The syntheses of poly (diethylene glycol adipate) in low-intensity ultrasound

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Abstract. Poly (diethylene glycol adipate) is an important product of chemical technology. Several grades of polyesters (P-9, P-9A) are produced in the industry, in which poly(diethylene glycol adipate) is the main component. These composites are used in production of binders of mixed rocket solid fuels, as well as consumer goods. Poly(diethylene glycol adipate) is obtained by polycondensation of diethylene glycol and adipic acid. Usually, the polycondensation is carried out using catalysts. The use of catalysts complicates this process: requires further purification process or in solvent free system might slow reaction rate due to the limiting diffusion between reactants and mass transfer limitations. Therefore, it was proposed to use low-intensity ultrasound, which allows to influence the kinetics of the process without complicating the system. In this work, the reaction of polycondensation of diethylene glycol and adipic acid in low-intensity ultrasound was studied. The results of applying low-intensity ultrasound to the preparation of poly(diethylene glycol adipate) showed an increase in the reaction rate of the formation of a high-molecular compound and a change in the thermal regime. Application of low-intensity ultrasound provides synchronization of vibration and rotation of self-organizing dissipative structures, which leads to the decrease in energy consumption for mass transfer, thereby increasing the reaction rate. The low-intensity ultrasound demonstrated to be an effective method to intensify the polycondensation reaction.

1. Introduction

Polycondensation is one of the most common methods of obtaining high-molecular compounds. The advantages of this method are a simple reaction system, which consists only of monomers and a product, and an easy-to-implement technological scheme. Catalysts are often used to obtain high-quality polymers with large molecular weight. For example, polycondensation of diacids with diols in the presence of organometallic catalysts was studied in works [1,2]. Sokolsky-Papkov and colleagues [3] suggest using H₃PO₄ or H₂SO₄ as polymerization catalysts to obtain safety polymers for medical purposes. In recent years, many researchers have proposed using enzymes as catalysts [4-6]. The use of catalysts complicates this process: requires further purification process or in solvent free system might slow reaction rate due to the limiting diffusion between reactants and mass transfer limitations [5]. Therefore, it seems particularly promising to use a method of non-reactive intervention in the kinetics of physical and chemical transformations in condensed media.
Application of ultrasound may activate various mechanisms in the fluid, depending on the modulation frequency [7-9]. In a recent study [5], the effect of ultrasound on lipase-catalyzed synthesis of poly(ethylene glutarate) has been investigated in detail: application of ultrasound significantly intensified the polyesterification reaction with reduction of the processing time from 24 h to 7 h. But the use of traditional ultrasonic transducers for mechanical agitation has several disadvantages: high-power regime of excitation and instrumental complexity. Application of low-intensity ultrasound allows to overcome it. More than 60 years low-intensity pulsed ultrasound is successfully used for various medical purposes [10], we propose to apply it in the chemical technologies [11]. Our previous study [12] was addressed the influence of low-intensity ultrasound on the thermal activation polymerization of plastic “Acrodent” and the photolytic curing of the composite “Charisma”. In the first case, an increase in the degree of polymerization of the binder was noted, which made it possible to achieve a twofold decrease in the concentration of the residual monomer in the product. In the second case, the concentration of the residual monomer in the polymer was reduced from 30% during curing under normal conditions to 1% in low-intensity ultrasound. These results allowed us to suggest the feasibility of using low-intensity ultrasound in the other methods of polymer synthesis.

In the present study, we investigated for the first time the synthesis of linear polyester poly(diethylene glycol adipate) from bifunctional monomers. Several grades of polyesters (P-9, P-9A) are produced in the industry, in which poly(diethylene glycol adipate) is the main component. These composites are used in production of binders of mixed rocket solid fuels [13], as well as consumer goods.

2. Materials and methods
Adipic acid (purity ≥ 99%) was obtained from GRANCHIM, Russia. Diethylene glycol (purity ≥ 99%) was obtained from Sibur-Neftekhim, Russia. The chemicals were used directly as received from the supplier without any further modification.

Polycondensation was carried out in a reactor (a three necked glass flask) equipped with a Dean-Stark trap with a deflegmator, a thermometer and a mechanical stirrer. The reactor was located in a thermostat. The thermostat was a metal container with a heat carrier (Wood alloy melt), which was heated by an electric heater with the maintenance of a set temperature.

The source of low-intensity ultrasound is the current pulse generator with the total power of 10 VA. The low-intensity ultrasonic pulses are generated in the loop (antenna) via electromagnetic-acoustic conversion as a result of the action of a surface force [14]. The average amplitude of acoustic pulses is 150 Pa, much weaker than in similar experiments with an ultrasonic transducer. The frequency of the resulting weak acoustic signal may be regulated manually within the range of 50-2000 kHz to fulfill the resonant-type synchronization of vortex dissipative structures or other type of dynamic instabilities in the fluid, which play an important role in self-organization of chemical systems [15,16], thus controlling the course of reactions. The antenna of the current pulse generator was attached to the container with Wood alloy using metal clips. The pulses of the current generator create low-intensity ultrasonic pulses of the same frequency with an intensity of 5-10 dB.

The reaction mixture consisted of equimolar ratio of adipic acid (0.28 mol, 41.0 g) and diethylene glycol (0.28 mol, 29.6 g) without any addition of solvents. The reaction mixture was loaded into the reactor and heated with constant stirring. The time was counted from the moment when the temperature of the reaction mixture began to drop. Six syntheses of poly(diethylene glycol adipate) were carried out: three in the standard (normal) regime and three using low-intensity ultrasound (regulatory regime) with the frequency of 2000 kHz.

