DILUTE SOLUTION PROPERTIES OF POLYOCTENE 1

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ABSTRACT

DILUTE SOLUTION PROPERTIES OF POLYOCTENE-1

by Larry E. Ballard

A sample of atactic polyoctene-1 was fractionated and characterized by light scattering, osmometry, viscometry and, phase equilibria measurements.

Three molecular weight-viscosity relationships were established by correlating molecular weights determined by light scattering with viscosity data. They are

in cyclohexane at 30°C [η] = 5.75 x 10⁻⁵ M^{0.78}

in bromobenzene at 25°C [η] = 2.90 x 10⁻⁵ M^{0.78}

in phenyl ethyl ether at 50.4°C [η] = 6.54 x 10⁻⁴ M^{0.50}.

Mean square end-to-end dimensions of the polymer in bromobenzene were calculated from light scattering data by the Zimm method as well as Debye's dissymmetry technique. The universal hydrodynamic parameter Φ from polymer viscosity theory was calculated and found to agree very well with the commonly accepted value.

From phase study data, the theta temperature of the polymer in phenyl ethyl ether was found equal to $50.4^{\circ}C$.

A comparison of the ratio of the average end-to-end dimensions to the degree of polymerization for a series of poly α -olefins was made. It was found that the ratios were in the order polystyrene > polyoctene-1 > polybutene > polypropylene \approx polyisobutylene. This indicates the dimensions are proportional to the size of the pendant groups. The lower critical solution temperatures for a series of solutions of polyoctene-1 fractions in n-pentane were measured. It was found that the precipitation temperature could be related to the molecular weight through the Flory interaction parameter, X_1 .

A plot of the lower critical solution temperatures against $1/x^{1/2}$ gave a straight line. The intercept of this line at infinite molecular weight, i.e., $1/x^{1/2} = 0$, was defined as Θ_L , that is, the lower critical miscibility temperature for polymer of infinite molecular weight. The Θ_L for polyoctene-1 in n-pentane was found experimentally equal to 434° K and was calculated from a relationship based on the Prigogine cell model of solutions (assuming $\boldsymbol{\chi}_{1_C} = 0.50$) to be 437° K.

DILUTE SOLUTION PROPERTIES OF POLYOCTENE-1

By

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INTRODUCTION

Since it was first demonstrated by Natta¹ that stereoregular \mathfrak{a} -olefins could be prepared by specific catalysis, a number of results have been published^{2,3,4} which indicate a dependence of certain physical measurements on the polymer configuration, i.e., the distribution of asymmetric centers. The present work is a continuation of a program, being carried on primarily in this laboratory, designed to study the relationship between physical properties of \mathfrak{a} -olefin polymers and their chain configuration. The present work was carried out with the purpose of characterizing a sample of atactic polyoctene-1 and thereby adding to the data which are available for the poly \mathfrak{a} -olefins in general.

In addition, polyoctene-1 is of interest because of its relatively large pendant group. One object of this study is to discover how the pendant group will effect such measurable quantities as the average end-to-end length of the molecule. At first thought, it would be expected that the end-to-end length of a polymer would be directly proportional to the length of its pendant groups. That is, a long pendant group would be more apt to interfere with other groups and the polymer backbone and thus have the effect of expanding the polymer. However, Chinai and collaborators^{5,6} have investigated a homologous series of n-alkyl methacrylate polymers and found that the ratio of the end-to-end dimensions of these polymers to the degree of polymerization fell off in the order n-hexyl > n-octyl > methyl > ethyl > n-butyl. This order is curious in that the size of the polymer is not dependent on the size of the pendant group. In like manner, the end-to-end dimensions measured for the polyoctene-1 will be compared with the data of other

a-olefins and any apparent order or anomalies with respect to the length of the side groups will be noted.

Aside from the standard characterization procedures, measurements of the lower critical solution temperature (L.C.S.T.) of polyoctene-1, as well as several other α -olefins in n-pentane were undertaken. The fact that polymers will precipitate from solution when the solution is heated sufficiently high has only recently been recognized⁷,⁸. It appears that this phenomena is related to the approach of the solvent to its critical temperature and is associated with a rapid decrease in the entropy of mixing and a negative heat of mixing. It is believed that this is a universal phenomena characterizing all polymer-solvent systems.

Several workers^{7,8} have determined the L.C.S.T. for polymer-solvent systems and found that the L.C.S.T. decreases with increase in molecular weight. Also the L.C.S.T. was related theoretically to the Flory interaction parameter χ_1 and the solvent molecule size⁹. However, no work has been carried out in which polymer fractions have been studied. It was therefore of interest to determine the L.C.S.T. of solutions of characterized polymer fractions and to relate the L.C.S.T. to polymer molecular weight.

Upon considering the relationship between molecular weight and L.C.S.T., a new parameter is immediately suggested. This new parameter, which shall be referred to as Θ_L , is analogous to the Flory Θ_U which is the upper critical miscibility temperature for infinite molecular weight polymer. On the same basis, Θ_L is the lower critical miscibility temperature for infinite molecular weight polymer. That is, below the temperature Θ_L (provided we are at the same time above Θ_U), polymer of any molecular weight is miscible with the solvent. Since no exact theory for this

phenomena is at present available, Θ_L will be determined in a manner similar to that used to find Θ_U . However, any relationship between molecular weight and the L.C.S.T. which is linear could be extrapolated to infinite molecular weight to find Θ_L .

THEORY

Thermodynamics of Polymer Solutions

Because of the size and conformations of dissolved polymer molecules, their solution behavior is considerably different from that of low molecular weight substances. Thus special theoretical treatment is required to explain their solution properties. Even at low concentrations, polymer solutions exhibit large deviations from ideal thermodynamic behavior. These deviations from ideality arise largely from very high entropies of mixing as a result of the large difference in molecular size between the polymer and the solvent. By a statistical mechanical treatment in which polymer segments and solvent molecules are allowed to occupy sites in a lattice, Flory¹⁰ and Huggins¹¹ independently were able to show that the conformational entropy of mixing was given by

 $\Delta S_{M} = -k(n_{1} \ln \mathcal{N}_{1} + n_{2} \ln \mathcal{N}_{2})$ (1.1)

where \mathcal{N}_1 and \mathcal{N}_2 are the volume fraction and n_1 and n_2 are the number of molecules of solvent and solute and k is the Boltzmann constant.

The heat of mixing can be seen to originate in the replacement of some of the contacts between like species in the pure solvent or polymer with contacts between unlike species in the solution. According to the lattice theory with each cell able to accommodate either a solvent molecule or a polymer segment, three types of first neighbor contacts are possible. That is, it is possible to have a solvent-solvent, a solvent-polymer, or a polymer-polymer contact. If the energies associated with these contacts are represented by w_{11} , w_{12} , and w_{22} respectively, the change in energy for the formation of an unlike contact pair can be represented by

$$\Delta w_{12} = w_{12} - (1/2)(w_{11} + w_{22}) \qquad (1.2)$$

Following the van Laar treatment for the heat of mixing, we can write

$$\Delta H_{M} = z \Delta w_{12} n_1 \mathcal{N}_2 \tag{1.3}$$

This equation can be written as

$$M_{\rm M} = kT \chi_1 n_1 \sigma_2 \tag{1.4}$$

where we define

$$\chi_1 = z \Delta w_{12} / kT$$
 (1.5)

as a dimensionless parameter which characterizes the interaction energy between polymer and solvent, z is the coordination number of a polymer segment, and n_1 is the number of solvent molecules.

If it is assumed that Δw_{12} is independent of temperature, that is, if Δw_{12} contains no entropy contribution and the only entropy contribution is from the conformational entropy as given by equation (1.1), one can find the free energy of mixing from equations (1.1) and (1.4). That is,

 $\Delta F_{M} = \Delta H_{M} - T\Delta S_{M} = kT[n_{1} \ln \mathcal{N}_{1} + n_{2} \ln \mathcal{N}_{2} + \chi_{1}n_{1}\mathcal{N}_{2}] (1.6)$ From this expression it is possible to derive several useful relationships involving experimentally obtainable quantities. For example, if (1.6) is differentiated with respect to n_{1} (realizing that \mathcal{N}_{1} and \mathcal{N}_{2} are functions of n_{1} and n_{2}), we can find the relative partial molar free energy, $\Delta \overline{F}_{1}$ (i.e., the chemical potential per mole of the solvent in the solution). Thus

$$\Delta \overline{F}_{1} = \mu_{1} - \mu_{1}^{0} = RT[\ln(1 - N_{2}) + (1 - 1/x)N_{2} + X_{1}N_{2}^{2}] \quad (1.7)$$
$$= RT \ln a_{1} \quad (1.8)$$

where x is the number of chain segments per polymer molecule and is given by the ratio of the molar volumes of the solute and the solvent, and a_1 is the activity of component 1.

In like manner, if we differentiate (1.6) with respect to n_2 , we obtain for the solute

$$\Delta \overline{F}_{2} = \mu_{2} - \mu_{2}^{0} = RT[\ln \mathcal{M}_{2} - (x-1)(1-\mathcal{M}_{2}) + X_{1}x(1-\mathcal{M}_{2})^{2}]$$
(1.9)
= RT ln a₂ (1.10)

The theory just discussed is based on the assumption that there is a uniform concentration of polymer throughout the solution. It is more likely, however, that in dilute solutions individual polymer molecules become separated from each other by regions of pure solvent and the concentration of polymer segments must become non-uniform in the solution. This problem is approached by deriving a general expression for the total free energy of interaction between all of the segments in a volume element, δV , which is considered small enough so that the expected segment density may be considered to be the same for all portions of δV . It has been shown that the free energy of mixing polymer segments with solvent in the volume element δV is given by

$$\delta(\Delta F_{M}) \approx kT[\delta n_{1} \ln(1-\omega_{2}) + \chi_{1}\delta n_{1}\omega_{2}] \qquad (1.11)$$

where \mathcal{N}_2 refers to the volume fraction of the polymer in δV . The chemical potential of the solvent in δV is given by

$$(\mu_1 - \mu_1^0) = \operatorname{RT}[\ln(1 - N_2) + N_2 + \chi_1 N_2^2]$$
 (1.12)

If (1.12) is expanded in series and if powers of \mathcal{N}_2 larger than the second are neglected, we have

$$(\mu_1 - \mu_1^0) = -RT[(1/2 - X_1)N_2^2]$$
 (1.13)

These expressions may be regarded as the excess chemical potential resulting from non-ideal contributions.

Equation (1.13) can be written in the form

$$(\mu_1 - \mu_1^0) = RT(K_1 - \psi_1)W_2^2$$
 (1.14)

where \mathcal{K}_1 and $\mathcal{\Psi}_1$ are heat and entropy parameters defined as

$$\Delta \bar{H}_{1} = RT K_{1} N_{2}^{2}$$
 (1.15)

$$\Delta \overline{S}_{1} = R \psi_{1} w_{2}^{2}$$
 (1.16)

Comparing equations (1.13) and (1.14), it is seen that

$$K_1 - \psi_1 = X_1 - 1/2$$
 (1.17)

It is sometimes preferred to use as a parameter the ideal temperature defined by

$$\Theta = K_1 T / \Psi_1 \tag{1.18}$$

so that

$$\Psi_1 - K_1 = \Psi_1(1 - \Theta/T)$$
 (1.19)

The excess chemical potential can be written

$$(\mu_1 - \mu_1^0) = -RT \psi_1 (1 - \Theta/T) N_2^2$$
 (1.20)

In a thermodynamically poor solvent, i.e. where both \mathcal{K}_1 and $\mathcal{\Psi}_1$ are positive, Θ will also be positive. When $T = \Theta$, the chemical potential due to segment-solvent interactions is zero according to equation (1.20). Thus at $T = \Theta$, the excess chemical potential is zero and deviations from ideality vanish and the molecules can interpenetrate one another freely with no net interaction. At temperatures below Θ , they attract one another, and at temperatures much below Θ , precipitation of the polymer occurs. It will be seen later that Θ is the critical miscibility temperature for polymers of infinite molecular weight.

Molecular Extension^{12^a}

In general, each molecule in a dilute solution will tend to exclude all others from the volume which it occupies. This leads to the concept of an excluded volume from which a polymer molecule effectively excluded all others. If this concept of excluded volume is extended to individual molecules, we find that, because of the obvious requirement that two segments cannot occupy the same space, the chain will extend over a larger volume than would be calculated theoretically. The extended conformation of a polymer molecule is determined by an equilibrium between an expansion force due to the excluded volume and a contraction force due to a distortion of the molecule beyond its most probable conformation as determined by bond length and valence and internal rotational angles. The distorted chain may be considered to be expanded by a factor \mathbf{a} over the unperturbed dimensions (the dimensions determined by the bond angles and the lengths only) of the molecule. Thus the actual root-mean-square end-to-end length of the molecule, $\overline{r^2}$, is given by $\mathbf{ar^2}_0$ where $\overline{r^2}_0$ is the unperturbed dimension determined experimentally from viscosity measurements.

The total free energy of mixing the polymer segments of a molecule with a solvent consists of the sum of the ΔF_{Mj} for each volume element plus a term ΔF_{el} for the free energy change associated with alteration in molecular conformation. Thus

$$\Delta F = \sum_{j} \Delta F_{Mj} + \Delta F_{e1}$$
 (2.1)

At equilibrium

$$(\partial \Delta F/\partial a)T, P = 0$$
 (2.2)

This leads to an evaluation of α given by

$$a^{5} - a^{3} = 2C_{M} \psi_{1} (1 - \Theta/T) M^{1/2}$$
 (2.3)

where

$$C_{M} = (27/2^{5/2} \pi^{3/2}) (\overline{\mathcal{W}}^{2}/Nv_{1}) (\overline{r}^{2}_{0}/M)^{-3/2}$$
(2.4)

and $\overline{\mathcal{N}}$ is the specific volume of the polymer, v_1 its molar volume, and N is the number of particles. Equation (2.3) predicts that a should increase without limit as molecular weight increases. Thus $(\overline{r}^2)^{\frac{1}{2}}$ should

increase more rapidly than in proportion to the square root of the molecular weight. This follows from the theory of random chain configuration which shows that the unperturbed root-mean-square distance $(\overline{r}_0^2)^{1/2}$ is proportional to $M^{1/2}$, whereas $\overline{r}^2 = a\overline{r}_0^2$.

