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Single-stage processes of polymer products photochemical synthesis with optical accuracy

V.M. Treushnikov [a,*], S.A. Chesnokov [b]

[a] *"Reper-NN" Enterprise, 37/23, Gagarin Ave., 603009 Nizhny Novgorod, Russia*
[b] *G.A. Razuvaev-Institute of Organometallic Chemistry, Russian Acad. Sci., 49, Tropinin Street, GSP-445, 603600 Nizhny Novgorod, Russia*

Abstract

The basic conditions necessary for realization of single-stage processes of synthesis of polymeric products with optical accuracy are considered in this work. It is shown, that this problem can be solved with a method, which is designated as a method of frontal photopolymerization. The essence of this method will consist in maintenance of process of polymerization as a running wave.

For fabrication of products with optical accuracy it is necessary, that polymerization passed actually only in infinitely thin layer on a polymer–monomer boundary.

The basic requirements to devices of exposure and to compositions for photopolymerization are considered in this work. It is shown, that only compositions, in which process of radical polymerization passes without breaking, are suitable for these purposes. Such process can be realized at imposing of certain restrictions on molecular movements of reagents, first of all, on their rotary movement.

Keywords: Level-by-level photopolymerization; Photochemical synthesis; Optical accuracy

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1. Introduction

Two schemes of polymer products formation are possible: two-staged and single-stage. The two-staged scheme is traditional—first a polymer (material) is synthesized and then a product is made from it by various ways (a thermo-pressing, moulding under the pressure, mechanical machining, etc.). A single-stage scheme assumes, that both a polymer and a product from it are formed simultaneously during a single stage. Therefore one can say rather about a synthesis of polymer products with given properties, including shapes and sizes of the product and physical–chemical characteristics of an obtained material, than about of a synthesis of a polymer as an initial raw material for its further transformation into a product.

There are two basic reasons to leave two-staged schemes of polymer products formation and to proceed to the single-stage ones.

The first reason is decreasing of energy and raw material expense in polymer products manufacture. As a rule, energy expense, connected with transformation of a polymer into a product, significantly exceeds one of polymer synthesis. In many cases, in particular, when products are made from blocks of a polymer by mechanical processing, the most part of material is loosed as a wastage (shaving).

The second reason is a quality of products, made from polymers. Firs of all it must be noted, that practically in all kinds of processing of polymer into a product there are such undesirable phenomena, as a partial destruction of the polymer, which leads to an occurrence of free radicals in it. These radicals initiate a thermo-oxidizing destruction of a polymer as a chain reaction with degenerated branching and also causes a formation of various defects (stresses, dislocations, cavities, molecular packing density fluctuations, etc.), which are able to concentrate on themselves any external influences (mechanical, chemical, etc.) and to promote by such a manner theirs increasing, which leads to a product destruction finally. The rather paradoxical situation arises—somebody spends grate efforts to get high quality polymer, and others spoil it during processing into a product. Very many polymers do not find an application namely because of

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* Corresponding author.
E-mail addresses: director@reper.ru (V.M. Treushnikov), sch@iomc.ras.ru (S.A. Chesnokov).

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absence of comprehensible way of their processing into products.

A task statement about creation of single-stage processes of polymer products formation is not new. This task was formulated definitely enough in the last quarter of the last century [1–3]. However, all attempts to solve this problem were not successful, especially in a field of getting polymer products with optical accuracy. There are two basic reasons, which explain negative results of these investigations. They are processes of a thermal emission and a contraction of a reaction medium (emission of a free volume), those take place during polymerization of practically all known monomers. The statement is even known, that creation of single-stage processes is impossible until non-contractive monomers will be created (synthesized).

The aim of this paper is to show, that single-stage processes of polymer products synthesis with optical accuracy can be realized and without of non-contractive monomers use. It is necessary for this to provide conditions, in which processes of heat-away and of extraction of a free volume from reaction zone occur much faster, than a polymerization reaction itself.

2. Methods

What is an essence of a problem? First of all it is necessary to note, that during polymerization not only polymer formation occurs

$$n \cdot M \xrightarrow{\text{polymerization}} M_n,$$

but simultaneously formation of a heat and a free volume take place:

$$n \cdot M \xrightarrow{\text{polymerization}} M_n + \text{“heat”} + \text{“free volume”},$$

where M is a monomer, M_n the polymer, n is the number of monomer molecules, formatting polymer molecule (a polymerization chain length).

A free volume one can interpret as quasi-particles of zero mass density, which can then cooperate with each other and form various kinds of defects in a polymer. Principally important is follows—an output of such quasi-particles from the volume can take place only through the surface, surrounding the reaction medium. This leads to decreasing of a volume of a polymer and to distortion of all the surfaces of a formed polymer product. Natural consequence of eduction of heat is the increase in temperature of the reaction medium. The last cannot be supposed for two reasons. First, the increase in temperature results in change of constants of velocities of the elementary reactions determining the mechanism of reaction of polymerization. Consequence of this can be increase in dispersiveness of various characteristics of obtained polymer (molecular mass, structure in case of copolymers, microtactfulness, etc.), that inevitably in itself is the reason of deterioration of optical properties of a material. Second, the increase in temperature results in volume expansion of formed products, that, naturally, is accompanied by change of their sizes.

From the aforesaid one conclusion follows only: formation of products with optical accuracy under the single-phase scheme is possible only in case of the organization of such processes in which the increase in temperature is excluded during polymerization (reaction of polymerization should take place in isothermal conditions) and the full output of free volume from polymer is provided.

Both distribution of temperature, and free volume in the reaction medium can be as a first approximation described by the equations of heat conductivity and the diffusion, having the same structure. In this connection, characteristic times of a relaxation of these processes (times of an setting of balance) depend on the linear sizes of formed products in the second power ($t_{\text{rel}} \sim L^2$, where L is a radius or diameter of the cylinder in case of cylinder formation, for example). Factors of proportionality depend both on the form of formed products, and from factors of heat conductivity of the reaction medium and diffusion of quasi-particles of free volume in these medium.

