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*Andrii Gladii, Fedir Tsyupko, Igor Polyugyn, Iosyp Yatchyshyn and Marta Laruk*

# KINETIC REGULARITIES OF HYDROXY(POLY)ALKYLENEOXY(METH)ACRYLATES ACYLATION BY PHTHALIC ANHYDRIDE

*Lviv Polytechnic National University*
*12, St. Bandera str., 79013 Lviv, Ukraine*

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**Abstract.** The kinetics of non-catalytic and catalytic processes of 2-hydroxyethylmethacrylate (HEMA) and hydroxyhexaoxypropylacrylate (PPA6) bulk acylation by phthalic anhydride (PA) has been investigated. The product of PA and PPA6 interaction has been synthesized for the first time. The structure of the synthesized compounds has been confirmed by IR-spectroscopy and molar refraction.

**Keywords**: acrylic monomer, polycarboxylate, phthalic anhydride, HEMA, PPA6.

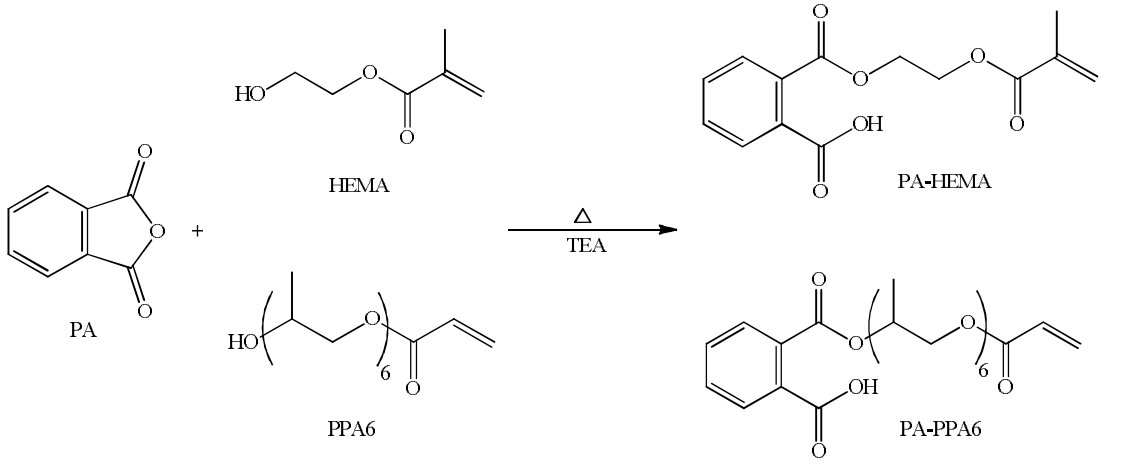
## 1. Introduction

Hydroxy(poly)alkyleneoxy(meth)acrylates (HPAMA) are used as monomers for the production of polycarboxylate hyperplastisizers [1-3] and polymeric demulsifiers for oil-water emulsions [4-9]. Polycarboxylates are acrylic polymers with carboxy groups of (meth)acrylic acids in the macromolecule of polymeric chain. There are no data in literature concerning the synthesis of polycarboxylates containing distant carboxy group non-bounded to aliphatic polymeric chain. The transfer from HPAMA end hydroxy group to carboxy one improves anticorrosive properties of polycarboxylates [10] and allows following modification of oil polymeric demulsifiers to increase their demulsifying ability.

In this work the acrylic monomers are synthesized *via* HPAMA acylation by phthalic anhydride without solvents, in contrast to the synthesis proposed by Z. Sedlakova *et al.* [11]. Our approach allows to simplify the process and reduce the price of monomers production.

O. Baranovska [12] shows that the kinetic regularities of alcohol acylation by acid anhydride are insufficiently illustrated in literature. The aim of this work was to investigate the kinetic regularities of HPAMA acylation by phthalic anhydride, as well as to ground and determine the optimum synthesis conditions for acrylic monomers with distant carboxy group.

The kinetic regularities of non-catalytic and catalytic acylation by phthalic anhydride are determined on the basis of commercial compounds HEMA and PPA6 without solvents with 10 % excess of HPAMA according to Scheme (1):




(1)

# 2. Experimental

## 2.1. Materials

The following compounds were used as the initial materials:

– PA (BASF, Germany): purity > 99 %; acid number (*AN*) 758 mgKOH/g; molar mass (*MM*) 148 g/mol;

– Bisomer® HEMA™ (GEO, UK): purity > 99%; *AN* < 0.3 mgKOH/g; *MM* 130 g/mol;

– Bisomer® PPA6™ (GEO, UK): purity > 99 %; *AN* < 0.3 mgKOH/g; *MM* 420 g/mol;

– Triethylamine (TEA), as a catalyst: purity > > 99.5 %; density 0.728 g/cm$^3$; *MM* 101 g/mol;

– Methoxyhydroquinone (MEHQ), as an inhibitor of thermal polymerization: purity > 99 %; *MM* 140 g/mol.

## 2.2. Analytical Methods

Average values of molar mass of the synthesized purified monomers were determined *via* cryoscopy in benzene as a solvent. The acid number was determined according to the procedure of conductometric analysis developed in [13].

## 2.3. Spectral Methods

IR-spectra of HEMA, PPA6 and products of their interaction with PA (PA-HEMA and PA-PPA6) were recorded at IR-spectrophotometer "Specord-M80" with integration number of 1 s according to the method of thin films applied over KBr plates for the area of 4000–400 cm$^{-1}$.

