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Abstract

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A NEW CAVITATION METHOD OF EMULSION POLYMERIZATION*

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Polymerization in dispersions, as is known, has a number of substantial advantages, leading to a considerable increase in the rate of the process (by 2–3 orders of magnitude) and to the possibility of increasing the molecular weight of the polymer. In addition, favorable steric conditions are thereby created for obtaining more homogeneous and ordered structures.

However, all these advantages, because of the use of extraneous additives—emulsifiers—are to a considerable extent reduced as a result of disruption of those optimal topochemical features of the process that should arise during the formation of the polymer in emulsions. ([1]). The use of emulsifiers also has an especially negative effect, because of the difficulties of removing them, in obtaining polymers with high insulating properties.

In this connection, both for studying the mechanism of dispersion polymerization in its pure form and for the technology of obtaining polymers, it is of interest to seek ways of emulsifying monomers without the use of specially introduced emulsifiers.

It is well known that, under the action of ultrasonic oscillations, very highly dispersed emulsions are obtained without emulsifiers, since stabilizing factors arise under the influence of cavitation. However, the complexity and poor economy of large installations for obtaining sufficiently powerful sources of acoustic energy practically exclude their broad use in industry. Analysis of the phenomena of the dispersing action of ultrasound leads to the conclusion that the solution of the problem of creating a powerful and at the same time accessible source of acoustic energy should be sought in the development of a simple method of exciting cavitation. The simplest and sufficiently effective method proved to be the use of the energy of collapse of cavitation cavities arising during the condensation of superheated vapor in the liquid phase.

Earlier we developed and successfully applied ([2,3]) a cavitation method for exciting acoustic oscillations, which proved highly effective for obtaining a wide variety of highly dispersed systems. Recently this method has also been tested by other investigators ([4]).

If superheated steam is passed through a capillary under a small pressure (2–3 atm.) into the liquid phase, then, as a result of the sudden condensation of the issuing steam, the space (directly at the end of the capillary) momentarily occupied by a certain element of the volume of the vapor phase sharply decreases to negligible dimensions, and the mechanical impact thereby arising (collapse of the cavity) must cause strong compression in the boundary layers, reaching very high values. Condensation of the steam

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and the phenomena associated with it, under certain experimental conditions—a sufficient difference between the temperatures of the liquid phase and the vapor—proceeds so rapidly that even in the immediate vicinity of the orifice it is already difficult to detect breaks in the continuity of the liquid phase. The elementary act described, namely the rupture of the continuity of the liquid phase by some element of vapor volume and the subsequent elimination of this rupture as a result of condensation, is nothing other than the process of formation and collapse of an individual cavity; and the sum total of such elementary acts gives the typical phenomenon of cavitation.

The calculation of the frequencies of the shock wave given below leads to values on the order of tens of kilohertz, which corresponds to the region of audible high tones bordering on ultrasonic vibrations.

If we assume that the initial radius of the collapsing cavity (r) does not differ too greatly from the mean free path of vapor molecules (on the order of 10^{-3} cm), and, consequently, that the time of condensation of vapor inside the cavity will be less than the time of its collapse, then the conditions will be present for the typical phenomenon of cavitation, i.e., the formation and destruction of vapor-free voids. Then the required collapse time of an individual cavity (τ) will be determined from the acceleration of a certain layer of liquid, freely moving toward its center, under the action of a unidirectionally directed force F.

Taking into account capillary pressure, we express the driving force acting on a unit surface of the collapsing cavitation by the following equation:

$$F_s = P_0 + 2\sigma/r,$$

where P_0 is atmospheric pressure.

The mass of the moving layer with an area of 1 cm^2 and thickness $v\tau$, where v is the propagation velocity of the elastic wave, is $m_s = \rho v\tau$, where ρ is the density of the liquid.

Then the required acceleration a is found from the equation:

$$a = \frac{P_0 + 2\sigma/r}{\rho v \tau}.$$

Further, since the radius of the cavity is the path traversed by the liquid layer during the collapse time of the cavity,

$$\tau = \sqrt{2r/a}.$$

Substituting the corresponding value for a, we find

$$\tau = \frac{2r\rho v}{P_0 + 2\sigma/r}.$$

If, in the equation found, we substitute the order of magnitude of the numerical values of the quantities involved, we obtain for τ a value of about 10^{-4}, which corresponds to frequencies on the order of tens of kilohertz. This shows that the process considered is a source of high-frequency acoustic vibrations.

The dispersing action of cavitation excited by the method described is highly effective. The formation of stable and concentrated emulsions of the oil–water type when the capillary is introduced near the interface proceeds, for most immiscible phases, in 5–10 sec. In this way we successfully dispersed various kinds of oils: vaseline, peach, castor, camphor (with an increased camphor content), paraffin, phenols, cresols, liquid wastes from petroleum cracking, as well as sulfonamide preparations poorly soluble in water, iodine, and other medicinal substances ([2,3]).

The application of the described method of exciting cavitation to polymerization in dispersions proved to be sufficiently effective and very promising. We successfully tested the applicability of this method to the processes of polymerization of styrene, methyl methacrylate, acrylonitrile, and also

various combinations of the indicated monomers with one another. At the same time we established that, under the influence of cavitation, both stages of the emulsion-polymerization process (both emulsification and polymerization proper) proceed more efficiently than with the usual method. The preparation of 100 g of emulsion (1 : 5) is usually completed in a few seconds, with the formation of highly dispersed emulsoids with an average size on the order of 10^{-4} cm.

The polymerization process, usually carried out at elevated temperatures, under the conditions of the cavitation method begins to proceed at a noticeable rate already during emulsification. Under the influence of the heat of condensation of superheated steam, which raises the temperature of the emulsion to 40–60°, and under the direct action of cavitation, which creates favorable microkinetic and topochemical conditions for the process, polymer formation in most cases is completed within a few minutes after emulsification, without additional heating. And for such monomers as acrylonitrile, or its mixtures with styrene or methyl methacrylate, polymerization proceeds rapidly even at room temperature. In this case, i.e., in the case of polymerization at a reduced temperature, polymers are formed with increased heat resistance in comparison with those obtained by generally accepted methods.

Thus, for example, the copolymer of acrylonitrile with styrene (in a ratio of 1 : 1) obtained by cavitation polymerization softens at 140°, while the copolymer of acrylonitrile with methyl methacrylate (in a ratio of 70 : 30) softens at 120°, i.e., 30° higher than that obtained by ordinary methods.

Of considerable interest is the effect of the direct mechanical action of cavitation on the energetic state of polymer molecules. Owing to the development of high pressures and temperatures at the moment of collapse of the cavity, the molecules in the boundary layers of the monomer may undergo cracking with the formation of free radicals. This is confirmed by the facts we observed: the polymerization of certain monomers, for example acrylonitrile, even without the introduction of initiators, as well as the partial polymerization of such monomers as cyclopentadiene, which usually polymerizes only under the influence of catalysts by an ionic mechanism.

In our opinion, the cavitation method of polymerization may find wide application also in the field of obtaining graft and block copolymers, as well as for other processes of structuring complex high-polymer systems, where the phenomena of destruction and reconstruction of polymer chains are of decisive importance.

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Note: Figure translations are in progress. See original paper for figures.