Square-law dependence of times of a relaxation of these processes on the linear sizes of formed products is the basic obstacle in a way of creation of single-phase processes of their formation. However, it is true only when process of polymerization occurs simultaneously in all points of volume of the reaction medium as it usually occurs at polymerization in flasks, reactors, etc. Such dependence can be excluded, if polymerization carries out as layer-by-layer growth of a product, providing course of reaction of polymerization only on border of separation of phases: liquid monomer–polymer. The essence of this statement is explained with the scheme shown in Fig. 1. This scheme explains also sense of designations used below.

In a quantitative sense for realization of such mechanism of polymerization fulfillment of three basic conditions is necessary:

1. depth of front of reaction of polymerization should be infinitesimal, i.e. $\Delta h \to 0$;
2. velocity of movement of front of reaction of polymerization should be equal to some constant, i.e. $\omega = \text{constant}$;
3. velocity of polymerization should be those that the inequality is satisfied: $t_{\text{pol}} \leq \Delta h/\omega$, where t_{pol} is the minimal time necessary for achievement of a degree of conversion of monomer α_k, which is equal 1 in an ideal case ($\alpha_k \to 1$).

These conditions are dictated by that the free volume had time to leave completely in a liquid phase, and reaction of polymerization in all points of volume of the reaction medium would carry

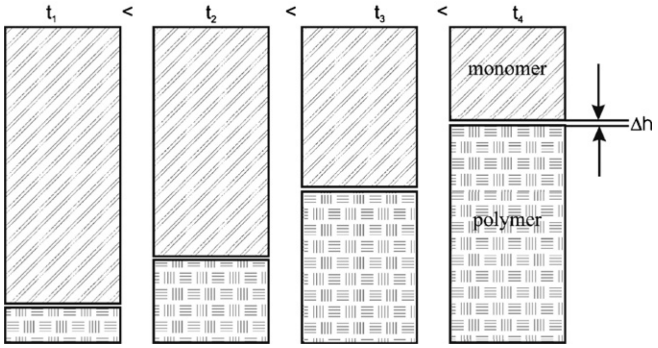

Fig. 1. Scheme of level-by-level polymerization, designations are in the text.

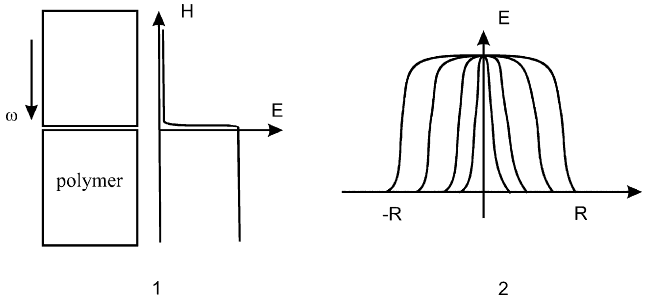

Fig. 2. Two principal schemes of devices for exposure allowing realize the frontal polymerization: (1) horizontal–vertical type; (2) centrifugal type.

out at the same temperature (at $\Delta h \to 0$ times of a relaxation $t_{\rm rel}$ tend also to zero for both these processes). Realization of these conditions in case of usual dark reactions is extremely difficult. But it can be carried out if one proceeds to photopolymerization, i.e. to polymerization initiated by light.

Fig. 2 shows two basic schemes of devices for exposure, allowing to realize two of three listed conditions: $\Delta h \to 0$ and ω = constant.

In case of devices of horizontal–vertical type the horizontal plane which passes through an axis 00′, divides space into two parts: bottom where intensity of light is equal E_0, and top, where $E = 0$. Change of intensity of light from E_0 up to 0 occurs within the range of a zone of thickness Δh shown on a curve of distribution of intensity of light along a vertical. Reducing of size Δh to minimally possible value is achieved with the help of optical system of division of a light beam specially developed for these purposes (achieved level $\Delta h \leq 10\,\mu$m). Clearly, that photopolymerization can take place in a transitive zone and in the bottom, lighted part of space. For this purpose a composition (we shall name it below a photopolymerization composition—PPC) is filling in the special form made from a transparent material for light, and with set constant velocity, ω = constant, is lowering gradually in the bottom zone. It is essentially important to choose a velocity ω such that reaction of polymerization had time to come to the end during passage of a transitive zone by thickness Δh. In this case process of polymerization represents a moving flat wave of length Δh. We have named such way of polymerization by frontal photopolymerization. Strictly speaking, here it is necessary to distinguish two waves: one light wave, generating polymerization, and a flat wave of polymerization generated by light. In an ideal case these two waves should move synchronously, with the same velocity ω.

In case of devices of exposure of centrifugal type (Fig. 2) light first is focused along a vertical axis 00′ (in case of manufacturing of lenses—along an optical axis of a lens), and then radius of a lighted zone is increased with constant velocity ω. Other requirements are the same, as in the previous case. Here both moving waves have the ring form.

3. Theory

What properties should have PPC to satisfy the condition $t_{\rm pol} \leq \Delta h/\omega$? For discussion of this question it is useful to use concept of threshold photosensitivity of PPC, which we shall define as value:

$$S_{\rm th}^{\lambda} = \frac{1}{E_0 \cdot t_{\rm th}}$$

The physical sense of values E_0 and $t_{\rm th}$ is defined above. Taking into account this definition, the basic requirement to PPC it is possible to write in the following view:

$$S_{\rm th}^{\lambda} \cdot E_0 > \frac{\omega}{\Delta h} \tag{1}$$

Theoretical expression for $S_{\rm th}^{\lambda}$ has the following view [4–6]:

$$S_{\rm th}^{\lambda} = -\frac{a_\lambda}{\ln(1-\alpha^*)} \tag{2}$$

where a_λ is a constant of velocity of photochemical reaction of decomposition of the photoinitiator in PPC, equal to multiplication of its molar extinction factor at the wavelength $\lambda(\varepsilon_\lambda)$ on a quantum output of its decomposition (Φ); α^* is the minimal degree of conversion of the photoinitiator in PPC, necessary for achievement of a degree of conversion of monomer in PPC equal $\alpha_k (\alpha_k \to 1)$.

