On kinetic features of photo- or γ-induced polymerization in *p*-diethynylbenzene crystals in the temperature range of 4.2–300 K

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The stereoregular radical polymerization in photo- or γ-irradiated crystals of *p*-diethynylbenzene (DEB) has been found to proceed in the temperature range of 4.2–300 K [*J. Low Temp. Phys.* **139**, 675 (2005)]. We have studied the kinetics of this process. The polymerization of acetylene monomers due to the system of conjugated bonds formation results in the shift of a crystal absorption band from UV to visible. Being compared with gravimetrical data on the polymer yield, it allowed the direct detection of polymerization process in a crystal. The monomer radicals, initiating the polymerization process, as well as propagating macroradicals were detected by ESR method. The rates of both radical formation and chemical reaction of polymerization retard, as it inherent to solid phase processes, already at small yields. Thus we applied a mechanism pertaining to the first stages of the processes only. It has been proved that both photo- and γ-induced polymerization have chain character in the temperature range 77–300 K but it is most probably not chained at 4.2 K and, for photo-polymerization, every act of monomer addition to the polymer needs an extra quantum of light. The kinetic chain length (the number of added monomer molecules per radical) turned out to be around of 200 at 300 K and of 20 at 77 K. It was interesting to note that polymer just formed was able to be modified — the radicals then created in polymer chain were able to add monomer molecules forming, in such a way, a *branched polymer*. This process, of course, is not chained too.

1. Introduction

The polymers with conjugated bonds are of great interest because of their properties. The fact of stereoregular polymer formation under photo- or γ-irradiation of para-diethynylbenzene (DEB) crystals may be thought of as proved [1]. The present work is concerned with study of polymerization mechanism and kinetics, in particular, with elucidation of the problem whether the process has chain character and with determination of polymerization efficiency. During increase of the irradiated samples temperature, to remove the nonreacted monomer, the contribution of post-polymerization in the process is prominent. Therefore the methods of optical and ESR spectroscopy were used because they allow to investigate the reaction and analyze products obtained directly in solid phase without the sample structure distraction. The γ- or UV irradiation of samples leads to a significant red shift of DEB absorption band: colorless crystals become yellow. That the yellow color is due to polymerization rather than to conversion of individual molecules was proved by experiments where DEB molecules were diluted by xenon; in the latter case the samples did not demonstrate red shift of the absorption band. The conjugated bonds formed during polymerization surely shall contribute to this red shift.

2. Experimental

The crystals of DEB for optical investigations were grown, from the melt, between two quartz plates in their central calibrated part, where it was possible to grow species of thickness L of 1–50 μm and area of 2–20 mm^2. Absorption spectra were recorded on a Hitachi spectro-

photometer; ESR spectra were recorded on EPR-21 spectrometer (3 cm) at microwave power 10^{-4} W. The polymerization was initiated by ^{60}Co irradiation or by light from DRSH-1000 or DRSH-500 mercury lamps. Low-temperature irradiation and investigation were performed using optical cryostats.

3. Results and discussions

As it is seen from Fig. 1, all kinds of radiation: γ-radiation, light with λ = 253.7 nm or with 300 nm < λ < < 340 nm, cause the appearance of an absorption band with the center near 400 nm; there is more red shift (up to 700 nm), contribution of which is different for different kinds of irradiation (Fig. 1,*a–d*). However, in the region 320–470 nm, where basic absorption takes place, spectra are absolutely identical. It means that their absorption cross-sections in this region shall be close. To establish an agreement between absorption density change and polymerization efficiency, the following approach has been used. In the case of polymerization at 300 K nonreacted monomer (or the monomer and solvent) was removed by evacuation. The optical spectra were then recorded and, after that, the polymer yields were determined gravimetrically.