Also **a** depends on the intensity of the thermodynamic interaction as expressed by $\psi_1(1-\Theta/T)$ which is equal to $\psi_1 - K_1$. The larger this factor, the greater the value of **a** for a given M. Hence, the better the solvent, i.e., the larger the ψ_1 , the greater the swelling of the molecule.

At $T = \Theta$ in a poor solvent, $a^5 - a^3 = 0$ and a must equal unity. Therefore, at $T = \Theta$, the molecular dimensions are unperturbed by intermolecular interaction and the excluded volume will equal zero at this temperature.

Phase Study 12b

When the temperature of a polymer solution is lowered, the solvent becomes thermodynamically poorer. Finally, a temperature is reached below which the polymer and solvent are no longer miscible in all proportions. At this and any lower temperature, a mixture of polymer and solvent will separate into two phases.

The condition for equilibrium between two phases in a binary system is that the partial molar free energy of each component be equal in each phase. Application of this condition to the partial molar free energy given by equation (1.7) gives for the critical concentration at which phase separation first appears

$$M_{2c} = 1/(1 + x^{1/2}) \approx 1/x^{1/2}$$
 (3.1)

The critical value of X_1 is given by

$$X_{\rm 1C} = (1 + x^{1/2})^2/2x \approx 1/2 + 1/x^{1/2}$$
 (3.2)

Thus the critical value of X_1 exceeds 1/2 by a small increment depending on the molecular weight and at infinite molecular weight equals 1/2. The temperature at which phase separation begins is given by

$$1/T_{c} = 1/\Theta[1 + (1/\psi_{1})(1/x^{1/2} + 1/2x)]$$
 (3.3)

Thus $1/T_{c}(^{0}K)^{-1}$ should vary linearly with $(1/x^{1/2} + 1/2x)$. The theta temperature is seen to be the critical miscibility temperature in the limit of infinite molecular weight.

Fractionation

Most polymerization procedures yield products which are heterogeneous with respect to molecular weight. Before the polymer is studied, it is desirable to separate the whole polymer into parts or fractions having a relatively narrow molecular weight distribution.

All of the methods used to fractionate polymers are based on the difference in solubility of the different species present. That is, the solubility, which is related to the chemical potential of the species in solution, decreases with increase in molecular weight. Thus if the solubility of a solvent is decreased by cooling a solution of a heterogeneous polymer, a point is reached when phase separation occurs and two layers form. The system will then consist of a dilute phase with low polymer concentration and a precipitated phase with high concentration. Because of the lower solubility of the higher molecular weight species, they will be contained mostly in the precipitated phase, and the more soluble lower molecular weight species will remain in the dilute solution phase. Likewise if the solubility of a solvent is decreased by adding a non-solvent to it, a point is reached when enough non-solvent is added to cause the high molecular weight species to precipitate. If this precipitated polymer is removed and additional non-solvent is added, the polymer of slightly lower molecular weight will precipitate. Thus a scheme is offered whereby a whole polymer can be separated into fractions of different molecular weight.

Osmometry and the Second Virial Coefficient

An osmometer is a device in which a solution is separated from pure solvent by a membrane permeable only to solvent molecules. The activity of the solvent in the solution is less than that of the pure solvent, and if the system is to be kept in equilibrium, the activity of the solvent on both sides of the membrane must be brought into equilibrium. This may be done by applying an excess pressure to the solution side, either mechanically or by developing a hydrostatic head. The excess pressure required to reach equilibrium is called the osmotic pressure, π , and the change in activity with pressure is given by the equation

$$(\partial \ln a_1/\partial P)_{T,N} = v_1/RT$$
 (4.1)

where v_1 is the molar volume of the solvent. Thus at osmotic equilibrium,

$$\int_{0}^{1} d \ln a_{1} = \int_{0}^{\pi} (v_{1}/RT) dP \qquad (4.2)$$

Since v_1 is essentially independent of pressure, we can write

$$-\ln a_1 = \pi v_1 / RT$$
 (4.3)

If the solution is sufficiently dilute, $a_1 = N_1$ where N_1 is the mole

fraction of the solvent, and since N_1 is near unity,

- $\ln N_1 \approx 1 - N_1 \approx N_2 \approx cv_1/M$ (4.4)

where c and M are the concentration and molecular weight respectively of the solute. Substituting these expressions in equation (4.3), we obtain

$$\pi/c \approx RT/M$$
 (4.5)

However, this expression holds only for ideal solutions and in order to treat polymer solutions, it is necessary to use the thermodynamic relationships discussed previously.

According to equation (1.8), we have for a polymer solution

RT In $a_1 = \ln(1-\mathcal{N}_2) + (1 - 1/x)\mathcal{N}_2 + \chi_1 \mathcal{N}_2^2$ (4.6) Substituting (4.6) directly into (4.3), we have

$$\mathbf{\pi} = -(\mathrm{RT/v}_1)[\ln(1-\omega_2) + (1 - 1/x)\omega_2 + \chi_1\omega_2^2] \quad (4.7)$$

If the logarithmic term is expanded and only terms in powers of v_2 of order three or less are retained, then

$$\boldsymbol{\pi} = (\mathrm{RT/v}_1) \left[\mathcal{N}_2 / \mathbf{x} + (1/2 - \boldsymbol{\chi}_1) \mathcal{N}_2^2 + \mathcal{N}_2^3 / 3 + \dots \right] \quad (4.8)$$

Since $\mathcal{N}_2 = c \overline{\mathcal{N}}$ where $\overline{\mathcal{N}}$ is the (partial) specific volume of the polymer and since x is the ratio of the molar volume of polymer and solvent, we have

$$\mathcal{N}_2/\mathrm{xv}_1 = \mathrm{c}\overline{\mathcal{N}}/\mathrm{xv}_1 = \mathrm{c}/\mathrm{M}$$
 (4.9)

Thus

 $\pi/c = RT/M + RT(N^2/v_1)(1/2 - X_1) c + RT(\overline{N^3}/3v_1)c^2 + ...$ (4.10) The first term on the right is the van't Hoff ideal term. At infinite dilution π/c must approach this limit. The higher order terms represent the deviation from ideality.

It has already been pointed out that the lattice model theory suffers from the invalid assumption that the interaction of the segments of a given polymer molecule with the segments of all other polymer molecules are the same as would be expected if these latter segments were randomly distributed over the entire volume. It is much more likely that at high dilution, the solution may be considered to consist of two more or less distinct regions; i.e., one containing clusters of polymer molecules and the other region consisting of pure solvent. The expressions for osmotic pressure derived from the lattice model theory are therefore invalid at high dilution.

The deviation of a polymer solution from ideal behavior may be thought to arise from interaction of molecules in the solution. Each molecule in a dilute solution of a good solvent will tend to interact with those in its vicinity and thus exclude them from the volume which it occupies. This excluded volume is calculated by considering the interaction between a pair of molecules in solution. Flory and Krigbaum¹³ derived a general expression for the free energy of mixing in terms of the excluded volume. Thus

$$\Delta F_{M} \approx -n_{2}kT[\ln V - (u/2)(n_{2}/V)] + Constant$$
 (4.11)

where u is the excluded volume. The excluded volume u can be expressed by the following relationship:

$$u = 2 \Psi_{1} (1 - \Theta/T) (\overline{N}^{2} m^{2} / v_{1}) F(J \xi^{3}) \qquad (4.12)$$

where m is the weight of a polymer molecule, V_1 is the volume of the solvent, and J has the value

$$J = \Psi_1(1-\Theta/T)(\overline{\sigma}^2/V_1)$$
(4.13)

The value of ξ^3 is given by

$$\xi^{3} = (3^{3}/2^{1/2}\pi^{3/2}) N_{A}^{-1}(\overline{r}_{0}^{2}/M)^{3/2} M^{-1/2}a^{3} \qquad (4.14)$$

where N_{A} is Avogadro's number. The function $F(J \xi^3)$ is of the nature

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that it decreases as the agrument increases. If we examine equation (4.13), we see that when $T = \Theta$, J vanishes. When J vanishes, $F(J \oint ^3)$ becomes unity. The dependence of the excluded volume on temperature is seen by examining equation (4.12). As the solvent becomes poorer by decreasing the temperature, the excluded volume decreases and at $T = \Theta$ it vanishes.

From equation (4.11) we can derive an expression for osmotic pres-

$$\pi/c = RT[1/M + (N_A u/2M^2)c]$$
 (4.15)

This equation holds only at very high dilution since only binary interaction between molecules was considered. If the osmotic pressure is expressed as a power series in concentration analogous to the virial expansion for a gas, we may adopt the convention form

$$\mathbf{\pi} = \mathrm{RT}[\mathbf{A}_{1}c + \mathbf{A}_{2}c^{2} + \mathbf{A}_{3}c^{3} + \dots]$$
 (4.16)

where c expresses the concentration of polymer in gm per unit volume. Recalling that $n_2/V = cN_A/M$ and comparing equations (4.15) and 4.16) it follows that

$$A_1 = 1/M$$
 (4.17)

$$A_2 = N_A u / 2M^2$$
 (4.18)

or from equation (4.12) we can show that

$$A_{2} = (\overline{\mathcal{W}}^{2}/v_{1}) \psi_{1}(1 - \Theta/T) F(J \xi^{3})$$
 (4.19)

$$= JF(J\xi^3)$$
(4.20)

When equation (4.16) is compared with the virial expansion of PV in powers of 1/V for a real gas, the analogy is at once obvious. Thus if the gas molecules are regarded as point particles which exert no forces on each other so that u = 0, the second and higher virial coefficients, A_2 , A_3 , etc., vanish and the gas behaves ideally. Likewise in a polymer solution when $T = \Theta$, u = 0, and equations (4.15) and (4.16) reduce to the ideal van't Hoff's law

$$\mathbf{n}/c = \mathrm{RT}/\mathrm{M} \tag{4.21}$$

which rearranges to

$$\pi V = n_2 RT$$
 (4.22)

and is a direct analogy to the perfect gas law. Thus the temperature $T = \Theta$ for a polymer solution is seen to be the analog of the Boyle point of a real gas, that is, the temperature at which a real gas obeys the relation PV = nRT except for terms in the square and higher powers of 1/V.

The value of A_3 depends on interactions involving three molecules. In order to evaluate A_3 , it is necessary to consider the region of space from which the center of gravity of molecule k is repelled by both of the molecules 1 and m. An accurate evaluation of the intergals resulting from considerations of the problem are difficult and so approximation procedures are used. In one model, the molecules are treated as inpenetrable non-interacting spheres. The results of these calculations show that

$$A_3 = (5/8)A_2^{2}M \tag{4.23}$$

A more detailed analysis¹⁴ shows that the numerical coefficient 5/8 should be replaced for polymer molecules by a slowly increasing function of A_2 . It is less than 5/8 and vanishes as A_2 goes to zero. Calling this function g, we have

$$A_3 = gA_2^2M$$
 (4.24)

For many purposes it is preferable to use instead of equation (4.16) the series expansion

$$\pi/c = (\pi/c)_0 [1 + \int_2 c + \int_3 c^2 + ...]$$
 (4.25)

where

$$\int_{2} = A_{2}/A_{1}$$
 (4.26)

$$r_{3} = A_{3}/A_{1}$$
 (4.27)

and

С

$$(\pi/c)_0 = RT/M \qquad (4.28)$$

An important consequence of the relationship between the second and third virial coefficient is that the contribution of the third virial coefficient decreases rapidly as the second is made smaller, that is, when poorer solvents are used. It follows that the decrease in slope for poorer solvents should be accompanied by a rapid decrease in curvature.

Osmotic pressure measurements are made to determine both the molecular weight of a polymer and the polymer-solvent interaction. These two values require that the first two terms in equation (4.25) be evaluated. Since the third term is important only as it aids in the accurate evaluation of the others, its value can be approximated, and since it makes a negligible contribution in poor solvents, it is sufficient to take for g its value in a good solvent, that is 0.25^{14} , and to treat it as a constant¹⁵. Thus if g = 0.25 is used and higher order terms are neglected we can write equation (4.25) as

$$\pi/c = (\pi/c)_0 [1 + (\lceil_2/2)c]^2$$
 (4.29)
The osmotic pressure data is then treated by plotting $(\pi/c)^{1/2}$ against c. The molecular weight is calculated from the intercept of the line and A_2 is determined from the slope and the intercept of the line.

If we examine equation (4.2), we see that A_2 is given by the molecular weight independent factor J, multiplied by the factor $F(J \xi^3)$ which decreases slowly from unity to approach zero asymptotically as the

molecular weight becomes larger. We can compute A_2 easily from the theoretical expression using experimentally obtained parameters. Thus

$$J = \Psi_{1}(1 - \Theta/T) \overline{v}^{2} / V_{1}$$
 (4.30)

is obtained easily by using values of ψ_1 and θ obtained from phase studies, and \overline{w}^2 and V_1 are found from density measurements. The factor ξ^3 can be computed using values of \mathfrak{a} obtained from viscosity studies. The factor $F(J\xi^3)$ can be found by successive approximation calculations. Also this factor has been expressed in closed form by Flory, Krigbaum, and Orofino¹⁶,¹⁷, and by Cassassa and Marrority¹⁸. The calculated values of A_2 can then be compared with those obtained from osmometry or light scattering measurements.