Values α^* and α_k are connected by the following equation [7,8]:

$$\bar{n} \cdot \alpha^* \cdot C_0 \cdot \bar{\nu} = \alpha_k \cdot C_{\rm M} \tag{3}$$

Taking into account the last equation, we find, that:

$$S_{\rm th}^{\lambda} = -\frac{a_\lambda}{\ln(1-(\alpha_k \cdot C_{\rm M})/(\bar{n} \cdot C_0 \cdot \bar{\nu}))} \tag{4}$$

where C_0 and $C_{\rm M}$ are concentrations of the photoinitiator and a monomer in PPC; $\bar{n}$ the average number of the free radicals formed at disintegration of one molecule of the photoinitiator, capable to lead a chain of polymerization; $\bar{\nu}$ is an average length of a chain of polymerization.

Further only those PPC will be interesting for us in which process of polymerization takes place under the radical mechanism. According to the standard theory of radical polymerization, true for a stationary regime of course of reaction, we have:

$$\bar{\nu} = \frac{k_{\rm p} \cdot C_{\rm M}}{\sqrt{a_\lambda \cdot E_0 \cdot C_0 \cdot k_0}} \tag{5}$$

where $k_{\rm p}$ and k_0 are the constants of velocities of reactions of growth and breakage of a chain of polymerization. The relation (5) assumes, that breakage of a chain of polymerization occurs as a result of reactions recombination of macroradicals or their disproportions. Taking into account (5), we find, that:

$$S_{\rm th}^{\lambda} = -\frac{a_\lambda}{\ln(1-(\alpha_k \sqrt{a_\lambda \cdot E_0 \cdot k_0})/(\bar{n} \cdot k_{\rm p} \cdot \sqrt{C_0}))} \tag{6}$$

From expression (6) unequivocally follows, that at

$$E_0 \geq \frac{\bar{n}^2 \cdot k_p^2 \cdot C_0}{a_\lambda \cdot k_0 \cdot \alpha_k^2} = E_{\rm cr} \tag{7}$$

this expression loses physical sense. In the practical sense it means, that at any as much as big times of exposure by light with $E_0 \geq E_{\rm cr}$ the set degree of conversion of monomer α_k in PPC is unattainable. For each type of PPC the relation $E_{\rm cr} \cdot \alpha_k^2 =$

constant should be satisfied. We have confirmed this relation by numerous experiments. It is true for systems in which really reaction of polymerization takes place in a stationary regime. Thus, it is possible to say, that the condition (7) excludes a possibility of creation of single-stage processes of synthesis of polymeric products with optical accuracy. The condition (1) demands, that PPC keep ability to polymerization at $E_0 \to \infty$. Only this condition can provide desirable quality of formed products ($\Delta h \to 0$) at maintenance of high enough velocity of wave movement ω (productivity of process).

However, as it has been marked above, expression (5) is true only for a stationary regime of course of reaction, i.e. when velocity of initiation of the free radicals, capable to lead a chain of polymerization, is equal to velocity of destruction of trailer macroradicals. Whether there can be other regimes of course of reaction of polymerization? One variant can be of interest for single-stage processes of synthesis of polymeric products only: when in (6) and (7) $k_0 \to 0$, i.e. when polymerization takes place without breaking. First we shall prove theoretically, that such mechanism of polymerization can be realized under some certain conditions.

The approach to the description of kinetic of chemical reactions in media with the limited mobility of the reagents, described earlier in Refs. [9–15] is used below. The basic assumption is, that according to representations about cellular effect bimolecular reactions in the condensed media can take place by one of two schemes mentioned below:

$$\text{I.}\quad \mathrm{A}+\mathrm{B} \to [\mathrm{A}\ldots.\mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (\mathrm{AB})*] \xrightarrow{k_2} \text{products}$$

$$\text{II.}\quad \mathrm{A}+\mathrm{B} \to [\mathrm{A}\ldots.\mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (\mathrm{AB})*] \rightsquigarrow \text{products}$$

where reactions in a cell are shown in square brackets. Basic difference of these two schemes is that the output of products from a cell in the first one is designated by a direct arrow, whereas in the second—by wavy one. This means we admit, that at transition from low viscous media to solid ones a qualitative change of character of molecular movements is possible at some values of viscosity. As for the reactions designated by direct arrows, we assume, that density of distribution of probabilities of lifetime of corresponding conditions (intermediate products) are described by indicative functions of type:

$$f(t) = k_i \mathrm{e}^{-k_i t} \tag{8}$$

This statement directly follows from the mass action law, in particular, from the equation for reaction of the first order. Basic importance is that if transformation of any intermediate product in complex reaction does not correspond to function (8) the mass action law impossible to use for the description of such reactions.

In process of change of viscosity of medium character of molecular movements of reagents should change—most likely, it should come closer to type of Brown movement (continual diffusion). For the description of continual diffusion in absence of action of external forces the one-dimensional Focker–Planck equation can be used [9–15]:

$$\frac{\partial f(x,t)}{\partial t} = D\frac{\partial^2 f(x,t)}{\partial x^2} \tag{9}$$

with the following boundary and initial conditions:

$$f(0,t) = f(a,t) = 0; \qquad f(z,0) = 1$$

The density of distribution of probability of reagents lifetime can be found by integration:

$$f(t) = \int_0^a f(x,t)\,\mathrm{d}x \tag{10}$$

Here the following designations are used: D is the factor of diffusion (more exactly, the factor of diffusion of rotary movement of the reagent, correlating with value of reversal time of correlation of rotary movement, for example, the paramagnetic probe determined experimentally by EPR method [16,17]); (0, a) the range within which a movement of a molecule on type Brown movement take place in one-dimensional representation until one of borders will be achieved—transformation of one type of a molecule into another; z the position (coordinate) of a molecule in this range at the moment of time $t=0$. The solution of Eqs. (9) and (10) under the set boundary conditions is function of probability density distribution [18]:

$$f(t) = \frac{2\pi D}{a^2}\sum_{\nu=1}^{\infty}\nu\left\{\sin\frac{\pi z\nu}{a} + \sin\frac{\pi(a-z)\nu}{a}\right\}\mathrm{e}^{-(D\pi^2\nu^2/a^2)t} \tag{11}$$

