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filament at a particularly favorable orientation come to thermal equilibrium with the surface. A small constant accommodation coefficient would follow from this. The postulated circumstances are reminiscent of the interpretation of the hydrogen molecule-hydrogen atom exchange reaction where the hydrogen atom must meet the hydrogen molecule close to the line of centers for a reaction to be effected.[10]

The author is deeply indebted to Professor Joseph E. Mayer who suggested this problem and continually guided its progress.

[10] J. O. Hirschfelder, H. Eyring, and B. Topley, J. Chem. Phys. 4, 170 (1936).

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(Received June 10, 1944)

Systems of linear polymer molecules are characterized by favorable heats of polymerization counterbalanced by unfavorable entropies of polymerization. Long chains are therefore formed and are stable at low temperatures while at sufficiently high temperature appreciable amounts of monomeric units split off. At any given temperature there exists a definite equilibrium distribution in sizes. This distribution is derived here by statistical methods and proves to be a very simple function of the heat of polymerization.

POLYMERIC materials occurring in nature or produced in the laboratory display a distribution in molecular sizes. The so-called molecular weight distribution curves have been rather intensively investigated in recent years from both the experimental and theoretical viewpoints.

The theoretical studies have been based on statistical or kinetic treatments of the postulated mechanism of formation of the polymers. For example, Flory[1] developed the theory for size distribution in condensation polymers by a statistical treatment. Kuhn,[2] Mark and Simha,[3] Montroll,[4] and others developed the theory for size distributions resulting from chain degradation. Flory[5] and Stockmayer[6] have investigated the theory of size distribution in branched polymers. Several authors[7-9] have discussed size distributions resulting from postulated chain mechanisms of polymerization by integrating the kinetic equations.

There have been, however, few attempts to discuss quantitatively the equilibrium distribution that must exist between polymerized and unpolymerized material as a function of temperature. It has generally been tacitly assumed that in a certain temperature range polymers will keep growing in size, restricted only by the kinetic situation, until all the monomer and short polymers are incorporated into one giant molecule.

It is, however, well known that polymers, such as polystyrene and many other chain polymers, will break down at high temperatures and give a large percentage of monomeric material. It is also known that polymers formed at high temperatures generally have a lower average molec-

[1] P. J. Flory, J. Am. Chem. Soc. 58, 1877 (1936).
[2] W. Kuhn, Ber. B63, 1503 (1930).
[3] H. Mark and R. Simha, Trans. Faraday Soc. 36, 611 (1940).
[4] E. W. Montroll and R. Simha, J. Chem. Phys. 8, 721 (1940).
[5] P. J. Flory, J. Am. Chem. Soc. 63, 3083, 3091, 3096 (1941).
[6] W. H. Stockmayer, J. Chem. Phys. 11, 45 (1943); ibid. 12, 125 (1944).

[7] G. V. Schulz, Zeits. f. physik. Chemie B32, 27 (1936); ibid. B43, 25 (1939).
[8] E. F. Herrington and A. Robertson, Trans. Faraday Soc. 38, 490 (1942).
[9] Hulbert, Harmon, Tobolsky, and Eyring, Ann. N. Y. Acad. Sci. 44, 371 (1943).

ular weight than those formed at low temperatures.* All polymerizations are exothermic, the heat of polymerization in vinyl polymerizations being generally of the order of 10–20 kcal. per mole of monomer. The favorable heat of polymerization is counterbalanced by an unfavorable entropy of polymerization. It is, therefore, to be expected that high temperatures would tend to favor depolymerization, whereas at low temperatures large polymeric molecules would be stable. At any given temperature, however, there should be an equilibrium distribution in sizes, corresponding to a condition where entropy and heat are balanced so as to give a minimum free energy.

