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PECULIARITIES OF PEROXIDE-CONTAINING REACTIVE COPOLYMERS SYNTHESIS

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Abstract. This work deals with the study of radical copolymerization of higher esters of (meth)acrylic acid with peroxide monomer, 5-*tert*-butylperoxy-5-methyl-2-hexene-3-yne showing the properties of a weak inhibitor. Due to the mentioned and other features of investigated process, the composition of obtained copolymer cannot be adequately described with known Mayo-Lewis and Scaits equations. The analysis of kinetic data has allowed to propose differential equation of copolymer composition for investigated systems. A technique of quasi-stationary concentrations was not used during its derivation. The obtained equation includes a rate constant of chain break to the monomer and allows to predict the composition of peroxide-containing copolymer adequately. It should be taken into consideration that the derived equation can be also applied for other polymeric systems where chain break significantly affects the reagent, especially during the formation of copolymers with low polymerization degree and in the absence of noticeable quadratic break of macroradicals in the system.

Keywords: copolymerization, kinetics, peroxide copolymer, higher (meth)acrylates, differential composition.

1. Introduction

The composition of binary copolymers can be estimated using the Mayo-Lewis equation (differential composition) and Scaits equation (integral one) [1-5]. The rather large data bank of experimentally determined binary copolymerization constants exists. The developed algorithms of the Mayo-Lewis and Scaits equations used for copolymer composition prediction and determination of copolymerization constants are presented in literature as well. This allows to widely use copolymerization constants despite the frequent deviations between calculated and experimental data. In the majority of cases, such deviations can be explained by the following factors: by the effect of penultimate unit of a propagating polymer chain [6]; by steric factors in those cases when monomers have bulky substituents; or by the considerable difference in monomers polarity [3, 7-10].

Studying a copolymerization of 5-*tert*-butylperoxy-5-methyl-2-hexene-3-yne peroxide monomer (VEP) with higher (meth)acrylates, a divergence of experimental composition from the calculated one using the Mayo-Lewis equation is observed. Such divergence can not be explained by above-mentioned factors. A set of curves demonstrating the divergence character is represented in Fig. 1. The constants of binary copolymerization are determined according to the technique described in literature [11] using starting segments of experimental curves for the calculations using the Mayo-Lewis method. Just these constants are used for the calculated curves shown as dotted in Fig. 1.

The pattern of divergence develops with VEP conversion which is always used in less amount than that of the second comonomer. Fig. 1a shows cymbatic experimental and calculated composition changes but in all cases the observed change is significantly less than the calculated one. In some cases (curves 1, 2) experimentally determined copolymer composition can be considered as the constant that cannot be described adequately by the Mayo-Lewis theory (apart from the case of alternating copolymers). Finally, within the Mayo-Lewis theory, the dependence at which insufficient content of monomer units increases with its conversion (Fig. 1b), cannot be obtained at all.

The purpose of this work is ester radical copolymerization study and influence of comonomers

structure peculiarities on the macromolecules of peroxide-containing copolymer structure and copolymerization mechanism.
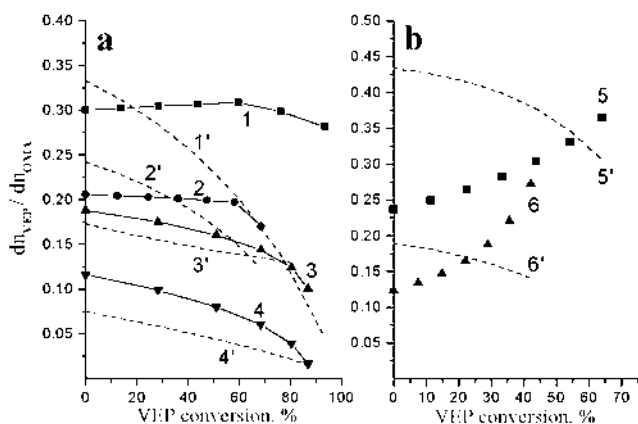