More simple solution we have at $z/a \to 0$

$$f(t) = \frac{z}{2\sqrt{\pi D t^3}}\exp\left(-\frac{z^2}{4Dt}\right) \tag{12}$$

Functions (11) and (12) essentially differ from (8), that makes use of the mass action law incorrect for the description of such processes.

According to representations about cellular effect the constant of velocity of bimolecular reaction can be defined as

$$k_{\mathrm{eff}} = k_1 \cdot P_{\mathrm{B}}(x) \tag{13}$$

where $P_{\mathrm{B}}(x)$ is the probability of an output of intermediate products from a cell towards the end-products formation.

According to Refs. [9–11], a value of $P_{\mathrm{B}}(x)$ is determined by integral:

$$P_{\mathrm{B}}(x) = \int_0^{\infty} f_a(\eta)\left\{\int_{\eta}^{\infty} f_b(\xi)\,\mathrm{d}\xi\right\}\mathrm{d}\eta \tag{14}$$

where for scheme I

$$f_a(\eta) = k_{-1}\mathrm{e}^{-k_{-1}\eta}; \qquad f_b(\xi) = k_2\mathrm{e}^{-k_2\xi}$$

$$P_{\mathrm{B}}(x) = \frac{k_2}{k_{-1}+k_2} = \frac{x}{1+x}; \quad x = \frac{k_2}{k_{-1}}$$

for the scheme II

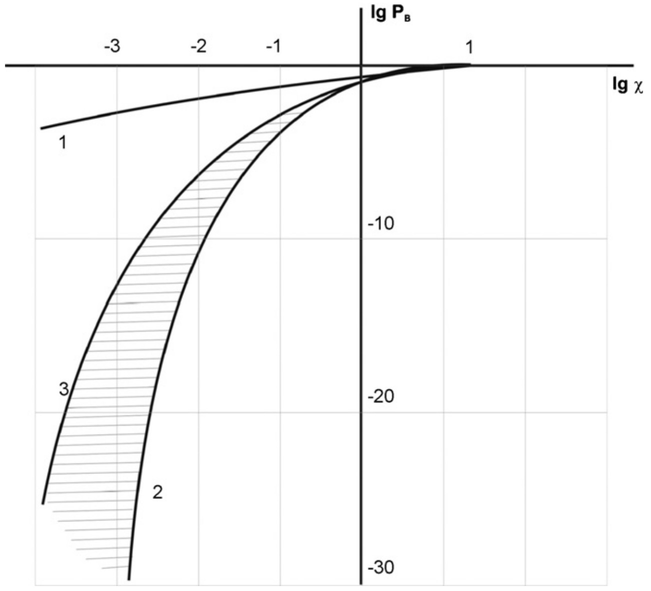

Fig. 3. Results of calculation by means of Eq. (14): (1) $\chi = 4\pi rD/k_2$; (2) $\chi = \pi^2 D/a^2 k_2$; (3) $\chi = 4D/Z^2 k_2$.

$f_a(\eta) = k_{-1}\mathrm{e}^{-k_{-1}\eta}$; $f_b(\xi)$ corresponds either (11) or (12). In case (12), in particular, we have:

$$P_\mathrm{B}(x) = \frac{1}{\sqrt{\pi}}\int_0^\infty t^{-3/2}\mathrm{e}^{-((1/t)+(1/x))}\,\mathrm{d}t; \quad x = \frac{4D}{z^2 k_{-1}}$$

Here everywhere designations η and ξ as well as t correspond to time parameter.

Results of calculations on Eq. (14) for schemes I and II are shown in Fig. 3.

At transition from function (8)–(11), that corresponds to qualitative change of character of molecular movements of reagents, significant reduction of values $P_\mathrm{B}(x)$ and accordingly of constants of velocities of bimolecular reactions are natural. At $x \le 0.04$ reduction of constants of velocities of chemical reactions more than in 10^5 times it is necessary to expect. This circumstance can be an explanation of significant reduction of constants of velocities practically of all reactions at their transitions from low viscosity media to solid ones, for example, to polymers [19–21]. Here one can note, that in the literature such phenomenon usually is named the phenomenon of a kinetic stop of chemical reactions which cannot be explained within the framework of the classical kinetic theory by transition of reactions in solid media to a diffusion-controllable regime of their course (constants of velocities of coming together of reagents in solid media is larger than constants of velocities of reactions themselves in 10^5 and more times [19–21]).

One can note two more very well-known facts which also can be considered as consequence of that in solid media molecular movements of reagents occur on type of Brown movement. These facts concern so-called compensation effect (CEF) which has no explanation within the framework of the classical kinetic theory [22,23], and substantial growth of energy of activation practically all chemical reactions at transitions from low viscosity media to solid ones [24,25]. We shall prove, that these facts are natural at transition from scheme I to the scheme II. First of all we note, that if in (14) function (12) is used as $f_b(\xi)$, and (8)—as $f_a(\eta)$, the obtained result can be approximated the following complex function:

$$P_\mathrm{B} = \begin{cases} 0.1x & \text{for } 0.4 \le x \le 4 \\ x^3 & \text{for } 0.04 \le x \le 0.4 \\ x^n & n > 3 \text{ for } x \le 0.04 \end{cases} \tag{15}$$