An attempt to obtain the equilibria obtaining among chains of all sizes in polymeric sulfur was made by Powell and Eyring.[10] These authors used empirical expressions for the entropy of polymerization, but were able to explain many of the observed phenomena pertaining to "elastic sulphur" by means of their equations. A treatment of random reorganization in linear condensation polymers was made by Flory.[11]

The basis for a more general theory of the equilibrium distribution in sizes for linear chain polymers is inherent in papers by Flory[12] and by Huggins[13] on the entropy of randomness of a mixture of solvent and polymer molecules. The method used by these authors is to construct a lattice upon whose sites solvent molecules or segments of the long chain polymers can be moved interchangeably, and to count the number of available distinct configurations. From this work in conjunction with a recent note by Flory[14] it can easily be inferred that the logarithm of the number of configurations Ω available to a mixture of n_0 solvent molecules and n_1 molecules of monomer, n_2 molecules of dimer, n_x molecules of

x-mer, etc., is

$$\ln \Omega = -\sum_{x=1} n_x \ln \frac{n_x}{n_0 + \sum xn_x} - n_0 \ln \frac{n_0}{n_0 + \sum xn_x}$$
$$+ \sum_{x=1} (x-1)n_x[\ln(\gamma-1)-1] - \sum n_x \ln \sigma, \quad (1)$$

where γ is the coordination number of the lattice and σ is the symmetry number of the long chain molecule (usually 2).

THE EQUILIBRIUM DISTRIBUTION

If the distribution of polymer sizes is known (by specification of the n_x's), Eq. (1) gives the number of available configurations. The energy of each distribution with specified values of the n_x's can easily be written in terms of the heat of polymerization per molecule, P.†

$$E = -\sum n_x(x-1)P. \quad (2)$$

The equilibrium properties of a system containing n_0 solvent molecules and N monomeric units (which may be linked together in any fashion into polymeric units) can be obtained in theory by evaluation of the partition function.

$$Z = \sum_i \Omega_i \exp\{-E_i/kT\} \quad (3)$$

where the subscript i refers to a particular set of the n_x's corresponding to a definite distribution in sizes among the polymer molecules.

Each term in the summation corresponding to any combination n_1, n_2, n_3, etc., consistent with condition (5) below corresponds to a macrostate of the system. The macrostate corresponding to "equilibrium" is the state for which the free energy is a minimum and can be found by maximizing the expression.

$$\ln \Omega_i - E_i/kT \quad (4)$$

with respect to the variables n_1, $n_2 \cdots n_x$, $\cdots$ subject to the condition that

$$\sum_{x=1} xn_x = N. \quad (5)$$

The problem of maximizing (4) subject to (5) can be best solved by the method of Lagrange multipliers. In other words, multiply Eq. (5) by $-\alpha/kT$ and add to Eq. (4) giving, after sub-

* Although this may in part be due to the different temperature coefficients of the rate constants involved in the kinetic mechanism, there is evidence that indicates that the molecular weights at temperatures of 130°C and above are definitely delimited by polymerization-depolymerization equilibria.

[10] R. Powell and H. Eyring, J. Am. Chem. Soc. 65, 648 (1943).

[11] P. J. Flory, J. Am. Chem. Soc. 64, 2205 (1942).

[12] P. J. Flory, J. Chem. Phys. 10, 51 (1942).

[13] M. L. Huggins, J. Phys. Chem. 46, 151 (1942).

[14] P. J. Flory, J. Chem. Phys. 12, 114 (1944). A similar but more detailed treatment has been made by R. Scott and M. Magat (soon to be published).