## 2.4. Experimental Results Processing

### 2.4.1. Calculation of kinetic regularities

HPAMA acylation by phthalic anhydride may be examined as irreversible reaction of the second order according to the following scheme:

$$A + B \rightarrow P, \qquad (2)$$

where *A* – PA; *B* – HEMA or PPA6 and *P* – reaction product (PA-HEMA or PA-PPA6).

The kinetic studies of non-catalytic and catalytic acylation of HEMA and PPA6 by phthalic anhydride were carried out relative to the acid number change. PA conversion was determined relative to acid number according to Eq. (3):

$$K_A(t) = \frac{AN_{0_{mix}}(theor.) - AN(t)}{AN_{0_{mix}}(theor.) - AN_P(theor.)} \cdot 100, \qquad (3)$$

where $K_A(t)$ – PA conversion, %; $AN_{0_{mix}}(theor.)$ – theoretical *AN* of the reaction mixture before the reaction, mgKOH/g; $AN_P(theor.)$ – theoretical *AN* of the end product, mgKOH/g; $AN(t)$ – *AN* value for time $t$, mgKOH/g; $t$ – time of sampling, s.

Theoretical *AN* were calculated according to Eqs. (4) and (5):

$$AN_{0_{mix}}(theor.) = \frac{2 \cdot MM(KOH) \cdot 1000}{MM(PA) + 1{,}1 \cdot MM(HPAMA)}, \qquad (4)$$

$$AN_P(theor.) = \frac{MM(KOH) \cdot 1000}{MM(P) + 0{,}1 \cdot MM(HPAMA)}, \qquad (5)$$

where $MM(KOH)$, $MM(PA)$, $MM(HPAMA)$, $MM(P)$ – molar masses of KOH, PA, HPAMA and reaction product (PA-HEMA or PA-PPA6), g/mol.

Transfer from conversion to PA concentration was carried out as follows:

$$C_A(t) = C_{A_0}\left(1 - \frac{K_A(t)}{100}\right), \qquad (6)$$

where $C_A(t)$ – PA current concentration, mol/l; $C_{A_0}$ – PA initial concentration, mol/l, calculated according to Eq. (7):

$$C_{A_0} = \frac{m(A) \cdot \rho_0 \cdot 1000}{MM(A) \cdot (m(A) + m(B))}, \qquad (7)$$

where $m(A)$, $m(B)$ – masses of PA and HPAMA loaded in a reactor, g; $MM(A)$ – PA molar mass, g/mol; $\rho_0$ – initial value of the mixture density, g/cm$^3$. Since reliable determination of $\rho_0$ value has experimental difficulties, we assume that the mixture density is not changed during the process and equal to the mixture density at the end of the process: $\rho_0 \approx \rho_P$ (Table 3).

In the absence of essential side reactions, ***i.e.*** regarding that the selectivity relative to the end product is 100 %, change of HEMA or PPA6 concentration is determined according to Eq. (8):

$$C_B(t) = C_{B_0} - (C_{A_0} - C_A(t)), \qquad (8)$$

where $C_B(t)$ – HPAMA current concentration, mol/l; $C_{B_0}$ – HPAMA initial concentration, mol/l. Taking into account 10 % molar excess of $C_{B_0}$ ($C_{B_0} = 1{,}1 \cdot C_{A_0}$), Eq. (8) takes the view of:

$$C_B(t) = 1{,}1 \cdot C_{A_0} - C_{A_0} + C_A(t) = 0{,}1 \cdot C_{A_0} + C_A(t). \qquad (9)$$

In accordance with [14] the integral kinetic equation of the second order reaction at non-equimolar ratio between reagents for one determined component has the view of:

$$\frac{1}{C_{B_0} - C_{A_0}} \ln \frac{C_{A_0} \cdot C_B(t)}{C_{B_0} \cdot C_A(t)} = kt, \qquad (10)$$

where k – rate constant of the non-catalytic reaction (or effective rate constant of the catalytic reaction $k_{ef}$), l/(mol·s). Substituting Eq. (9) into Eq. (10) and further reduction we obtain:

$$Y = kt, \quad (11)$$

where $Y$ – left part of Eq. (10) after reduction, l/mol:

$$Y = \frac{1}{0{,}1 \cdot C_{A_0}} \ln \frac{0{,}1 \cdot C_{A_0}{}^2 + C_{A_0} \cdot C_A(t)}{1{,}1 \cdot C_{A_0} \cdot C_A(t)}. \quad (12)$$

Activation energies of the non-catalytic and catalytic acylation were obtained on the basis of temperature dependence according to Arrhenius equation. To obtain kinetic data we took experimental points till maximal conversion 50–80 %.

### 2.4.2. Synthesis of Carboxy-Containing Monomers

The general procedure of the synthesis is the following. Definite amount of HPAMA and MEHQ (an inhibitor of thermal polymerization) were loaded into a glass reactor equipped with a mechanical stirrer and temperature control device. The mixture was heated to the definite temperature and PA was added under constant stirring. The calculated amount of the catalyst (TEA) was added to the mixture after achieving necessary temperature for the catalytic processes. The temperature was sustained within ± 2 K. Synthesis was carried out for no more than 4 h till PA conversion was 100 %. Table 1 represents loadings for the reaction mixture and temperature ranges.

