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SYNTHESIS OF A NON-ISOCYANATE URETHANE OLIGOMER BASED ON PHTHALIC ANHYDRIDE

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Abstract:

Objective. The purpose of this work is to study the method of synthesizing an oligomer containing urethane groups without the isocyanate method, as well as to conduct an infrared spectroscopic analysis to determine the formed chemical bonds and functional groups in the resulting urethane oligomer. The

influence of the temperature of the reaction mass and the reaction time on the average molecular weight of the resulting urethane oligomer is shown. The optimal temperature-time parameters for carrying out the synthesis process without an isocyanate urethane oligomer have been established.

Methods. To achieve the goal of this study, a method was used to determine the formed chemical bonds and functional groups. Ethylene glycol, urea, formaldehyde, and phthalic anhydride were used to synthesize the urethane oligomer. The urethane oligomer was obtained by the chemical reaction of polycondensation under vacuum. To determine the optimal temperature and time of the polycondensation reaction, samples were selected that differ in the duration of the reaction, as well as in the temperature of the reaction system. The molecular weights of the samples were determined by cryoscopy. A graph of the dependence of the molecular masses of the samples on the duration of the polycondensation reaction at different temperatures was plotted.

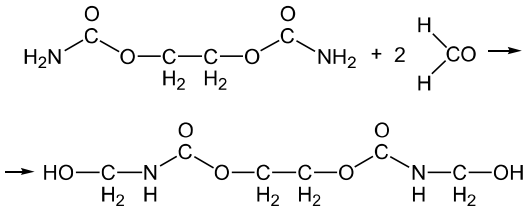
Results. The results of the experiments showed that an absorption band in the region of 1640.55 cm-1 was found in the IR spectrum, explaining the presence of the -CO-NH2 group and an absorption band in the region of 1732.08 cm-1, proving the presence of an unsubstituted urethane group.The study of the molecular weight of the obtained urethane oligomer by the cryoscopic method showed that the molecular weight of the oligourethane reaches 3921. The optimal temperature-time condition for the synthesis of this oligourethane is a chemical reaction at 160 ° C and for 120 minutes.

Conclusion. The results obtained from the study of the urethane oligomer synthesis method without the isocyanate method indicate that the optimal condition for obtaining a urethane oligomer based on phthalic anhydride is the polycondensation reaction for 120 minutes at a temperature of 160 °C. this method allows to obtain without isocyanate urethane oligomer based on ethylene glycol, urea, formaldehyde and phthalic anhydride, with an average molecular weight reaching 3921.

Keywords. Synthesis, isocyanate-free method, urethane oligomer, cryoscopy, IR spectroscopy.

Introduction. This paragraph includes information on the latest scientific advances in the chemistry and technology of non-isocyanate type urethane polymers. Polyurethanes are one of the most used polymers in many modern technologies [1, 2]. However, the use of toxic components, such as isocyanates, in the production process can make the production of polyurethanes extremely toxic and dangerous [3, 4]. For a long time, non-isocyanate sources have been sought for the production of polyurethanes. A significant problem in the technologies for producing non-isocyanate-type polyurethane by the method using cyclic carbonates is the lack of commercially available multifunctional cyclic carbonates [5, 6]. Recent works in the field of new methods for the preparation of cyclic carbonates are primarily devoted to the development of new catalytic systems and the synthesis of monofunctional compounds [7]. Similar catalytic systems are also used for the copolymerization of epoxides with CO2 and ring-opening polymerization of cyclic carbonates, with one or another direction of the reaction depending on the process conditions [8, 9].

Methods. Obtaining a urethane oligomer based on phthalic anhydride begins with a chemical reaction of the interaction of urea with ethylene glycol in a molar ratio of two to one. Next, a chemical reaction of the interaction of the resulting diurethane with formaldehyde in a molar ratio of one to two, respectively, is carried out. As a result, diurethane with terminal hydroxyl groups is formed. The chemical reaction equation for this process is shown below.



