polystyrene–diethylbenzene[56], poly(methyl methacrylate)–diethyl phthalate[57], and polyisobutylene–xylene[50]. For the first of these systems, taking T'_g = = -110°, good agreement was found between theory and experiment. The agreement was good also for the third system at 25° (T'_g = -50°) and for the second system at 120° and 140° (T'_g = -65°). At 60° the second system showed significant discrepancies between theory and experiment.

Calculated and experimental data for the polystyrene–ethylbenzene, polystyrene–decalin[65], and polyisobutylene–toluene[64] systems are reproduced in Fig. 6. The experimental points for the latter system lie on the theoretical

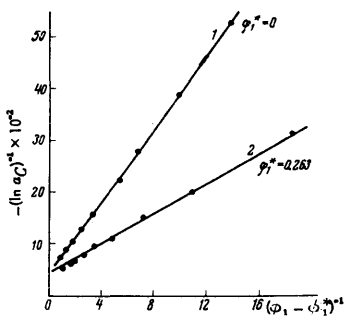


Fig. 5. Plot of $\ln a_C = f(\varphi_1)$ at 20°: 1) polyisobutylene–toluene; 2) polystyrene–ethylbenzene.

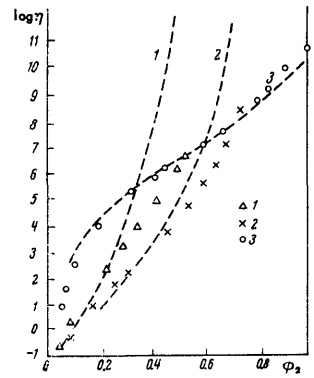


Fig. 6. Variation of viscosity with volume fraction of the polymer in solution at 20°: 1) polystyrene–decalin; 2) polystyrene–ethylbenzene; 3) polyisobutylene–toluene. The broken curves were calculated theoretically using Eqn. (29).

curve, whereas for the first two systems the theoretical and the experimental curves do not coincide.

The better agreement between theory and experiment at temperatures above the glass point of the polymer itself is striking, and cannot be fortuitous. It arises from the fact that the packing density of the macromolecules of polymers in the elastic state is very close to that of molecules of their low-molecular-weight analogues[75]. Hence there is practically no contraction when polymers such as polyisobutylene are mixed with iso-octane or other similar liquids of low molecular weight[76]. In systems of this type the principle of additivity of free volumes, which underlies the theoretical treatments, is valid to a first approximation. But it is very doubtful whether this principle can be applied to solutions of glassy polymers, particularly those which are loosely packed, and which undergo considerable contraction on dissolution[76]. Also, Eqns. (27) are evidently generally applicable only at temperatures above T_g for the polymer[1].

2. Variation of the Viscosity of Solutions with the Molecular Weight of the Dissolved Polymer

The early investigations of the viscosity of concentrated polymer solutions were made over a narrow range of molecular weights of the polymer: from 8.6×10^4 to 1.0×10^5,[47] or from 0.32×10^6 to 1.10×10^6.[50] Under these conditions Ferry showed that the viscosity of the solutions varied as the 3.4th power of the molecular weight of the polyisobutylene.

Bueche's papers describe a detailed study of the influence of the molecular weight of polymers on the viscosity of their concentrated solutions. This worker examined 15 polystyrene fractions (molecular weights between 5.0×10^4 and 10×10^6 [58]) and 14 fractions of poly(methyl methacrylate) covering molecular weights from 5.0×10^3 to 5.0×10^6,[57] at two concentration levels and one concentration level respectively. He showed that the variation of the logarithm of viscosity with the logarithm of chain length for a polystyrene solution of concentration 0.44 and a poly(methyl methacrylate) solution of concentration 0.25 weight fraction of the polymer is expressed, as in the case of the polymer itself,

by two intersecting straight lines. The lines corresponding to the longer chains are steeper and all have the same slope of 3.4, i.e. they are described by Eqn. (1). It was subsequently found that the viscosity data for solutions of polyacrylonitrile [44,46] and poly(vinyl alcohol) [29,33] are also described by this equation. The variation of viscosity with chain length of the dissolved polymer was established over wide concentration limits in the work of Porter and Johnson [59,77] and of Tager and coworkers [63]. Fig. 7 shows the results obtained for solutions of 7 samples of polyisobutylene of molecular weight between 0.9×10^3 and 1.2×10^6. It is obvious from the figure that in the concentration range which was investigated (from 0.05 volume fraction of the polymer upwards) the variation is described by two intersecting straight lines. The slope of the lines corresponding to the higher values of molecular weight is independent of the concentration of the solution, but the slope of the left-hand branches (corresponding to low molecular weights) increases with concentration. The slope of the right-hand branches is 3.4, i.e. these lines obey Eqn. (1). In agreement with Bueche's theoretical predictions [56] (p. 364) and with his data for polystyrene solutions, both the straight lines and their points of intersection are shifted towards larger Z values by decreasing the concentration of the polyisobutylene solution. However, the product of the critical chain length Z_C (given by the intersection of the straight lines) and of the concentration of the solution remains approximately constant (see Table).

The value of the product of critical chain length and concentration depends on the nature of the dissolved polymer: the more rigid the polymer chain, the lower is $Z_C\varphi_2$. Thus, values of 180 and 80 have been reported for solutions of polyisobutylene [63,69] and of poly(vinyl alcohol) [33] respectively. The same investigations reveal that Z_C varies with temperature and that increase of temperature causes a slight increase in the value of $Z_C\varphi_2$.