### 2.4.3. Purification

The synthesized unpurified monomers with the mass of approximately 100 g were dissolved in 100–150 ml of benzene. The obtained solution was washed in separating funnel by 250 ml of 10 % HCl solution to remove TEA and HEMA (or PPA6) excess. Then the benzene layer with PA-HEMA (or PA-PPA6) was extracted by 5 % solution of $NaHCO_3$ in the amount of 1.5-fold molar excess relative to the theoretical amount of the final product. Aqueous layer with sodium salt PA-HEMA (or PA-PPA6) was rapidly washed by benzene and acidified by concentrated HCl till pH was 2. The obtained oily product was extracted by benzene. After drying over $Na_2SO_4$ the benzene was distilled under 2.1 kPa and 333 K. Then the products were purified from remains of volatile components under 13.3 Pa and 298 K. The purified products yield exceeded 95 %.

## 3. Results and Discussion

### 3.1. Kinetics of HEMA and PPA6 Acylation by Phthalic Anhydride in the Presence of TEA Catalyst and without it

The kinetic anamorphoses of HEMA and PPA6 non-catalytic bulk acylation by phthalic anhydride (without solvents) are represented in Figs. 1 and 2 and results for the catalytic acylation at different temperatures – in Figs. 3 and 4. In the case of HEMA acylation the concentration of TEA catalyst was 1 mol % relative to $C_{A0}$ (Fig. 3) and in the case of PPA6 acylation – 1.25 mol % relative to $C_{A0}$ (Fig. 4) because the induction period is observed here (Fig. 2).

So, the kinetics of PPA6 catalytic acylation (Fig. 2) differs from that of HEMA acylation (Fig. 1) by the presence of the induction period (Fig. 2). Its maximum is 60 min at 378 K. While increasing temperature the induction period decreases and is 20 min at 388 K and 10 min at 398 K. The presence of the induction period during PPA6 acylation by PA is in agreement with our previous investigations [15] and apparently caused by high viscosity of the reaction mixture.

Using TEA in the amount of 1 mol % relative to $C_{A0}$ during HEMA acylation allows to decrease the temperature range owing to faster homogenation of the reaction mixture at 368 K after adding catalyst (Fig. 3). TEA addition to the mixture PA+PPA6 in the amount of 1.25 mol % relative to $C_{A0}$ does not allow to decrease the temperature interval but results in disappearance of the induction period (Fig. 4), which is observed without TEA (Fig. 2).

*Table 1*

**Loadings for the reaction mixture and temperature ranges**

| Reaction | PA, g·(mol) | HPAMA, g·(mol) | Loadings range TEA, mg (mol % relative to $C_{A_0}$) | MEHQ, mg (mol % relative to $C_{A_0}$) | Temperature range, K |
|---|---|---|---|---|---|
| PA+HEMA | 44.4 (0.30) | 42.9 (0.33) | 75.90–303.6 (0.25–1) | 42 (0.1) | 368–398 |
| PA+PPA6 | 22.2 (0.150) | 69.3 (0.165) | 189.7–758.8 (1.25–5) | 21 (0.1) | 378–398 |

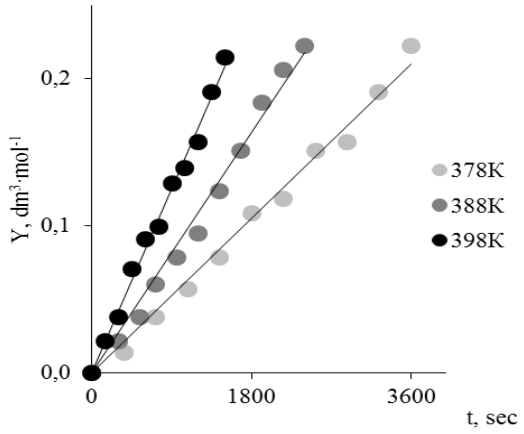



**Fig. 1**. Kinetic anamorphoses of HEMA non-catalytic acylation by PA at 378–398 K

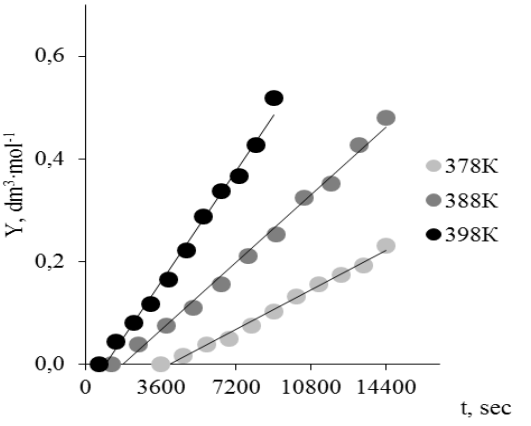



**Fig. 2**. Kinetic anamorphoses of PPA6 non-catalytic acylation by PA at 378–398 K

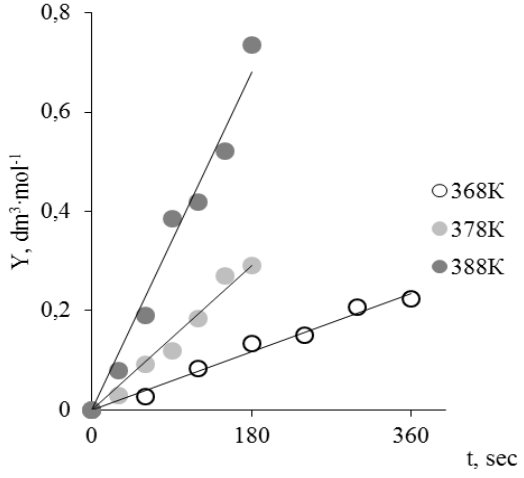



**Fig. 3**. Kinetic anamorphoses of HEMA acylation by PA at 368–388 K and TEA concentration of 1 mol %, relative to $C_{A0}$