Fig. 1. Dependence of differential content of VEP-units (mole part) upon a VEP conversion at its copolymerization with octyl methacrylate (OMA) in cyclohexanone and initiation with azobisisobutyronitrile (AIBN): experimental data (1–6); data calculated using the Mayo-Lewis equation (1'–6'). $T = 343$ K; $[AIBN]_0 = 0.0142$ mol/dm^3. Examples are separated for cymbate (a) and antibate (b) changes of experimental and calculated values. Initial concentration of comonomers $[VEP]_0$ and $[OMA]_0$, respectively, mol/dm^3: 0.3 and 2.0 (1); 0.26 and 2.0 (2); 0.16 and 2.0 (3); 0.06 and 2.0 (4); 0.16 and 0.8 (5); 0.16 and 1.6 (6)

2. Experimental

2.1. Materials and Methods

2-tert-Butylperoxy-2-methylhexene-5-yne-3 (VEP) was synthesized using the known procedure [12]. 3.27 g of 2-hydroxy-2-methylhexene-5-yne-3 Nazarov's alcohol (NA) and 2.94 g of tert-butylhydroperoxide (tBHP) (Aldrich) were loaded into a three-neck reactor equipped with a stirrer. The reactor was cooled to 278 K. Then 3.78 g of H_3PO_4 was slowly added using drop funnel. At the same time the reactor temperature was held not higher than 298 K. NA : tBHP : H_3PO_4 molar ratio was 1 : 1.1 : 1.3. After H_3PO_4 addition synthesis was carried out at 298 K for 5 h under constant stirring. Then the reaction mixture was carried to the separating funnel and washed with twice-distilled water till pH values became neutral. After additional washing with 10% solution of Na_2CO_3 and again with water the mix was dried over $MgSO_4$. Before using VEP was distilled under vacuum at vapor temperature of 291–298 K. After its purification VEP had the following characteristics: active

oxygen content 8.7 % (theoretical value 8.75 %); d_{20} 0.867 g/cm^3 (ref. 0.867 g/cm^3); $n^d_{20} = 1.4482$ (ref. 1.4482).

Esters of (meth)acrylic acid: butyl acrylate (BA) (Aldrich) 99 %; hexyl acrylate (HAT) (Aldrich) 97 %; octyl methacrylate (OMA) 96 % synthesized using a known technique [13, 14]; lauryl methacrylate (LAMA) (Fluka) 97 % and 2-ethylhexyl acrylate (EHA) (Fluka) 99 % were purified by washing with 10 wt % Na_2CO_3 solution first, then by washing with water and drying over $MgSO_4$. After vacuum distillation, the characteristics of these substances coincided with reference values.

N,N'-azo-isobutyronitrile (AIBN) (Fluka) 98 % was used as received.

Solvents were of "chemical purity" grade. Additionally, solvents were purified using the standard techniques.

VEP copolymerization with higher esters of (meth)acrylic acid was carried out in solutions of propanone, cyclohexanone, ethyl acetate and heptane using AIBN as an initiator. VEP concentrations were 0.10–0.42 mol/dm^3, (meth)acrylic acid esters – 0.5–2.8 mol/dm^3, AIBN – 0.01–0.02 mol/dm^3. Reaction mixtures were prepared from preliminary made solutions of VEP, of the corresponding (meth)acrylic acid ester and AIBN. Syntheses were carried out at 343 K in sealed ampoules (in propanone, heptane, ethyl acetate) or in the reactor (in cyclohexanone). The timed sampling was performed for obtaining kinetic data. This technique results in the formation of linear copolymers since initiation by VEP peroxide group may be neglected at 343 K.

Reagent consumption was controlled using a chromatography analysis of the samples. (Meth)acrylic acid esters were analyzed by means of a gas-liquid chromatograph Selmichrom-1 (Selmi, Ukraine). Chromatographic analysis of VEP was performed by means of liquid chromatograph (Laboratorni Pristroje, Czechoslovakia, with UV VIS Detector LCD 2563).

