Synthesis of water-soluble polycarboxylates on the base of phthalic anhydride

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Abstract – The process of synthesis (meth)acrylic monomers with carboxyl group near aromatic nucleus by reacting of phthalic anhydride (PA) and hydroxypolyoxyalkylen (meth)acrylate are investigated. The basic laws of process of non-catalytic acylation of hydroxyethylmethacrylate (Bisomer HEMA) and hexapropyleneglycolmonoacrylate (Bisomer PPA6) by phthalic anhydride are found. The values of the activation energy (E_A) for examined reaction systems are calculated on the base of obtained kinetic parameters. The effect of structure of polyoxyalkylene chain on the reaction rate with PA without the use of solvents.

Key words – phthalic anhydride, Bisomer HEMA, Bisomer PPA6, (meth)acrylic monomers, polycarboxylates, water-soluble polymers.

I. Introduction

The water-soluble polycarboxylates are applied in the building industry as superplasticizers for cement mixtures, in the composition of detergents, as well as anticorrosive component of heat carriers in the heating and cooling systems. They are synthesized via copolymerization of (meth)acrylic acids and their derivatives.

The disadvantage of polycarboxylates of this type is unfavorable spatial location of carboxyl groups, which are tied to aliphatic polymer chain, which restrains the plasticizing and anticorrosive properties of polycarboxylates. The synthesis of (meth)acrylic monomers with space available carboxyl group, which are tied with aromatic nucleus, will give us an opportunity to investigate the properties of obtained oligomeric materials on their base, as plasticizers for concrete, which have an anticorrosive ability. The most acceptable variant of obtaining of the monomers of this type is an application as the raw material for PA and hydroxypolyoxyalkylen (meth)acrylates of different structures (Fig. 1).

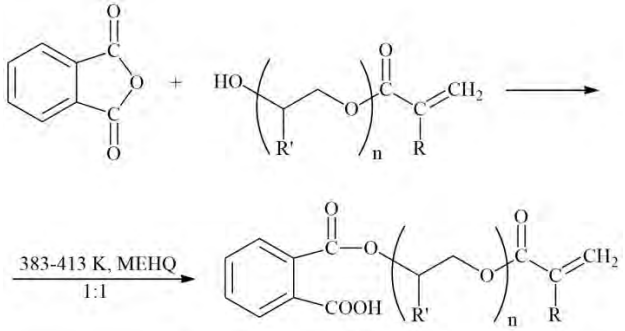

Fig. 1 The reaction scheme of acylation of hydroxypolyoxyalkylen(meth)acrylate by PA (R, R': –H, –CH_3; n = 1, 8)

The synthesis of only one monomer of this type is described in the literature; it is obtained via interaction between PA and HEMA in the environment of benzene at the temperature of 333K [1]. However, the described method doesn't fulfill to the basic requirement of industrial production – absence of using of solvents.

II. Experimental part

The synthesis of products of interaction between PA and HEMA and between PA and PPA6 was conducted into the thermostatical reactor with a stirrer in the temperature range 383-413K in the presence of an inhibitor of polymerization – methoxyhydroquinone (MEHQ). The kinetics of processes were investigated by the change of concentration of PA after homogenization of the reaction mixture using morpholine method for determination anhydrides of carboxylic acids [2].

Synthesis of PA-HEMA: 56,1 g of HEMA (0,4312 mol) with the addition of 0,12 g MEHQ were loaded into the reactor with capacity of 0,25 dm^3. The mixture was heated to the reaction temperature (383-413 K), then 63,9 g of PA (0,4312 mol) were added. After homogenization of the reaction mixture, a calculated sample test was taken for the determination of content of phthalic anhydride. The obtained results are shown in Fig. 2.

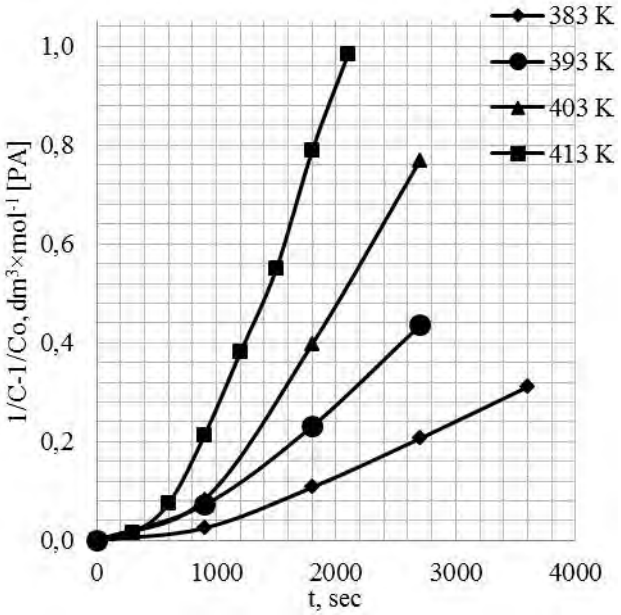

Fig. 2 The kinetics of acylation of HEMA by PA

The kinetics of reaction is described by second-order equation. The difference between the achieved values of the conversion of PA in the range 1,5-5 hours at temperatures of 393-413 K did not exceed 2-4%, indicating that the establishment of some reaction equilibrium is taking place. The optimal conditions of reaction conduction: temperature 413 K, reaction time 1,5 h at 84,3% conversion of PA.