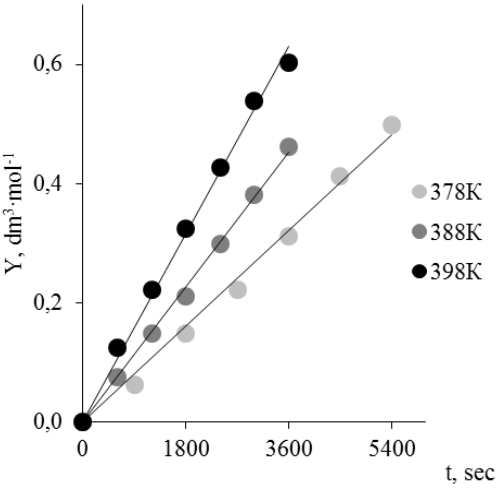



**Fig. 4**. Kinetic anamorphoses of PPA6 acylation by PA at 378–398 K and TEA concentration of 1.25 mol %, relative to $C_{A0}$

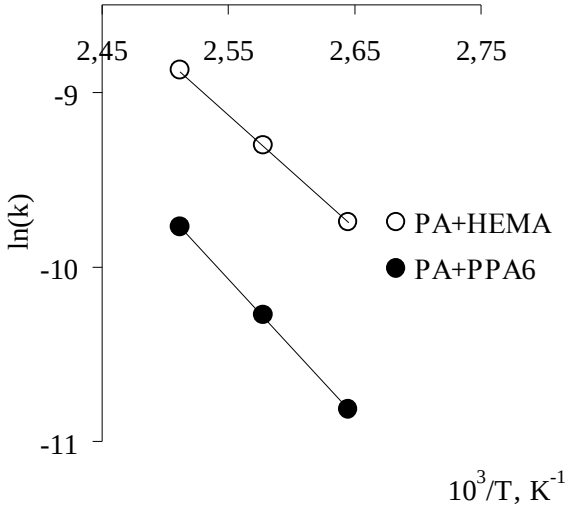



**Fig. 5**. Temperature dependence of rate constant of HEMA and PPA6 non-catalytic acylation by PA according to Arrhenius equation

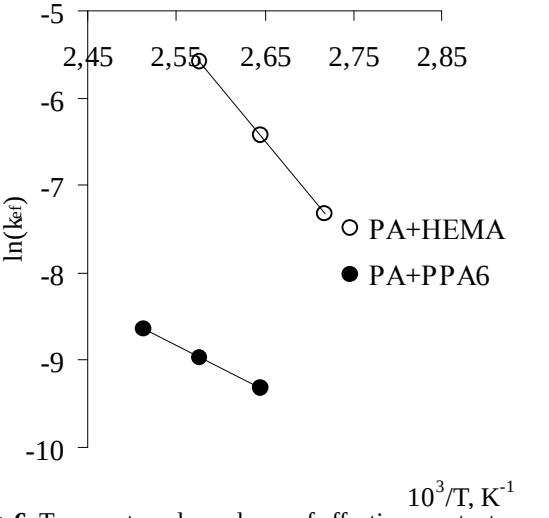



**Fig. 6**. Temperature dependence of effective constant of HEMA and PPA6 catalytic acylation by PA according to Arrhenius equation

*Table 2*

**Kinetic parameters of HEMA and PPA6 bulk acylation by PA in the presence of TEA and without it**

| Reaction | $T$, K | $k_{ef}\cdot 10^4$, $dm^3\cdot mol^{-1}\cdot s^{-1}$ | | $E_a$, $kJ\cdot mol^{-1}$ | | $\ln(k_0)$ | |
|---|---|---|---|---|---|---|---|
| | | Non-cat. | Cat. | Non-cat. | Cat. | Non-cat. | Cat. |
| PA+HEMA | 368 | - | 6.53 ± 0.48 | 54.4 ± 2.59 | 104 ± 2.11 | 7.54 | 26.7 |
| | 378 | 0.58 ± 0.02 | 16.1 ± 1.56 | | | | |
| | 388 | 0.91 ± 0.04 | 37.8 ± 3.65 | | | | |
| | 398 | 1.39 ± 0.04 | - | | | | |
| PA+PPA6 | 378 | 0.20 ± 0.01 | 0.89 ± 0.04 | 65.0 ± 2.51 | 42.1 ± 2.19 | 9.86 | 4.08 |
| | 388 | 0.34 ± 0.02 | 1.26 ± 0.03 | | | | |
| | 398 | 0.57 ± 0.03 | 1.75 ± 0.07 | | | | |

On the basis of kinetic anamorphoses (Figs. 1-4) we obtain the effective constants $k_{ef}$ and rate constants $k$ for HEMA and PPA6 bulk acylation by PA in the presence of TEA and without it (Table 2). Plotting logarithmic dependence $\ln(k)$ and $\ln(k_{ef})$ on inverse temperature (Figs. 5 and 6) allows to obtain values of activation energy $E_a$ and logarithm of near-exponential multiplier for non-catalytic ($\ln(k_0)$) and catalytic ($k_{0ef}$) processes (Table 2).

