P-30: Effect of Polymer Molecular Weight on the Constants of their Degradation in Aqueous Solution under the Influence of Ultrasound

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Proposed an expression for the dependence of the rate constant of polymer degradation on its molecular weight and molecular weight distribution of the calculation of polymers during the degradation under the action of ultrasound, which satisfactorily describe the experimental data

1. Introduction

The dispersion of mineral and organic compounds under the action of ultrasound in polymer solutions is widely used to obtain stable dispersions with particle sizes up to several hundred nanometers, and a narrow distribution of their size. In particular, the processing products of starch aqueous solutions by ultrasound improves the technological and physiological properties such as solubility, viscosity, stabilizers, food and drugs. This is achieved by a slight decrease in polymer molecular weight and a reduction of its molecular weight distribution. Therefore the mathematical description of the process of polymers degradation in solution under the action of ultrasound is an important issue.

2. Results and Discussion

Changing the molecular weight of macromolecules in solution under the influence of ultrasound takes place on the first order equation in the initial stage of the process, and then considerably slows down, reaching a minimum value. The speed of the process increases with increasing of polymer molecular weight. Calculated from the equation of the first order rate constants for polymers degradation are shown in Table 1.

Table 1

Influence of high molecular weight compounds on the rate constant of its decomposition

Polymer	Solvent	Molecular weight, g/mol	Rate constant, min^{-1}
Dibutyryl chitin (DBC)	2 M HCl in water	350000	0,0469±0,0006
DBC	2 M HCl in water	280000	0,0363±0,0008
DBC	2 M HCl in water	190000	0,0315±0,0004
DBC	2 M HCl in water	124800	0,0208±0,0002
Starch	water	5930000	0,173±0,002

Investigation of changes in molecular weight distribution of high-molecular substances in their destruction under the action of ultrasound has shown that it is much narrower, i.e., the ratio of weight average molecular weight of the polymer number-average (M_w/M_n) is markedly reduced in the process of degradation.

In order to describe the dependence of the rate constant of degradation of high molecular weight compounds in solution from its molecular weight, assume that the constant depends on the ratio of the size of the volume of the globule macromolecules in solution and the size of a cavitation bubble, which arises in the liquid under the action of ultrasound. Dependence of the volume of the globule of macromolecule in solution of molecular weight can be described by the expression:

$$V_M = [h] \cdot M / N_A \quad (1)$$

Where [η] - intrinsic viscosity of the polymer, M - its molecular weight, N_A - Avogadro's number.

$$[h] = K_M \cdot M^a \quad (2)$$

Where K and α – constants in equation of Mark-Houwink.

Given the fact that low molecular weight compounds practically degraded under the action of ultrasound, and to increase the size of the globule of macromolecule leads to an increase in the rate constant of destruction, reaching a maximum at approximately the same size of the globule and the cavitation bubble, the rate constant on molecular weight can be described by the expression:

$$k = k_p \cdot V_M / (V_M + V_p) \tag{3}$$

where k_p - aspect ratio, Vp - volume of the cavitation bubble.

In view of (1) and (2) from equation (3) we obtain the expression:

$$k = \frac{k_p \cdot \frac{K_M}{N_A} \cdot M^{a+1}}{k_p \cdot \frac{K_M}{N_A} \cdot M^{a+1} + V_p} \tag{4}$$

Transforming equation (4) and the fact that k_p is close to 1 and taking logarithms, you can get a linear dependence of the rate constants of degradation of the polymer from its molecular weight:

$$\lg(1/k - 1) = \lg(V_p \cdot N_A / K_M) - (a+1) \cdot \lg M \tag{5}$$

The rate constant of degradation of the polymer on the molecular weight is well described by a straight line in coordinates of equation (5). The coefficient of correlation line is 0.963, the value of $\lg(V_p N_A/K_M)$ is 5,630 ± 0,002, and the value of $(\alpha + 1)$ = 0,7779 ± 0,0005.

Thus, the dependence of the rate constant of polymer degradation in solution of high molecular weight of the compound can be written by the expression:

$$k = k_p \cdot M^{a+1} / (M^{a+1} + V_p \cdot N_A / K_M) \tag{6}$$

To verify the adequacy of the expression (6) to experimental data was calculated modified molecular weight distribution of DBC and starch, its weight average molecular weight and value of M_w/M_n under the influence of ultrasound.

Change the number of macromolecules per unit volume of the system (N_i) with a molecular mass of M_i calculated using the formula:

$$N_i = -N_{i_0} \cdot e^{-k_i t} + 2(1 - N_{2i_0}(-k_{2i} \cdot t)) \tag{7}$$

where N_{io} and N_{2io} - the initial number of macromolecules with molecular weight M_i, and M_{2i} per unit volume of the system, k_i and k_{2i} - the rate constant of degradation of high molecular weight compounds with molecular weight M_i, and M_{2i}, t - time.

For the calculations used experimental data from the source of DBC with molecular weight distribution, molecular weight 124 800 g/mol and the value of M_w/M_n, equal to 2.26

Calculated from equation (7) the molecular mass distributions of degraded under the action of ultrasound DBC satisfactory agreement with experimental data. It should be noted that the observed small difference in molecular weight distribution of polymer degradation after 240 min under the action of ultrasound is obviously due to inaccuracies in the description of the molecular weight distribution of the source DBC taken for the calculations.

Weight average molecular weight calculated by the formula:

$$M_W = \sum c_i \cdot M_i \tag{8}$$

where c_i - the mass fraction of polymer with a molecular weight M_i.

Average molecular weight calculated by the formula:

$$M_N = i / \sum \frac{1}{M_i} \tag{9}$$

References

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