To obtain a urethane oligomer based on phthalic anhydride, a polycondensation reaction is carried out between the previously synthesized diurethane diol and phthalic anhydride. Figure 1 shows the chemical reaction equation for the polycondensation of diurethane diol and phthalic anhydride.

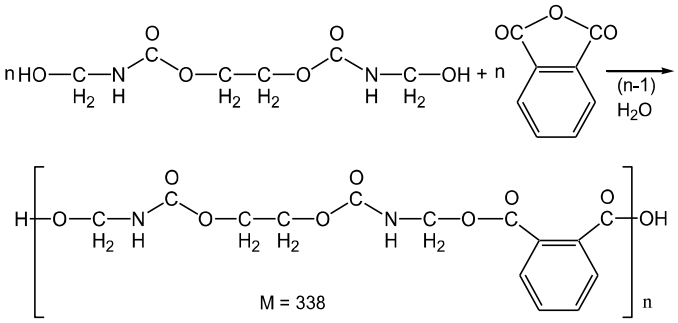


Figure 1. Polycondensation reaction equation between diurethane diol and phthalic anhydride

The mass of one link of the polycondensation oligomer based on phthalic anhydride is 338.

The process of synthesis of urethane oligomer based on phthalic anhydride. The procedure for obtaining diurethane based on ethylene glycol is the first step in the synthesis of urethane oligomer based on ethylene glycol. Based on this product, diurethane diol based on ethylene glycol is obtained. To do this, 100 grams of ethylene glycol diurethane is placed in a flask equipped with a stirrer, dropping funnel, reflux condenser and thermometer. Connect the heating, set to 65 ° C. after the temperature of the reaction mass reaches 65 °C, the stirrer is connected at a rotation speed of 280-300 rpm. Then, through a dropping funnel, 152 grams of a formaldehyde solution with a 20% concentration and 10 grams of ammonia water with a 20% concentration begin to be poured. This stage of the chemical reaction lasts for 150 minutes. After completion of the reaction, water is distilled off from the reaction mass using a vacuum at 60°C for 40 minutes. The resulting diurethane diol is a viscous liquid with a light yellowish tint.

To carry out the process of polycondensation of diurethane diol and phthalic anhydride, 71.5 grams of phthalic anhydride are added to the flask. Then, during 30 minutes with intensive stirring, the temperature of the reaction mass is raised from 60 °C to 130 °C. After, a vacuum is connected to the flask and 10 grams of sulfuric acid solution with a 40% concentration is poured. Next, raise the temperature of the reaction mass to 160 °C. The reaction at the reached temperature proceeds for 120 minutes.To obtain an oligourethane with a terminal urethane group, the temperature of the reaction mass is reduced from 160 °C to 135 °C and 6 grams of urea are added. This reaction step lasts 30 minutes at a given temperature. After completion of the reaction, the vacuum is removed and the resulting product is held at 70°C with slow stirring for 50-60 minutes. The product obtained is a whitish-yellow solid mass, soluble in water.

Determination of the molecular weight of the oligomer by the cryoscopic method. A relatively simple method for determining the molecular weight of a substance is to measure the drop in freezing point of dilute solutions of that substance in a solvent. As one of the colligative properties of dilute solutions, the freezing point decrease depends only on the amount of dissolved particles, but not on their type.

To determine the temperature difference, first determine the freezing point

of the pure solvent, and then the solution of the urethane oligomer in this solvent in a cold mixture using, for example, a Beckmann thermometer. To do this, usually determine the temperature profile near the freezing point and depict it graphically. From the above formula, the molar mass (M) is calculated using formula 1 [10, 11].

$$M = \frac{K \cdot m1 \cdot 1000}{\Delta T \cdot m2} \qquad (1)$$

where: K - cryoscopic constant. For water it is 1.86, for benzene 5.07; ΔT is the temperature difference between the solvent and the solution; m1 is the mass of the dissolved substance; m2 is the mass of the solvent.

Results. Infrared spectroscopy of a urethane oligomer based on phthalic anhydride. To determine the chemical bonds formed during the chemical synthesis of a urethane oligomer based on phthalic anhydride, the samples were studied by infrared spectroscopy (Figure 2).