Viscosity

A property common to all high polymers is that when dissolved, the viscosities of the resulting solutions are considerably larger than those of the pure solvents. This ability to produce a viscous solution is a property of polymers related to the voluminous nature of the randomly coiled chain molecules and so is basically a measure of the size or extension in space of the polymer molecule.

The viscosity of a liquid is commonly determined by timing the flow of a known volume of the liquid through a capillary (viscometer) and is calculated using the relation

$$\eta = A\rho t - B\rho/t$$
 (5.1)

where **A** and **B** are viscometer constants, ρ is the density of the liquid, and t is the flow time. The factor **B** is used to correct for kinetic energy effects. If t is large and if well-designed viscometers are used, the kinetic energy effect is small and can be neglected. If the kinetic energy effects are small, the viscosities of the solvent and solution, \mathcal{M} and \mathcal{M}_0 , can be replaced by the flow times, t and t₀, since only the relative values are required. (The subscript o refers to solvent flow time.)

It is customary in polymer science to represent polymer solutions concentrations, c, in gm./100 ml. On this basis, if the viscosity of the solution is η and that of the solvent is η_0 , we can define several useful quantities. If the viscosity of the solution is divided by the viscosity of the solvent, we obtain the relative viscosity, η_{re1} . The specific viscosity is defined as $\eta_{sp} = \eta_{re1} - 1$ and expresses the incremental viscosity attributable to the solute. The ratio η_{sp}/c , the viscosity number (or reduced specific viscosity), is a measure of the specific capacity of the polymer to increase the relative viscosity. The limiting value of this ratio at infinite dilution is called the intrinsic viscosity¹⁹ which is designated by [η]. Thus in mathematical language

$$[\eta] = (\eta_{sp}/c)_{c} \rightarrow o = [(\eta_{re1} - 1)/c]_{c} \rightarrow o$$
 (5.2)

When the concentration c is expressed in gm./100 ml., the intrinsic viscosity is given in the reciprocal of this unit, deciliters per gm. Intrinsic viscosity may also be defined as the following:

$$[\eta] = [(\ln \eta_{re1})/c]_{c \to 0}$$
 (5.3)

Huggins ¹⁹ found, for a series of polymer fractions at different concentrations in the same solvent at the same temperatures, that the slopes of the linear portions of the plots of $\eta_{\rm sp}$ /c against c were proportional to the square of the intercept, and he proposed the empirical relationship

$$\eta_{\rm sp}/c = [\eta] + k' [\eta]^2 c$$
 (5.4)

In this equation, k^{*} is constant for a given polymer-solvent system provided the polymer is pure and homogeneous. It is generally in the range of 0.30 to 0.40. Another relation, due to Kraemer²⁰, similar to (5.4) is

$$(\ln \eta_{rel})/c = [\eta] - k''[\eta]^2c$$
 (5.5)

If the left side of equation (5.4) is expanded in terms of $\eta_{
m sp}/c$, we obtain

$$[\ln(\eta_{rel})/c]/c = \frac{\eta_{sp}}{c} - \frac{\eta_{sp}}{c}^{2} - \frac{\eta_{sp}}{c}^{2} + \frac{\eta_{sp}}{c}^{3} - \dots$$
(5.6)

from which we have

$$\lim_{c \to o} [\ln(\eta_{rel})/c] = \lim_{c \to o} (\eta_{sp}/c)$$
(5.7)

If equation (5.4) is substituted into equation (5.6) and powers of c higher than the first are neglected, it is seen that k' + k'' = 0.50. This furnishes a convenient aid for extrapolating viscosity data.

Usually $[\eta]$ is found by plotting both η_{sp}/c against c and $\ln(\eta_{rel})/c$ against c on the same graph. This procedure facilitates extrapolation since both intersect the ordinate at zero concentration.

If log $[\eta]$ of a series of polymer fractions is plotted against log M, a general empirical relationship, known as the Mark-Houwink equation²¹, is obtained. The relationship may be expressed by the equation

$$[\gamma] = \mathbf{K} \cdot \mathbf{M}^{\mathbf{a}} \tag{5.8}$$

where **K'** and a are constants for a given polymer, solvent, and temperature. The value of the constant a, when applied to measurements of flexible chains, usually lies between 0.50 and 0.80. Although equation (5.8) is empirical in origin, it can be closely approximated by more complex theoretical expressions. It has been shown that the viscosity measurement gives a viscosity average molecular weight²² defined by the equation

$$M_{v} = \left[\sum_{i=1}^{\infty} w_{i} M^{a}\right]^{1/a} = \left[\sum_{i=1}^{\infty} N_{i} M_{i}^{1+a} / \sum_{i=1}^{\infty} N_{i} M_{i}\right]^{1/a}$$
(5.9)

If fractionated polymers are available so that $M_n \approx M_v \approx M_w$, any absolute molecular weight measurement can be used with values of intrinsic viscosity to evaluate the constants in equation (5.8). However, since M_v is nearer to M_w than to M_n , weight average molecular weights are preferred for determining the constants.

The theories of the frictional properties of polymers in solution conclude that the intrinsic viscosity is proportional to the effective hydrodynamic volume of the molecule in solution divided by the molecular weight^{12^C}. The effective volume is shown to be proportional to the cube of a linear dimension of the polymer chain. When $(\overline{r}^2)^{1/2}$ is chosen as the linear parameter, it is shown that^{12^C}

$$[\mathcal{N}] = \mathfrak{P} \left(\overline{r}^2\right)^{3/2} / \mathfrak{M}$$
(5.10)

where Φ is a universal constant independent of solvent temperature and polymer. We can separate $(\overline{r}_2)^{1/2}$ into the factors $\alpha(\overline{r}_0^2)^{1/2}$, and since $(\overline{r}_0)^{1/2}/M$ is independent of the solvent and molecular weight, we can write

$$[\gamma] = \Phi(\overline{r}_{0}^{2}/M)^{3/2} M^{1/2} \alpha^{3} = KM^{1/2} \alpha^{3}$$
(5.11)

where

$$K = \Phi \left(\bar{r}_{0}^{2} / M \right)^{3/2}$$
 (5.12)

which is constant for a given polymer and independent of solvent and molecular weight. It was shown previously that at $T = \Theta$, $\alpha = 1$. Therefore at $T = \Theta$ we have

$$[\eta]_{e} = KM^{1/2}$$
 (5.13)

The constant Φ can be calculated from equation (5.10) if \overline{r}^2 has been determined from light scattering measurements or by some other means and if is measured in the same solvent at the same temperature at which the light scattering measurements were made. From the value of Φ , $(\overline{r}^2/M)^{1/2}$ can be calculated from (5.10) and compared with similar values calculated, assuming free rotation about the bonds. Thus it is possible to obtain information on the effect of hindered rotation about bonds and other perturbing effects, such as side groups on the main polymer chain.

Light Scattering

When a beam of light passes through a non-absorbing liquid, it is found that the medium is not perfectly transparent but scatters a small amount of the incident radiation. This scattering in pure liquids was shown by Einstein²³ to be related to local thermal fluctuations in the density of the liquid which made it optically inhomogeneous. If the inhomogeneity of the medium is increased by adding a solute, the scattering intensity increases.

The intensity of the light scattered from a solution depends on the polarizability of the molecules compared with that of the solvent, the size of the molecules, and the concentration of molecules. The intensity of the light scattered in a given direction from a single molecule is proportional to the square of its size or molecular weight. This means, for example, that the light scattered from one molecule of molecular weight 2M will be greater by a factor of 2 than the light scattered by two molecules of molecular weight M. This dependence of scattered intensity per particle on a power of molecular weight greater than the first make possible the determination of molecular weight and polymer size.

The problem of measuring molecular weights of polymers by light scattering therefore becomes a matter of determining the intensity of scattered radiation. The intensity of scattered light is expressed in terms of the turbidity 2, defined as the fraction of the light scattered in all directions from the primary beam per cm. of path. The turbidity is measured experimentally by comparing the scattered intensity at a given angle to the incident intensity of the light. Debye²⁴ related molecular weight to scattered intensity by the expression

$$\frac{HC}{Z} = \frac{1}{M} + 2A_2c \qquad (6.1)$$

where

$$H = \frac{32\pi^3}{3N_A} \frac{n_o^2}{\lambda^4} \left(\frac{dn}{dc}\right)^2$$
(6.2)

is constant for a given polymer-solvent system and a specific wave length of light, λ . The other constants are Avogadro's number N_A , the refractive index of the solvent n_0 . The (dn/dc) is the refractive index increment of the solution due to dissolved polymer. This is a measurable quantity which is proportional to the excess polarizability of the molecules in the solvent. A_2 is the second virial coefficient and c is the concentration of the polymer expressed in terms of weight per volume.

Equation (6.1) is satisfactory for particles smaller than about $(\lambda/20)^{\circ}A$. For larger particles, interference occurs in the scattering pattern and the scattering envelope becomes unsymmetrical. In this

case, it is necessary to correct equation (6.1) with a factor $P(\Theta)$ which is a shape factor that corrects the observed scattering to that which it would be if there were no interference. Thus equation (6.1) becomes

$$\frac{HC}{2} = \frac{1}{MP(\Theta)} + 2A_2c \qquad (6.3)$$

Zimm was able to show²⁵ that the shape factor for randomly coiled polymer molecules (that is, those whose radial segmental density distribution can be represented by a Gaussian function) may be represented approximately as

$$\lim_{\sigma \to 0} \overline{\mathbf{P}^{-1}}(\Theta) = 1 + \frac{8\pi^3}{9\lambda^2} \overline{\mathbf{r}^2} \sin^2 \frac{\Theta}{2} + \dots \qquad (6.4)$$

where $\sin \Theta$ is the viewing angle as measured from the direction of the incident light. Combining (6.4) with equation (6.3), we have

$$\lim_{c \to 0} \frac{Hc}{2} = \frac{1}{MP(\Theta)} = \frac{1}{M} \left(1 + \frac{8\pi^2}{9\lambda^2} \overline{r}^2 \sin^2 \frac{\Theta}{2} + \ldots \right)$$
(6.5)

If the dissymmetry method of Debye is used to calculate the molecular weights and sizes, it is necessary to measure the scattering intensity, i_{Θ} , at two angles symmetrical about 90°, for example, at 45° and 135°. The dissymmetry coefficient, $z = i_{90-45}/i_{90+45}$, thus obtained can be used to calculate the value of $(\overline{r}^2)^{1/2}$ for the molecules being measured. We can then use $(\overline{r}^2)^{1/2}$ with equation (6.4) to calculate the shape factor, $P(\Theta)$, and then use $P(\Theta)$ in equation (6.3) to calculate the molecular weight.

If the dissymmetry is large, the scattered intensity, and therefore the turbidity, will be functions of the angle at which it is determined, as well as the concentration. $Zimm^{26}$ solved this problem by plotting the data simultaneously as a function of angle and concentration. Thus Hc/γ in equation (6.3) is plotted against $sin^{2\Theta} + kc$ (k is an arbitrary

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constant chosen so that kc $\approx \sin^2 \frac{\Theta}{2}$) and the curves are extrapolated both to zero angle and zero concentration. These limiting values are then extrapolated to the common intercept at zero. The limiting slope of the zero angle line yields the second virial coefficient, A₂; the ratio of the limiting slope of the zero concentration line to the intercept gives the mean-square end-to-end dimension of the molecule, and the intercept gives the reciprocal of the weight average molecular weight, \overline{M}_{w} .

The dimensions of the molecules obtained in this way are the zaverage values, and some knowledge of the molecular weight distribution is required in order to convert them to weight average values. Many molecular weight distributions can be approximated by a function of the form

$$f(M) = \frac{y^{h+1}}{h!} M^{h} e^{-yM}$$
 (6.6)

where h is a parameter characterizing polydispersity. Zimm has $shown^{25}$,²⁶ that for such a distribution, h is given by

h =
$$(\overline{M}_{u}/\overline{M}_{n} - 1)^{-1}$$
 (6.7)

and that

$$\frac{M_z}{h+2} = \frac{M_w}{h+1} = \frac{M_n}{h}$$
(6.8)

If we assume that a polymer has this particular distribution, we can convert the z-average dimensions to the weight average dimensions by use of the relation

$$r_z = r_w(h + 2)/(h + 1)$$
 (6.9)

Lower Critical Solution Temperature

If two unlike liquids are mixed, two results are possible. The liquids will either dissolve each other completely to form a single phase or the liquids will not dissolve each other completely and two phases (each of which is a solution) will form. If the homogeneous mixture of two liquids is not miscible at all temperatures and at all compositions, then at some other temperature or composition, the two will separate into two phases. For example, n-hexane and nitrobenzene are miscible in all proportions, if the temperature is above 19°C. Likewise, outside the limits of about 0.15 and 0.80 mole fraction nitrobenzene, the two liquids will be miscible at all temperatures.

If we plot the phase separation temperature against the mole fraction of nitrobenzene, the results will be as shown in Figure 1. At the point C, the maximum in the curve, the two liquid layers become identical and the liquids will be miscible in all proportions. This point is called the upper critical solution temperature (U.C.S.T.) and also called the upper critical consolute temperature.

In other two component systems, a different type of behavior may be observed. For example, in the system diethylamine and water, shown in Figure 2, there exists a temperature below which the liquids are miscible in all proportions. This point represents a lower critical solution temperature (L.C.S.T.). Finally, there are liquid systems which exhibit both an upper and a lower critical solution temperature. An example of this is the system n-toluidine and glycerol as depicted in Figure 3. In this particular case, the two phase region is a closed loop and the L.C.S.T. is lower than the U.C.S.T. In another case, the







Fig. 2.27^a Phase diagram of the system diethylamine plus water.