Ferry and coworkers [51,52] found that the viscosity of solutions of polyisobutylene, cellulose trinitrate, and cellulose tributyrate, when referred to the viscosity of the solvent, is a unique function of the product $Z^{3.4}\varphi_2^5$: the curves

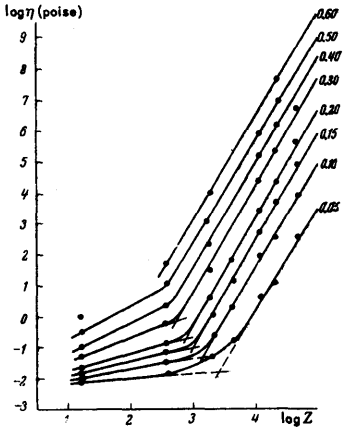


Fig. 7. Variation of the viscosity of polyisobutylene solutions in iso-octane with degree of polymerisation of the polymer [63]. The numbers by the straight lines denote the volume fraction of polyisobutylene in solution.

TABLE. Product of the critical chain length Z_C and of the volume fraction of the polymer φ_2 for polyisobutylene solutions in iso-octane at 20°. [69]

φ_2	$Z_C\varphi_2$	φ_2	$Z_C\varphi_2$
0.05	140	0.30	210
0.10	160	0.40	200
0.15	150	0.50	180
0.20	140		

for solutions of all three polymers coincide. This relationship was shown to be valid also for solutions of poly(vinyl alcohol) [33]. However, the authors themselves point out that the expression does not apply at high concentrations [51]. Tests of the expression over a wide range of concentrations and molecular weights of dissolved polymer, using solutions of polyisobutylene [69] and poly(methyl methacrylate) [66], showed that the expression does not hold.

3. Effect of Temperature on the Viscosity of Polymer Solutions

Most investigations of the viscosity of concentrated polymer solutions have been confined to a fairly narrow temperature interval of 40–60° [25,27,28,36,37,47-51,62-65,78,79], and only a few studies [56,57,66-68] have dealt with temperature changes of 100–200°. The results indicate that over a 40–60° temperature interval the logarithm of the viscosity varies linearly with reciprocal temperature, but over a wider range of temperatures non-linearity sets in, and the curvature increases with the concentration of the solution (Fig. 8).

As we have already pointed out, curvature in the plot of $\log\eta = f(1/T)$ is associated with the nature of the liquid state [19]. A similar variation of the logarithm of the viscosity is found with low-molecular liquids, their solutions, and polymer melts and solutions. Measurements of specific heat, mechanical properties, volume changes, and viscosity indicate that the molecules of a multicomponent liquid form a single continuous system [19].

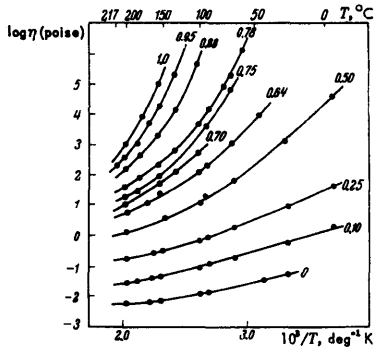


Fig. 8. Temperature dependence of the viscosity of polystyrene solutions in dibenzyl ether [20]. The numbers by the curves denote the weight fraction of the polymer in solution.

A concentrated solution of a polymer is also a single continuous system, differing from the polymer itself by having shorter relaxation times. Since the nearest neighbours of the polymer segments are solvent molecules, mutual friction takes place, and the jumps of segments and small molecules alike require a definite activation energy. Hence the term "energy" or "heat of activation" can be applied to concentrated solutions of polymers just as it can to the polymers themselves. (Very dilute solutions of polymers are an exception, and involve a radically different friction mechanism[80].) These terms are applied to concentrated solutions of polymers[48,52,56,57] and to plasticised systems[72].

The heat of activation for viscous flow depends on the concentration of the solution. It increases with increasing volume fraction of the polymer: linearly over a relatively narrow concentration range (from $\varphi_2 = 0.05$ to $\varphi_2 = 0.5$)[27,28,36,37,47,49] and non-linearly over a wider range of compositions[56,57,62-65]. It can be seen from Fig. 9 that the heat of activation for flow rises most steeply at high concentrations for solutions of polymers close to the glassy state: at $\varphi_2 = 1$ (polymer), ΔH_{visc} is of the order of hundreds of kilocalories per mole.

The slope of the function $\log\eta = f(1/T)$ increases when the material (or the solution concentration) is changed because the intermolecular interaction energy increases[19], as a result (in the present case) of a decrease in the free volume, or of approaching the glass point of very concentrated solutions[70].

The heat of activation for the flow of a solution depends also on the molecular weight of the dissolved polymer: this was demonstrated for solutions of cellulose tributyrate[52] and of poly(vinyl alcohol)[33,46], which were investigated over the composition range up to $\omega_2 = 0.40$ and $\omega_2 = 0.25$ respectively. Measurements were made over the whole composition range and a wide range of molecular weights for solutions of polyisobutylene[63,77]: the results are shown in Fig. 10. For not too high concentrations ($\varphi_2 < 0.35$) the heat of activation increases with the molecular weight of the polymer; at concentrations $\varphi_2 > 0.35$ we find a sharp increase in ΔH_{visc} on going from $M = 10^2$ (iso-octane) to 0.9×10^3 (from 1.9 to 14.5 kcal mole^{-1}).