To study the effect of low-intensity ultrasound during reaction the amount of formed water and the temperature of the reaction mixture in the standard and regulatory regimes were controlled. The data were statistically processed, their accuracy was 3%.
3. Results and discussions

The interaction of adipic acid with diethylene glycol is a well-studied reaction and is described by the equation:

\[ n \ HOOC - (CH_2)_4 - COOH + nHO - (CH_2)_2 - O - (CH_2)_2 - OH \rightarrow \]
\[ \rightarrow \ [ - COO - (CH_2)_4 - COO(CH_2)_2 - O - (CH_2)_2 - ]_n + 2n \ H_2O \]

The process of formation of poly(diethylene glycol adipate) is a set of series-parallel reactions. It is described by a third-order kinetic equation at a conversion rate of 50% to 90%. In the reaction system, a large number of reactions occur at almost any time, differing in the degree of polymerization of the incoming molecules. Due to the Flory principle, they are indistinguishable, so we can only talk about the probabilistic course of the process.

The kinetic curves of the formation of water in the normal and in the regulatory regimes are presented in figure 1. It can be seen that the use of low-intensity ultrasound leads to the intensification of polycondensation of poly(diethylene glycol adipate): in the normal regime 3.6 g of water is formed within 90 minutes and at 2000 kHz in 62 minutes.

![Figure 1. Kinetics of water formation during polycondensation of adipic acid and diethylene glycol.](image)

The difference of water volumes (ΔV) formed in fixed time intervals in the regulatory and normal regimes is shown in table 1.

| Time, min | ΔV, ml |
|-----------|--------|
| 10        | 0.4    |
| 30        | 0.4    |
| 60        | 0.4    |
| 90        | 0.5    |
| 120       | 0.6    |

Analysis of the course of temperature changes in the reaction mixture during synthesis of poly(diethylene glycol adipate) (figure 2) shows that at first the process proceeds in a non-isothermal regime. This is due to the melting of adipic acid.
Figure 2. The temperature of the reaction mixture during polycondensation of adipic acid and diethylene glycol.

During the first 10 minutes, there is a decrease in the temperature of the reaction mixture by 10 °C in normal and by 7 °C in regulatory regimes. After that the temperature increases. At 2000 kHz temperature stabilizes faster. The application of low-intensity ultrasound influences the thermal conductivity of the reaction mixture.

In two hours of synthesis, it is possible to achieve a conversion of 30% - 40%. The reaction proceeds in a non-isothermal regime, temperature fluctuations reach 10 °C. As a result, it is impossible to quantify the reaction rate constant. However, we can compare the degree of transformation $\xi$ in the normal and regulatory regimes (table 2).

Table 2. The degree of transformation $\xi$ in the normal and regulatory regimes.

| Time, min | The degree of transformation $\xi$ |
|-----------|-----------------------------------|
|           | Normal regime | Regulatory regime |
| 10        | 0.06 | 0.09 |
| 30        | 0.18 | 0.21 |
| 60        | 0.29 | 0.32 |
| 90        | 0.33 | 0.38 |
| 120       | 0.34 | 0.40 |

Analysis of the tables 1 and 2 shows that the “average” rate of the process in the regulatory regime increases.

Polycondensation is a nonlinear and nonequilibrium process. The combination of driving forces (chemical potentials) and friction forces in the system create conditions for the formation of vortex dissipative structures of an autogenerating type - percolation clusters and self-organization processes. At this level of structural and thermodynamic organization of autogenerating dissipative structures, there are Langevin internal and external sources. Low-intensity ultrasonic wave is an external Langevin source, which is included in the system. There are two possible models of the effect of an acoustic wave on a condensed medium: either direct pumping by energy of clusters due to mechanical work performed by periodic compression, or parametric resonance and synchronization of clusters due to periodic disturbances of energy-intensive parameters of their external connections. In the second case, a decrease in stochastic noise occurs, and the kinetics of the process in the area of effective...
regulation becomes globally consistent. According to the theory, the synchronization of periodic motions (oscillations and rotations) of convective structures that form and determine interphase reaction-diffusion flows leads to an increase in the reaction rate, which is observed during polycondensation. At the beginning of the process the temperature drops due to the melting of adipic acid; therefore, the reaction rate at this stage is significantly reduced both in normal and regulatory regimes. But the inclusion of a regulatory low-intensity ultrasonic signal leads to an increase in the thermal diffusivity of the mixture, which, in turn, decreases the depth of the thermal well and leads to an increase in the "average" reaction rate. The reduction in the reaction time established the positive effect of low-intensity ultrasound on the poly(diethylene glycol adipate) reaction meeting the demand for green chemistry and a sustainable development. Compared with the traditional ultrasound methods, the key features of our method are the relatively low-power regime of excitation and instrumental simplicity.

4. Summary
Polyester poly(diethylene glycol adipate) was synthesized using low-intensity ultrasound with the frequency of 2000 kHz. Application of low-intensity ultrasound significantly influences the process of polycondensation. The positive effects were achieved without affecting other technological parameters of the process. Therefore the results of can be summarized as follows:
- increasing the reaction rate of polycondensation;
- reducing the reaction time;
- increasing the thermal diffusivity of the reaction mixture.

5. References
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