Fig. 3.^{27^a} Phase diagram of the system m-toluidine plus glycerol showing upper and lower critical temperatures with L.C.S.T. J.C.S.T.



Fig. 4. Phase diagram of polymersolvent system showing upper and lower critical temperatures with L.C.S.T. > U.C.S.T.

L.C.S.T. is higher than the U.C.S.T. and there are two, two phase regions separated by a one phase region. This type of behavior has been observed for polymer systems and is the one which will be of primary interest. An example of this type is shown in Figure 4.

The stability of a binary phase can be characterized in terms of the chemical potential. If we consider a binary system whose two components are in equilibrium, thermodynamic arguments^{27^a} show that for equilibrium with respect to diffusion for a two component system

$$\left(\frac{\partial \mu_1}{\partial n_2}\right) = \left(\frac{\partial \mu_2}{\partial n_1}\right) < 0$$
 (7.1)

Making use of the Gibbs Duhem relation, it can be shown that

$$\frac{\partial \mu_1}{\partial x_2} = \frac{n}{x_1} \begin{pmatrix} \partial \mu_1 \\ \partial n_2 \end{pmatrix}$$
 and $\frac{\partial \mu_2}{\partial x_2} = \frac{n}{x_1} \begin{pmatrix} \partial \mu_2 \\ \partial n_2 \end{pmatrix}$ (7.2)

and so equation (7.1) is equivalent to

$$\left(\frac{\partial \mu}{\partial x_2} \right) < 0 \text{ and } \left(\frac{\partial \mu}{\partial x_1} \right) < 0$$
 (7.3)

For example, these conditions may be illustrated by the hexane-nitrobenzene system shown in Figure 1. If the chemical potential of hexane is plotted as a function of the mole fraction of nitrobenzene, the curves shown in Figure 5 result. Above $19^{\circ}C$ (curve 1) a single phase only exists and the conditions of (7.3) are always satisfied. However, below $19^{\circ}C$, curve 3 consists of three parts: one corresponding to the phase rich in nitrobenzene, one for the phase rich in hexane, and a horizontal line joining these two, corresponding to the simultaneous presence of two phases. The curve at $19^{\circ}C$ represents the transition temperature between these two types of curves. The horizontal portion is reduced to a single point of inflection at C which mathematically satisfies the restrictions

$$\frac{\lambda \frac{\partial \mu_1}{\partial x_2}}{\partial x_2} c = \left(\frac{\partial^2 \mu_1}{\partial x_2^2}\right)_c = 0$$
 (7.4)

(7.5)

and



Fig. 5.^{27^a} Variation of chemical potential of n-hexane as a function of nitrobenzene concentration.

The conditions of stability as given by equation (7.1) can be written also in terms of the free energy of mixing since we can write

$$\left(\frac{\partial \mu_1}{\partial x_2}\right)_{T,P} = -x_2 \left(\frac{\partial \overline{F}}{\partial x_2}\right)_{T,P} \qquad (7.6)$$

Therefore, for stability we can write from (7.1) and (7.6).

$$\left(\frac{\partial^2 \mathbf{F}}{\partial x_2^2}\right) > 0 \tag{7.7}$$

This inequality has a simple geometric interpretation. If \overline{F} is plotted as a function of x_2 , then equation (7.7) requires that for a stable system to exist, the curve must be concave upward at all points. This is illustrated in Figure 6, curve 1. However, if we consider curve 2, we see that the portion of the curve BC is unstable with respect to material fluctuations and is surrounded by the portions AB and CD which are materially stable but are metastable with respect to the heterogeneous mixture represented by the line AD.



energy with composition.

The two phases in equilibrium have compositions A and D. That is, the common tangent AD satisfies the equilibrium conditions,

$$\mu_{1}' = \mu_{1}''$$

$$\mu_{2}' = \mu_{2}''$$
(7.8)

where the primes refer to phase' and phase". Furthermore, at the critical point, we can write

$$\left(\frac{\partial^2 \overline{F}}{\partial x_2^2}\right) = \left(\frac{\partial^3 \overline{F}}{\partial x_2^3}\right) = 0$$
 (7.9)

and

$$\frac{\partial^{4}\overline{F}}{\partial x_{2}^{4}} > 0$$

We will now investigate the conditions which determine whether the critical point shall be a maximum or a minimum, that is, an U.C.S.T. or a L.C.S.T. Referring to Figures 1 and 2 we have from Prigogine and Defay^{27b} that the slope of the curve CA is given by

$$\frac{dx_{2}'}{dT} = -\frac{x_{2}''\Delta''_{1} \quad \overline{H}_{2} + (1 - x_{2}'')\Delta''_{1} \quad \overline{H}_{1}}{T(x_{2}'' - x_{2}')(\partial^{2}\overline{F'}/\partial x_{2}'^{2})}$$
(7.10)

where Δ_{j} " refers to a change in a thermodynamic variable from phase' to phase" and \overline{H}_{i} is the partial molar enthalpy of component i. If we adopt the convention of calling the first phase that which is more dilute in component 2, we have

$$x_2" > x_2' \text{ or } (x_2" - x_2') > 0$$
 (7.11)

If equation (7.10) is positive in the neighborhood of C on the curve AC, then C is an U.C.S.T., and if the slope is negative on AC, then C is a L.C.S.T.

The denominator is always positive for stable phases because of (7.11) and the fact that

$$\left(\frac{\partial^2 \overline{F}}{\partial x_2}\right) > 0 \qquad (7.12)$$

Therefore, the sign of (7.10) is determined by the numerator.

Now we consider two phases very close to the critical point. We let their temperature and concentrations be defined as $T_c + \delta T$, $(x_2)_c + \delta x_2$ and $T_c + \delta T$, $(x_2)_c + \delta x_2$ ". The partial molar enthalpy of component 1 in these solutions can be obtained from the following expressions

$$\overline{H}_{1}' = (\overline{H}_{1})_{c} + (\frac{\partial \overline{H}_{1}}{\partial x_{2}})_{c} \delta x_{2}' + (\frac{\partial \overline{H}_{1}}{\partial T})_{c} \delta T$$
(7.13)

and

$$\overline{H}_{1}" = (\overline{H}_{1})_{c} + (\frac{\partial \overline{H}_{1}}{\partial x_{2}})_{c} \delta x_{2}" + (\frac{\partial \overline{H}_{1}}{\partial T})_{c} \delta T \qquad (7.14)$$

The heat of transfer of component 1 from the first phase to the second is therefore

$$\Delta_{I}^{"}\overline{H}_{1} = \overline{H}_{1}^{"} - \overline{H}_{1}^{'} = \left(\frac{\partial \overline{H}_{1}}{\partial x_{2}}\right)_{c} \left(\delta_{x_{2}}^{"} - \delta_{x_{2}}^{'}\right)$$
(7.15)

From the Gibbs-Duhem relationship we can write

$$x_1 \left(\frac{\partial \overline{H}_1}{\partial x_2}\right)_{T,P} + x_2 \left(\frac{\partial \overline{H}_2}{\partial x_2}\right)_{T,P} = 0$$
 (7.16)

Therefore, the numerator in (7.10) can be written

$$-\delta x_{2}" \left[\left(\frac{\partial \overline{H}_{2}}{\partial x_{2}} \right)_{c} - \left(\frac{\partial \overline{H}_{1}}{\partial x_{2}} \right)_{c} \right] \left(\delta x_{2}" - \delta x_{2}" \right)$$
(7.17)

To simplify the expression, we make use of the following relationships. The derivative of \overline{H} with respect to x_2 can be written in the form

$$\frac{\partial \overline{H}}{\partial x_2} = \overline{H}_2 - \overline{H}_1 \tag{7.18}$$

and therefore

$$\left(\frac{\partial^2 \overline{H}}{\partial x_2^2}\right) = \frac{\partial \overline{H}_2}{\partial x_2} - \frac{\partial \overline{H}_1}{\partial x_2}$$
(7.19)

Since the change of component 2 in phase' must be equal to and the negative of the change of component 2 in phase", we can write

$$\delta x_2' = -\delta x_2''$$
 (7.20)

Hence, if we substitute (7.19) and (7.20) into (7.17), we have for the numerator of (7.10)

$$-2(\frac{\partial^{2}H}{\partial x_{2}^{2}})_{c} (\delta x_{2}')^{2}$$
 (7.21)

As we have seen, the sign of (7.10) must be the same as that of (7.21), that is, opposite to $(\partial^2 \overline{H}/\partial x_2^2)_c$. Therefore, we have at an U.C.S.T.

$$\left(\frac{\partial^2 H}{\partial x_2^2}\right)_c < 0$$
 (7.22)

and for a L.C.S.T. we have

$$(\frac{\partial^2 H}{\partial x_2^2}) > 0$$
 (7.23)

These conditions relate the nature of the consolute temperature to the curvature of the line \overline{H} as a function of x_2 . For an U.C.S.T., the curve of $\overline{H}(x_2)$ must be concave up as curve 1 in Figure 7, whereas for a L.C.S.T., the curve must be convex down as curve 2. In the first case, the heat content of the mixture is larger than that of the pure substances. The mixture will be formed from the pure substances with an absorption of heat, that is, it will be an endothermic reaction. In the other case, the mixture will be formed by an evolution of heat, that is, it will be an exothermic reaction.



Fig. 7.^{27^b} Molar enthalpy as a function of composition.

If we consider the relation

$$\overline{F} = \overline{H} - T\overline{S}$$
 (7.24)

and remember that at the critical point $(\partial^2 \overline{F}/\partial^2 x_2^2)$ is zero, we can write

$$\left(\frac{\partial^{2} \overline{H}}{\partial x_{2}^{2}}\right)_{c} = T\left(\frac{\partial^{2} \overline{S}}{\partial x_{2}^{2}}\right)_{c}$$
 (7.25)

The curvature of $\overline{H}(x_2)$ and $\overline{S}(x_2)$ have the same sign at the critical point. Therefore, in addition to (7.22) and (7.23) we have as a further condition at an U.C.S.T.

$$\left(\frac{\partial^2 S}{\partial x_2^2}\right)_c < 0$$
 (7.26)

and at a L.C.S.T.

$$\left(\frac{\partial^2 S}{\partial x_2^2}\right)_c > 0 \qquad (7.27)$$

It will be beneficial to express these conditions in terms of the excess thermodynamic functions. Thus we have

$$\overline{F}^{E} = \overline{F}^{M} - RT(x_{1} \ln x_{1} + x_{2} \ln x_{2})$$
 (7.28)

$$\overline{\mathbf{H}}^{\mathbf{E}} = \overline{\mathbf{H}}^{\mathbf{M}} \tag{7.29}$$

$$T\overline{S}^{E} = \overline{H}^{E} - \overline{F}^{E}$$
(7.30)

The superscript E indicates the function to be the thermodynamic excess function, that is, the difference between the thermodynamic function of mixing (denoted by M) and the value corresponding to an ideal solution. So from equations (7.28, 7.29, 7.30) we can write

$$\left(\frac{\partial}{\partial}\frac{{}^{2}\overline{F}^{M}}{x^{2}}\right)_{c} = \frac{RT_{c}}{x_{1}x_{2}} + \left(\frac{\partial}{\partial}\frac{{}^{2}\overline{F}^{E}}{x^{2}}\right)_{c} = 0 \quad (7.31)$$

$$\left(\frac{\partial}{\partial}\frac{{}^{2}\overline{H}^{M}}{x^{2}}\right)_{c} = \left(\frac{\partial}{\partial}\frac{{}^{2}\overline{H}^{E}}{x^{2}}\right)_{c} < 0 \quad (U.C.S.T.) \text{ or } > 0 \quad (L.C.S.T.) \quad (7.32)$$

$$\left(\frac{\partial}{\partial}\frac{{}^{2}\overline{S}}{x^{2}}\right)_{c} = -\frac{R}{x_{1}x_{2}} + \left(\frac{\partial}{\partial}\frac{{}^{2}\overline{S}^{E}}{x^{2}}\right) < 0 \quad (U.C.S.T. \text{ or } > 0 \quad (L.C.S.T.) \quad (7.33)$$

These conditions can be illustrated as shown below.



Thermodynamic excess functions in the neighborhood of an U.C.S.T. (Fig. 8) and a L.C.S.T. (Fig. 9).

Thus for an U.C.S.T., the excess functions appear as in Figure 8 and for a L.C.S.T., they appear as in Figure 9. So it can easily be seen that the following conditions hold: for an U.C.S.T.,

$$\overline{F}^{E} > 0, \ \overline{H}^{E} > 0, \ \overline{S}^{E} > 0$$
 (7.34)

and for an L.C.S.T.,

$$\overline{F}^{E} > 0, \ \overline{H}^{E} < 0, \ \overline{S}^{E} < 0$$
 (7.35)

The conditions above can be summarized²⁸ by saying that U.C.S.T.'s are related to large positive deviations of the enthalpy of the system from ideality while L.C.S.T.'s result from sufficiently large negative deviations of the entropy from ideality.

