

Analysis method of binary concentration-inhomogeneous systems.

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Abstract

A method for the analysis of binary concentration-inhomogeneous polymer-monomer systems, in which the concentration of components varies continuously from point to point, is proposed. As a characteristic of inhomogeneity serves the distribution function of the polymerization mass over concentrations. The method is based on measuring the dependence of the heat capacity of the polymerization mass on temperature in the temperature range, which includes the glass transition range, and comparing it with the dependence of the heat capacity of homogeneous systems on temperature and concentration, followed by the solution of the Fredholm integral equation of the first kind.

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As was shown in the works of Dyachkov et al., devoted to the mechanism of radical bulk polymerization of methyl methacrylate (MMA) [1–4], at the stage of auto-acceleration, the spatially homogeneous distribution of the concentration of components is destabilized, as a result of which the polymerization system becomes concentrations inhomogeneous. In this regard, there is a need for a method for analysing the concentration inhomogeneity of such systems. The quantitative characteristic of inhomogeneity can be the distribution function of the polymerizing mass over concentrations $M(x)$, which has the following sense: $M(x)dx$ – is the mass fraction of the system with the concentration (mass fraction) of the polymer from x to $x + dx$.

To illustrate the idea of the analysis method, we consider a binary system that forms true solutions over the entire concentration range, such as the MMA - polymethylmethacrylate (PMMA) system, and consider any extensive property of the system, such as specific heat capacity, or specific volume, or dielectric constant. Let the temperature of some phase (or relaxation) transition of the system (for the MMA–PMMA system, this is the glass transition temperature T_g) be a monotonic function of the composition. We will consider this function as

known, because it is easy to determine experimentally. On the dependence of heat capacity on temperature $C(T)$ the glass transition appears as an S-shaped inflection, with the abscissa of the inflection point being the glass transition temperature of the system (from which its composition can be determined), and the step height is proportional to the mass of the system. If now an inhomogeneous system consists of two fractions of different composition, then the $C(T)$ curve will have two inflection points, the abscissas and jump heights of which can be used to determine the compositions and mass percent of the fractions. This kind of analysis for a binary system consisting of two fractions was carried out by Rabinovich and co-workers [5].

To visually illustrate the idea of the proposed method of analysis, let us consider the schematic dependence of the specific heat of the MMA–PMMA system on temperature at three different concentrations (x) of PMMA (see Fig. 1). On it, the black curves refer to homogeneous systems of compositions x_1 , x_2 and x_3 , (wherein $x_2 = \frac{x_1+x_3}{2}$), the red curve refers to heterogeneous one, consisting of two fractions of compositions x_1 and x_2 in a ratio of 1:1 (its integral composition is thus $x_4 = x_2$)

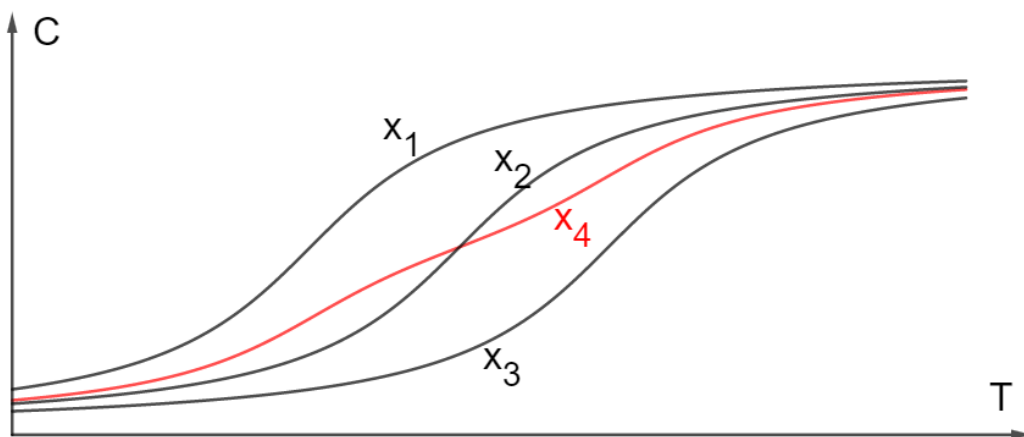


Fig. 1. Schematic dependence of heat capacity on temperature at three various concentrations of PMMA. Further explanations are in the text.

It is easy to see that the heat capacity of an inhomogeneous system differs from that of a homogeneous one of the same composition. From here it can also be seen that the dependence of the heat capacity from concentration of a homogeneous system at a constant temperature is essentially non-linear. This is explained by the fact that different compositions at the same temperature correspond to different aggregate states (vitreous and rubber elastic).

Differences in the heat capacities of homogeneous and inhomogeneous systems make it possible to calculate the distribution function of the polymerization mass over conversions $M(x)$, using the following considerations:

When the compositions of the fractions do not differ much, the two S-shaped curves merge into one wider S-shaped curve. In this case, for the specific heat capacity (or any other extensive property), one can write the equality

$$C_{\Sigma}(T) = C(x_1; T)m_1 + C(x_2; T)m_2 \quad (1)$$

with $C_{\Sigma}(T)$ – specific heat capacity of an inhomogeneous system, $C(x; T)$; – dependence of the specific heat capacity of a homogeneous system on the composition and temperature, x_1 and x_2 – compositions of the first and second fractions, m_1 and m_2 – their mass fractions. The solution of the task is reduced to finding of three numbers: x_1 , x_2 and m_1 ($m_2 = 1 - m_1$), for what man can apply the linear regression analysis.

In the case of an arbitrary number N of fractions of various composition, equation (1) is modified as follows:

$$C_{\Sigma}(T) = \sum_{n=1}^N C(x_n; T)m_n$$

In the limit, when the composition of an inhomogeneous system changes continuously from point to point, the sum turns into an integral, and the equation takes the form:

$$C_{\Sigma}(T) = \int_0^1 C(x; T)M(x)dx \quad (2)$$

with $M(x)$ is the desired distribution function.

Equation (2) is an Fredholm integral equation of the first kind with respect to the function $M(x)$ and belongs to the class of so-called ill-conditioned tasks. Methods for solving such tasks were developed by the school of mathematicians under the guidance of Academician Tikhonov [6].

The first experience of using the above method of analysis on the example of a polymerizing MMA–PMMA system was undertaken by us in [7].

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