Synthesis of PA-PPA6: 88,7 g PPA6 (0,2110 mol) with the addition of 0,12 g MEHQ were loaded into the reactor with capacity of 0,25 dm^3. The mixture was heated to the reaction temperature (393-413 K) and then 31,3 g of PA (0,2110 mol) were added. After homogenization of the

reaction mixture, a calculated sample test was taken for the determination of content of phthalic anhydride. The obtained results are shown in Fig. 3. As we can see, with the decreasing of temperature the duration of the induction period is increasing (Fig. 3), which may be due to the steric factor due to the large molecular size PPA6 (M = 420 g/mol). After the induction period, the average length of which is 45 min., the reaction kinetics is described by the equation of the second order.

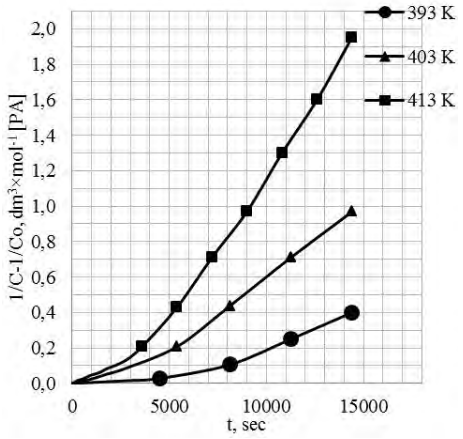

Fig. 3 Kinetics of acylation PPA6 by PA

The maximum achieved value of the conversion of PA was 80% at stirring the reaction mixture for 4 hours at the temperature of 413 K.

III. Calculation of energy activation

The kinetic parameters of the process of acylation of HEMA and PPA6 by PA were calculated based on the obtained kinetic regularities (Figs. 2 and 3). The constants of the reaction rates of examined systems are presented in Table 1.

TABLE 1

THE KINETIC PARAMETERS OF THE PROCESS OF ACYLATION OF HEMA AND PPA6 BY PA

		PA-HEMA	PA-PPA6
		$k \times 10^5$, $dm^3/(mol \times sec)$	
T, K	383	7,41	-
	393	12,3	2,33
	403	19,9	5,32
	413	29,6	9,60
E_A, kJ/mol		61,1	95,6

With increasing of the size of oxyalkylene fragment, a significant reduction in the rate constant of the reaction is observed. Acylation reaction rate decreases significantly in a number of HEMA-PPA6. This is probably due to the increased viscosity of the reaction system by increasing the molecular weight of molecule hydroxypolyoxyalkylen (meth)acrylate.

The dependence of the negative logarithm of the calculated reaction rate constants from the inverse temperature is shown in Fig. 4. As we can see, the value of the linear approximation in both cases close to unity ($R^2 \approx 1$), indicating the reliability of the received results. The tangent of the angles of direct lines enables us to calculate the value of E_A. The calculated values of E_A for the reaction systems PA-HEMA and PA-PPA6 equal to 61,1 kJ/mol and 95,6 kJ/mol, accordingly.

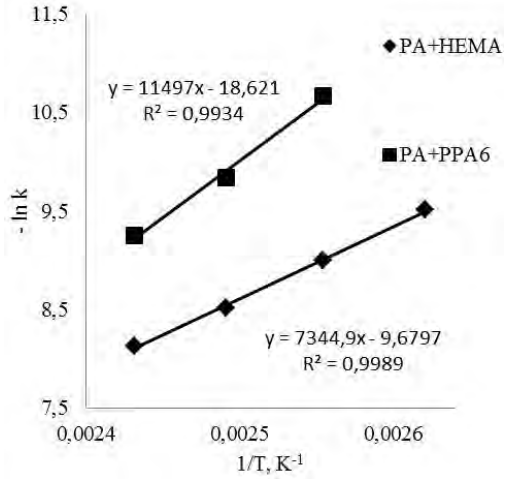

Fig. 4. The dependence of the negative logarithm of the reaction rate constant from the inverse temperature

With the increase of molecular weight of alkoxyalkylene chain, the E_A is increasing. This indicates an increase in steric obstacles which depends on the size and structure of the original molecule.

Conclusion

The process of obtaining of the product of the interaction between PA and Bisomer HEMA in the temperature range 383-413 K at an equimolar ratio of reagents without the use of solvents are investigated. The absence of solvent enables to accelerate the synthesis process, eliminates the technological stage of its regeneration and increases the productivity of the reaction unit.

For the first time the kinetics of synthesis of monomer with higher molecular weight by the example of interaction between PA and industrial available Bisomer PPA6 in the temperature range 393-413 K are investigated. The existence of the induction period for this reaction that lasts 45 min. (due to the high viscosity of the reaction system) is found.

The values of E_A of reaction systems PA-HEMA and PA-PPA6 are calculated. Found that by increasing of the size of hydroxypolyoxyalkylene chain in the molecule of polyoxyalkylen(meth)acrylate, acylation reaction rate is slowing down, and E_A is increasing.

References

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