At an U.C.S.T., the critical value of \overline{F}^{E} can arise only from energetic factors which affect the enthalpy of the system though not necessarily the entropy. However, a L.C.S.T. point will occur only if the system has a large negative excess entropy and a small negative excess enthalpy. The difficulty of satisfying the conditions for a L.C.S.T. can be shown in the following way²⁸. Consider a one phase system which satisfies the conditions of (7.35) and is therefore potentially capable of having a L.C.S.T. Suppose that at a temperature T_0 the system has at O a value of \overline{F}_0^E (Point O in Figure 10). Since \overline{S}^E is negative, \overline{F}^E will increase with T. If \overline{C}_{p}^{E} is positive, however, \overline{S}^{E} will become less negative as T increases and so the slope of $\overline{F}^{E}(T)$ will decrease with increase of T. The curvature of $\overline{F}^{E}(T)$ will be larger, the larger the ratio $\overline{S^E}/\overline{C_p^E}$. Thus system A will show a L.C.S.T.; system B will show a closed loop and C will not show a phase separation. However, almost any system at O having excess entropy greater than $-\overline{F}^{E}(critical)$ will separate into two phases on lowering the temperature, for example, OE, OF (corresponding to a regular solution), and OG. So for a L.C.S.T. there must exist the proper combination of \overline{H}^{E} , \overline{S}^{E} , and \overline{C}_{p}^{E} , but almost any system having \overline{S}^{E} larger than $-\overline{F}_{c}^{E}$ will show a U.C.S.T. For example,

E, F, G are systems showing an U.C.S.T. Since \overline{H}^E must change from negative at a L.C.S.T. to positive at an U.C.S.T., it follows that for a closed loop \overline{C}^E_p must be positive.



An alkane polymer that is above its melting point is generally miscible in all proportions with a paraffin solvent⁸ and according to the original Hildebrand-Scatchard solubility parameter theory, the heat of mixing should be small and positive. The polymer is often incompletely miscible with aromatic and polar solvents in which the heat of mixing is large and positive. The polymer becomes more soluble as the temperature is raised until complete miscibility is attained at the U.C.S.T. However, Freeman and Rowlinson⁷ have shown recently that hydrocarbon polymers can also be precipitated from hydrocarbon solvents whether aliphatic or aromatic by raising the temperature sufficiently above the normal boiling point of the solvent. The minimum temperature at which immiscibility occurs is the L.C.S.T. for the system. As we have seen, in order to satisfy the thermodynamic requirements for a L.C.S.T., the heat of mixing must be negative at this point. A modified Hildebrand-Scatchard solubility parameter theory was used by Delmas, Patterson and Somcynsky⁹ to show the variation of ΔH_M with solubility parameters δ_1 and δ_2 . Thus

$$\Delta H_{M} = 2V_{M} \sigma_{1} \sigma_{2} (\delta_{1} - \delta_{2}) T (\partial \delta_{1} / \partial T)$$
 (7.36)

where

$$\delta_{i} = (\Delta E_{i}^{vap} / V_{i})^{1/2}$$
 (7.37)

 $\Delta \mathbf{E}_{i}^{vap}$ is the energy of vaporation, V_{i} the molar volume, and \mathcal{N}_{i} is the volume fraction of species i. As the temperature increases, $\Delta \mathbf{E}_{1}^{vap}$ will decrease. Therefore, δ_{1} will also decrease. Since δ_{2} is less temperature dependent than δ_{1} , a point will eventually be reached where δ_{2} will be larger than δ_{1} and the difference ($\delta_{1} - \delta_{2}$) becomes negative. So ΔH_{M} will be positive or negative according to whether δ_{1} is greater or less than δ_{2} .

A quantative treatment of this problem has been given by Delmas, Patterson, and Somcynsky⁹ and by Bellemans and Naar-Colin²⁹. The derivation of ΔH_{M} is carried out using the quasicrystalline lattice or cell theory developed by Prigogine³⁰. Thus it was shown that ΔH_{M} is given by

$$\frac{\Delta H_{M}}{\text{no. base moles } x \mathcal{N}_{1}} = A - B(T/r_{A})^{2} \quad (7.38)$$

where A and B are constants which depend on the solvent-polymer system and are given by

$$A = z_{W} N_{A} = z \in {}^{*}_{11} \delta^{2} N_{A} / 8$$
 (7.39)

$$B = 10.5 (k^2/z \epsilon_{12}^*) N_A$$
 (7.40)

 ϵ_{ij}^* is the minimum potential energy of interaction of two segments of type i and j (a solvent and polymer segment for example). δ is given by

$$\delta = \left(\frac{\epsilon_{22}^{*} - \epsilon_{12}^{*}}{\epsilon_{11}^{*}} \right)$$
(7.41)

Prigogine has shown³¹ that r_{A} should be given by

$$r_{A} = (n + 1)/2$$
 (7.42)

where n is the number of carbon atoms in the solvent molecule. Further, it was shown that

$$R X_1 = A(r_{\dot{A}}/T) + (BT/r_{\dot{A}})$$
 (7.43)

Thus we have an expression which shows the dependence of X_1 on the temperature. Or conversely, for every X_1 , we can find two corresponding critical temperatures.

If A does not equal zero, we find the change of X_1 with T for constant r_A is given by

$$\frac{\partial X}{\partial T} = -\frac{Ar}{RT^2} + \frac{B}{r_A R}$$
(7.44)

For X_1 to be a minimum we find that

$$T_0^2 = (A/B)r_A^2$$
 (7.45)

The significance of X_1 being a minimum at this point means that above or below T_0 , X_1 will increase and the solvent quality becomes poorer. As T increases or decreases, X_1 will reach the critical value and the polymer will precipitate from the solution. So if we solve for T_c/r_A , we find

$$\Gamma_{c}/r_{A} = \frac{R \chi_{1} \pm [(R \chi_{1})^{2} - LAB]^{1/2}}{2B}$$
 (7.46)

Depending on the relative values of A and B, we can distinguish three possible cases. If A is zero (the polymer liquids differ only in chain length), the U.C.S.T. is zero and the L.C.S.T. is given by

$$T_{c}/r_{A} = R/2B$$
 (7.47)

If $4AB < (1/2 R)^2$, two real roots exist corresponding to the L.C.S.T. and the U.C.S.T. If $4AB > (1/2 R)^2$, there are no critical temperatures and the polymer and the solvent are not soluble in all proportions. These three cases are illustrated in Figure 11, 12, and 13.



 $x_2 \rightarrow$ Fig. 13. LAB > (1/2 R)².

EXPERIMENTAL

Fractionation

The sample of polyoctene-1 used for this study was supplied by the Union Carbide Corporation. The polymer as received was a dark yellowish, rubber-like substance. No measurements were made on the bulk polymer prior to purification.

The polymer was fractionated by precipitation according to the method described by $Flory^{12^d}$ using cyclohexane as the solvent and acetone as the non-solvent. The solution from which the polymer was precipitated was prepared by dissolving approximately ten gm. of polymer in 1000 ml. of cyclohexane. Acetone was slowly added to the stirred solution until a slight turbidity (due to precipitated polymer) persisted. The precipitated polymer was redissolved by warming and the resulting solution was placed in a thermostat maintained at $25\pm0.5^{\circ}C$ for 24 hours to allow the precipitated phase to settle. After the two phases had separated, the supernatant phase was removed leaving the polymer rich phase in the flask. The polymer was removed from the flask by dissolving it in cyclohexane. The solution was filtered through glass wool to remove impurities and the polymer was recovered by freezedrying. The procedure was repeated using the supernatant phase until a total of twelve fractions was recovered.

After the first fractionation, it was discovered that the discoloration was due to a residue, probably catalyst, left in the polymer. When the polymer was dissolved in n-nonane, the residue remained insoluble and could be removed easily by centrifugation. After the residue

was separated, the recovered polymer was transparent and colorless. The insoluble residue did not ignite when heated over a gas flame and an Xray powder photograph produced a typical crystalline pattern. Thus it was concluded that the residue was predominantly inorganic in nature. In view of the amount of work entailed in extracting the residue from each individual fraction and in repeating several measurements which had been made using the impure polymer, a sample of the polymer from which the residue had been removed was refractionated in order to obtain pure fractions.

Ten gm. of the polymer were dissolved in 1000 ml. n-nonane and the resulting mixture was centrifuged on the high-speed Servall centrifuge. The purified polymer was recovered by pouring the solution into an excess of acetone. The precipitated polymer was dried under vacuum, weighed, and then fractionated according to the procedure discussed previously. This second fractionation yielded eleven fractions. In addition, several of the first fractions were purified and later used for measurements. Henceforth, the fractions from the first fractionation will be designated by a primed number, and those of the second fractionation will be designated by a number followed by the letter A.

Phase Studies

Precipitation temperatures, T_p , of polyoctene-1 in ethyl phenyl ether were determined by the method described by Shultz and Flory³². A polymer solution was prepared by weighing solvent and polymer directly into a test tube. The solution in the tube was then diluted after each determination of T_p to obtain the next solution. T_p was determined for four to seven concentrations for each of the six polymer fractions studied.

After the solution was prepared, it was placed in a stirred water bath and cooled rapidly to determine the approximate T_p . The precipitated polymer was redissolved by heating and replaced in the water bath. The bath was cooled slowly (about $0.2^{\circ}/\text{min.}$) until the polymer precipitated. The temperature at which the solution first became turbid was noted, and when the solution became opaque, the temperature was again noted. The mixture was defined as opaque when a black line behind the tube was no longer visible through the tube. The two temperatures were in most cases within $0.2^{\circ}C$ of each other and T_p was taken to be the temperature between the two.

After the polymers had been precipitated by cooling, the mixture was warmed slowly. The polymer would, in most cases, redissolve about 1°C higher than the precipitation temperature. This difference in temperature probably resulted because the warming took place too rapidly for equilibrium conditions to be established and because some of the precipitated phase settled.

The specific volume of the polymer between $20^{\circ}C$ and $50^{\circ}C$ was determined by measuring its density at 5° intervals from 20° to 50° . A cyclohexane solution of the polymer was placed in a calibrated specific gravity bottle and the solvent was evaporated leaving a polymer film. The bottle was filled with water and the total weight of the bottle, water, and polymer was measured over the temperature range. Thus the volume of the polymer at each of the seven temperatures was easily calculated. From a knowledge of the weight and volume of the polymer, its density, and thus its specific volume, was calculated over the 30° C temperature range. The density of the solvent was calculated using the equation given in the International Critical Tables³³.

Viscosity

All viscosity measurements were made with a No. 75 Cannon-Ubbelohde semi-micro dilution type viscometer. The intrinsic viscosities of the polyoctene-1 fractions were determined in cyclohexane, bromobenzene, and ethyl phenyl ether. The temperature of the solutions was maintained to within $\pm 0.5^{\circ}$ C by placing the viscometer in a thermostat. The solution flow times were measured by an electric timer accurate to ± 0.1 sec. The relative viscosities of all solutions were between 1.2 and 2.0.

The viscosities of three solutions at different concentrations were measured for each fraction. The first solution was prepared by weighing polymer and solvent directly into a flask whereas the other two were obtained by successive dilutions of the solution within the viscometer.

Viscosity measurements in the theta solvent presented problems not encountered ordinarily when working with solutions of thermodynamically good solvents since incipient precipitation of the polymer occurs a few degrees below the measurement temperature. It was therefore essential the polymer solution did not cool below the theta temperature. All apparatus used in the transfer of the solution from the preparation flask to the viscometer was preheated to prevent precipitation of the polymer. In addition, the solvent used for the dilutions was heated above the theta temperature before it was added to the solution in the viscometer. It has been shown by Cannon, Manning, and Bell that the kinetic energy correction is negligible for the type of viscometer used in this study³⁴. Therefore, no corrections due to kinetic energy effects were applied to the viscosities.

The intrinsic viscosities of all the fractions measured in bromobenzene were equal to or less than about 4 deciliters/grm. Flory and others have shown^{12^e},³⁵ that for intrinsic viscosities less than about 4 deciliters/gm. it is not necessary to correct the intrinsic viscosity for rate of shear effects. The effect of shear rate on the viscosities measured in cyclohexane was investigated by plotting [η] bromobenzene against [η] cyclohexane since some [η] values in the latter solvent are larger than 4. As seen in Figure 14, the relationship was linear over the range of the fractions studied. This linearity indicates that no shear corrections were necessary for the viscosity measurements in cyclohexane. In addition the linear relationship between log [η] cyclohexane and log M_w indicated that shear rate corrections were unnecessary.

Osmometry

The number average molecular weight of the polymer fractions was determined by osmometry. A modified Zimm-Myerson osmometer designed by Stabin and Immergut was used for the measurements³⁶. The instrument was designed to facilitate removal of the solution while the instrument remained in the thermostat making successive readings much faster. Another feature of the instrument is the large ratio of membrane area to capillary radius which decreases the time required to reach equilibrium.



Since the osmotic pressure of a solution is directly proportional to the absolute temperature. the temperature needs to be measured to within $\pm 0.1^{\circ}C$. The error of the temperature measurement will not affect the molecular weight significantly. However, more stringent requirements upon temperature control are imposed by the following considerations. The osmometer encloses a volume of liquid which is large compared to the volume of liquid per millimeter of capillary. The osmometer acts toward temperature fluctuations as if it were a sensitive thermometer. For example, cyclohexane at 30°C has a temperature coefficient of volume of 0.0011 ml. per ml. per ^OC whereas the volume of liquid contained by a 0.1 mm. length of 0.5 mm. diameter capillary is 7.8×10^{-5} Therefore for an osmometer containing 10 ml. of solution, a change m1. of 0.05°C corresponds to a change in scale reading of 0.7 mm. In order to fulfill the requirement for accurate temperature control, the osmometry measurements were carried out in a 30° thermostat whose temperature was controlled to within $\pm 0.01^{\circ}$ C. The temperature fluctuation was determined by a Beckmann thermometer.

The membranes used in the osmometer were de-nitrated gell cellophane grade 450. The membranes were treated in a 5% NaOH solution for one hour to render them more permeable to the solvent. After the membranes were treated with the NaOH solution, they were conditioned gradually to the solvent, cyclohexane, following the method described by Yanko³⁷. When the osmometer was assembled, the permeability of the membranes was measured. The importance of the permeability measurement is to establish that the membranes are free from imperfections and that the osmometer is assembled correctly. It is also used to decide the minimum time required for the establishment of osmotic equilibrium.

