

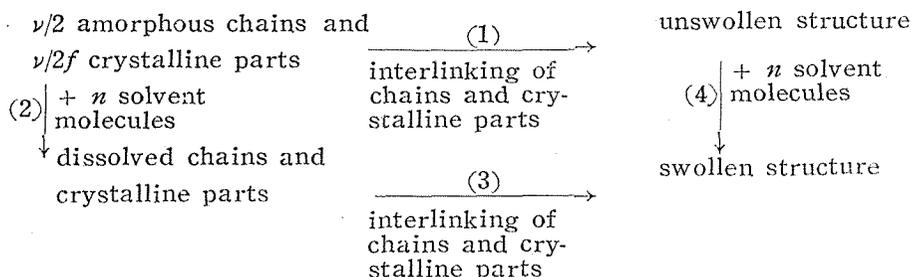
## 15. Statistical Mechanics of Anisotropic Swelling of Crystalline Polymers

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In the present study the entropy of anisotropic swelling was derived in a similar manner as the previous study for isotropic swelling, except that a modification factor on elastic entropy of swelling had been introduced.

Let us consider the following cycle:



As the sum of the entropy of process (1),  $S_1$ , and the entropy of process (4),  $\Delta S_s$ , is equal to the sum process (2),  $S_2$ , and the entropy of process (3),  $S_3$ , the entropy of swelling,  $\Delta S_s$ , is given by the following equation.

$$\Delta S_s = S_2 + S_3 - S_1 \quad (1)$$

Introducing the calculated values of  $S_2$ ,  $S_3$  and  $S_1$  in the above equation, we obtain

$$\Delta S_s = -k(n \ln(1-v_2) + \nu \ln v_2 + \nu/4 (\lambda_1'^2 + \lambda_2'^2 + \lambda_3'^2 - \lambda_1^2 - \lambda_2^2 - \lambda_3^2) - \nu/2f \ln \left( \frac{V/V - \sigma}{1 - \sigma} \right)) \quad (2)$$

$$v_2 = \nu/2 V_2 / (nV_1 + \nu/2 V_2), \quad Z = V_2/V_1.$$

where  $V_1$ ,  $V_2$ ,  $V$ ,  $V'$  and  $\sigma$  represent respectively molar volume of solute, molar volume of anamorphous chain, volume of system before swelling, volume of the system after swelling and the fraction of amorphous parts;  $\lambda_1$  and  $\lambda_1'$  represent principal extension ratios of unswollen and swollen structure.

The partial molal-free energy of dilution obtained by differentiating Eq. (2) and introducing heat of mixing of the van Laar form, is then

$$\Delta \bar{F}_1 = RT \left[ \ln(1-v_2) + v_2(1-2/Z) + v_2^{3/2} / 3Z \left\{ (a_1'^2 + a_2'^2 + a_3'^2) - \frac{1}{b^2} (a_1^2 + a_2^2 + a_3^2) \right\} \right. \\ \left. \cdot (a_1' \cdot a_2' \cdot a_3')^{-3/2} + \mu v_2^2 - \frac{1}{fZ} \frac{1}{(1/v_2 - 2 + 1/\sigma)} \right] \quad (3)$$

$$\lambda_1 = a_1 \lambda_1, \quad \lambda_2 = a_2 \lambda_1, \quad \lambda_3 = a_3 \lambda_1, \quad \lambda_1' = b \lambda_1$$

$$\lambda_1' = a_1' \lambda_1', \quad \lambda_2' = a_2' \lambda_1', \quad \lambda_3' = a_3' \lambda_1'.$$

At equilibrium between swollen structure and pure solvent,  $\Delta F_1$  is zero and we obtain

$$Z = V_2/V_1 = \frac{\left[ v_2^{3/3} \left\{ (a_1'^2 + a_2'^2 + a_3'^2) - \frac{1}{b^2} (a_1^2 + a_2^2 + a_3^2) \right\} (a_1' \cdot a_2' \cdot a_3')^{-2/3} - 2v_2 - \frac{1}{f(1/v_2 - 2 + 1/\sigma)} \right]}{v_2^2 \left[ \left( \frac{1}{2} - \mu \right) + \frac{v_2}{3} + \frac{v_2^2}{4} + \dots \right]} \quad (4)$$

## 16. Studies on the Temperature rise and its Influence on the Degree of Polymerisation in the Emulsion Polymerisation of Vinyl acetate

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By many investigations on the emulsion polymerisation, it has already been recognized that the locus of polymerisation is in the micelles of detergent molecules in the earlier stage of polymerisation and is in the monomer-polymer particles in the later one. Recently through the studies by S. Okamura ("Synthesis and Applications of Polyvinyl Emulsion" (in Japanese) 1949.) and by M. Matsumoto ("J. Chem. High Polymer (Japan) 7, 390, 1950) it has also been found the different relationships between the degree and the conversion of polymerisation in both stages.

In the paper reported here are considered the relations between the degree of polymerisation and the rise of temperature in the emulsion polymerisation of vinyl acetate. By the usage of sodium lauryl sulphate as emulsifier, the size of emulsion particles and also the amount of heat accumulated in the polymerising particles are both found to diminish markedly. From these effects, the branching polymerisation occurs to the less extent than in the case without any emulsifiers, and so the difference of the degree of polymerisation as polyvinyl-acetate ( $\bar{P}_{Ac}$ ) and as alcohol ( $\bar{P}_A$ ) is very small. The effects of agitation on the relationships mentioned above are shown in Figure-1. At the strong agitation the polymerisation occurs mainly in the swollen polymer particles and so  $\bar{P}_{Ac}$  are found to increase but  $\bar{P}_A$  to decrease during the polymerisation proceeds.

Assuming that the heat of polymerisation is spent to warm the emulsion liquid and the emulsion particles and also to escape at constant rate through the wall of reaction vessel, the elevation of temperature in the emulsion particles is evaluated as shown in Figure 2. At the maximum temperature shown in figure (e. g. ca. 77°C.), the amount of monomer remaining in particles reaches 50% or more. The boiling point of monomer in swollen state is considered to be higher than normal value (73°C) and these relations are calculated by the Huggins-Boyer's equation