Viscosity averaged molecular weight (M_n) of copolymers was measured after determination of the constants for the Mark-Houwink equation [15] *via* fractionating of copolymer samples and determination of fraction molecular weights by gel permeating chromatography using a HP 5890 CasChromat equipped with HP 7694 detector (Hewlett Packard, Japan). Prepared copolymers had low molecular weights and appear as viscous-flow liquids under ambient conditions. Depending on synthesis conditions, M_n (g/mol) of VEP copolymers were: 6000–12000 with BA; 5000–9000 with HAT; 5000–8000 with OMA; 7000–12000 with LAMA and 6000–10000 with EHA. All these copolymers had

good solubility in aliphatic and aromatic solvents and limited one in acetone and ethyl acetate. They may be precipitated from the solutions by methanol and ethanol.

3. Results and Discussion

3.1. Theoretical Grounds

The radical copolymerization of peroxide monomers has been widely studied [16-18, 20, 23]. Peroxide monomers can be copolymerized with vinyl and diene monomers without any additional radical initiators because of the peroxide groups decomposition.

The new class of reactive polymers, called functional polyperoxides (FPP), is based on the peroxide monomers. They have been recently designed and employed for synthesis and modification of polymer composites. Along peroxide-containing fragments, there are hydroxyl, carboxyl, anhydride, or alkyl ($-C_6H_{13}$ to $-C_{15}H_{31}$) fragments that provide functional groups to the FPP structure. The ability of the functional groups to form chemical and/or physical bonds, combined with the homolytic decomposition of peroxide groups at elevated temperatures, makes FPP a unique experimental system for development of polymer composites, both *ex situ* and *in situ* [16-20, 22, 24-29].
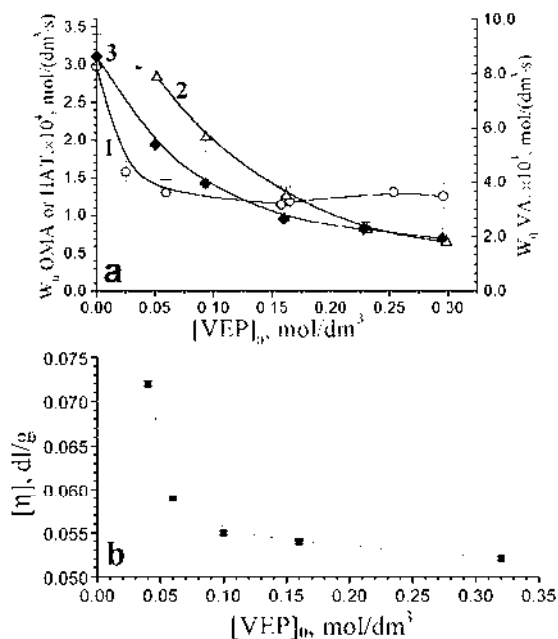
Studies of VEP copolymerization with a series of comonomers reported in [16-20] had shown that the reaction proceeds in a weakly inhibited mode. VEP molecules play a role of weak inhibitor: kinetic and material chains are terminated by an elementary reaction of chain transfer to VEP molecule. This fact, in the case of VEP copolymerization with higher esters of (meth)acrylic series, demonstrates the dependence shown in Fig. 2.

1. Initiation:

2. Chain propagation
($R_3 = C\equiv C-C(CH_3)_2-OO-C(CH_3)_3$):

3. Break of material and kinetic chains *via* chain transfer to the monomer with the formation of low active radical (LR):