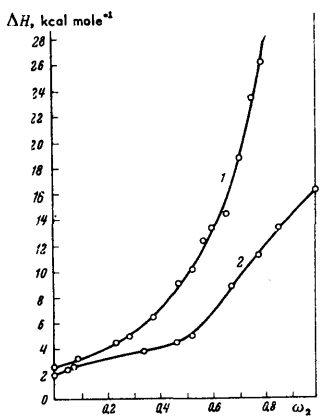


Fig. 9. Variation of the heat of activation for viscous flow with weight fraction of the polymer in solution:
1) polystyrene–diethylbenzene[56]; 2) polyisobutylene–toluene.[64]

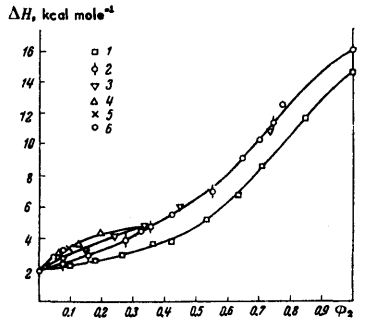


Fig. 10. Concentration dependence of the heats of activation for viscous flow of polyisobutylene solutions in iso-octane[63]:
1) $M = 0.9 \times 10^3$; 2) $M = 2.0 \times 10^4$; 3) $M = 1.1 \times 10^5$; 4) $M = 2.4 \times 10^5$; 5) $M = 6.5 \times 10^5$; 6) $M = 1.2 \times 10^6$.

Increasing the molecular weight of the polymer from 0.9×10^3 to 2×10^4 raises ΔH_{visc} by 1.6 kcal mole^{-1} (from 14.5 to 16.1). Further increase of molecular weight has no effect on the heat of activation for viscous flow.

The lack of dependence of the heat of activation for the flow of concentrated polymer solutions upon the molecular weight of the dissolved polymer, like the general validity of Eqn. (1), argues for a general mechanism of flow in polymers and their concentrated solutions. Hence we may suggest that other relationships, derived for the flow of polymers, should also be valid for solutions of polymers. Thus, Ferry[1] states that the temperature dependence of the viscosity of concentrated solutions of polystyrene, poly(vinyl chloride), poly(vinyl acetate), and cellulose tributyrate is satisfactorily described by the WLF equation.

A similar relationship was recently proposed[67] for polymer solutions: the equation obtained is

$$-\frac{T-T_0}{\log a_T} = \frac{[f(\varphi_1,T_0)]^2}{a_f(\varphi_1)} + (T-T_0)f(\varphi_1 T_0) \qquad (30)$$

where T and T_0 are the experimental and the reference temperature respectively; $f(\varphi_1, T_0)$ is the relative free volume of a solution of the given concentration φ_1 at the reference temperature T_0; $a_T = \eta(\varphi_1, T)/\eta(\varphi_1, T_0)$, and $a_f(\varphi_1)$ is a function of concentration. The plot of $-(T - T_0)/\log a_T = f(T)$ is a straight line whose slope measures $f(\varphi_1, T_0)$ and whose intercept on the ordinate axis measures $a_f(\varphi_1)$. The linearity of this function was confirmed in the poly(n-butyl methacrylate)–diethyl phthalate system.

4. Effect of the Nature of the Solvent on the Viscosity of Polymer Solutions

The effect of the nature of the solvent on the viscosity of concentrated solutions of polymers has been least thoroughly investigated, in spite of the essential relevance of intermolecular interaction and of its influence on all rheological properties. As already stated, the addition of small, readily mobile molecules to a polymer causes a dramatic increase in the fluidity and free volume of the system. Hence we can suggest that the addition of solvents and plasticisers to a polymer should affect the viscosity and all related properties in direct proportion to the volume fraction of the solvent and irrespectively of the nature of the solvent: the same conclusion follows also from a number of

theoretical equations. The earliest studies of the problem appeared to confirm this point of view. Thus, Ferry and coworkers[49-51] examined solutions of poly(vinyl acetate) in five solvents, of polyisobutylene in two solvents, and of polystyrene in two solvents up to weight fractions of the polymer of $\omega_2 = 0.5-0.6$, and showed that the viscosities are similar at a given volume fraction, but differ if the solutions are compared at a given weight fraction†.

The influence of the nature of the solvent on the viscosity of polymer solutions has been studied also by other workers[26,38,42,47,59], but either over a limited concentration range or over a limited range of solvents. A detailed study of the problem was made with solutions of polyisobutylene in six chemically different liquids, and of polystyrene in five liquids, over a wide range of compositions and at temperatures between 20° and 50°.[62,64,65,69] It was shown that even the viscosity of solutions of a polymer as elastic as polyisobutylene, whose chains contain only groups of a single type, depends on the nature of the solvent. The effect of solvent on the viscosity of polymer solutions is specially marked when the polymer is close to T_g under the conditions of the experiment. Thus, the viscosities of decalin and ethylbenzene solutions of atactic polystyrene at 20° and equal volume fractions differ by a factor of several hundreds.

With rise in temperature the concentration–viscosity curves of solutions in different solvents tend to coalesce, and at temperatures above T_g for polystyrene the viscosities of decalin and ethylbenzene solutions differ only by the viscosity difference between the solvents themselves.

The fall of viscosity with increase of temperature is not the same in solutions in different solvents: in other words, the heat of activation for viscous flow also depends on the nature of the solvent. It is important to note that the order of the plots of $\log\eta = f(C)$ and $\Delta H_{visc} = f(C)$ is the same, both for polyisobutylene and for polystyrene solutions. This suggests that the viscosity of concentrated solutions of polymers, like the viscosity of low-molecular liquids and their mixtures, is determined by the heat of activation for flow[19].

Several workers have suggested[26,42,49-51] that the viscosity of a polymer solution is controlled by the viscosity of the solvent. Thus, there is evidence[62,64,65,69] that the viscosity of the solution is highest in the most viscous solvent and lowest in the least viscous solvent. However, the viscosities of decalin and toluene (or ethylbenzene) at 20° differ by about a factor of 5, as compared with a factor of 12 for polyisobutylene solutions and a factor of several hundreds for polystyrene solutions in these solvents. Hence, viscosity differences between solutions of polymers depend on the viscosity of the solvent but are not wholly determined by it. The basic reason for differences in fluidity of solutions in different solvents is component interaction. Therefore it is very important to compare viscosities with parameters which characterise the interaction: as far as possible, the comparison should apply to the same concentration region.