For scheme I at $x \ll 1$

$$k_\mathrm{eff}^\mathrm{I} = \frac{k_1 k_2}{k_{-1}} = \frac{A_1\mathrm{e}^{-(E_A^{(1)}/RT)}A_2\mathrm{e}^{-(E_A^{(2)}/RT)}}{A_{-1}\mathrm{e}^{-(E_A^{(-1)}/RT)}} = \bar{A}\mathrm{e}^{-((E_A^{(1)}+E_A^{(2)}-E_A^{(-1)})/RT)} \tag{16}$$

For the scheme II at $x < 1$

$$k_\mathrm{eff}^\mathrm{II} = A_1\left(\frac{\pi^2 A_D}{z^2 A_{-1}}\right)^n \mathrm{e}^{-((E_A^{(1)}+nE_A^D-E_A^{(-1)})/RT)} \tag{17}$$

where A_1, A_2, A_{-1}, A_D are the before-exponential multipliers in Arrenius equation for corresponding reactions; $E_A^{(1)}$; $E_A^{(2)}$; $E_A^{(-1)}$; E_A^D are the energy of activation in Arrenius equation for the same reactions.

If in schemes I and II condition $(\mathrm{AB})^*$ is interpreted as a transitive condition, one can assume that $k_2 \approx k_{-1}$ and

$$E_A^{(2)} = E_A^{(-1)} \ll E_A^{(1)} \tag{18}$$

In this connection, from the point of view of the stated theory it is necessary to expect, that at transition from scheme I to the scheme II the energy of activation practically of all chemical reactions should grow from a value $E_A^{(1)}$ up to $E_A^{(1)} + nE_A^D$, where $n > 1$, and E_A^D is the energy of activation of rotary movement of reagents in a cell. In other words, dependence of constants of velocities of chemical reactions on temperature in Arrenius coordinates should look how is shown in Fig. 4.

The numerous researches described, in particular, in Refs. [24,25], confirm this conclusion. One can say that these effects connected to increase of activation energies of chemical reactions at transitions of reactions from low viscosity solvents to solid polymers, one consider as one of the basic attributes of solid-phase reactions which are not finding explanations in the traditional kinetic theory. This phenomenon finds quite logic explanation within the framework of considered representations.

Now let us consider the next phenomenon. As it follows from (15), value n in (17) can depend on temperature. Taking into account (18), Eq. (17) can be rewritten so:

$$k_\mathrm{eff}^\mathrm{II} = A_\mathrm{eff}\mathrm{e}^{-E_\mathrm{eff}/RT} = A_1 A^n \mathrm{e}^{-((E_A^{(1)}+nE_A^D)/RT)}$$

$$A = \frac{\pi^2 D}{z^2 A_{-1}}$$

or

$$\ln A_\mathrm{eff} - \frac{E_\mathrm{eff}}{RT} = \ln A_1 + n\ln A - \frac{E_A^{(1)} + nE_A^D}{RT}$$

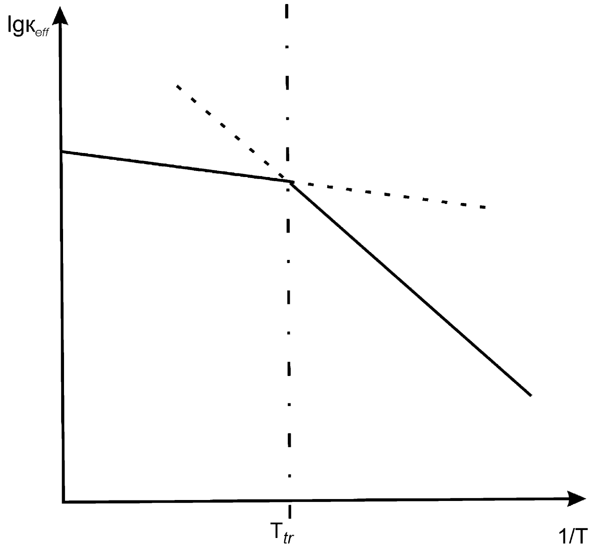

Fig. 4. Prospective dependence of constant of chemical reaction velocity on temperature with taking into account a transition from a scheme I to a scheme II. T_{tr} is a temperature, by which a change of reagents molecular movements character occurs.

If n is some function of T, than last equality will be true at any values T, when

$$n = \frac{\ln A_{\text{eff}} - \ln A_1}{\ln A} = \frac{E_{\text{eff}} - E_A^{(1)}}{E_A^D}$$

Last relation can be rewritten as:

$$\ln A_{\text{eff}} = \ln A_1 - \ln A \frac{E_A^{(1)}}{E_A^D} + \frac{\ln A}{E_A^D} E_{\text{eff}},$$

that corresponds to

$$\log A_{\text{eff}} = a + bE_{\text{eff}} \tag{19}$$

Eq. (19) represents essence of compensation effect (CEF), which is widely spread in case of many chemical, biochemical and physical processes [22,23]. One can also note here, that CEF is logic consequence of transition from scheme I to the scheme II, caused by imposing of restrictions on molecular movements of reagents.

Summing up above-stated, we can accept, that as the fact of possibility of course of chemical reactions under the scheme II, and a possibility of transition from scheme I to II, does not contradict experimental data available in the literature. To carry out transition to non-breakage polymerizations, it is necessary to brake selectively only reactions of breakage of a chain of polymerization under the second order, having kept thus velocity of reactions of growth of a chain of polymerization so high, as well as in low viscosity solutions. From the formal point of view, the last is possible, if at change of parameter x transitions from a curve 1 in Fig. 3 on the curves which are between curves 2 and 3, occur for each concrete reaction at certain characteristic for the given reaction value x. Basic our assumption is that there should be some interval of values x, for example $x_{\min} \leq x \leq x_{\max}$ within which there is non-breakage polymerization with the maximal possible velocity. What ways of detection of non-breakage polymerization can be? In what media can it take place? These are the basic questions which are considered below.

