

Copolymerization of Systems of Three and More Components

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In a paper to be published shortly we have constructed and solved the Schrödinger equation for a hole in a liquid and determined the eigenvalues of its energy. On this theory we are led to an expression for the intrinsic pressure which does not contain the temperature but only the surface tension and density of the liquid. This gives for the intrinsic pressure the value

$$p_0 = 3.5\sigma(7\pi\sigma/15E)^{1/2},$$

and for the van der Waals' force constant the value

$$a_2 = 3.5\sigma V^2(7\pi\sigma/15E)^{1/2}, \quad (5)$$

where $E = 3.1h^{4/7}\sigma^{5/7}/\rho^{2/7}$, h being the Planck constant. In Fig. 2 $\log(10^5 a_2)$ has been plotted against $\log(10^5 a)$ and

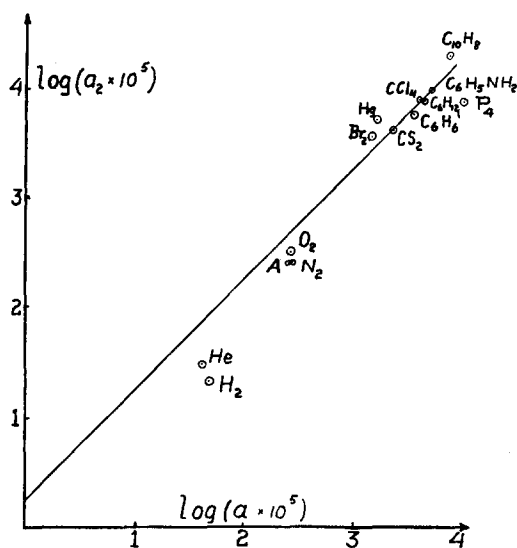


FIG. 2. The abscissae denote the experimental values for van der Waals' constant a and the ordinates the values of a_2 obtained from Eq. (5).

the agreement is satisfactory. The constant of proportionality is again 0.6 instead of being unity.

In the paper referred to above various other applications of the modified hole theory have been discussed, but it is interesting to find that the hole theory leads immediately to a relation between surface tension and van der Waals' constant.

We are very grateful to Dr. Kothari for his kind interest in the work.

¹ Fürth, Proc. Camb. Phil. Soc. **37**, 252 (1941).

² See also R. S. Silver, Nature **150**, 605 (1942). It is interesting to note that water passes up through the conduit of trees in a state of tension [Dixon, Proc. Roy. Soc. **B125**, 1 (1938)].

³ Handbook of Chemistry and Physics (Chemical Rubber Publishing Company, Cleveland, 1937-1938), 22nd edition.

Copolymerization of Systems of Three and More Components

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IN a recent paper¹ these authors have shown that with a steady state assumption the course of copolymerization of a system of two components can be calculated without restricting assumptions as to the relative values of the rate constants involved.

Similarly it is possible to calculate the course of copolymerization of a system of any number of components. This, however, is rather involved because of the great number of rate constants which must be considered. Even the answer to the limited question of the polymer as a function of monomer composition involves $x(x-1)$ rate constant ratios (where x is the number of components). Thus, for a system of three components, A , B , and C , where nine rates of growths are involved, six ratios are required; namely,

$$\alpha^b = k_2^{ab}/k_2^{aa}; \quad \alpha^c = k_2^{ac}/k_2^{aa}; \quad \beta^a = k_2^{ba}/k_2^{bb};$$

$$\beta^c = k_2^{bc}/k_2^{bb}; \quad \gamma^a = k_2^{ca}/k_2^{cc}; \quad \gamma^b = k_2^{cb}/k_2^{cc},$$

where the first upper index denotes the nature of the active group in which the growing chain ends and the second upper index the monomer added in the process. Then the initial polymer composition $a/b/c$ is:

$$\frac{a}{b} = \frac{\beta^a \gamma^b AB + \gamma^a A(\beta^a A + \beta^c C)}{\alpha^b \gamma^a AB + \gamma^b B(\alpha^b B + \alpha^c C)} \cdot \frac{A + \alpha^b B + \alpha^c C}{B + \beta^a A + \beta^c C} \quad (1)$$

$$\frac{a}{c} = \frac{\beta^a \gamma^b AB + \gamma^a A(\beta^a A + \beta^c C)}{\alpha^c \beta^a AC + \beta^c C(\alpha^b B + \alpha^c C)} \cdot \frac{A + \alpha^b B + \alpha^c C}{C + \gamma^a A + \gamma^b B} \quad (2)$$

Equations (1) and (2) indicate the possibility of predicting the composition of a multipolymer from information gathered from a separate study of each pair of monomers involved. The knowledge of the ratios of the propagation rate constants for each pair of monomers also permits the calculation of the size distribution curve of sequences of units of one kind. This is worth-while information which, in most cases, cannot be obtained otherwise. Thus if the monomer mixture is made up of the monomers A , B , C , \dots Y , the resulting initial copolymer will consist of sequences of a , b , \dots and y monomer units. The fraction of all a sequences which possess n_a monomer units will be given by a distribution function $N(n_a)$.

$$N(n_a) = \left(\frac{A}{A + \alpha^b B + \alpha^c C + \dots + \alpha^y Y} \right)^{(n-1)} \times \left(1 - \frac{A}{A + \alpha^b B + \alpha^c C + \dots + \alpha^y Y} \right) \quad (3)$$

In many cases of interest the a sequences will consist mainly of one member—i.e., isolated a units. In other cases relatively long sequences of a 's will be present in the copolymer.

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¹ T. Alfrey and G. Goldfinger, J. Chem. Phys. **12**, 205 (1944).