Fig. 2. Initial consumption rate (W_0) of higher (meth)acrylate (a) and VEP-OMA copolymer characteristic viscosity (b) *vs*. VEP initial concentration. [VEP]$_0$: OMA (1); HAT (2) and BA (3)
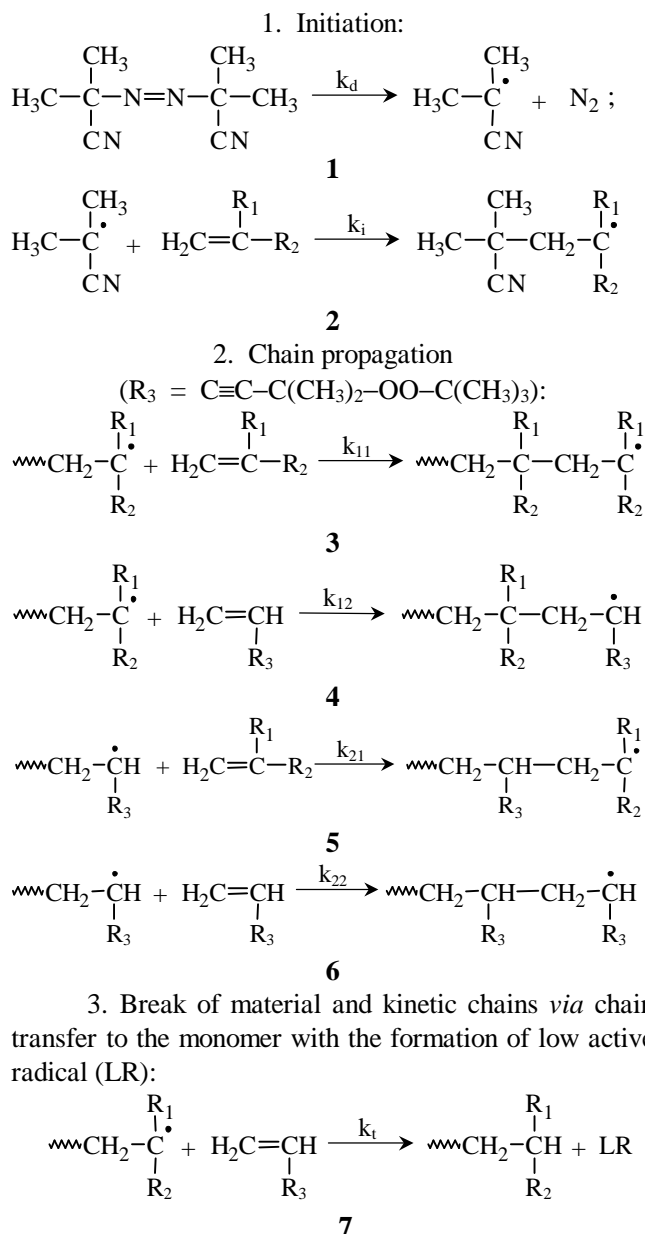
Scheme 1. Reactions taking place during the synthesis of copolymers of VEP with higher esters of (meth)acrylic series (R_1 = H, CH_3; R_2 = $C(O)OC_nH_m$; C_nH_m = butyl, hexyl, octyl, lauryl, 2-ethylhexyl)

One can observe from Fig. 2 the decrease of both polymerization rate and copolymer molecular weight with an increase of VEP initial concentration in polymerizate. This fact and the number of additional studies results (determination of the first kinetic order of the reaction by initiator and acrylate comonomer, C^{13} NMR and PMR studies) have also allowed to confirm that VEP copolymerization with higher esters of (meth)acrylic series proceeds in the weakly inhibited mode. The latter allows to propose the process scheme (see Scheme 1).

The proposed polymerization scheme differs from the classic [1, 3, 5, 7, 10, 30] one only by the part that describes the break of material and kinetic chain: there is no quadratic break (it is confirmed by the first kinetic order by initiator) and there is a chain break mainly over VEP molecules.

3.2. Equations of Copolymer Differential Composition

The data presented above allow to derive an equation of differential composition of copolymer for those cases, when the chain breaks *via* monomer molecules.

The absence of quadratic break allows to form the following differential equations:

• differential equation for the rate of macroradical total concentration change:

$$\frac{d[R]}{dt} = W_{in} - k_t \cdot [R] \cdot [V] \tag{8}$$

• differential equation for the rate of the concentration change of radicals with peroxide end fragment:

$$\frac{d[R_V]}{dt} = k_{12} \cdot [R_A] \cdot [V] - k_{21} \cdot [R_V] \cdot [A] \tag{9}$$

