

On The Kinetics of Polymerization in a Water - Monomeric Highly Dispersed Heterogeneous System

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Abstract

Polymerization in a highly dispersed heterogeneous monomer-water system has specific properties that strongly distinguish it from polymerization in solution and in bulk. One of the specific phenomena is the high polymerization rate when the monomer is in the nano-dispersed state (in emulsifier micelles) in the aqueous phase [1-3]. It can be assumed that the kinetic effect is possible due to the occurrence of polymerization reactions at the monomer-water-phase interfaces. The theoretical rationale for this assumption is given in this article.

Keywords: Polymerization; Emulsion; Micelles

Editorial

A drop of the monomer in water should have at least two qualitatively different polymerization zones. This requirement proceeds from the thermodynamics of heterogeneous systems, according to which it is necessary to differentiate the homogeneous phase and border area in system of two immiscible liquids, attributing the latter a certain layer thickness [4,5]. This layer thickness is referred to as a distance from the interface within which the parameters of liquids are considerably differ from those in their bulk phases [5]. The thickness of the surface layer of the monomer is a state parameter and depends on the physicochemical parameters of the individual phases of the heterogeneous system. (density, tangential pressure, chemical potential, etc.).

The thickness of the boundary layer can be determined by different parameters and its size depends on the selected

parameter. In [5] using methods of statistical mechanics an asymptotic formula describing the changes in the density of the liquid depending as a function of the distance h from the interface was introduced:

$$\rho = \rho_0 + \frac{\pi \rho_0^2 \chi_0 (B' \rho' - B \rho_0)}{6} \cdot \frac{1}{h^3} \quad \text{Equation 1}$$

Where ρ_0 is the density and χ_0 - the isothermal compressibility of the liquid; B and B' are constants of Van der Waals interaction between fluid molecules themselves, as well as their interactions with molecules of the other phase, ρ - density of the fluid in the boundary layer, ρ' - the density of the other phase.

Using this formula, the thickness of the boundary layer (t) was determined by the formula:

$$t = \{ \pi \rho_o \chi_o (B'\rho' - B\rho_o) / 6C \}^{1/3} \text{ Equation 2}$$

Where $C = \rho - \rho_o / \rho_o$ (C depends on the selected value of ρ)

The density of many liquid monomers is less than the density of water ($\rho' > \rho_o$) and with $B'\rho' > B\rho_o$ density of monomer at the interface must be higher than its bulk density and the polymerization in this layer should proceed at an increased rate.

The difference between the parameters of the monomer on the surface and in the volume is due to the interaction of molecules of neighboring phases. At the interface, the dipole-dipole interaction between the monomer and water molecules leads to orientation of the molecules and thus ensures the maximum interaction of the unsaturated bond of the monomer molecules with the water molecule. Orientation effects at the liquid-liquid interface considerably increased in the presence of polar groups in the monomer molecules [5], which lead to decrease in the surface entropy [6].

Adamson's basic researches devoted intermolecular interactions at the hydrocarbon-water interface showed that aimed dipole-dipole and dipole-polarization interaction have a decisive influence on the energy state of molecules in the vicinity of the interface. Because of these interactions, the aromatic hydrocarbon-water interface highly subjected to structural changes, as a result of which clathrate compounds are formed [7].

From the foregoing material it could be concluded that heterogeneous monomer-water systems have at least four qualitatively different polymerization zones, which are shown schematically in Figure 1:

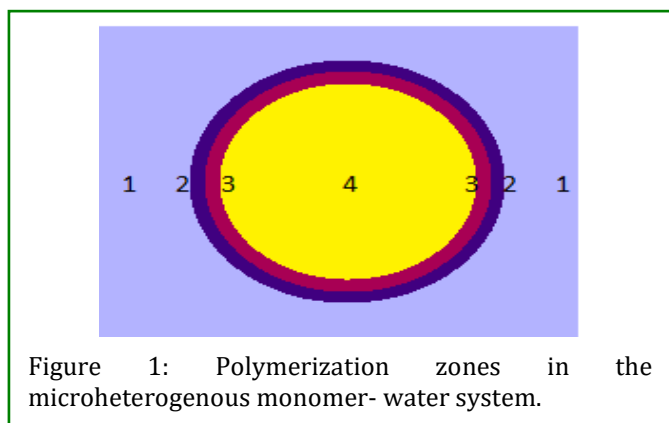


Figure 1: Polymerization zones in the microheterogeneous monomer-water system.

1. Aqueous phase
2. Boundary layer of the aqueous phase
3. Monomer boundary layer
4. Monomer phase

Obviously, for the detection of kinetic effects associated with the proceeding of polymerization reactions in 3 - zone it will be necessary to carry out the process in systems which have highly developed interface.

In nanodispersed systems (micellar emulsion), the thickness of the boundary layer is comparable with the diameter of dispersed particles, and it will be possible to detect the kinetic effect.

Conclusion

The above theoretical material allows us to conclude that the boundary layer of the monomer phase is qualitatively different from other polymerization zones and, depending on the nature of the monomer, polymerization in this zone can proceed at relatively high rates.

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