Both the yield of polymerization determined in such a way and the polymer absorption intensities decrease with an increase of irradiation dose (Fig. 2). This is typi-
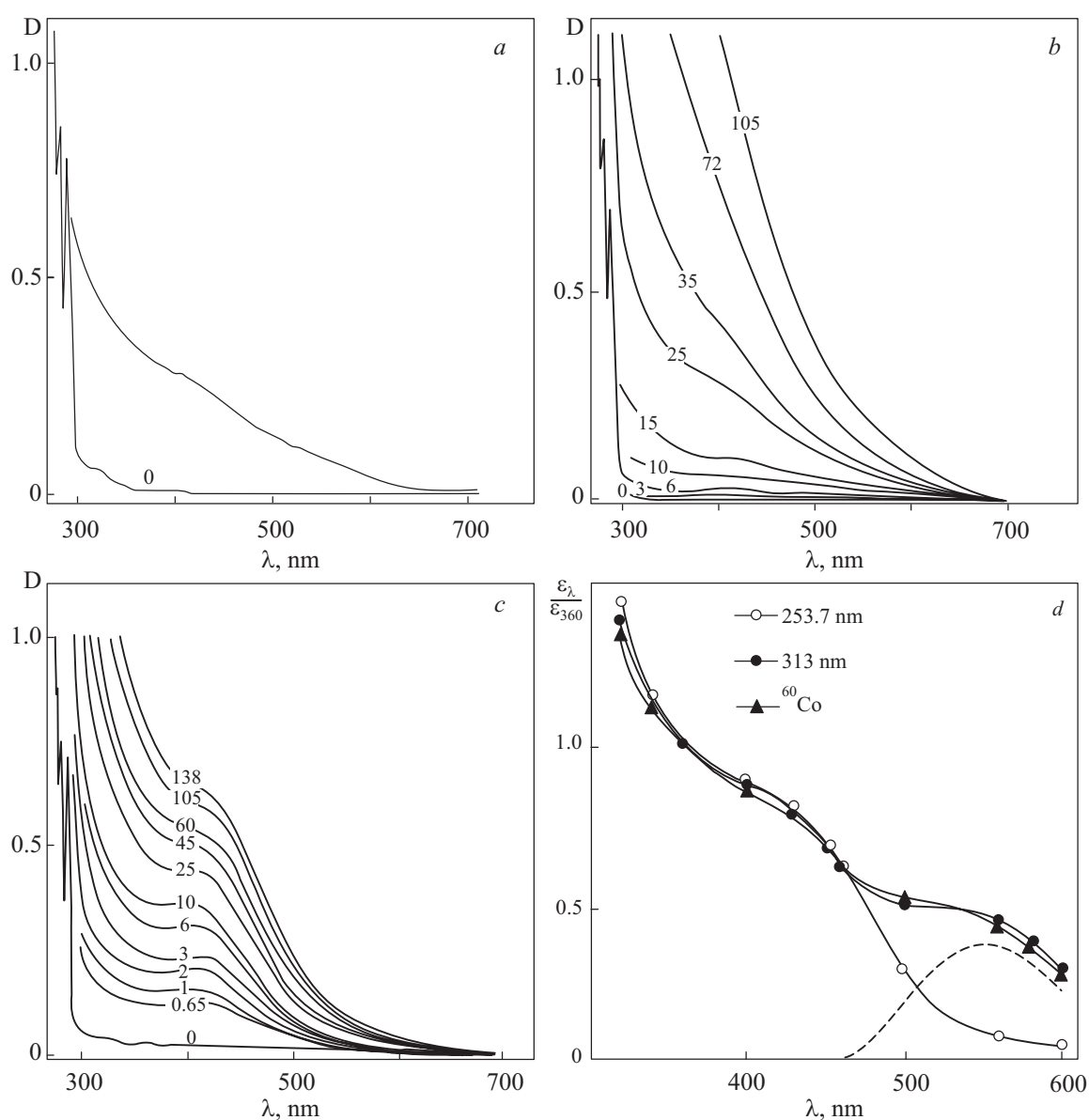