• differential equation for peroxide comonomer consumption:

$$\frac{d[V]}{dt} = -k_{12} \cdot [R_A] \cdot [V] - k_{22} \cdot [R_V] \cdot [V] - k_t \cdot [R] \cdot [V] \tag{10}$$

written on the basis of Scheme 1 with the following designations: W_{in} – initiation rate, mol/(dm^3·s); $[R]$ – total macroradical concentration; $[R_V]$ – concentration of macroradicals with end VEP-units; $[R_A] = [R]–[R_V]$ – concentration of macroradicals with end acrylate unit; $[A]$ – concentration of (meth)acrylic comonomer; $[V]_0$, $[V]$ – initial and current VEP concentration, respectively;

• and, using the equation of the part of radicals with end monomer V unit:

$$ch = \frac{[R_V]}{[R]} = \frac{d[R_V]/dt}{d[R]/dt} - \tag{11}$$

allows to derive the following differential equations of monomer consumption in elementary reactions leading to the propagation of material chain:

• equation of acrylate comonomer consumption:

$$\frac{d[A]}{dt} = -k_{11} \cdot (1-ch) \cdot [R] \cdot [A] - k_{21} \cdot ch \cdot [R] \cdot [A] \tag{12}$$

• equation of peroxide comonomer consumption which does not account its consumption for the chain break, because VEP molecule residue is not incorporated into a copolymer at chain break:

$$\frac{d[V]^P}{dt} = -(k_{12} \cdot (1-ch) \cdot [R] + k_{22} \cdot ch \cdot [R]) \cdot [V] \tag{13}$$

The equations derived allow to develop an expression describing the differential composition of the copolymer:

$$dm = \frac{d[V]^P}{d[A]} = \frac{d[V]^P/dt}{d[A]/dt} =$$

$$= \frac{k_{12} \cdot ((k_{22} - k_t) \cdot [V] + k_{21} \cdot [A]) \cdot [V]}{((k_{21} \cdot k_{12} - k_{11} \cdot k_t) \cdot [V] + k_{11} \cdot k_{21} \cdot [A]) \cdot [A]} \tag{14}$$

The latter equation is of interest introducing the designations: $[V]/[A] = M$; $k_{11}/k_{12} = r_1$; $k_{22}/k_{21} = r_2$, – and rewriting the Eq. (14) in the next form:

$$dm = \frac{M \cdot r_2 + 1 - k_t/k_{21} \cdot M}{r_1/M + 1 - k_t/k_{21} \cdot r_1} \tag{15}$$

The obtained equation is an equation of instant (differential) composition of the copolymer accounting the effect of chain transfer to peroxide comonomer.

If polymerization (or copolymerization) proceeds with the formation of polymer molecules with high polymerization degree, it means that chain propagation constant is much higher than the chain break constant. In our case this may become true if $k_{21} \gg k_t$. Then, $k_t/k_{21} \to 0$, and summands $k_t/k_{21} \cdot M$ and $k_t/k_{21} \cdot r_1$ become insignificant resulting in the transformation of the Eq. (15) to the Mayo-Lewis equation:

$$dm = \frac{M \cdot r_2 + 1}{r_1/M + 1} \tag{16}$$

The same transformation takes place if there is no chain transfer reaction to the one of comonomers in the system. In this case, k_t equals to zero, and the Eq. (15) transforms into (16) without additional limitations.

The investigated copolymerization cannot be attributed to those processes leading to the formation of copolymers with high polymerization degree. At VEP content of 15–20 mol % in the copolymer an average polymerization degree changes within 16–40 range depending upon a comonomer nature. It should be noted that maximum divergence of obtained copolymer differential composition from the calculated one is observed at maximum ratio of VEP to (meth)acrylate concentration within the studied concentrations. Under such conditions the copolymer samples with the highest content of peroxide group but with the least molecular

weight are obtained. This verifies that chain transfer has an indirect effect on copolymer composition.