† Consideration of the vibrational entropy of the lattice model is omitted as being of secondary importance.

stituting Eq. (1),

$$\phi = \sum_{x=1} n_x \frac{(x-1)P}{kT} - \sum_{x=1} n_x \ln \frac{n_x}{n_0 + \sum xn_x}$$

$$- n_0 \ln \frac{n_0}{n_0 + \sum xn_x}$$

$$+ \sum_{x=1} (x-1)n_x[\ln (\gamma-1) - 1]$$

$$- \sum n_x \ln \sigma - \frac{\alpha}{kT}\sum xn_x. \quad (6)$$

Differentiating ϕ with respect to each of the n_x's and setting these derivatives equal to zero, the following expression is obtained upon solving for $\ln \frac{n_x}{n_0 + \sum xn_x}$:

$$\ln \frac{n_x}{n_0 + \sum xn_x} = \frac{x-1}{kT}P - v_p\left(1 - \frac{x}{\bar{x}_n}\right)$$

$$+ (x-1)(1-v_p) - \ln \sigma$$

$$+ (x-1)[\ln (\gamma-1) - 1] + \frac{\alpha x}{kT}, \quad (7)$$

$x = 1, 2, 3, \cdots$, where

$$v_p = \frac{\sum_{x=1} xn_x}{n_0 + \sum_{x=1} xn_x}, \quad (8)$$

and

$$\bar{x}_n = \frac{\sum_{x=1} xn_x}{\sum_{x=1} n_x}. \quad (9)$$

From Eq. (7) the following is immediately derived:

$$\frac{xn_x}{n_0 + \sum xn_x} = x \exp \left\{ \frac{(x-1)}{kT}P + \frac{\alpha x}{kT} \right.$$

$$- v_p\left(1 - \frac{x}{\bar{x}_n}\right) + (x-1)(1-v_p)$$

$$\left. - \ln \sigma + (x-1)[\ln (\gamma-1) - 1] \right\}$$

$$= \left(\frac{x}{\beta}\right) \exp x\left[\frac{P}{kT} + \frac{\alpha}{kT} + \frac{v_p}{\bar{x}_n} - v_p + \ln (\gamma-1)\right]$$

$$= \left(\frac{x}{\beta}\right) y^x e^{-P/kT}, \quad (10)$$

where

$$y = \exp \left\{ \frac{P}{kT} + \frac{\alpha}{kT} + \frac{v_p}{\bar{x}_n} - v_p + \ln (\gamma-1) \right\}, \quad (11)$$

and

$$\beta = \sigma(\gamma-1). \quad (12)$$

The value of α must be obtained by summing Eq. (10) over all values of x and setting the result equal to v_p. This operation leads to the following equation

$$\frac{y}{(1-y)^2} = v_p\beta e^{P/kT}. \quad (13)$$

Solution of the quadratic equation for y leads to the following:

$$y = 1 + \frac{1}{2(v_p\beta e^{P/kT})}$$

$$- \frac{1}{2}\left[\frac{4}{v_p\beta e^{P/kT}} + \frac{1}{(v_p\beta e^{P/kT})^2}\right]^{\frac{1}{2}}. \quad (14)$$

Upon substituting Eq. (14) in (10) an exact expression for the equilibrium size distribution is obtained. A normalized approximate result (based on the assumption that $e^{P/kT} \gg 1$) is:

$$\frac{\frac{xn_x}{n_0 + \sum xn_x}}{v_p} = x\frac{1}{\beta v_p e^{P/kT}}\left(1 - \frac{1}{(\beta v_p e^{P/kT})^{\frac{1}{2}}}\right)^{x-1}. \quad (15)$$

The distribution in sizes for polymer molecules at equilibrium thus obtained is of the same form as distributions previously derived by statistical treatments for the formation of linear condensation polymers or for the degradation of "infinite" linear polymers. The latter is particularly easy to visualize: If an infinite polymer is degraded by a random scission process, and the probability that any given bond is cut is p, then the weight fraction of x-mer is

$$W(x) = xp^2(1-p)^{x-1}. \quad (16)$$

Comparing (16) with (15) we see that the equilibrium distribution can be considered to be the result of a random scission process on an "infinite" linear polymer, the probability of scission at any temperature being equal to

$$p = \frac{1}{(\beta v_p e^{P/kT})^{\frac{1}{2}}}. \quad (17)$$