The increment of rate constants for HEMA and PPA6 non-catalytic acylation by PA is 1.5 and 1.6 times, respectively, while increasing temperature by 10 K (Table 2). Rate constants of HEMA acylation are 2.7 times higher compared with those of PPA6. For example, for 1.5 h at 398 K PA conversion for HEMA acylation is 89 % and for PPA6 – only 36 % (2.5 times).

The effective rate constants of HEMA catalytic acylation at 378 and 388 K are respectively 18 and 30 times higher compared with those of PPA6 (Table 2). The increment of rate constants for HEMA catalytic acylation (at TEA constant concentration) is 2.4 times higher compared with 1.4 times for PPA6. Obviously, it is connected with the length of hexaoxypropylene chain and conformation of PPA6 molecule affecting the formation of catalytic complex intermediate, *i.e.* decreases conversion relative to PA. For example, for 9 min at 378 and 388 K (TEA concentration is of 1 mol % relative to $C_{A0}$) PA conversion of HEMA acylation is 83 and 100 %, respectively. For PPA6 acylation (TEA concentration is of 1.25 mol % relative to $C_{A0}$) at the same temperatures PA conversion is 9 and 12 %, respectively. TEA concentration of 1.25 mol % relative to $C_{A0}$ after 4 h of PPA6 acylation does not allow to achieve 100 % PA conversion. Maximum values of PA conversion after 4 h at 378, 388 and 398 K are 77, 85 and 88 %, respectively. Thus, to achieve 100 % PA conversion for HEMA acylation the optimum temperature is 368 K and TEA concentration – less than 1 mol % relative to $C_{A0.}$ For PPA6 the optimum temperature is 388 K and TEA concentration – more than 1.25 mol % relative to $C_{A0.}$

The long hexaoxypropylene chain in PPA6 molecule (compared with HEMA) increases the activation energy of non-catalytic acylation by 10.6 kJ and correspondingly decreases the reaction rate. While using the catalyst we observe the increase of $E_a$ for HEMA acylation and its decrease for PPA6 acylation. The kinetic compensative effect (Fig. 7) is clearly observed for the obtained values of activation and kinetic parameters of temperature dependencies. There is a straight connection between the activation energy and near-exponential multiplier.

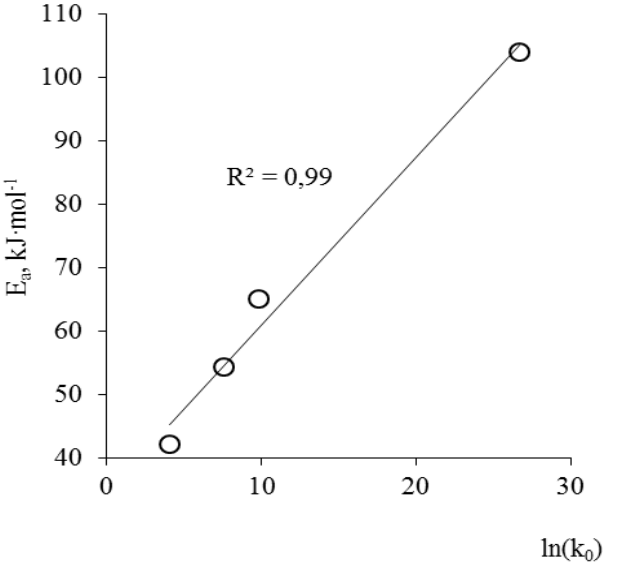



**Fig. 7.** Correlation between the activation energy and near-exponential multiplier for HEMA and PPA6 bulk acylation by PA in the presence of TEA and without it

Compensative effects are observed for the one-type reactions which differ by the structure of one of the components or by reaction conditions (catalyst, medium). When summarizing the greater amount of data they may be used for prediction.

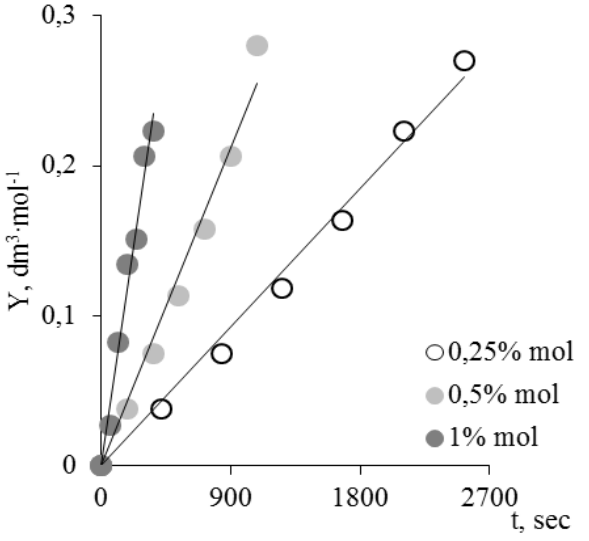



**Fig. 8.** Kinetic anamorphoses of HEMA acylation by PA at 368 K and different TEA concentration (mol % relative to $C_{A0}$)