4. Results and discussion

From point of view of considered representations by the most significant for definition of velocity of chemical reactions under the scheme II is mobility of reagents in a cell, i.e. not so much transmitting diffusion of reagents in reactor media, how their rotary diffusion. This conclusion finds many the experimental confirmations described, in particular, in Refs. [24,25]. For many reactions proceeding in conditions of a solid media, linear correlation between constants of velocities of chemical reactions and frequency of paramagnetic probe (PP) rotation is found out. Rotary diffusion of reagents depends not only on temperature of the medium, but, that has the most important value for its practical regulation, it depends also on viscosity of the reactor medium and the molecular sizes of reagents. In other words, we have completely new mechanisms of control of velocities of the chemical reactions, not connected with change only temperature of the medium. In various media it is possible to evaluate the velocity of rotary movement of reagents, in particular, on the basis of measurements by EPR method of times of correlation of rotary movement of various PP [16,17]. In this connection, it is interesting to compare times of correlations τ_c in polymers and some liquid oligomers and the monomers presented in Tables 1 and 2. From these tables it is visible, that times of correlation τ_c in some liquid oligomers have the same values, as in such solid polymers, as PS, PMMA and others. From point of view of considered representations display of kinetic effects in these media, characteristic for solid media, should be quite natural. This statement appeared correct. Namely it opens a way to creation of PPC, satisfying a condition (1).

Table 1
Correlations times in some polymers

Polymer matrix	T_c (°C)	Time of correlation τ_c, 10^9 s at 20 °C
Cycled natural caoutchouck (CNC)	28	9–5
Polystyrene (PS)	110	1–2
Polyphenylene quinoxalines (PPQ)	360–380	2
Polyphenylenes (PP)	–	20–30
Phenolphormaldehyde pitch (PPP)	–	More than 100
Siloxane caoutchoucks (SC)	About 50 °C	1–3

Table 2
Correlations times in some liquid oligomers and monomers

Medium	($\times 10^{-6}$ m^2/s at 20 °C	Time of correlation (τ_c), 10^9 s at 20 °C
TGM-3[a]	10–30	0.05–0.06
MGF-9[a]	100–150	0.25
MDF-2[a]	800–900	0.7
OKM-2[a]		0.4–0.7
OUMA-2100[a]		1.2–1.9

[a] Abbreviations of monomers correspond to classification, presented in Ref. [1].

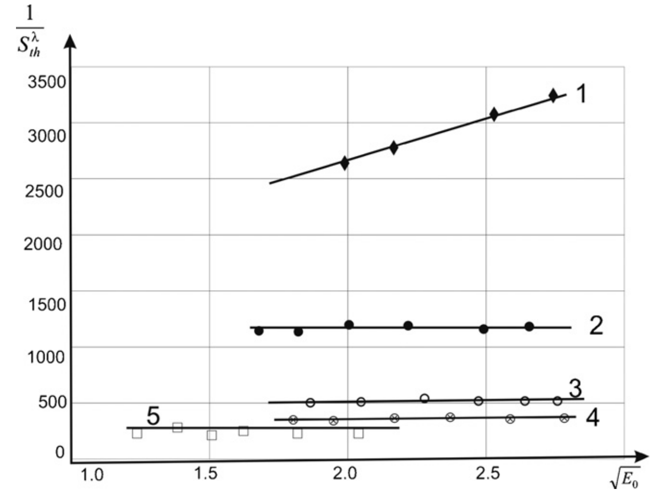

Fig. 5. Dependence of threshold photosensitivity of liquid PPC of various composition on intensity of light: (1) benzyl methacrylate $\tau_c = 0.1 \times 10^{-10}$ s; (2) phenoxyethil methacrylate $\tau_c = 0.3 \times 10^{-10}$ s; (3) TGM-3 $\tau_c = 0.4 \times 10^{-10}$ s; (4) OKM-2 $\tau_c = 4 \times 10^{-10}$ s; (5) OUMA $\tau_c = 8 \times 10^{-10}$ s.

We present some results of the experimental investigations confirming this statement. From (6) follows, that at small enough values E_0/C_0 dependence of threshold photosensitivity of PPC on intensity of light should satisfy the equation:

$$\frac{1}{S_{\text{th}}^{\lambda}} = \frac{C_k}{a_\lambda C_0} + \frac{\alpha_k \sqrt{k_0}}{\bar{n} \cdot k_{\text{p}} \sqrt{a_\lambda} C_0} \sqrt{E_0} \qquad (20)$$

It is taken into account here in addition, that in PPC highly effective inhibitor of radical polymerization can present with concentration C_x.

From (20) follows, that at $k_0 \neq 0$ in coordinates $1/S_{\text{th}}^{\lambda} \div \sqrt{E_0}$ these dependences should be the straight lines directed under some non-zero angle to a coordinate axis. At $k_0 \to 0$ an angle of an inclination of these straight lines should approach to zero too. From Fig. 5 follows, that in a case of oligomers (monomers), in which $\tau_c \geq 0.4 \times 10^{-10}$ s an angle of inclination of mentioned straight lines is equal to zero. In such systems velocity of reaction of polymerization is proportional E_0 in the first degree that means an absence of the second order reactions of breakage of a chain of polymerization, i.e. polymerization is non-breakage. One can note, that synchronously with reduction of an angle of an inclination of the mentioned above straight lines threshold photosensitivity of PPC grows significantly (in tens and more times).

On the basis of data presented in Fig. 5, it would be possible to make conclusion that for entering into a non-breakage regime of polymerization such condition must be satisfied: $\tau_c \geq 0.4 \times 10^{-10}$ s. But it is not absolutely so.

Fig. 6 shows the generalized curve of dependence of a threshold photosensitivity of various PPC on correlation time τ_c, representing system matrix polymer–liquid oligomer.