† It may be useful to stress that when comparing any property of solutions in different solvents one should not use weight fractions, since their value depends on the density of the liquid. The concentration of the solution should be given in mole or volume fractions. Using the former units we compare the solutions at a constant concentration of solvent molecules, using the latter units we compare them at a constant degree of filling of space by different solvents. With a property such as viscosity it is more correct to compare solutions of equal volume fraction.

We must first of all consider the thermodynamic affinity between the polymer and the solvent, measured by the chemical potential difference $\Delta\mu_1$ or by the second virial coefficient A_2. Experimentally measured values of $\Delta\mu_1$ and A_2 show that iso-octane is a good solvent for polyisobutylene whereas butyl propionate is a poor solvent[81]. In the composition range between $\varphi_2 = 0.5$ and $\varphi_2 = 1$ the viscosity coefficients of polyisobutylene solutions in the two solvents are identical. Decalin is a poor solvent for polystyrene, whereas ethylbenzene is a good solvent. In the former the viscosity and the heat of activation are much higher than in the latter. But ethyl acetate also is a poor solvent for polystyrene, yet the viscosities of ethyl acetate and ethylbenzene solutions are very similar. Thus, there is no correlation between the viscosity coefficient of a solution and the thermodynamic affinity of the polymer for the solvent. Hence, it is not generally correct to assume, over a wide concentration range, that the viscosity or the heat of activation of a solution in a thermodynamically more active solvent must be higher (or lower) than in a poor solvent.

It must be noted that no correlation is observed between viscosity and the heat of dissolution (i.e. the enthalpy change). Knowing the differences in chemical potential of a component, $\Delta\bar{\mu}_i$, and its partial enthalpy, $\Delta\bar{H}_i$, we can calculate the partial entropy of mixing, $\Delta\bar{S}_i$:

$$\Delta\bar{\mu}_i = \Delta\bar{H}_i - T\Delta\bar{S}_i. \qquad (31)$$

The entropy of mixing is largely determined by the flexibility of the polymer chain[72,75]. When flexible polymers are dissolved the partial entropy of mixing of the solvent $\Delta\bar{S}_i$ is always greater than in the dissolution of polymers with rigid chains, since in the former case the number of configurations which the chains can adopt in solution (and therefore also the thermodynamic probability of the solution) is greater than in the latter.

For polyisobutylene solutions, the values of $\Delta\bar{S}_i$, which characterise the flexibility of the polymer chain, decrease along the following series of solvents: toluene > CCl_4 > > iso-octane ≃ cyclohexane[81].

Thus, in solutions of elastic polymers solvent interactions take the form of changes in the flexibility of the chain. The viscosity of the solution is lowest in the solvent which makes the polymer chain most flexible, as was to be expected from the general theoretical considerations outlined above. However, the viscosity of the solvent itself also plays a role, and on occasions these two factors can be mutually opposing. Thus, the viscosity of CCl_4 is greater than that of iso-octane by about a factor of two, but the polyisobutylene chain is less flexible in iso-octane solutions than in CCl_4. The two factors cancel each other out, and the two solutions have identical viscosities.

At elevated temperatures the rate [amplitude?] of the torsional vibrations of the units increases: the kinetic flexibility of the polymer chain increases, the whole set of conformations becomes available[82], and the influence of the nature of the solvent becomes less marked. At a certain temperature, solutions of equal φ_2 in solvents of equal viscosities have the same viscosity. This is very clearly seen for solutions of polyethylene at $T > T_f$: the viscosities of solutions in decalin, dodecane, xylene, and monochlorobenzene lie on a common curve[69].

Thus, we can make the following statement regarding the viscosity of polymer solutions at experimental temperatures higher than T_g: the lower the viscosity of the

solvent and the greater the flexibility of the polymer chain in that solvent, the lower will be the viscosity of the solution.

The situation is a great deal more complicated when T_g for the dissolved polymer is significantly higher than the experimental temperature: this is particularly true of polymers with polar side-chain substituents which interact strongly both with each other and with the solvent molecules. In this case it is impossible to explain the effect of solvent on the viscosity of concentrated polymer solutions without detailed consideration of the structure of solutions.

II. NEWTONIAN VISCOSITY AND STRUCTURE OF THE SOLUTIONS

Studies of the viscous, optical, and other properties of very dilute polymer solutions show that the individual macromolecules have a coiled, globular form, and can move independently of each other[80]. This model applies only to very dilute solutions; when the concentration is increased the molecules begin to interact. The problem, therefore, is to identify the concentration at which these interactions set in and the configuration of the interacting molecules.

As long ago as in 1931 Staudinger[83] proposed the idea of a "critical" concentration, i.e. a concentration at which rod-shaped polymer molecules begin to touch. Boyer and Spencer[84] prefer to redefine the "critical concentration" as the concentration at which a random distribution of globular molecules becomes close packed. Their calculations show that the critical concentration depends on the molecular weight of the polymer and on the nature of the solvent. Thus, for solutions of polystyrene in benzene C_{crit} (g/100 ml) = $= 30.6M^{-1/2}$, whilst for solutions of polystyrene in ethyl methyl ketone $C_{crit} = 69.1M^{-1/2}$. When the molecular weight is $\sim 10^6$, $C_{crit} = 0.03-0.06$ g/100 ml (i.e. is very small). Using modified Ostwald viscometers with very narrow capillaries (d = 0.2 mm and 1600–3900 s outflow time for the pure solvent), Streeter and Boyer[85] observed anomalies in the viscosity at high dilutions. Their results show that the corrected viscosity varies linearly with concentration only down to 0.1 g/100 ml: further dilution gives a sharp upward bend in the curve, and still further dilution (below C = 0.002 g/100 ml) makes the curve bend down again, forming a maximum. Critical concentration values of 0.03–0.07% were obtained from these experiments[85], but subsequent work failed to confirm the results. Thus, Frank[86] did not observe any anomalies in the concentration dependence of the light-scattering asymmetry of the same solutions. Öhrn suggested[87], as a result of his calculations, that the phenomena observed by Boyer and coworkers were due to adsorption of polymer molecules on the viscometer walls, resulting in a decrease in diameter as well as a decrease in concentration. By working with a viscometer provided with three capillaries of different diameters he found that the largest anomalies are observed with the narrowest capillaries. Batzer's studies[88] of the viscosity of poly(vinyl chloride) solutions with different degrees of chain branching support this explanation. Therefore we must conclude that the effects observed by Streeter and Boyer have no bearing on the existence of a critical concentration.