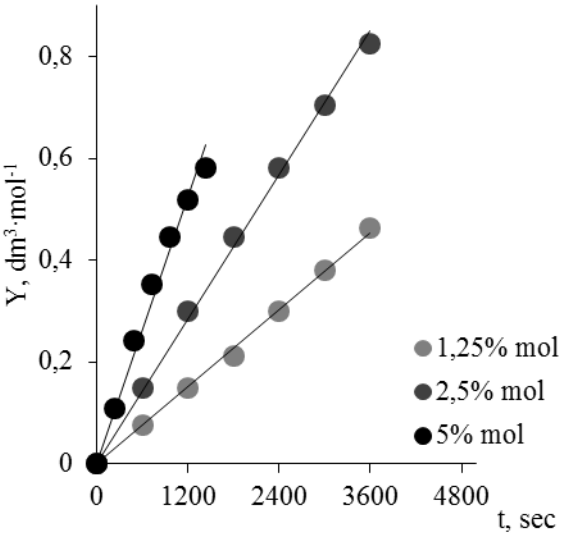



**Fig. 9.** Kinetic anamorphoses of PPA6 acylation by PA at 388 K and different TEA concentration (mol % relative to $C_{A0}$)

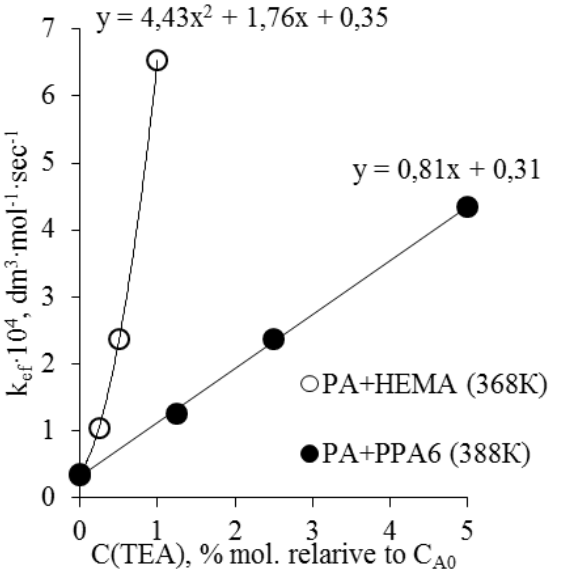



**Fig. 10**. Effective rate constants for HEMA and PPA6 catalytic acylation by PA depending on TEA concentration

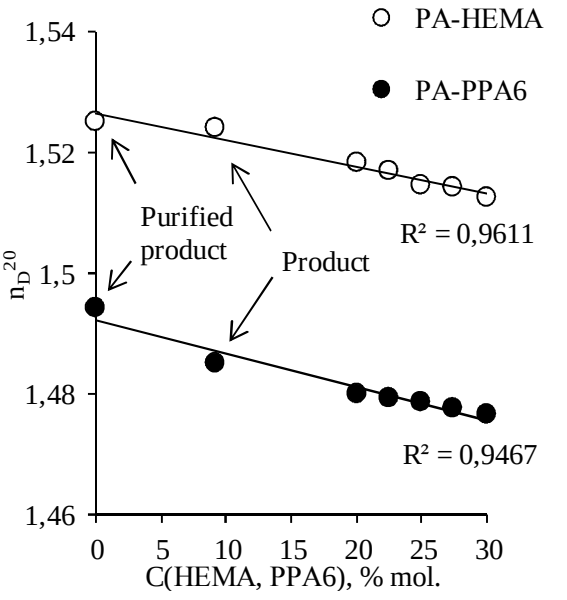



**Fig. 11.** Dependence of refractive index of PA-HEMA/PA-PPA6 on HEMA/PPA6 excess, respectively

*Table 3*

**Physico-chemical characteristics of PA-HEMA and PA-PPA6 before and after purification**

| Reaction | | *MM*, g·mol$^{-1}$ | $\rho$, g·cm$^{-3}$ | $n_D^{20}$ | $M_{R(exp)}$ | $M_{R(theor)}$ |
|---|---|---|---|---|---|---|
| PA+HEMA | Before purification | 260 | 1.2281 | 1.5240 | 64.78 | - |
| | After purification | 280 | 1.2280 | 1.5252 | **69.90** | **69.46** |
| PA+PPA6 | Before purification | 550 | 1.1073 | 1.4850 | 142.4 | - |
| | After purification | 570 | 1.1150 | 1.4942 | **148.9** | **147.6** |

## 3.2. Effect of TEA on the Acylation Rate

The kinetic anamorphoses of HEMA and PPA6 bulk acylation by PA are represented in Figs. 8 and 9 at optimal temperatures and different TEA concentrations.

On the basis of data from Fig. 8 and 9 we determined the dependence of the effective rate constant for HEMA and PPA6 catalytic acylation on TEA concentration (Fig. 10).

The dependence of effective rate constant for HEMA and PPA6 acylation on TEA concentration at 368 and 388 K is described by second and first order polynomials, respectively (Fig. 10). The efficiency of TEA as the catalyst is higher for HEMA acylation than that for PPA6. This fact is confirmed by quadratic dependence of the effective rate constant on TEA content for HEMA acylation and practically linear dependence – for PPA6. PA conversion of 100 % may be achieved for HEMA for 1 h and for PPA6 – for 4 h at optimum temperature and TEA maximum concentration of 1 and 5 mol %, respectively.

## 3.3. Physico-Chemical Characteristics of the Reaction Mixture and Purified Products

Fig. 11 represents the values of refractive index for PA-HEMA and PA-PPA6 products depending on HEMA or PPA6 excess.

The dependence of refractive index on HPAMA content ill 30 mol % is practically linear. It confirms the efficiency of the proposed purification method. The obtained dependencies may be used for the simple determination of residual alcohol in the final product. On the basis of physico-chemical characteristics of the obtained products before and after purification we calculate the value of molar refraction $M_{R(exp)}$ (Table 3). Theoretical values of molar refraction $M_{R(theor)}$ for PA-HEMA and PA-PPA6 were calculated using ACD Lab program [16] *via* increments method. After purification of the obtained products $M_{R(exp)} \approx M_{R(theor)}$, that means correspondence of the synthesized monomers to their structure.