Fig. 1. Absorption spectra of DEB crystals (L = 1 μm, 300 K) before (0) and after irradiation (time in min shown in figure) by: *a*) γ-radiation (500 kGy); *b*) light (300 nm < λ < 340 nm, I_0 = 2.4·10^{17} quant/cm^2·s); *c*) light (λ = 253.7 nm, I_0 = = 1·10^{16} quant/cm^2·s); *d*) DEB crystals absorption spectra for different types of irradiation.
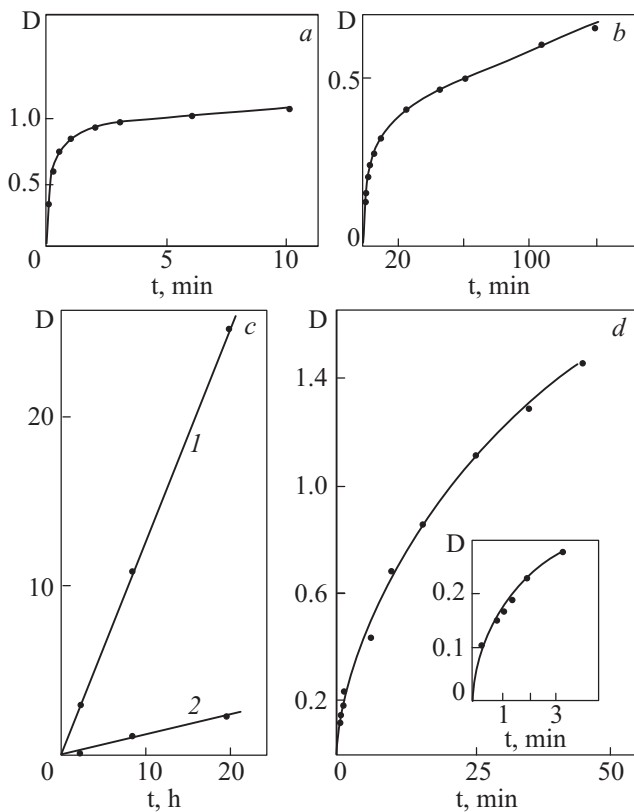
Fig. 2. Dependence of polymer optical density *D* (at λ = = 400 nm) on time of DEB crystals irradiation (*L* = 1 μm, 300 K) by light: *a*) λ = 230–340 nm, I_0 = 4.2·10^{17} quant/cm^2·s; *b*) *λ = 253.7 nm,* I_0 = 1·10^{16} quant/cm^2·s; *c*) γ-radiation (*L* = = 1 μm (curve *1*), *L* = 10 μm (curve *2*), *I* = 22 kGy/h); *d*) light (300 nm < λ < 340 nm, I_0 = 2.4·10^{17} quant/cm^2·s, *L* = 50 μm).

cal for radiation-chemical processes in solid phase, e.g., for the processes of radical accumulation, including radical formation in DEB [2], and for chemical reactions in solid state [3], including polymerization reaction [4]. It is commonly agreeable to call these effects *kinetic stop effect* («*kinetic*», because the changes of process conditions may lead to its «*reviving*» [2,4,5]). Similarly as in these cases, the effect observed in our work is not associated with reagents expenditure because, during temperature rise, the process rate sharply increases and significant conversion yield can be reached. It is not connected with a decay of radical centers. ESR investigations have shown that process «reviving» is not due to formation of new radicals but due to propagation of «stilled» macromolecules. Since this effect was observed for reactions of radical recombination and for low-temperature oxidation of macro-radicals, it is hard to assume that in polymerization reactions it has been caused by macromolecules lengthening or by their interlock.

3.1. Connection between absorption spectra and poly-merization characteristics

At very small irradiation doses, the polymerization yield and optical absorption (in the polymer absorption range) depend linearly on the absorbed dose, which allows one to determine correctly the radiation and/or quantum yields. In the case of gamma-irradiation, it is possible because one can use sample as large as is wished, but in the case of UV irradiation it is hard to accomplish. Therefore, it was necessary to create models which could help to describe correctly the linearity of polymerization yield at small doses and reaching the limit of yield at large doses, and help to make correct interpolation for the range of middle doses.

The simplest interpolation is

$$\frac{dD}{dt} = 0.43 \frac{D_0}{t + \tau}. \tag{1}$$

Its solution

$$D = 0.43 D_0 \ln\left(1 + \frac{t}{\tau}\right) \tag{2}$$

gives the obvious asymptotes:

$$D = 0.43 \frac{D_0}{\tau} t \text{ (short times)}, \tag{3}$$

$$\frac{D}{D_0} = \log t - \log \tau \text{ (long times)}. \tag{4}$$

The convenience of this equation lies in the possibility of simple parametric description of kinetic curves obtained experimentally, as well as in correct determination of initial incline of kinetic curves, which enables to find real values of polymerization quantum and/or radiation yields. Actually, initial incline is equal, in our designations, to D_0/τ and it is governed by the value of D_0 — its inclination in the coordinates (*D*, log *t*) and by the parameter τ which can be found from the point of these lines intersection with abscissa axis. As it seen from Fig. 2,*d* kinetic curve may have logarithmic character already at very low conversions and, therefore, the observed initial incline can differ from that found by interpolation formula (2) by an order of magnitude. From the accepted model, it follows that τ is a time when (in the range of more intensive polymerization, for strongly absorbing monomer — in the front of sample) some critical concentration of polymer molecules $N_p^c(T)$ can be reached, at which point the polymer just formed retards further polymerization. One can show that