Interest in this problem has been renewed in recent years. Horth and Rinfret[89] studied the concentration dependence of the density of poly(vinyl acetate) solutions, and concluded that a "critical" concentration exists, varying from 0.75 to 0.09 g/100 ml as the molecular weight varies from 80 000 to 3 200 000. From their measurements of the concentration dependence of the heat of mixing of poly(vinyl acetate) with methanol and tetrachloroethane Parent and Rinfret[90] obtained appreciably lower values of the critical concentration (φ_2 = 0.02–0.005).

We feel that the term "critical" is an unfortunate one, because the properties of the solutions as a rule do not vary discontinuously with concentration. The so-called singular points on property–composition curves are due to the presence of specific interactions between the components[91]. Experimental observations of density discontinuities at a strictly defined concentration are also unconvincing: no discontinuities were observed in analogous measurements on polystyrene and polyisobutylene solutions[76]. What is undeniable, however, is that the macromolecules begin to interact at some definite level of concentration which must be a function of the molecular weight of the polymer and of the nature of the solvent: under these conditions the solutions contain aggregates or associations of molecules rather than individual molecules. Polymer association effects have been discussed even in dilute solutions[92–95]. The interaction forces will depend, of course, on the nature of the polymer and of the solvent: dipole–dipole interaction predominates in poly(vinyl chloride) solutions in polar solvents, whilst in solutions of polybutadienes in octane or chloroform dispersion interactions are predominant. The latter are quite substantial if allowance is made for the increase in polarisability with molecular length. But this interaction is invariably present, and associations are formed.

It remains to be established what these associations consist of, how the macromolecules are distributed within the associations, and what is the configuration of the macromolecules. Boyer and Spencer assumed, in their first paper, that the globular molecules remain unchanged in form when they come into contact, but they were subsequently forced to postulate unwinding or uncoiling during interaction. The view that uncoiling must take place when the macromolecules interact follows directly from our knowledge of the structure of the polymers themselves, which are often prepared by concentrating their solutions. With the exception of a few ("globular") polymers, the polymers themselves do not contain unchanged globular formations. According to the views current until very recently, an amorphous polymer consists of a conglomeration of entangled, more or less straight, molecular chains, whereas in a crystalline polymer ordered regions alternate with regions of entangled chains. The entangled chain model was adopted in the theory of the viscosity of concentrated solutions, whose basic postulate is that all the chains are mutually intertwined as in a ball of tangled threads. The number of interlocks increases with the molecular weight of the polymer.

However, as Kargin and coworkers were the first to point out[96], the concept of tangled chains does not apply to a real polymer. Very large numbers of so-called supermolecular structures have been reported in polymers, and it has been shown that even in the amorphous state polymers have an ordered bundle-like structure[97]. The formation of bundles of chains, observed in amorphous polymers, must be preceded by uncoiling and mutual orientation of the chains.

Since very dilute solutions contain globular molecules whereas in the polymers themselves the chains are rela-

tively straight, the first effect must be an unfolding or uncoiling of the globular molecule as the solution becomes more concentrated: this has been confirmed by an electron-microscopic study of poly-α-butylene solutions[98]. Colophony (a substance whose glass point is above room temperature) was used as the solvent, thus enabling the structure of the solution to be "frozen" during the investigation. It was found that in poly-α-butylene solutions of concentration 0.1–0.5%, the molecules have a linear configuration and interact with each other to give appreciably ordered formations. These experiments suggest that individual globular molecules are to be found only in the more dilute solutions.

Unfortunately, it is impossible at present to examine the structure of the more concentrated solutions in the electron microscope, and therefore the indirect methods of investigation such as light scattering and viscosity studies play an important role. The first indications of the uncoiling of chains in polyelectrolyte solutions with increase of concentration and of degree of ionisation came from viscosity studies[99]. Zubov and Lipatov explain the sharp increase in viscosity obtained by concentrating aqueous solutions of poly(methacrylic acid) by postulating uncoiling of molecular chains and the formation of supermolecular structures[100]. A similar unfolding of globular molecules occurs in solutions of polymeric non-electrolytes.

Recently, an attempt was made[101] to estimate the shape of interacting macromolecules by comparing the concentration dependence of the relative viscosity of polymer solutions with that of suspensions of rigid spherical particles. It was concluded that the ratio $\log\eta_{rel}/C$ (where η_{rel} is the relative viscosity) increases gradually with the former, but decreases with the latter, when the concentration increases. The author[101] ascribes this difference to different interaction mechanisms. The collision of two rigid spheres produces a "dumb-bell", which contributes to the viscosity more than each isolated sphere. On the other hand, when two polymeric molecules collide, molecular aggregates are formed, and these contribute less to the viscosity than the two separate macromolecules. The papers by Maron and coworkers[102,103] contain similar conclusions, from viscosity data, on the change in shape of interacting particles.

Thus, when the concentration of a polymer solution is increased the globular molecules unfold, and the chains, more or less straightened, begin to interact. This is accompanied by a sharp increase in light scattering by the solution, which decreases, however, when the concentration is increased still further[104].