The measurement of the time constant of an osmometer, from which the permeability is obtained, may be made with the osmometer filled with pure solvent. The initial level in the measuring capillary, h_1 , is set 1-5 cm. above that for the reference capillary, h_2 , and the descent noted at a series of times. The logarithm of the hydrostatic head (the difference between h_1 and h_2) is then plotted vs. time. The time necessary for the natural logarithm to decrease by 1 is the time constant³⁸. An example of this measurement is shown in Figure 15.

When the results of the measurement indicated that the osmometer was functioning properly, the solvent was removed from the cell and it was filled with the polymer solution by means of a syringe and a long hypodermic needle. (To prevent the membranes from drying, the osmometer was never left free of solvent.) The cell was rinsed with a few ml. of solution before it was filled so that the final concentration of the solution would not be affected by the small amount of liquid which remained in the cell.

Care was taken to remove all air bubbles from the osmometer cell after it was filled. This presented no problem since the bubbles could be seen easily through the glass cell and were easily removed.

The polymer solution was preheated to the operating temperature before it was placed in the cell. However, it cooled slightly when transferred to the cell. Thus when it was placed in the cell, it warmed and expanded. The expansion of the solution caused an immediate capillary rise which continued for several minutes. After this expansion ceased, it was assumed that temperature equilibrium was established and the readings were begun.



Osmotic pressure was determined by measuring the difference between the level in the solution capillary, h_1 , (previously referred to as the measuring capillary) and the level in the reference capillary, h_2 . The heights, h_1 and h_2 , were measured by a cathetometer accurate to ± 0.001 cm. The difference between h_1 and h_2 , i.e., Δh , was therefore accurate to ± 0.002 cm.

It is usual for Δh to pass through a maximum and then decrease slowly with time. The level in the measuring capillary and therefore Δh should increase with time until an equilibrium height is reached. If Δh is plotted against time, it will increase to a maximum and then drop slowly. The decrease in Δh (or in the level of the measuring capillary) is caused by polymer molecules diffusing through the membranes. Actually the polymer molecules diffuse through the membranes from the beginning of the measurements and so the maximum Δh is not the true equilibrium value.

Assuming that the polymer diffusion has been constant throughout the determination, the effect can be corrected by extrapolating Δh to zero time. The intercept at zero time gives the equilibrium Δh value. An example of this extrapolation is shown in Figure 16.

After the reading of the first solution was completed, it was removed from the cell and the cell was rinsed with pure solvent. The first solution was diluted and the procedure just described was repeated. Finally this second solution was removed and diluted and a third reading was made. Thus three concentrations of each fraction were measured.



Fig. 16. Osmotic equilibration curve at $30^{\circ}C$ for polyoctene-1, FlOA in cyclohexane. C = 0.8047 gm/100 cc.

Light Scattering

The weight average molecular weights of six polymer fractions were determined by light scattering. All of the measurements were performed using the Brice-Phoenix Light Scattering Photometer series 1000.

Light scattering measurements were performed on six of the higher molecular weight fractions with bromobenzene as the solvent. Preliminary investigation of the solvent indicated that the solvent exhibited no fluorescence at the wave length used for the light scattering measurements. All reported measurements were taken with the unpolarized green (5416\AA) line of mercury.

The techniques and procedures for making the light scattering measurements were, with a few exceptions, the same as those described by McCoy^{39^a}. One difference in technique involved the method of measuring the scattering intensities over the range of angles. Since the light scattering calculations depend upon the ratio of the scattering intensity at a given angle Θ , G_{Ω} , to the intensity at zero angle, G_0 , it is important that G_0 remain constant throughout the measurements. However, it was found that G_0 would drift slightly during the time of the measurement and thus the ratio of G_0/G_0 was affected. This change in the G_0 reading which was attributed to instrument drift or photo tube fatigue changed the G_{α}/G_{0} ratio by as much as two to three percent. The technique used by McCoy did not take into consideration the change in ${\rm G}_{\rm O}$ with time and, in fact, assumed it to be constant over the range of angles covered. In order to correct for this drift, it was deemed advisable to check G_0 after the intensity at each angle was measured. The photo tube was set at the sero angle position and the galvanometer deflection

was arbitrarily set at 95. The photo tube was then rotated to the first angle, the 45° position, and the intensity measured. The photo tube was returned to the zero angle position and if necessary the galvanometer deflection adjusted to 95. The intensity at the second angle was then read. This procedure was continued throughout the entire range of angles. Thus the zero angle intensity, G_{\circ} , was the same for all angles.

The anomalous readings between 70° and 80° mentioned by McCoy^{39^b} were also observed during this investigation. As McCoy noted, these anomalous readings were probably due to extraneous reflections. This effect was corrected by using a rectangular tube between the cell table diaphragm and the cell. This tube, although allowing the parallel light beam from the lamp to pass unhindered, fit tightly against the cell so that no extraneous light reached the photo tube.

The data obtained from these measurements were treated in the manner outlined by McCoy with the exception that, because of larger dissymmetry ratios, the Fresnel corrections for the back reflection of light at the glass/air interface were applied.

The specific refractive index increment, (dn/dc), of the solution due to the polymer was measured using the Brice-Halwer⁴⁰ type differential refractometer. The instrument was calibrated with standard sucrose and alkali chloride solutions. The (dn/dc) was measured for the whole polymer and for several fractions at the temperature at which the light scattering measurements were made. Details of the measurements and calibration procedure are given by McCoy^{39^C}.

If the technique just described was used, the ratio G_{Θ}/G_{0} should be independent of any instrument fluctuations. That is, G_{Θ} , the intensity of scattered light at Θ , is directly proportional to the incident

intensity, G_0 . Any fluctuation in G_0 will cause a fluctuation in G_0 . The ratio G_A/G_0 will remain constant. However, it was found that the ratio G_{Ω}/G_{0} tended to decrease with time. A definite correlation was seen to exist between the decrease in this ratio and the increase in the solution temperature. The temperature of the solution increased as a result of the increase of the temperature inside the instrument. It is believed that as the temperature of the solvent increased, its solvent qualities changed which caused the polymer coil size to change. Although this effect would not change the measured value of the molecular weight, it would, however, change those parameters which depend on the solvent-polymer interaction such as the second virial coefficient. Although no extensive study was made of this effect, it was found that the change did not effect the value of the data to an appreciable extent and so no direct attempt was made to maintain the solution at a constant temperature. That is, the temperature of the solution was determined by the temperature inside the photometer.

Lower Critical Solution Temperature

Lower critical solution temperatures were made of n-pentane solutions of polyoctene-1 and two other α -olefins, isotactic and atactic polypropylene and polybutene. For the polyoctene-1 and the atactic polypropylene and polybutene, n-pentane solutions of known concentrations were prepared and transferred to capillary tubes by means of a long hypodermic needle. Because they were insoluble at room temperature in n-pentane, the isotactic polymers were weighed directly into the tubes. The solvent also was weighed directly into the tubes. When the solutions, or solvent and polymer, had been placed in the tubes, they were cooled to dry ice temperature and evacuated. The tubes were then sealed while under vacuum.

On several occasions during the sealing, it was observed that solution was lost due to "bumping" of the solutions while under vacuum. It was found that this problem could be solved if the solution was frozen with liquid nitrogen before the tube was evacuated. To determine if any solution was lost during the sealing, the liquid level in the tube was measured with a cathetometer before and after sealing.

The tubes were heated by immersing them completely in a heating bath of Dow-Corning 550 silicone oil. The temperature of the phase separation, T_p , was found by heating the bath slowly (0.1°C per min.) until the solution became turbid. The phase separations, in most cases, took place over a range of one degree or less and were reproducible to within one degree with two or three repeated heatings. No evidence for decomposition of the polymer upon heating was observed.

Above T_p , the two phases separated, the polymer rich phase being the denser. If the bath was cooled immediately after the solution became turbid so that the phases did not separate, the polymer would redissolve immediately at the precipitation temperature.

RESULTS

Fractionation

Two samples of polyoctene-1 were fractionated from a dilute cyclohexane solution. The first fractionation was carried out on the untreated whole polymer, while the second fractionation was carried out using a sample from which the metallic residue had been extracted. This second fractionation yielded eleven fractions. With the exception of two extracted fractions, no studies were made of the fractions from the first fractionation.

The results of the fractionation were determined by viscosity measurements. Thus the intrinsic viscosity of each of the eleven fractions from the second fractionation and the bulk polymer were determined in cyclohexane at 30° C.

The results of the second fractionation are shown in Table I. It is seen that the molecular weights (as determined by intrinsic viscosity) of the first three fractions are in reverse order. It is suspected that this resulted either because of non-uniform temperature throughout the fractionation or because the polymer separated on the basis of tacticity rather than molecular weight alone. Another possibility is that some branching was present in the molecules and that this caused the solubility of lower molecular weight species to be decreased. No information was available concerning either the tacticity or the possible presence of branching of the polymer and no measurements were made to determine either tacticity or branching of the fractions.

Table I. Fractionation data.

Fraction	[7]] cyclo- hexane 300	wt.gm.	wt. %	[η] _i w _i
Second Fractionation				
1 A	6.37	0.634	7.50	0.48
2 A	6.72	0.133	1.54	0.10
3 A	9.30	0.290	3.45	0.32
Ц А	9.64	0.285	3.33	0.32
5 A	8.60	0.741	8.10	0.76
6 A	5.71	1.59	18.92	1.08
7 A	4.19	1.05	12.50	0.53
8 A	2.90	0.94	11.19	0.32
9 A	1.75	1.30	15.47	0.27
10 A	1.00	0.75	8.93	0.09
11A	0.30	0.70	8.33	0.02
	Σ	w _i 8.40	$\sum [7]$];w _i 4.29
First Fra	actionation			
21	6.64	`		
7 '	2.61			
8*	1.58			

.

Bulk intrinsic viscosity, $[\eta]_{B} = 4.57$ $\sum [\eta]_{i}w_{i} = 4.29$

Of the 8.52 gm. of polymer which were fractionated, a total of 8.40 gm. were recovered for a recovery of over 98%. The fractionation data was checked by the equation $[\eta]_B = \sum_{i=1}^{n} [\eta]_i w_i$ where $[\eta]_B$ and $\left[\, \mathcal{N} \,
ight]_{i}$ are the intrinsic viscosities of the bulk polymer and the ith fraction respectively and w; the weight fraction of the respective polymer fractions. The value of 4.29 for $\sum_{i=1}^{11} [\eta]_i w_i$ is somewhat lower than the intrinsic viscosity of the bulk polymer, $[\eta] = 4.57$. Since the recovery of the polymer was high, this discrepancy can not be explained by the loss of higher molecular weight species. It is believed that a small amount of degradation occurred between the time the polymer was fractionated and the intrinsic viscosities were determined. However, this degradation was shown to be negligible over a long time period by redetermining the intrinsic viscosities of fractions. Another possible explanation for this discrepancy is that no corrections were made for the shear effect at high intrinsic viscosity. The shear effect would cause the measured viscosity to be lower than the true value for higher molecular weight species while having no effect on the viscosity of lower molecular weight species. The overall effect would therefore cause the sum $\sum_{i=1}^{n} [\eta]_i w_i$ to be smaller than $[\eta]_B$.

The molecular weight distribution of the polymer was not constructed because not enough fractions were recovered from the whole polymer for an accurate representation.

Phase Studies

Liquid-liquid phase diagrams were constructed for five fractions of polyoctene-1 in phenetole near the critical miscibility temperature.

The diagrams were constructed by plotting the precipitation temperatures, T_p , against the volume fractions, \mathcal{N}_2 , of the polymer. The resulting phase diagrams are shown in Figure 17.

The critical miscibility temperatures, T_c , correspond to the maximum point in the phase diagrams. In Figure 18, the reciprocal of the critical temperatures is plotted against the molecular size function, $1/x^{1/2} + 1/2 x$, in accordance with equation (3.3). The intercept of the y-axis gives the reciprocal of the theta temperature and the ratio of the intercept to the slope of the line gives the value of the entropy of dilution parameter χ_1 . These values are then used with equations (1.15), (1.16), and (1.18) to calculate the excess entropy and heat of dilution respectively. These results are shown below in Table II.

Table II. Thermodynamic parameters from phase equilibria studies. Polyoctene-1 in phenetole.

θ(°K)	ψ_1	$\Delta \overline{H}, \mathcal{V}_2^2$ cal./mole	$\Delta \overline{S}, \mathcal{V}_2^2$ cal./mole deg.
50.4	.813	788	1.66

The value of x in equation (3.3) was calculated from \overline{M}_{w} rather than \overline{M}_{n} since it was only possible to measure \overline{M}_{n} for two fractions. To determine if the use of M_{w} rather than M_{n} to calculate x would affect the value of $1/\Theta$, a value of 1.2 for the ratio M_{w}/M_{n} was assumed and calculated values of M_{n} were used to calculate new values of x.

The important parameter Θ , which is obtained at the y intercept, was unaffected by using M_W rather than M_n ; however, a small change of slope is noted which introduces approximately six percent uncertainty in Ψ_1 .






Light Scattering

The weight average molecular weight of the polymer fractions was determined using the Zimm method as outlined previously. The Zimm plots for the polyoctene-1 fractions five through ten are shown in Figures 19 through 24.