In such systems mobility of reagents depends not only on the molecular sizes of monomers (oligomers), but also on ratio polymer–monomer (in detail these investigations are described in Refs. [26,27]). In a full view, as it shown in Fig. 6, these curves have been found out only in case of use of oligomers (monomers), in which $\tau_c \leq 1 \times 10^{-10}$ s. It is possible to select three areas in Fig. 6. In an area I photosensitivity of PPC does not depend on τ_c, that corresponds to a stationary regime of course of polymerization reaction. In the area II S_{th}^{λ} grows significantly with increase of τ_c, that corresponds to a condition $k_0 \to 0$. In the area III S_{th}^{λ} decreases with growth of τ_c, that can be connected with braking of reactions of growth of a chain of polymerization ($k_{\text{p}} \to 0$).

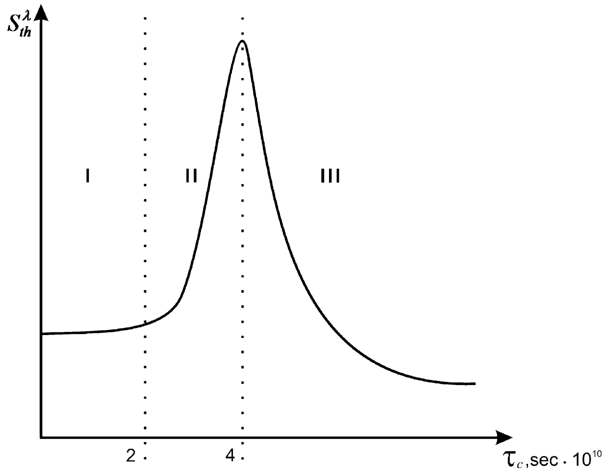

Fig. 6. Dependence of threshold photosensitivity of PPC layers of composition: matrix polymer–oligomer TGM-3 on time of correlation of rotary movement of paramagnetic probe.

Data presented in Fig. 6, have essentially important from our point of view semantic loading. First, they show, that process of braking of various reactions begins at different values τ_c (different values of parameter x). Second, transition to non-breakage polymerizations comes to an end at $\tau_c \approx 4 \times 10^{-10}$ s, i.e. the completely non-breakage polymerization begins not at $\tau_c \geq 0.4 \times 10^{-10}$ s, but only at $\tau_c \approx 4 \times 10^{-10}$ s. What is the reason of so big distinction in estimations of correlation time τ_c, at which polymerization begins as non-breakage? The mentioned above contradiction arises in connection with that at $0.4 \times 10^{-10}\,\text{s} \leq \tau_c \leq 4 \times 10^{-10}$ s in case of polymerization of liquid oligomers a mechanism of microheterogeneous polymerization becames more preferable. Really, if at formation of the first molecules of polymer local microareas (microreactors) arise, in which $\tau_c \geq 4 \times 10^{-10}$ s it is natural, that in these microareas reaction of polymerization will take place further according to a non-breakage mechanism with a velocity, which exceeds the polymerization velocity in other parts of the reactor in many orders. Further it is easy to image, that at the certain concentration of such “points of growth” and diffusion run of the free radicals formed in these media at decomposition of the photoinitiator, polymerization outside such microreactors may be excluded practically completely. The last means, that in such media process of polymerization will occur basically due to growth of microreactors (“grains”, “points of growth”), formed on the initial stage of this reaction. In this connection, we assume, that really non-breakage polymerization begins at $\tau_c \gg 0.4 \times 10^{-10}$ s. More correctly, that it occurs at $\tau_c \geq 4 \times 10^{-10}$ s as it displays the data in Fig. 6.

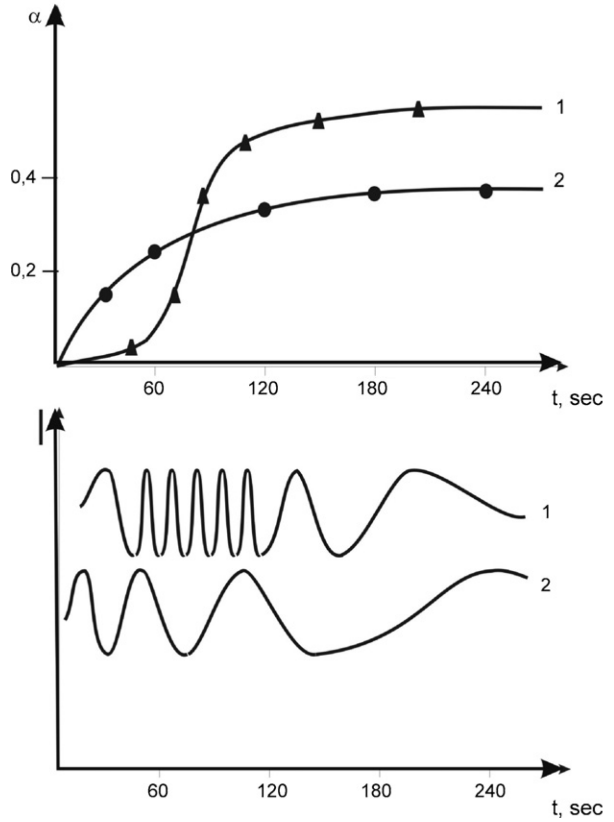

Fig. 7. Kinetic curves of photopolymerization of PPC with various viscosities: (1) $\tau_c < 4 \times 10^{-10}$ s; (2) $\tau_c > 4 \times 10^{-10}$ s.

These conclusions are confirmed directly also by kinetic curves of photopolymerization of various PPC, distinguished only with viscosity (Fig. 7).

According to the data presented in Fig. 6, in systems, where $\tau_c \geq 4 \times 10^{-10}$ s, velocity of polymerization should be slowed down monotonously in process of course of reaction (increase of medium viscosity). It is in full conformity with the data presented in Fig. 7. If at $0.4 \times 10^{-10}\ \mathrm{s} \leq \tau_c \leq 4 \times 10^{-10}$ s polymerization occurs on the microheterogeneous mechanism than against those conclusions which it would be possible to make from Fig. 6, velocity of polymerization should remain a constant for a long time (before connection of growing grains), instead of to grow significantly in process of increase of a degree of conversion of a monomer.