In the concentration region where light scattering decreases, the viscosity rises steeply, evidently due to the formation of a continuous disordered network in the solution. However, this network is composed of aggregates of more or less linear chains rather than of interlocking and entangled long molecular chains. Interlocking of macromolecules in solutions is as unlikely as it is in polymers, because it would be inconsistent with the observed rapid establishment of equilibrium in solutions following temperature or concentration changes. The relaxation time of chains is very large, and unravelling processes should be exceedingly slow. In practice (in the neighbourhood of a phase separation temperature, say) a turbid solution becomes instantly transparent, corresponding to the appearance of a maximum on the viscosity polytherm[105,106]. This is evidence that the solution contains aggregates which can rapidly regroup in response to a temperature change.

When the concentration of the solution is increased the degree of aggregation also increases, the network becomes more ordered, and fluctuations in concentration decrease. This is accompanied by a continuous increase in viscosity and by a decrease in the intensity of excess light scattering.

The non-linearity of the changes in heat of activation for the viscous flow of polymer solutions and the sharp increase of ΔH_{visc} at $\varphi_2 > 0.5$ are evidence for the existence of a concentration region in which interactions between chains are very strong. In this region of compositions we are evidently dealing with the highly ordered supermolecular structures which are found in the polymers themselves.

Hirai has derived[107], on the basis of the concept of bundles or "beams" of chains in solutions, a theoretical equation for the dependence of the heat of activation for viscous flow upon concentration and molecular weight of the polymer: this equation corresponds exactly to the experimental curves shown in Fig. 10.

Thus, the whole of the available experimental data on the viscosity and light scattering properties of concentrated polymer solutions points to the existence, in polymer solutions, of a number of concentration regions with different degrees of order and chain conformations: (1) the region of dilute solutions, in which the globular molecules become uncoiled and form aggregates as φ_2 is increased; (2) the concentration region in which the aggregates combine into a continuous network whose degree of order increases with φ_2; (3) the region of very concentrated solutions, in which highly ordered supermolecular structures are formed. All the transitions are reversible both towards concentration and towards dilution.

Thus, when a polymer comes into contact with a low-molecular liquid the molecules of the latter penetrate only between the ordered supermolecular structures (interbundle swelling). This is true whether the liquid is a good solvent or a poor solvent. According to the size of the solvent molecules, and to their affinity for the polymer, disintegration of the bundles may occur in different ways; hence the size of the supermolecular structures at a given value of φ_2 depends on the nature of the solvent. In decalin solutions of polystyrene the bundles do not break down appreciably, whilst in ethylbenzene solutions substantial disintegration occurs: the viscosity of the former solutions at 25° is much greater than that of the latter. In the high concentration region the viscosity of polyisobutylene solutions is the same in a good solvent (iso-octane) as in a poor solvent (butyl propionate). This also suggests that the molecules of these liquids penetrate only between the bundles, whose existence has been proved for the case of rubber-like polymers[108]. Butyl propionate cannot penetrate into the bundles and the swelling is limited. Iso-octane can enter the bundles, so that the latter disintegrate and the degree of ordering decreases. At a definite concentration (which is lower the better the solvent) the molecules begin to break apart and only at very low concentrations can we expect isolated globular macromolecules to form.

All that has been said agrees satisfactorily with Kargin and Kozlov's recent views[109,110] on interbundle plasticising, and is in keeping with a general flow mechanism common to polymers and their solutions. According to generally accepted ideas, based on the fact that polymers and low-molecular liquids have very similar heats of activation for viscous flow, the elementary unit of flow of a polymer is a

chain segment. However, the heats of activation [fluidity?] of polymers and of their concentrated solutions are higher than those of liquids by one order of magnitude, and those of glassy polymers are higher by two orders of magnitude. This suggests that the jumps involve portions of a bundle rather than individual segments, i.e. that the viscous-flow properties are determined by the collective motion of chains[1].