For determination of the constant values from the Eq. (15), a minimization of the square sum of divergence between experimental values and those calculated by this equation has been performed. The means of Excel 97 for the implementation of non-linear least-squares method has been applied. Fig. 3 represents the most typical cases of the optimized curves (curves 1) in comparison both with the experimental points and curves calculated using the Mayo-Lewis equation (16) (curves 2).
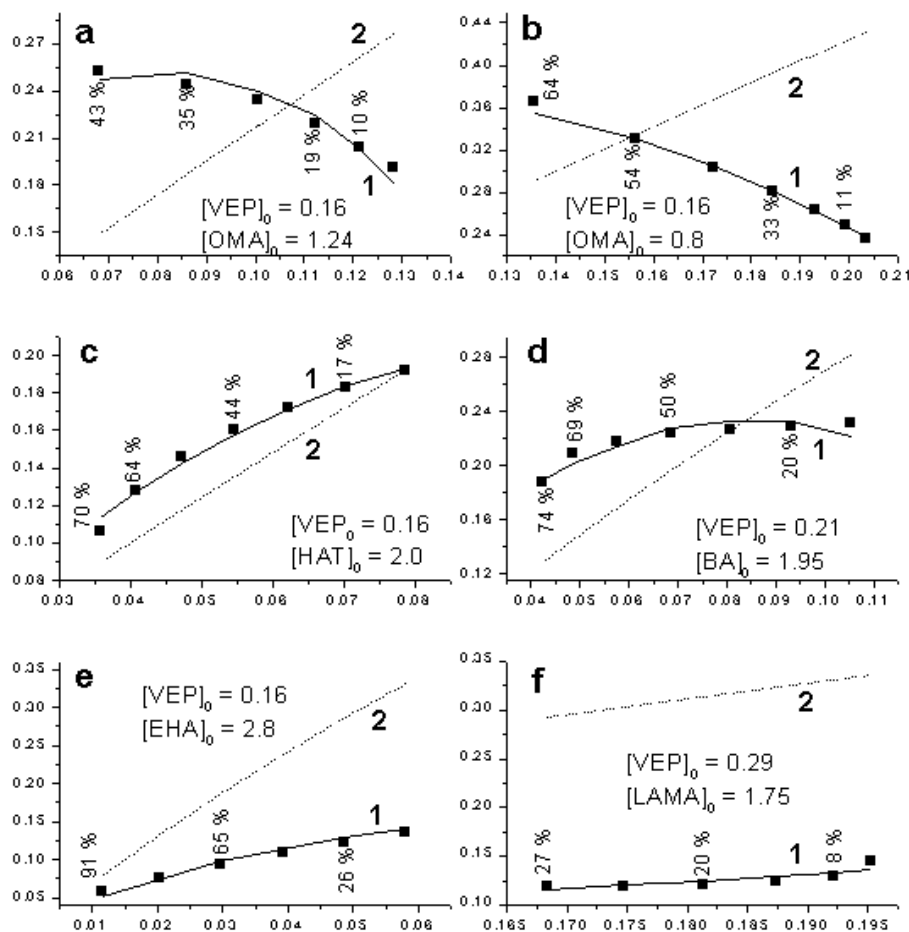

Fig. 3. Dependence of VEP-unit content in copolymers with higher esters of (meth)acrylic series (axes of ordinates) upon a ratio between comonomer concentrations [*V*]/[*A*] (axis of abscissae). Points at figures correspond to the experimental values: Eq. (15) simulation (1) and the Mayo-Lewis equation simulation (2). The values next to points correspond to the VEP conversion. Synthesis conditions: $T = 343$ K; $[AIBN]_0 = 0.0142$ mol/dm^3; cyclohexanone. Examples are given for VEP copolymerization with OMA (a, b), HAT (c), BA (d), EHA (e) and LAMA (f)

One can conclude from this figure that the prediction of copolymer composition is more exact using the Eq. (15) compared with the Mayo-Lewis equation.

Fig. 4 represents the dependence of k_t/k_{21} parameter, obtained as a result of optimization performance upon the ratio of comonomer initial concentrations $[A]_0/[V]_0$.

