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Molecular Distribution in Condensation Polymers

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Some time ago the writer extended the theory of three-dimensional condensation polymers[1] to include cases more general than those treated in previous papers.[1,2] Since the calculations merely involved straightforward (though tedious) application of the method previously employed, there was no urge to communicate them; but several recent inquiries prompt their publication without proof at this time.

The general system here treated is defined by the statement that the original mixture of monomers consists of $A_1, A_2, \ldots, A_i \ldots$ moles of reactants bearing respectively $f_1, f_2, \ldots, f_i, \ldots$ functional groups of type A each, together with $B_1, B_2, \ldots, B_j, \ldots$ moles of reactants of functionalities $g_1, g_2, \ldots, g_j, \ldots$ in groups of type B. The A groups (*e.g.*, carboxyl) can react only with B groups (*e.g.*, hydroxyl) and *vice versa*.

As in the previous work, it is assumed that all functional groups of a given kind are equally reactive, and that ring formation does not occur in molecular species of finite size. Although the first of these assumptions can be realized in many practical cases, the second is never correct and may cause considerable error in calculations for systems close to the gel point.[1] Such error could be reduced, though not entirely eliminated, by assigning effective functionalities, less than the true stoichiometric ones, to the monomeric reagents.

Let the system condense until a fraction p_A of the A groups and a fraction p_B of the B groups have reacted. These quantities are not independent, for:

$$p_A(\textstyle\sum_i f_i A_i) = p_B(\sum_j g_j B_j) \tag{1}$$

The distribution of molecular species in the system is then described by the following equation, in which $N\{m_i, n_j\}$ represents the number of moles of species consisting of $m_1, m_2, \ldots, m_i, \ldots$ monomer units of the A type combined with $n_1, n_2, \ldots, n_j, \ldots$ units of the B type:

$$N\{m_i, n_j\} = K \frac{(\sum_i f_i m_i - \sum_i m_i)!(\sum_j g_j n_j - \sum_j n_j)!}{(\sum_i f_i m_i - \sum_i m_i - \sum_j n_j + 1)!(\sum_j g_j n_j - \sum_j n_j - \sum_i m_i + 1)!} \times \prod_i \frac{x_i^{m_i}}{m_i!} \prod_j \frac{y_j^{m_j}}{n_j!} \tag{2}$$

where:

$$x_i = \frac{f_i A_i}{(\sum_i f_i A_i)} \frac{p_B(1 - p_A)^{f_i - 1}}{(1 - p_B)}$$

$$y_j = \frac{g_j B_j}{(\sum_j g_j B_j)} \frac{p_A(1 - p_B)^{g_j - 1}}{(1 - p_A)}$$

$$K = (\sum_i f_i A_i)(1 - p_A)(1 - p_B)/p_B = (\sum_j g_j B_j)(1 - p_A)(1 - p_B)/p_A$$

Equation (2) permits the computation of various average properties, the required summations being conveniently found by means of the appropriate generating functions.[2] We shall be content here to give the weight-average molecular weight. Let the effective molecular weight of monomer species i be M_i, this being less than the molecular weight of the original monomer species because of the loss of condensation by-product; for example, if this by-product is water, M_i will be less than the original monomer molecular weight by $18f_i/2$. The weight-average molecular weight of the whole polymer is then given by:

$$\bar{M}_w = \frac{\sum_{\text{(all species)}} (\sum_i m_i M_i + \sum_j n_j M_j)^2 N\{m_i, n_j\}}{\sum (\sum_i m_i M_i + \sum_j n_j M_j)\, N\{m_i, n_j\}}$$

$$= p_B \frac{(\sum_i M_i^2 A_i)}{(\sum_i f_i A_i)} + p_A \frac{(\sum_j M_j^2 B_j)}{(\sum_j g_j B_j)} + \frac{p_A p_B[p_A(f_e - 1)M_a^2 + p_B(g_e - 1)M_b^2 + 2M_a M_b]}{1 - p_A p_B(f_e - 1)(g_e - 1)} \Big/ p_B \frac{(\sum_i M_i A_i)}{(\sum_i f_i A_i)} + p_A \frac{(\sum_j M_j B_j)}{(\sum_j g_j B_j)} \tag{3}$$

where:

$$f_e = (\sum_i f_i^2 A_i)/(\sum_i f_i A_i)$$

$$g_e = (\sum_j g_j B_j)/(\sum_j g_j B_j)$$

$$M_a = (\sum_i M_i f_i A_i)/(\sum_i f_i A_i)$$

$$M_b = (\sum_j M_j g_j B_j)/(\sum_j g_j B_j)$$

This equation reduces to previously given formulas for simpler cases.[1,2] The gel point of the system occurs when the last term in the numerator (and hence M_w) becomes indefinitely large, or:

$$(p_A p_B)_{\text{gel}} = (f_e - 1)^{-1}(g_e - 1)^{-1} \tag{4}$$

as can also be directly established by a simpler procedure.[1]

The number-average molecular weight $\bar{M}_n$ can always be obtained by elementary stoichiometry, since without ring formation the number of molecules is just the original number less the number of new bonds formed.

It will not be given here, but we note that computation of $\bar{M}_n$ by summing over the distribution of equation (2) afforded a check on the distribution formula.

No attempt has been made to explore sol–gel relationships beyond the gel point, although this could presumably be done by Flory's methods.[1,3] One can be sure that the monomer units of higher functionality will be preferentially incorporated into the gelled network.

Extension of the general theory to include monomers endowed with both types of functional groups (*e.g.*, hydroxy acids) would present a new combinatory problem, and no attempts in this direction have been made. In view of the shortcomings of the theory, it is questionable whether such extensions would be worth while.

References

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3. P. J. Flory, *J. Am. Chem. Soc.*, **69**, 30 (1947).

Synopsis

The theory of molecular distribution in condensation polymers has been extended to include systems of a rather general type. Equations for the distribution and the weight-average molecular weight are given.

Résumé

La théorie de distribution moléculaire des polymères obtenus par condensation a été étendue de façon à inclure des systèmes d'un type plus général. Des équations pour la distribution des poids moléculaires ainsi que pour les poids moléculaires moyens sont données.

Zusammenfassung

Die Theorie der Molekularverteilung in Kondensationspolymeren wurde ausgedehnt, um Systeme von ziemlich allgemeinem Typus zu umfassen. Es werden Gleichungen für die Verteilung und das Gewichtsmittel-Molekulargewicht gegeben.

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