1. J.D. Ferry, "Viscoelastic Properties of Polymers" (Translated into Russian), Inostr. Lit., Moscow, 1963.
2. W. Philippoff, Kolloid Z., 71, 7 (1935).
3. W. Philippoff and K. Hess, Ber., 70, 639 (1937).
4. E. Jenkel and K. Ueberreiter, Z. phys. Chem., A182, 361 (1938).
5. A. P. Aleksandrov and Yu. S. Lazurkin, Zhur. Tekh. Fiz., 9, 1250 (1939).
6. J. D. Brodnyan, F. H. Gaskins, and W. Philippoff, Trans. Soc. Rheol., 1, 109 (1957).
7. G. M. Bartenev, Vysokomol. Soed., 6, 2155 (1964).
8. G. V. Vinogradov, A. Ya. Malkin, N. V. Prozorovskaya, and V. A. Kargin, Dokl. Akad. Nauk SSSR, 150, 574 (1963); 154, 890 (1964).
9. A. Ya. Malkin and G. V. Vinogradov, Kolloid. Zhur., 27, 234 (1965).
10. T. G. Fox and P. J. Flory, J. Phys. Colloid. Chem., 55, 221 (1951).
11. T. G. Fox and S. Loshaek, J. Appl. Phys., 26, 1080 (1955).
12. M. L. Williams. R. F. Landel, and J. D. Ferry, J. Amer. Chem. Soc., 77, 3701 (1955):
13. I. Z. Fisher, "Statisticheskaya Teoriya Zhidkostei" (Statistical Theory of Liquids), GIFML, Moscow, 1961.
14. A. Ya. Frenkel', "Sobranie Izbrannykh Trudov" (Collection of Selected Works), Vol. 3, Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1959.
15. G. Kanig, Kolloid Z., 190, 1 (1963).
16. A. I. Bachinskii, Z. phys. Chem., 84, 643 (1913).
17. A. K. Doolittle, J. Appl. Phys., 22, 1471 (1951); 23, 236 (1952).
18. S. Glasstone, K. Laidler, and M. Eyring, "The Theory of Rate Processes" (Translated into Russian), Inostr. Lit., Moscow, 1948.
19. P. P. Kobeko, "Amorfyne Veshchestva" (Amorphous Materials), Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1952.
20. T. G. Fox, S. Gratch, and S. Loshaek, in "Rheology" (F. Eirich, Editor) (Translated into Russian), Inostr. Lit., Moscow, 1962, Ch. 12.
21. F. Bueche, J. Chem. Phys., 20, 1959 (1952); 25, 599 (1956); J. Polymer Sci., 43, 527 (1960).
22. F. Bueche, "Physical Properties of Polymers" Interscience, New York–London, 1962.
23. P. A. Rebinder and A. S. Kolbanovskaya, Kolloid. Zhur., 12, 194 (1950).
24. A. B. Bestul and H. V. Belcher, J. Colloid Sci., 5, 303 (1950).
25. L. H. Cragg, L. M. Faichney, and H. T. Olds, Canad. J. Res., 26B, 551 (1948).
26. D. J. Streeter and R. F. Boyer, Ind. Eng. Chem., 43, 1791 (1951).
27. D. J. Plazek and J. D. Ferry, J. Phys. Chem., 60, 289 (1956).
28. M. Katayama and K. Sakaba, Chem. High Polymers (Japan), 13, 152 (1956).
29. S. Onogi, J. Hamana, and H. Hirai, J. Appl. Phys., 29, 1503 (1958).
30. J. Sone and J. Sakurada, Chem. High Polymers (Japan), 10, 206 (1953).
31. M. Matsumoto and J. Oyanagi, J. Polymer Sci., 26, 389 (1957).
32. J. Oyanagi, Chem. High Polymers (Japan), 15, 31 (1958).
33. J. Oyanagi and M. Matsumoto, J. Colloid Sci., 17, 426 (1962).
34. T. I. Zatsepina and A. A. Trapeznikov, Vysokomol. Soed., 3, 113 (1961).
35. A. A. Trapeznikov and T. V. Assonova, Kolloid. Zhur., 21, 485 (1959).
36. E. A. Pakshver, B. E. Geller, and G. V. Vinogradov, Khim. Volokna, No. 2, 21 (1959).
37. V. K. Pshedetskaya and B. E. Geller, Khim. Volokna, No. 2, 15 (1961).
38. B. E. Geller, "Khimiya i Tekhnologiya Khlorinovogo Volokna" (Chemistry and Technology of Chlorinated PVC Fibres), Gizlegrpom., Moscow, 1958.
39. Yu. S. Lipatov and P. I. Zubov, Vysokomol. Soed., 1, 88 (1959).
40. Yu. S. Lipatov and P. I. Zubov, Vysokomol. Soed., 1, 432 (1959).
41. Yu. S. Lipatov and P. I. Zubov, Vysokomol. Soed., 1, 1655 (1959).
42 K. S. Akhmedov and I. N. Shpilevskaya, Uzbek. Khim. Zhur., No. 2, 19 (1960).
43. I. N. Shpilevskaya, Abstract of Thesis, Tashkent, 1961.
44. M. Takahashi, Chem. High Polymers (Japan), 19, 16 (1962).
45. H. Asai, Chem. High Polymers (Japan), 19, 19 (1962).
46. S. Yugushi, Chem. High Polymers (Japan), 19, 113 (1962).
47. R. S. Spencer and J. L. Williams, J. Colloid Sci., 2, 115 (1947).
48. J. D. Ferry, J. Amer. Chem. Soc., 64, 1330 (1942).
49. J. D. Ferry, E. L. Foster, G. V. Browning, and W. M. Sawyer, J. Colloid Sci., 6, 378 (1951).
50. M. F. Johnson, W. W. Evans, J. Jordan, and J. D. Ferry, J. Colloid Sci., 7, 498 (1952).
51. J. D. Ferry, L. D. Grandine, Jnr., and D. C. Udy, J. Colloid Sci., 8, 529 (1953).
52. R. F. Landel, J. W. Berge, and J. D. Ferry, J. Colloid Sci., 12, 400 (1957).
53. L. V. Ivanova-Chumakova and P. A. Rebinder, Kolloid. Zhur., 18, 429 (1956).
54. P. J. Flory, J. Phys. Chem., 46, 870 (1942).
55. A. B. Bestul, H. V. Belcher, F. A. Quinn, Jnr., and C. V. Bryant, Kolloid. Zhur., 56, 432 (1952).
56. F. Bueche, J. Appl. Phys., 24, 423 (1953).
57. F. Bueche, J. Appl. Phys., 26, 738 (1955).
58. F. Bueche, J. Appl. Phys., 30, 1114 (1959).
59. R. S. Porter and J. F. Johnson, J. Polymer Sci., 50, 379 (1961).
60. H. Nakayasi and T. G. Fox. Trans. Soc. Rheol., 5, 381 (1961).
61. W. F. Busse and R. Longworth, J. Polymer Sci., 58, 49 (1962).
62. A. A. Tager and V. E. Dreval', Dokl. Akad. Nauk SSSR, 145, 136 (1962).
63. A. A. Tager, V. E. Dreval', and N. G. Trayanova, Dokl. Akad. Nauk SSSR, 151, 140 (1963).
64. A. A. Tager, V. E. Dreval', and F. A Khasina, Vysokomol. Soed., 5, 432 (1963).
65. V. E. Dreval', A. A. Tager, and A. S. Fomina, Vysokomol. Soed., 5, 1404 (1963).
66. H. Fujita and E. Maekawa, J. Phys. Chem., 66, 1053 (1962).
67. A. Teramoto, R. Okada, and H. Fujita, J. Phys. Chem., 67, 1228 (1963).
68. S. Kishimoto, J. Polymer Sci., A2, 1421 (1964).
69. V. E. Dreval', Thesis, Sverdlovsk, 1963.
70. T. G. Fox and P. J. Flory, J. Appl. Phys., 21, 581 (1950).
71. T. G, Fox and P. J. Flory, J. Amer. Chem. Soc., 62, 3113 (1940).
72. V. A. Kargin and G. L. Slonimskii, "Kratkie Ocherki po Fiziko-Khimii Polimerov" (Synopsis of the Physical Chemistry of Polymers), Izd. Moskov. Univ., Moscow, 1960.
73. H. Fujita and A. Kishimoto, J. Chem. Phys., 34, 393 (1961).
74. F. N. Kelley and F. Bueche, J. Polymer Sci., 50, 549 (1961).
75. A. A. Tager, "Fiziko-Khimiya Polimerov" (Physical Chemistry of Polymers), Goskhimizdat, Moscow, 1963.