## 3.4. IR-Spectral Characteristics

IR-spectroscopic investigations were carried out to confirm the structure of the synthesized products. The spectra of initial HEMA and PPA6 were recorded for the comparison.

While comparing HEMA and PA-HEMA spectra (Fig. 12) one can see that the absorption band typical of vibrations of OH-group in HEMA alcohol molecule disappears in PA-HEMA molecule. The absence of characteristic absorption band of hydroxy group at 3224 $cm^{-1}$ in PA-HEMA spectrum confirms this fact. The appearance of aromatic carboxy group is confirmed by the presence of wide absorption band within 3200–2580 $cm^{-1}$ (νOH), as well as at 896, 890 (δOH) and 1320 $cm^{-1}$ (δOH + νC–O). The formation of phthalic acid ester is confirmed by the shift of absorption band typical of

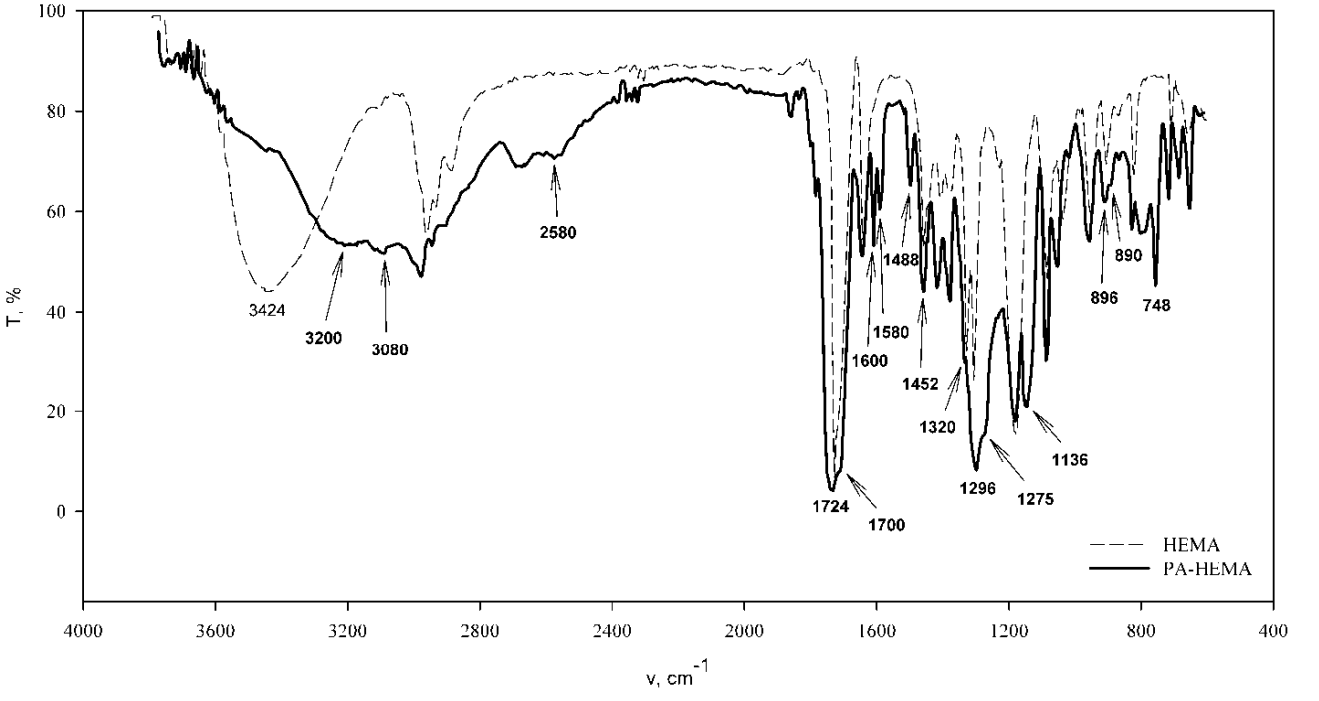



**Fig. 12.** IR-spectra of HEMA and PA-HEMA

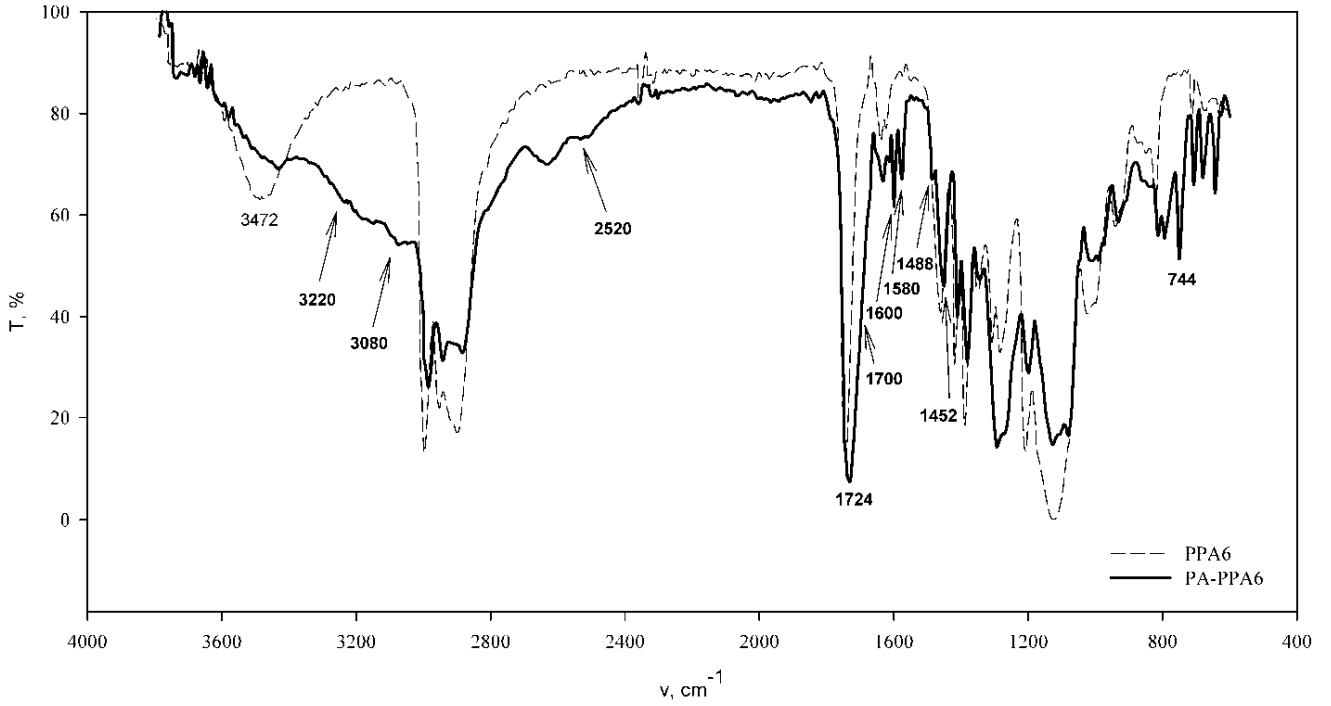



**Fig. 13.** IR-spectra of PPA6 and PA-PPA6

carbonyl vibrations towards 1724 $cm^{-1}$ and absorption bands at 1136 (νC–O), 1274 and 1296 $cm^{-1}$. The obtained aromatic acid has the form of dimer that is confirmed by absorption band at 1700 $cm^{-1}$. The presence of benzene ring in the structure of PA-HEMA is confirmed by absorption bands typical of benzene ring at 1452, 1488 and 1580 $cm^{-1}$ and band at 3080 $cm^{-1}$ (νC–H). The characteristic absorption bands at 1580 and 1600 $cm^{-1}$ confirm the conjugation of benzene ring with carbonyl; band at 748 $cm^{-1}$ indicates 1,2-substitution of the benzene ring.

While comparing PPA6 and PA-PPA6 spectra (Fig. 13) we observe the disappearance of PPA6 secondary OH-group in the molecule of PA-PPA6. It is confirmed by the absence of absorption band typical of hydroxy groups at 3472 $cm^{-1}$ in PA-PPA6 spectrum. The appearance of aromatic carboxy group is confirmed by absorption band within 3220–2520 $cm^{-1}$ (νOH) and appearance as a shoulder of absorption band at 1700 $cm^{-1}$. The