The dimensions of the polymer molecules were calculated both by the Zimm technique and Debye's dissymmetry method. To calculate the dimensions by the Zimm method, the limiting slope of the zero concentration line of the Zimm plot was divided by the intercept and this ratio set equal to $(8\pi^2/9\lambda^2)\overline{r^2}$. This value for the ratio is used because we assumed that the molecules in solution are in theform of random coils (see equation (6.4)). The wave length of the light in the solution is given by λ and $\overline{r^2}$ is the mean-square end-to-end length of the polymer molecule. Since $(\overline{r^2})^{1/2}$ obtained by this method is a z-average length, it was converted to the weight average length by the use of equation (6.9)

$$\bar{r}_{W}^{2} = \bar{r}_{Z} (h + 1)/(h + 2)$$

The h is a parameter characterizing the molecular weight distribution and can be found from equation (6.8)

$$M_n \neq M_w (h/h + 1)$$

Since M_n was determined from only two fractions, it was necessary to assume that the average value calculated from the two M_w/M_n ratios was the same for all of the fractions. The average for the ratio was 1.09 and the value of h calculated from this ratio was 12.10. Using this value of h, the ratio (h + 1)/(h + 2) was found equal to 0.93. Therefore, r_z^2 was multiplied by 0.93 to obtain \overline{r}_w^2 .

















A source of error in the Zimm method for determing the dimensions of the polymer coils arises from the difficulty in determining the limiting slope of the zero concentration line which generally becomes non-linear near the intercept. Furthermore, the Zimm method becomes less accurate as the molecular weight of the polymer decreases. It is possible, however, to obtain better results under these conditions by Debye's dissymmetry method.

Since dissymmetry is generally a function of solution concentration, it is necessary to use the limiting or intrinsic dissymmetry, [z], for the calculations. The dissymmetry is usually not a linear function of c. Therefore, the extrapolation to zero c is improved by plotting 1/z-1 against c. The chain dimension can then be obtained from published tables⁴¹ which relate the dimensions to z.

The values of z for the different concentrations were not calculated directly from the observed Hc/γ values at 45° and 135°. Rather, the values were taken from the averaged plot of Hc/γ against $\sin^2\theta/2$ + kc at 45° and 135° for each concentration. The values of z determined by this method are independent of individual readings at 45° and 135° and so are not effected by anomalous readings at these angles.

The second virial coefficient, A_2 , for polyoctene-1 in bromobenzene at 25° was obtained from the slopes of the zero concentration lines of the Zimm plots. The usual decrease of A_2 with molecular weight is observed.

The parameter \mathbf{D} in equation (5.10) was calculated from both the Zimm and the dissymmetery data using the values of $[\mathcal{N}]$ measured in the light scattering solvent, bromobenzene. The values calculated for \mathbf{D}

agree well with the most commonly accepted value of 2.1×10^{21} as given by Flory^{12C}. This agreement indicated that the polymer molecules have random coil configurations in solution.

The results of these calculations from the light scattering data are shown in Table III. The dimensions of fraction 10 were not calculated by the dissymmetry method because it was not possible to obtain an accurate measurement for z. A value of 0.105 for the specific refractive index increment (dn/dc) of polyoctene-1 in bromobenzene at 25°C was used for the calculations.

Viscosity

In addition to determining intrinsic viscosities of the deven fractions of the second fractionation in cyclohexane at 30° C, the intrinsic viscosity of two fractions from the first fractionation was also measured in cyclohexane at 30° C. Also the intrinsic viscosities of five fractions were determined in bromobenzene at 25° C and the intrinsic viscosities of four fractions were measured in the theta solvent, phenetole, at 50.4° C. The data were treated according to the quations of Huggins (5.4) and Kraemer (5.5). The results of the viscosity measurements are shown in Table IV with the values of the Huggins constants k' and k".

The sums of the Huggins constants, k' + k", in cyclohexane and bromobenzene are near the theoretical value of 0.5 in thermodynamically good solvents. However, Huggins constants, k', and the sums, k' + k",
obtained in phenetole were considerably larger. This effect has been observed previously in poor solvents⁴².

By plotting log $[\eta]$ cyclohexane 30°C against log \overline{M}_w , the constants for the Mark-Houwink equation were determined for each solvent from the

						
Fraction	n Mar 10 ^{−6}	(r²) Zimm	1/2,A Dissym.	∑ x Zimm	10 ⁻²¹ Dissym.	$A_2 \times 10^4$ ml mole/gm ²
5 A	4.00	2070	1995	1.83	2.01	1.62
6 A	2.50	1530	1392	1.97	2.61	1.98
7 A	1.68	1239	1172	1.87	2.03	2.15
8 A	1.25	940	1040	2.27	1.64	2.22
9 A	0.607	646	765	2.25	1.40	2.95
10 A	0.250	366		2.25		3.12

Table III. Light scattering results in bromobenzene at 25° C.

Fractio	n	[η]	k'	k"	k ' + k '
	A.	In cyclohexan	e at 30°C		
1 A		6.37	0.241	0.230	0.47
2 A		6.72	.263	.212	.48
3 A		9.30	.257	.224	.48
4 A		9.64	.238	.224	.46
5 A		8.60	.270	. 200	.47
6 A		5.71	.249	.208	.46
7 A		4.19	.322	.164	.49
8 A		2.90	.264	.200	.46
9 A		1.75	.290	.250	.54
10 A		1.00			
11 A		0.30			
2'		6.64	.212	.234	.45
7 '		2.61	.281	.208	.49
whole		4.57	.390	.110	.50
	Β.	In bromobenze	ne at 25°C		
7 A		1.95	.294	.262	.56
8 A		1.51	.255	.264	.52
9 A		1.00	.300	.290	•59
10 A		0.44	.264	.232	.50
2'		3.41	.510	. 103	.61
	с.	In phenetole	at 50.4°C (the	ta)	
7 A		0.86	.833	079	•75
9 A		.51	.865	096	•77
2'		1.26	.317	.198	.52
7 '		0.65	· ⁸ 97	064	.83

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Table IV. Viscosity results for polyoctene-1 from fractionations 1 and 2.

resulting relationships. (See Figure 25). The following relationships were established:

in	cyclohexane at 30°C,	[7]=	5.75	x	10-5	M0 • 7 8	(8.1)
in	bromobenzene at 25°C,	[7]=	2.9	x	10 ⁻⁵	M0.78	(8.2)
In	phenetole at 50.4°C,	[η] =	6.54	x	10 -4	M0.5	(8.3)

Osmometry

The number average molecular weights of fractions F9A and F1OA were determined by osmometry. The molecular weight of fractions higher than F9 were too large to be determined accurately.

The data were treated according to equation (4.29) by plotting $(\pi/c)^{1/2}$ against c. The results of this plot are shown in Figure 26. The second virial coefficient, A_2 , was found from the slope and intercept of the lines. Also the interaction parameter, χ_1 , was calculated from the relation^{12C}

$$A_2 = (\overline{N_2}/V_1)(1/2 - X_1)$$
 (9.1)

The results of the molecular weight measurements and the calculations are shown below in Table V.

Table V. Osmotic pressure data for polyoctene-1 in cyclohexane at 30°C.

Fraction	$\overline{M}_n \times 10^{-5}$	[_(cc./gm.)	A ₂ (cc. mole/gm. ² x10 ⁴)	. X1
9A .	5.40	210	3.89	.498
10A	2.38	109	4.58	.498



Fig. 25. Intrinsic viscosity - molecular weight relationship for polyoctene-1 in (1) cyclohexane at 30°C □, (2) bromobenzene at 25°C Δ and (3) phenetole at 50.4°C 0.



Fig. 26. Osmotic pressure vs. concentration for polyoctene-1 in cyclohexane at $30^{\circ}C$.

Lower Critical Solution Temperatures

Lower critical solution temperatues were determined for four fractions of polyoctene-1 in n-pentane. In addition, the L.C.S.T. of single fractions each of atactic polypropylene and polybutene and isotactic polypropylene were determined in n-pentane solution.

Phase diagrams were constructed by plotting precipitation temperatures, T_p , against weight fraction of polymer. These phase diagrams are shown in Figures 27 and 28. The L.C.S.T. was taken from the minimum of the T_p vs. weight fraction curve. These results are given in Table VI.

Fraction	T _{CL} (°K)	$M_{W} \times 10^{-6}$
Polyoctene-1		
5 A	438.1	4.00
6 A	439.0	2.50
8 A	440.0	1.25
11 A	446.1	0.06
Atactic polypropylene JK5	425.3	0.0758
Isotactic polypropylene JKE3	425.1	0.124
Isotactic polybutene-1 M17	424.3	0.499
Atactic polybutene-1 A121	422.3	2.3

Table VI. Lower critical solution temperatures for poly α -olefin fractions in n-pentane.





Fig. 28. Lower critical solution phase diagrams. T_{CL} vs wt. fraction polymer.

Fractio	n	M × 10 ⁻⁶	$a^{3}=[\eta]/[\eta]_{\Theta}$	$[(a^{5}-a^{3})/M^{1/2}]x10^{3}$
	Α.	In cyclohexane		
5 A		4.00	6.62	8.40
6 A		2.50	5.54	7.52
7 A		1.68	4.78	6.80
8 A		1.25	4.44	6.76
9 A		0.607	3.38	5.45
10 A		0.250	2.95	6.74
	в.	In bromobenzene		
5 A		4.00	3.13	1.78
6 A		2.50	2.74	1.65
7 A		1.68	2.22	1.19
8 A		1.25	2.06	1.13
9 A		0.607	1.93	1.22
10 A		0.250	1.31	0.52

Table VII. The expansion factor and its dependence on the molecular weight of polyoctene-1 in cyclohexane and bromobenzene.

DISCUSSION OF RESULTS

The molecular expansion factor α was calculated from the following relationship^{12C}

$\alpha^{3} = [\eta] / [\eta]_{\Theta}$

where $[\eta]$ is the intrinsic viscosity of the fraction in the thermodynamically good solvent and $[\eta]_{\theta}$ is the intrinsic viscosity in the theta solvent. The measurements of the $[\eta]$ values for the polymer fractions in both cyclohexane and bromobenzene were made at temperatures below that for the $[\eta]_{\theta}$ values. It has been shown that $[\eta]$ for polyisobutylene in several good solvents has a small temperature dependence^{12C}. It is presumed that this is true for other polymer-solvent systems and so it is assumed that **a** is not greatly affected by this difference in temperature.

The values of a^3 calculated for six fractions of polyoctene-1 in cyclohexane and in bromobenzene and are listed in Table VII. It is seen that there is a definite increase of a^3 with molecular weight. This agrees with equation(2.3) which predicts that a should increase without limit as the molecular weight increases.

According to equation (2.3), the factor $(a^5-a^3)/M^{1/2}$ should be independent of molecular weight. However, as seen in Table (VII), there is a considerable dependence on molecular weight. This suggests that the function a^5-a^3 is not exactly the correct one to use for this relationship.

The unperturbed dimensions of the molecules are related to the molecular weight and intrinsic viscosity by equation (5.11)

$$[\eta] = \Phi(\bar{r}^2_0/M)^{3/2M^{1/2}} a^3$$

Since, according to theory, the factor $(\overline{r}_0^2/M)^{3/2}$ is independent of molecular weight, we can write

$$[\eta] = KM^{1/2a^3}$$

where

$$K = \Phi (\bar{r}^2 / M)^{3/2}$$

At the theta temperature when a = 1, we can write equation (5.11) as

$$[\boldsymbol{\eta}]_{\Theta} = \mathrm{KM}^{1/2}$$

Thus from the values of $[\eta]_{\theta}$ and $M^{1/2}$, we can calculate K for a particular polymer. According to theory, K should be a constant independent of both solvent and molecular weight. It may be somewhat dependent on temperature, however. The results of the intrinsic viscosity measurements at the theta temperature (shown by (8.3)) (see page 71) gave results which are in complete agreement with theory as expressed by equation (5.13). That is, the exponent a is equal to 0.5. The value of K for polyoctene-1 was found experimentally to be equal to 6.54 x 10^{-4} .

If we use the commonly accepted value of Φ as being 2.1 x 10^{21} , we can use equation (5.11) to calculate $(\overline{r^2}_0/M)^{1/2}$ for polyoctene-1. This factor is characteristic of each type of polymer. Using the K calculated above, it was found that for polyoctene-1

$$(r^2_0/M)^{1/2} = 67.6 \times 10^{-10}$$

From the relationship $r_0 = r/a$, $(r^2_0/M)^{1/2}$ for the polymer was calculated for the six polymers studied by light scattering. The r_0 values were calculated using dimensions obtained from both the Zimm method and the dissymmetry technique. The values calculated from the dissymmetry dimensions tend to increase with decrease in molecular weight. It is thought that this is a result of larger errors which result at lower dissymmetry values at the lower molecular weights. The values calculated from the Zimm dimensions are reasonably constant as predicted by theory and their average, $(\overline{r}_0^2/M)^{1/2} = 68.9 \times 10^{-10}$, agrees very well with the value calculated from K. The results of these calculations are shown in Table VIII.

Fraction	Dissy	mmetry	Zimm		
	$(\bar{r}_{0}^{2})^{1/2}$	$(\bar{r}^{2}_{0}/M)^{1/2} \times 10^{10}$	$(\bar{r}^{2}_{0})^{1/2}$	$(\bar{r}^{2}_{0}/M)^{1}/2_{x1010}$	
5 A	1366	66.8	1418	70.9	
6 A	994	62.9	1093	69.2	
7 A	902	69.6	953	73.6	
8 A	819	73.1	740	66.1	
9 A	612	78.8	517	66.5	
10 A			336	67.2	

Table VIII. Values of $(\overline{r}_0^2/M)^{1/2}$ as determined by light scattering.