76. A.A.Tager, A.Smirnova, and N.Sysueva, Nauch.Dokl.Vys. Shkoly, Khim.i Khim.Tekhnol., No. 1, 135 (1958).
77. R.S.Porter and J.F.Johnson, Polymer, 3, 11 (1962).
78. R.Naito, J.Ukida, and T.Komianami, Chem.High Polymers (Japan), 14, 117 (1957).
79. R.Naito, Chem.High Polymers (Japan), 15, 191, 195 (1958).
80. V.N.Tsvetkov, V.E.Eskin, and S.Ya.Frenkel', "Struktura Makromolekul v Rastvorakh" (Structure of Macromolecules in Solution), Izd.Nauka, Moscow, 1964.
81. A.A.Tager, M.V.Tsilipotkina, V.E.Dreval', and O.V.Nechaeva, Vysokomol.Soed., 5, 94 (1963).
82. G.M.Pavlyuchenko, T.V.Gatovskaya, V.A.Berestnev, and V.A.Kargin, Vysokomol.Soed., 6, 1190 (1964); Dokl.Akad. Nauk SSSR, 143, 590 (1962).
83. H.Staudinger, "Die hochmolekularen organischen Verbindungen" (Translated into Russian), ONTI, Khimteoret, Leningrad, 1935, p.184.
84. R.F.Boyer and R.S.Spencer, J.Polymer Sci., 5, 375 (1950).
85. D.J.Streeter and R.F.Boyer, J.Polymer Sci., 14, 5 (1954).
86. H.R.Frank, J.Polymer Sci., 17, 130 (1955).
87. O.E.Öhrn, J.Polymer Sci., 17, 137 (1955).
88. H.Batzer, Markromol.Chem., 12, 145 (1954).
89. A.Horth and M.Rinfret, J.Amer.Chem.Soc., 77, 503 (1955).
90. M.Parent and M.Rinfret, Canad.J.Chem., 33, 971 (1955).
91. V.Ya.Anosov and S.A.Pogodin, "Osnovnye Nachala Fiziko-Khimicheskogo Analiza" (Basic Principles of Physicochemical Analysis), Izd.Akad.Nauk SSSR, Moscow-Leningrad, 1947.
92. S.Newman, W.R.Krigbaum, and D.K.Carpenter, J.Phys. Chem., 60, 648 (1956).
93. P.Trementozzi, J.Polymer Sci , 36, 113 (1959).
94. I.Ya.Poddubnyi, E.G.Erenburg, E.P.Chernova-Ivanova, and G.G.Kartashova, Dokl.Akad.Nauk SSSR, 148, 384 (1963).
95. J.Henstenberg and E.Schuch, Makromol.Chem., 74, 55 (1964).
96. V.A.Kargin, A.I.Kitaigorodskii, and G.L.Slonimskii, Kolloid.Zhur., 19, 131 (1957).
97. V.A.Kargin, "Sovremennye Problemy Nauki po Polimerakh" (Contemporary Problems in Polymer Science), Izd.Moskov. Univ., Moscow, 1963.
98. V.A.Kargin, S.Kh.Fakirov, and N.F.Bakeev, Dokl.Akad. Nauk SSSR, 159, 885 (1964).
99. A.Katchalsky, J.Polymer Sci., 6, 145 (1951); 7, 393 (1951); 12, 159 (1954).
100. Yu.S.Lipatov, P.I.Zubov, and E.A.Andryushchenko, Kolloid.Zhur., 21, 598 (1959).
101. T.Gillespie, J.Polymer Sci., C1, 31 (1963).
102. S.H.Maron, N.Nakajama, and J.M.Krieger, J.Polymer Sci., 37, 1 (1959).
103. S.H.Maron and T.T.Chiu, J.Polymer Sci., A1, 2051 (1963).
104. A.A.Tager, V.M.Andreeva, and E.M.Evsina, Vysokomol. Soed., 6, 1901 (1964).
105. P.Debye, B.Chu, and D.Woermann, J.Polymer Sci., A1, 249 (1963).
106. A.A.Tager, V.E.Dreval', and K.T.Khabarova, Vysokomol. Soed., 6, 1593 (1964).
107. N.Hirai, J.Polymer Sci., 39, 435 (1959); 40, 255 (1959).
108. V.A.Kargin, V.G.Zhuravleva, and Z.Ya.Berestneva, Dokl. Akad.Nauk SSSR, 144, 1089 (1962).
109. P.V.Kozlov, V.G.Timofeeva, and V.A.Kargin, Dokl.Akad. Nauk SSSR, 148, 886 (1963).
110. P.V.Kozlov, Zhur.Vses.Khim.Obshch.im.Mendeleeva, 9, 660 (1964).

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