$$\tau = N_p (\sigma N_m \eta I_0)^{-1}, \tag{5}$$

where η (λ_{irrad} ,*T*) is the quantum (radiation) yield, I_0 is intensity of incident light with λ_{irrad} (or dose intensity of
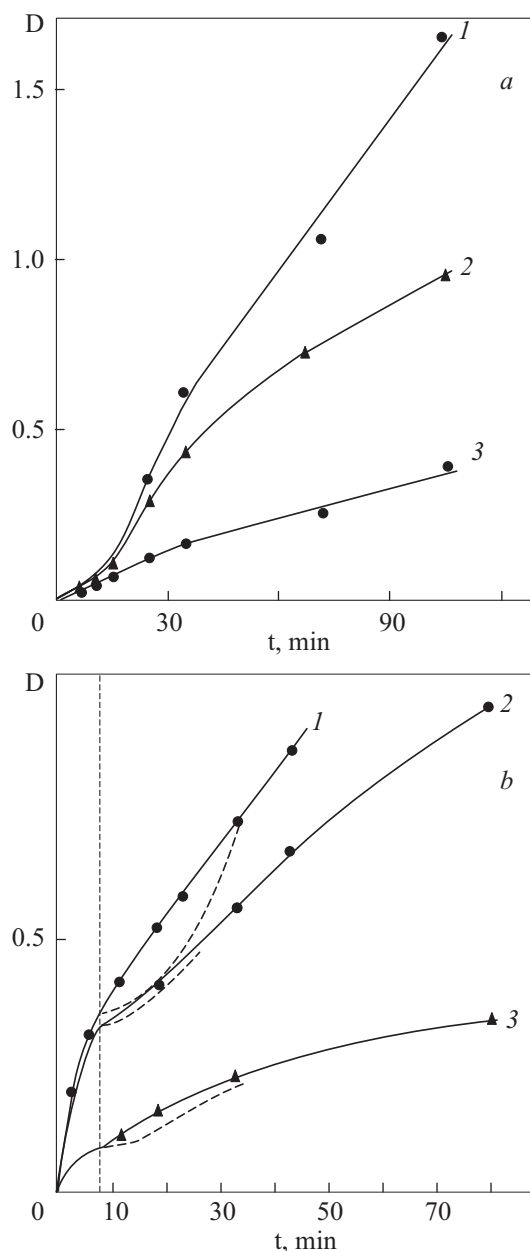
Fig. 3. Dependence of polymer optical density D on time of DEB crystals irradiation ($L = 1$ μm, 300 K) by light: *a*) 300 nm < λ < 340 nm, $I_0 = 2.4 \cdot 10^{17}$ quant/cm²·s; *b*) during first 9 min (vertical line) sample was irradiated by light with λ = 253.7 nm, $I_0 = 1 \cdot 10^{16}$ quant/cm²·s, then it was irradiated by light with 300 nm < λ < 340 nm, $I_0 = 2.4 \cdot 10^{17}$ quant/cm²·s. Dashed lines are the dependence of D on t during irradiation of sample by light (300 nm < λ < 340 nm, $I_0 = 2.4 \cdot 10^{17}$ quant/cm²·s) without preliminary irradiation (data of Fig. 3,*a*). At λ = 360 (curve *1*), 400 (*2*), and 500 (*3*) nm.

gamma-irradiation), N_m is monomer density, $N_p \equiv N_p^c$, and σ is polymer cross-section. It is important to point out that the temperature dependence of the kinetic curves for short and long times of irradiation has different nature. At short times, it is determined by polymerization quantum

yield changes with temperature (that is, by microscopic characteristics of the process); at long times it does not depend on quantum yield but it is determined by macroscopic parameter — critical concentration of polymer formed — N_p^c.

Two important features of the kinetic curves, following from the accepted model, are worth to be noted:

1. If the spectrum of polymer absorption does not depend on dose, the curves of D dependence on time for different λ in coordinates (D, log t) at long times present bunch of lines rising from point (0, log t).