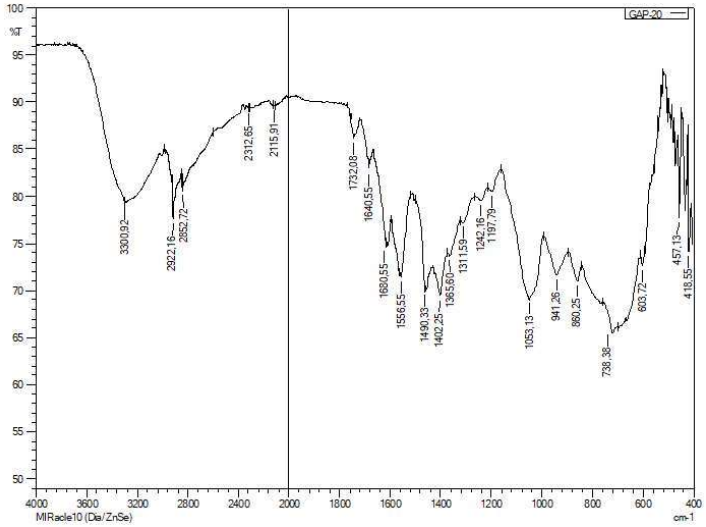


Figure 2. IR spectrum of oligourethane based on phthalic anhydride

The presence of an absorption band in the region of 1640.55 cm^{-1} in the IR spectrum explains the presence of the -CO-NH2 group. The absorption band at 1732.08 cm^{-1} indicates the presence of an unsubstituted urethane group. The absorption band in the region of 1680.55 cm^{-1} corresponds to non-planar bending vibrations of the O-H bond of the carboxyl group associated with the aromatic ring. The absorption band in the region of 1242.16 cm^{-1} corresponds to the stretching vibrations of –O-CO-O-groups. The IR spectrum contains absorption bands of stretching vibrations of -C-H bonds in the region 2922.16 - 2852.72 cm^{-1}. C-O-NH-groups in the IR spectrum are observed in the region of 3300.92 cm^{-1}. When a hydrogen bond is formed, the vibration frequency decreases and the bands broaden. Hydrogen bond absorption occurs in this region in the case of oligomers or polymers. In the IR spectrum, no absorption bands were found in the region caused by stretching vibrations of the hydroxyl group.

The results of infrared spectroscopy confirm the possible chemical structure of the phthalic anhydride-based urethane oligomer shown in Figure 1.

To determine the optimal temperature and time of the polycondensation reaction, samples were selected that differ in the duration of the reaction, as well as in the temperature of the reaction mass. Three polycondensation reactions were carried out at temperatures of 145, 160 and 175 °C.

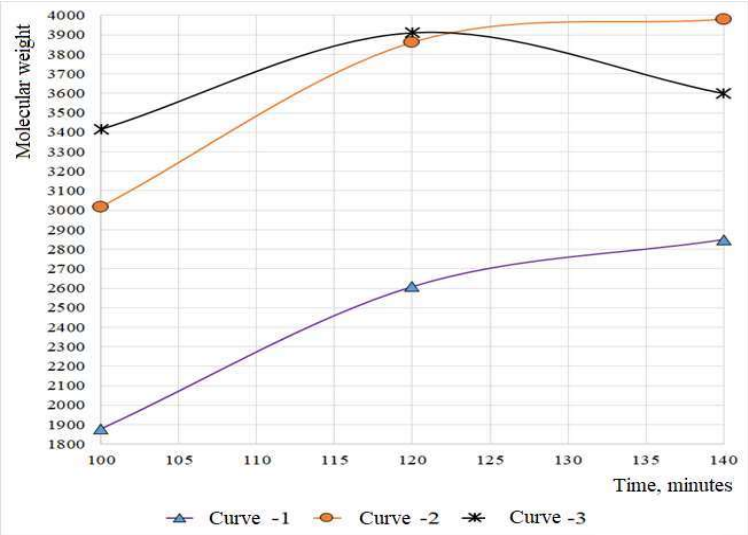
The duration of the three reactions was up to 140 minutes. Oligourethane samples were obtained at 100, 120 and 140 minutes from each reaction system. As a result, 9 samples of urethane oligomer based on phthalic anhydride with different temperature and time conditions were obtained. Then, the molecular weights of the samples were determined by the method of cryoscopy and a graph of the dependence of the molecular weights of the samples on the duration of the polycondensation reaction was plotted. Table 1 sets out the temperature-time parameters of the polycondensation reaction for samples of urethane oligomer based on phthalic acid.