Summing up to the aforesaid, we come to the conclusion, that for realization of non-breakage polymerization necessary for realization of single-stage processes of synthesis of polymeric products such PPC can suit, in which $4 \times 10^{-10}\ \mathrm{s} \leq \tau_c \leq 8 \times 10^{-10}$ s. This statement is one of the basic criteria of PPC selection for these processes for us. It was not revealed any case that this statement has been subjected to any doubts.

However it is necessary to mean, that this statement is a necessary condition for realization of single-stage processes of synthesis of polymeric products, but it is not sufficient. Other important requirement is to provide performance of condition $\alpha_k \to 1$. Performance of this condition depends both on nature of used oligomers in PPC, and on type of the used photoinitiators, capable to generate free radicals for initiation of a chain of polymerization. As for oligomers (or their mixes) from the formal point of view of the representations stated in this article are suitable only those, for which transitions from a curve 1 to any of curves between curves 2 and 3 in Fig. 3 occur for reactions of growth of a chain of polymerization at such values of parameter x which are unattainable even at $\alpha_k = 1$. In this article we shall not discuss in details this question, we note only, that the last is quite possible. First, it is possible because in many solid polymers times of correlation τ_c are of the same order, as in liquid oligomers (most likely because of “friable” packing of molecules of polymer). Second, there is a possibility of regulation both of flexibility of chains of obtained polymer, and of density of its packing by optimal choice of initial structure of PPC. For the present we do not have theoretically proved recommendations about search of PPC structures for single-stage processes, there is only knowledge about properties, which they must have.

More definitely it is possible to say about criteria of selection of photoinitiators for these processes. The photoinitiators containing carbonyl group are most widely presented in the market. It is possible to divide these photoinitiators into two types which differ from each other by mechanisms of generating of free radicals: generating free radicals on reaction such as Norrish I and such as Norrish II [28,29]. Our investigations have shown, that for single-stage processes photoinitiators, in which free radicals are formed as a result of a straight dissociation of a carbon–carbon couple next with carbonyl group (reactions type of Norrish I), better suit. This statement is illustrated by data in Fig. 8.

Various ethers of benzoin belong to such type of photoinitiators. It is possible to say, that these connections represent exception of a rule—the majority of connections generate free radicals as a result of a photo-redox process (reactions type of

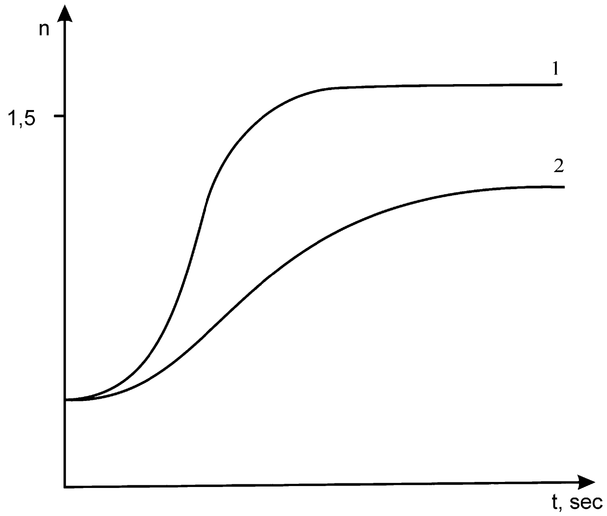

Fig. 8. (1) System OKM-2–isobutyl ether of benzoin—generation of free radicals by reaction of Norrish type I; (2) system OKM-2–2,4-di-tert-butylorthoquinone—generation of free radicals by reaction of Norrish type II.

Norrish II), in which relatively long-living molecules in excited triplet conditions participate as intermediate products. Namely last circumstance is the reason of braking of reaction of initiation of free radicals in process of increase of viscosity of the reactor medium during polymerization (the probability of transition of a molecule of the photoinitiator from excited triplet condition into the basic one significantly increases due to braking of bimolecular reaction of breakoff of an hydrogen atom by a molecule in a triplet condition from any donor of hydrogen). The basic role plays here also a restrictions on molecular mobility of reagents for the reasons considered above.

There are restrictions also on photoinitiator concentration, entered into PPC. It has been established, that the following relation should be satisfied:

$$C_0 \cdot \varepsilon_\lambda \cdot h_{\max} \leq 0.3 \qquad (21)$$

where ε_λ is a molar extinction factor of the photoinitiator for a wavelength of a of light, which carries out an exposure; $h_{\max}$ is the maximal thickness of a formed product in a light beam direction.

The condition (21) follows directly from a Buger law. It is easy to show, that if the condition (21) is satisfied, that during an exposure of samples from two sides an intensity of light will be practically identical along of light beams directions on any distance from walls of the form.

5. Conclusions

In summary we note the following. We have stated all basic requirements necessary for realization of single-stage processes of photochemical synthesis of polymeric products with optical accuracy. Necessity and sufficiency of these requirements are proved by a 10 years' operational experience of an enterprise "Reper-NN" in which all production is made under the single-stage scheme. We shall not describe here assortment and quality of polymeric products made in this enterprise, one can find all them in a site http://www.reper.ru. It is important, that all this works.

It would be desirable to pay attention once again that at a substantiation, first of all, of the requirements showed to PPC, it was necessary to refuse traditional concepts about the major factors determining velocities of chemical reactions. There is also some practical expedience in this. The matter is that single-stage processes of photochemical synthesis of polymeric products inherently are necessary for attributing to isothermal processes in the same understanding, as well as in case of alive organisms. Both in those and in other systems the methods allowing to control processes taking place in them, are necessary. In our case it is a variation of reagents mobility. It is interesting, that this method also is effectively used in alive organisms [30,31]. It is possible, that transition to single-stage processes of synthesis of polymeric products can give not only economic and ecological effects in the near future, but also come nearer to reproduction under industrial conditions the organic synthesis used in wildlife.

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