One can see from the figure that parameter k_t/k_{21} linearly depends upon a ratio of comonomer concent-rations. Correlated nature of the parameter is connected with a more complicated process of chain break than it was shown by the reaction scheme (7), and which is not studied enough. In this connection, it is advisable to introduce the following equation:

$$k_t / k_{21} = F \cdot \frac{1}{M} \qquad (17)$$

As a result, the Eq. (15) can be rewritten as follows:

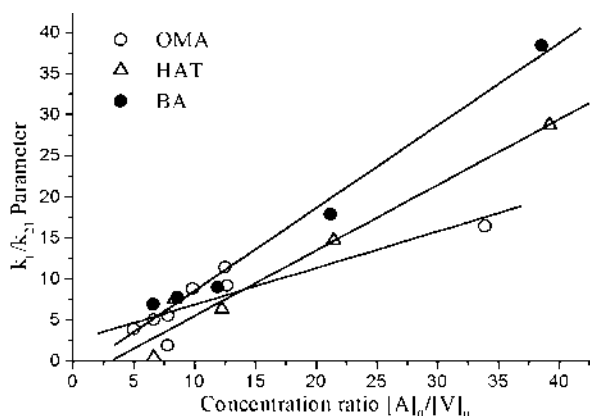$$dm = \frac{M \cdot r_2 - F + 1}{r_1 / M \cdot (1 - F) + 1} \qquad (18)$$

Fig. 4. Dependence of optimized k_t/k_{21} parameter upon a ratio of comonomer initial concentrations $[A]_0/[B]_0$

The values of the parameters from the latter equation obtained as a result of experimental data optimization are listed in Table 1.

Table 1

Numeric values of the Eq. (18) parameters

Comonomer	r_1	r_2	F
Octyl methacrylate	0.19±0.05	0.5±0.1	0.7±0.1
Hexyl acrylate	0.33±0.08	1.36±0.3	0.62±0.1
Butyl acrylate	0.26±0.04	1.1±0.4	0.85±0.1
2-Ethylhexyl acrylate	0.52±0.09	3.4±0.4	1.2±0.2
Lauryl methacrylate	0.85±0.12	3.7±0.6	1.4±0.3

These parameters should be considered as integral copolymerization coefficients since they describe the composition of the synthesized copolymers till 50–80 % of VEP conversion that corresponds to 35–60 % of total conversion.

4. Conclusions

Copolymerization of peroxide monomer VEP with higher esters of (meth)acrylic series due to the peculiarities of its mechanism has an interesting property – constant copolymer composition within rather wide limits of comonomer initial concentration. In the theoretical aspect, the study of such type of copolymerization demonstrates that under certain conditions the copolymer composition may depend not only upon a relative reactivity of comonomers and concentrations but also upon other elementary reactions, in particular, upon the type and rate of chain break. Radical copolymerization of higher (met)acryl acid esters with peroxide monomer 5-*tert*-butylperoxy-5-methyl-5-hexene-3-yne (VEP) was studied.

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ОСОБЛИВОСТІ СИНТЕЗУ ПЕРОКСИДОВМІСНИХ РЕАКЦІЙНОЗДАТНИХ КОПОЛІМЕРІВ

Анотація: *В роботі представлено дослідження радикальної кополімеризації вищих естерів (мет)акрилової кислоти з пероксидним мономером, 2-трет-бутилперокси-2-метил-5-гексен-3-іном, який проявляє властивості слабого інгібітора. Показано, що склад отримуваного кополімеру не може бути адекватно описаний за допомогою відомих рівнянь Майо-Льюіса та Скейтса. Аналіз кінетичних даних дав можливість побудувати математичну модель кополімеризації та запропонувати диференціальне рівняння складу кополімеру для всіх досліджуваних систем, при виведенні якого не використовується метод квазістаціонарних концентрацій. Отримане рівняння включає константу швидкості обривання ланцюга на мономер та дає можливість адекватно прогнозувати склад пероксидовмісного кополімеру. Отримане рівняння може бути застосоване і для інших полімеризаційних систем, в яких вплив обривання ланцюга на реагент є суттєвим, особливо при утворенні кополімерів з низьким ступенем полімеризації та за відсутності у системі помітного квадратичного обривання макрорадикалів.*

Ключові слова: *кополімеризація; кінетика; пероксидний кополімер; вищі (мет)акрилати; диференційний склад.*