formation of phthalic acid ester is confirmed by intensification of absorption band at 1724 $cm^{-1}$ (νC=O). The presence of benzene ring in the structure of PA-PPA6 molecule is confirmed by absorption bands typical of benzene ring vibrations at 1452, 1488 and 1580 $cm^{-1}$ and band at 3080 $cm^{-1}$ (νC–H). The characteristic absorption bands at 1580 and 1600 $cm^{-1}$ indicate the conjugation of benzene ring with carbonyl; band at 744 $cm^{-1}$ – 1,2-substitution of the benzene ring.

Thus, the results of IR-investigations completely confirm the structure of the synthesized compounds.

## 4. Conclusions

The optimum conditions for the synthesis of new acrylic monomers with distant carboxy group were determined during the reaction proceeding without solvent on the basis of kinetic parameters and in accordance with the scheme of irreversible reaction of the second order.

Using TEA as a catalyst allows to decrease the HEMA acylation temperature to 368 K and remove the induction period of the process for PPA6.

The determined optimum conditions for the synthesis of PA-HEMA and PA-PPA6 carboxy-containing monomers, respectively, are: temperature 368 and 388 K; process time 1 and 4 h; TEA concentration 1 and 5 mol % relative to PA initial concentrations.

The structure of the synthesized products was confirmed by refractometric and IR-spectroscopic investigations.

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## КІНЕТИЧНІ ЗАКОНОМІРНОСТІ РЕАКЦІЇ АЦИЛЮВАННЯ ГІДРОКСИ(ПОЛІ)АЛКІЛЕНОКСИ-(МЕТ)АКРИЛАТІВ ФТАЛЕВИМ АНГІДРИДОМ

***Анотація.*** *Досліджено кінетику некаталітичних та каталітичних процесів ацилювання в масі 2-гідроксиетилметакрилату (НЕМА) і гідроксигекса-оксипропілакрилату (РРА6) фталевим ангідридом (ФА). Вперше синтезовано продукт взаємодії ФА та РРА6. Підтверджено структуру синтезованих сполук методами ІЧ-спектроскопії та молярної рефракції.*

***Ключові слова:*** *акриловий мономер, полікарбоксилат, фталевий ангідрид, НЕМА, РРА6.*