Table 1

Temperature-time parameters of polycondensation of samples of oligourethane based on phthalic acid

Samples No.	Reaction conditions		Molecular weight determined by the method of cryoscopy
	Time minutes	Temperature °C	
1	100		1878,3
2	120	145	2607,6
3	140		2848,9
4	100		3018,4
5	120	160	3862,4
6	140		3981,0
7	100		3417,2
8	120	175	3910,7
9	140		3600,1

Discussions. According to the data obtained from Table 1, a diagram of the dependence of the molecular weight of samples of the resulting urethane oligomer on the time of the chemical reaction of polycondensation and the temperature of the reaction mass was compiled (Figure 3). This dependence diagram helps to compare the indicators of the table and determines the direction of the polycondensation reaction.



Curve-1 – samples obtained at 145°C; Curve-2 - samples obtained at 160 °C; Curve-3 - samples obtained at 175 °C

Figure 3. Effect of temperature and time of polycondensation on the molecular weight of urethane oligomer samples based on phthalic anhydride

The diagram of the dependence of the molecular weight on the time of the temperature flow shows that when the polycondensation reaction is carried out at 145 ° C, the molecular weight of the urethane oligomer based on phthalic anhydride increases from 1878 to 2607 at a noticeable rate up to the 120th minute of the reaction, but then a slowdown in the growth of the molecular weight is observed (Figure 3 , curve-1). The molecular weight of the oligourethane obtained at 160°C increases by 844 units at the 120th minute and reaches 3862, but the continuation of polycondensation up to 140 minutes shows an increase in molecular weight by only 119 units (Figure 3, curve-2). The direction of curve-3 shows the course of the polycondensation reaction at 175°C. Observing the direction of curve-3, we can conclude that the reaction system begins the reaction of transesterification or thermal destruction of the urethane oligomer based on phthalic anhydride.

Based on the data obtained, it should be concluded that the optimal condition for obtaining a urethane oligomer based on phthalic anhydride is to carry out the polycondensation reaction for 120 minutes at a temperature of 160 °C.

Table 2 shows the process parameters for obtaining an oligomer containing urethane groups based on phthalic anhydride.

Table 2

Parameters for the synthesis of a urethane oligomer based on phthalic anhydride

Stages	Synthesis parameters				
	Time, minutes	Temperature, °C	Pressure, atm.	pH environment	Mechanical impact
1. Synthesis of diurethane based on ethylene glycol	150	130	atmospheric	8,5-9,5	Mixing, 150-200 rpm
2. Condensation reaction of formaldehyde with the resulting diurethane	150	65	atmospheric	8,5-9,0	Mixing, 280-300 rpm

3. Residual water distillation	40	60	-0,8 atm.	7,5-8,0	Mixing, 140-150 rpm
4. Polycondensation	120	160	-0,4 – -0,5 atm.	6,0-6,5	Mixing, 100-130 rpm

Conclusion. Thus, the experiments carried out in this article indicate the possibility of obtaining an oligomer containing urethane groups based on ethylene glycol, urea, formaldehyde, and phthalic anhydride. The results obtained by studying the method of synthesis of a urethane oligomer without the isocyanate method indicate that the optimal condition for obtaining a urethane oligomer based on phthalic anhydride with a molecular weight of 3862 is to carry out the polycondensation reaction for 120 minutes at a temperature of 160 °C. The results of infrared spectroscopy confirm the possible chemical structure of the phthalic anhydride-based urethane oligomer shown in Figure 1.

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