It is of interest to examine an equation due to Kurata and Stockmayer which relates [η] to the molecular weight of the polymer. They show⁴³ that equation (10.1)

$$[\eta]^{2/3}/M^{1/3} = K^{2/3} + K^{5/3}(a^5 - a^3)M^{1/2}/[\eta]$$
(10.1)

due to Flory⁴⁴ should be modified and the resulting equation becomes

$$[\eta]^{2/3}/M^{1/3} = K^{2/3} + 0.363\Phi B[g(\alpha)M^{2/3}/[\eta]^{1/3}] \quad (10.2)$$

where B is a parameter characteristic of a particular polymer and g(a) is given by

$$g(a) = \frac{8a^3}{(3a^2 + 1)^{3/2}}$$

If we plot $[\eta]^{2/3}/M^{1/3}$ against $g(a)M_w^{2/3}/[\eta]^{1/3}$, a linear relationship results and the intercept will give $K^{2/3}$. The results of this plot for polyoctene-1 in the three solvents are shown in Figure 29.

K obtained from the theta solvent data, at 54°, was 7.50 x 10^{-4} and the K from the bromobenzene data at 25°C was 7.08 x 10^{-4} . Both these values are somewhat larger than the observed $[\eta]_{0}/M^{1/2}$ value, i.e., 6.54 x 10^{-4} . The value from the cyclohexane data, at 25°C, was 8.89 x 10^{-4} which is larger still.

It would be expected that K decreases as the temperature increases. That is, the chain length decreases with increase in temperature. This trend is observed as the temperature decreases from 54° to 25° C. However, the K from the cyclohexane data is in the reverse order as that expected. The explanation for this is not known.

The unperturbed dimensions of polyoctene-1 at the theta temperature were calculated from the Flory-Fox equation, $(\overline{r}^2_0)^{3/2} = [\eta]M/\Phi$, assuming $\Phi = 2.1 \times 10^{21}$, for the four fractions measured in the theta solvent. The values for fractions 7A and 9A whose unperturbed dimensions were calculated from the light scattering results using the dissymmetry method and the value of the expansion factor, α , agree fairly well. This indicates that a value for $\Phi = 2.1 \times 10^{21}$ is reasonable. Also the assumption that α for polyoctene-1 can be calculated from [N2] at temperatures different than the temperature at which the intrinsic viscosities in the good solvents is measured, appears to be valid. The unperturbed dimensions as measured in the theta solvent, are 2.4 times the values calculated assuming free rotation about the bonds, i.e., $\overline{r^2} = 2n1^2$, where 1 is assumed to be $1.5A^{12C}$. The perturbed dimensions in bromobenzene, as



measured by light scattering and calculated from viscosity measurements using the Flory-Fox equation and $\Phi = 2.1 \times 10^{21}$, are about 3.3 times as large, and the dimensions of the molecules in cyclohexane are about 4.2 times as large as the freely rotating dimensions. A comparison of these dimensions are shown in Figure 30. The dimensions calculated from the viscosities measured in bromobenzene compare very well with those measured by light scattering. Again the value of 2.1 x 10^{21} for Φ is shown to be correct, at least within experimental error.

Finally it will be of interest to compare the dimensions of polyoctene-1 with several other poly α -olefins. It has been reported by Chinai and collaborators⁵ that for a series of methacrylates, the ratio of the square of a linear dimension to the degree of the polymerization falls in the order n-hexyl > n-octyl > methyl > ethyl > n-butyl. The dimensions of polyoctene-1 were therfore compared with several other poly a-olefins, the purpose being to discover if any such curious order existed for the poly a-olefins. A comparison was made using the ratio of $(\overline{r}^2_{0})^{1/2}$ to the square root of the degree of polymerization to determine if any order existed. Table IX shows the results of this comparison. These calculations indicate that the dimensions are dependent on the pendant group and are proportional to their size. Thus, with respect to the pendant group, the average end-to-end dimensions fall in the order phenyl > hexyl > ethyl > two methyls \approx methyl. This order results when the data of Wilkins⁴⁸ or Natta⁴⁷ are used to determine the ratio $(\bar{r}^2_0/D.P.)^{1/2}$ for polybutene. The ratio calculated from the data of Krigbaum⁴⁶, however, results in a ratio for polybutene which is larger than both polystyrene and polyoctene-1.





Polymer	$(\bar{r}^{2}_{0}/M)^{1/2} \times 10^{10}$	(r ² ₀ /D.P.) ^{1/2}	Pendant group
polystyrene	70 45	7.16	phenyl
polyoctene	68	7.08	hexy1
polybutene	10046	7.48	
polybutene	81 47	6.00	ethy1
polybutene	780 48	5.81	
polypropylene	83.5 ²	5.32	
polypropylene	92 49	5.98	methyl
polyisobutylene	7650	5.66	two methyls

Table IX. Comparison of $(\overline{r}_0^2/D.P.)^{1/2}$ for atactic poly a-olefins.

The results of the L.C.S.T. studies substantiate the findings of other studies with bulk polymers^{7,8} which indicate that the L.C.S.T. decreases as the chain length of the solute species increases.

Using the theory developed by Delmas, Patterson, and Somcynsky, an attempt will be made to relate L.C.S.T. to the Flory interaction parameter, X_1 . Before studying the results of the present work, it will be of interest to use the theory and the resulting equation

$$T_{c}/r_{A} = \frac{R \chi_{1} + [(R \chi_{1})^{2} - LAB]^{1/2}}{2B}$$
(11.1)

to try to predict the results of the work carried out by Baker \underline{et} $\underline{a1}$? in which they determined the L.C.S.T. for four samples of polyisobutylene of different molecular weights in n-pentane.

The value of A used in the equation was that determined by Delmas, Patterson, and Somcysky from the heat of mixing of polyisobutylene with n-paraffins. B was also that determined by the above workers; it being the value which gave the best fit for the data. The values of these constants are

$$A = 10.1 \text{ cal./mole}$$
 (11.2)

$$B = 8.2 \times 10^{-3} \text{ cal./deg.}^2 \tag{11.3}$$

According to equation (7.42), r_A for n-pentane is equal to three. If we assume that the L.C.S.T. occurs at the same value of χ_{1c} as the U.C.S.T., we can use the simple Flory approximation relating χ_{1c} to the molecular weight. That is,

$$\chi_{1c} = 1/2 + (1/x^{1/2} + 1/2 x)$$
 (11.4)

Using the above values for A and B and the Flory approximation for χ_{1c} , the T_{CL} values for the polyisobutylene in n-pentane were calculated. The results of the calculations are shown in Table X. The data shown is that of Freeman and Rowlinson⁷ and Baker et al.⁸

Table X. The thermodynamic interaction parameter as a function of molecular weight and the observed and calculated T_{CL} for polyisobutylene in n-pentane.

Polymer	М	$1/x^{1/2}$	X _{1c}	T _{CL} (⁰ K) (observed)	T _{CL} (° K) (calculated)
(ref. 7)	1,584,000	.007	.507	348	334
III ⁸	14,000	.086	.586	373	396
IV ⁸	62,000	.040	.540	366	360
V8	2,250,000	.007	.507	344	334

If we plot T_{CL} against $1/x^{1/2}$, we obtain the relationship shown in Figure 31. Although this plot is not strictly justified by equation (11.1), there should be a linear dependence of T_{CL} or $1/x^{1/2}$ if the factor LAB is much smaller than $R(\chi_{1c})^2$. Polymer II from Baker <u>et al</u>. does not fit this linear relationship. It is believed that the molecular weight of polymer II was too small (1,170) to justify using the preceding method for calculating T_{CL} . Also the fact that unfractionated polymers were used would lead to uncertainty in determining the precipitation temperature. That is, T_{CL} values measured for polymers having true weight average molecular weights equal to the molecular weights given in Table X would probably be different than those observed.

An attempt was made to calculate the A and B from the observed data of Freeman and Rowlinson. Two equations were obtained by substituting two sets of the data, i.e., values of χ_{1c} and T_{CL} , into equation (11.1) and the equations were solved for A and B. It was found that the values of A and B are very sensitive to T_{C} and unless accurately known values are available, these constants can not be obtained by this method.

It should be mentioned that the χ_{1c} calculated from thermodynamic data by Baker <u>et al</u>. for polymer V is somewhat larger than the χ_{1c} calculated from the Flory approximation. However, the value for polymer V of $\chi_{1c} = .53$ gives $T_{CL} = 346^{\circ}$ K which is much closer to the observed value of 344° K. Thus the use of the Flory approximation for calculating χ_{1c} to determine the L.C.S.T. should be taken with reservation and at best should be considered an approximation which can be used if thermodynamic data are not available.

Independent values for A and B were not available for polyoctene-1 and so it was necessary to assume A equal to zero and to calculate B



from one of the T_C values. A is equal to zero if the solvent and polymer differ only in chain length. Therefore, this assumption is not unreasonable since the polymer is predominately methylene groups. Also if A is zero, the U.C.S.T. should be zero. A solution of polyoctene-1 F5 ($M_w = 4 \times 10^6$) was cooled to the freezing point of the solvent (142°K) without observing precipitation. Thus this criteria is obeyed, at least as far as can be observed. Hence if A is equal to zero, equation (11.1) becomes

$$T_{C}/r_{A} = RX_{I_{C}}/B \qquad (11.5)$$

If we use the T_C for F5A, B is equal to 6.84 x 10^{-3} cal./deg.². The results of the calculation of T_C for the remainder of the fractions are shown in Table XI.

Table XI. The thermodynamic interaction parameter as a function of molecular weight and the observed and calculated T_{CL} for polyoctene-1 in n-pentane.

Fraction	M _w x 10 ⁻⁶	1/x ^{1/2}	χ_{i_c}	T _{CL} (°K) (observed)	T _{CL} (°K) (calculated)
5 A	1.32	.005	.505	438.1	438
6 A	1.18	.009	.509	439	441
8 A	•75	.010	.510	440	442
11 A	.06	.040	.540	446	468

An attempt was also made with this data to calculate A and B. However, as before, it was not possible to obtain satisfactory results from the T_{C} data alone. The agreement of the calculated L.C.S.T. with the observed values becomes worse as the molecular weight increases. This indicates that A is not equal to zero as was assumed and/or that, as was decided before, the interaction parameter can not be calculated accurately by the Flory approximation.

So in order to be able to calculate the L.C.S.T. with more accuracy, it is necessary that A and B be determined independently or from highly precise L.C.S.T. data and that true values for X_{1c} be known. Although the calculations do not fit the observed data exactly, the equation seems to fulfill the need of predicting the dependence of L.C.S.T. on molecular weight.

If we extrapolate the T_{CL} to infinite molecular weight, i.e., to $1/x^{1/2} = 0$, we obtain the L.C.S.T. for infinite molecular weight polymer. This is an analogy to the familiar Flory theta temperature which is the U.C.S.T. for polymer of infinite molecular weight. On the basis of this analogy to the Θ_U for U.C.S.T., we will tentatively refer to the L.C.S.T. for infinite molecular weight as Θ_I .

Using equation (11.5) and a value of 0.5 for χ_{1c} , the T_{CL} 's for polyisobutylene in n-pentane and polyoctene-1 in n-pentane were calculated. This is compared with θ_L as determined from the extrapolation just described. (See Figure 31)

The results of the calculation and the extrapolation are shown below in Table XII. The results for polyoctene-1 agree to within less than 1%. This agreement is very good considering the assumption made. The agreement for the polyisobutylene results is about 3%. This agreement indicates that equation (11.5) predicts values of $T_{\rm CL}$ fairly well if the proper χ_{1c} is used.

Polymer	θ _L (extrapolation)	θ _L (calculated from 11.5)
polyisobutylene	34 3 °K	338 °K
polyoctene-1	437 °K	434 °K

.

Table XII. Values of Θ_L obtained by extrapolating T_{CL} to infinite molecular weight and calculating from equation 11.5 using χ_{1c} = 0.5.

SUMMARY

A sample of atactic polyoctene-1 was fractionated and characterized by light scattering, osmometry, viscometry and phase equilibria measurements. Molecular weight-viscosity relationships were established for the polymer in cyclohexane, bromobenzene, and phenyl ethyl ether. The mean-square end-to-end dimension of the polymer in bromobenzene was calculated from light scattering data using both the Zimm method and Debye's dissymmetry technique. The dimensions calculated by the two methods agree within experimental accuracy. The average value of the universal hydrodynamic parameter, Φ , was found equal to 2.01 x 10²¹. This agrees very well with the most commonly accepted value, $\Phi =$ 2.1(±0.2) x 10²¹. This close agreement indicates that the polymer molecules in solution are in the shape of random coils (as determined by a Gaussian distribution) and so can be treated in accordance with the standard theories of dilute solutions. The molecular weights of all but two fractions were too high to be studied by osmometry.

The dimensions of a series of poly α -olefins were compared by calculating the ratio of the average end-to-end dimensions of the polymers. It was found that the order, with respect to the size of the pendant groups, was phenyl > hexyl > ethyl > 2 methyls \approx methyl. This is the order expected since the larger groups should cause the polymer molecules to be more expanded due to a higher probability of chain interference.

The lower critical solution temperatures, L.C.S.T., for a series of solutions of polyoctene-1 fractions in n-nonane were measured. The decrease in T_{Cl} with increase in molecular weight was tentatively

explained in terms of the Flory interaction parameter, χ_1 . Also it was shown that fairly accurate values of $T_{\rm CL}$ could be calculated using χ_1 calculated from the molecular weight or thermodynamic measurements using a relationship based on the Prigogine cell model of solution. It was found that a plot of $T_{\rm CL}$ against $1/x^{1/2}$ gave a linear relationship. The intercept of this line at infinite molecular weight, i.e., at $1/x^{1/2} = 0$, was defined as $\Theta_{\rm L}$, that is, the L.C.S.T. for polymer of infinite molecular weight. The parameter, $\Theta_{\rm L}$, was also found by calculating from the relationship mentioned above using $\chi_{1c} = 0.5$. The two values agree to within less than 1% for polyoctene-1. Thus the relationship between $T_{\rm CL}$ and χ_1 appears to be correct for the system investigated.

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