2. The kinetic curves inclinations for given λ in logarithmic range at photo-irradiation shall: a) not depend on irradiation intensity; b) weakly depend on irradiation λ; c) not depend on thickness of samples. In case of gamma-irradiation of thin samples, the inclinations shall be 2 to 3 times greater than those at optical excitation.

We observed that polymerization takes place at irradiation by light with λ > 300 nm, which is longer than that of monomer absorption red edge (300 nm). In this case, very small part of incident light will be absorbed by the monomer. Nevertheless, at comparable intensities of short wave and long wave incident light, the rate of color change (in the range of significant D) appeared to be comparable (Fig. 2,*b* and Fig. 3,*a*). This fact suggests that polymer formed is able (by absorbing the light) to produce radicals which lead to further polymerization. The autocatalytic character of $D(t)$ dependence at irradiation by light of 300 nm < λ < 340 nm (Fig. 3,*a*) supports this idea: polymer just formed stimulates further polymerization. It is not clear, if polymerization first occurs due to weak absorption of light with λ = 313 nm (red wing of monomer absorption line) or due to action of the traces of light with more short waves on the sample (in the range of monomer absorption). A comparison of initial portion of kinetic curves of sample irradiated by light with 300 nm < λ < 340 nm and curves of sample first irradiated by light with λ = 253.7 nm (Fig. 3,*b*) demonstrated disappearance of autocatalytic character in the sample where polymer was preliminarily obtained. Autocatalytic character retains its nature until reaching significant optical density, when practically all incident light is absorbed and polymer volume begins linear growth with time.

3.2. Experimental determination of polymer cross-section, quantum and/or radiation yields of polymerization, and polymer critical concentration

The most simple case is gamma-irradiation one. Since the absorption is uniform across the whole sample thickness, it is possible to work with samples of such thickness that significant absorption by the just formed polymer would occur at low conversions. As a result, the dependences of D on the dose show as lines (Fig. 2,*c*) and their inclination give the polymerization radiation yield.

A divergence from the linear law appeared only at large doses (> 1000 kGy). At photo-irradiation, notable absorption by polymer molecules takes place when polymer local concentration is significant and correct determination of quantum yield can be done only taking in consideration the «kinetic stop» effect. Our experiments have shown that absorption spectra characteristics of irradiated DEB crystals are well described by simple phenomenological model given above. In fact, practically for all irradiation times, the dependence of D on log t constitutes straight lines for all used types of irradiation, intensities, and different sample thickness (Fig. 4). Moreover, for different observation wavelengths, kinetic dependence in these coordinates constitutes a bunch of lines rising from the same point located on abscissa axis (Fig. 4,*a,b*). As mentioned above, this is a proof that polymer absorption spectra even at significant conversion rates are irrelevant. Ten times light intensity enhancement (Fig. 4,*c*) as well as ten times sample thickness increase does not lead to notable change of lines incline in coordinates (D, log t). Interpolation expression (2) gives good description of the dependence (D, log t) for samples irradiated by light with
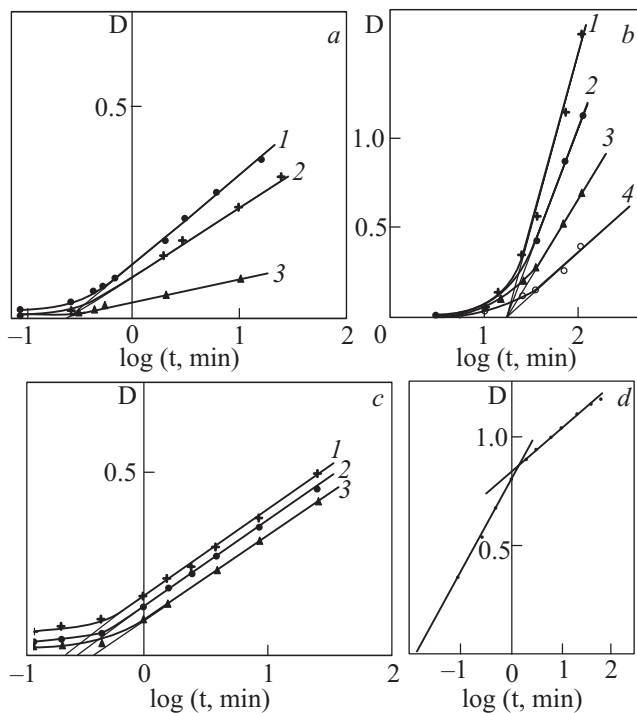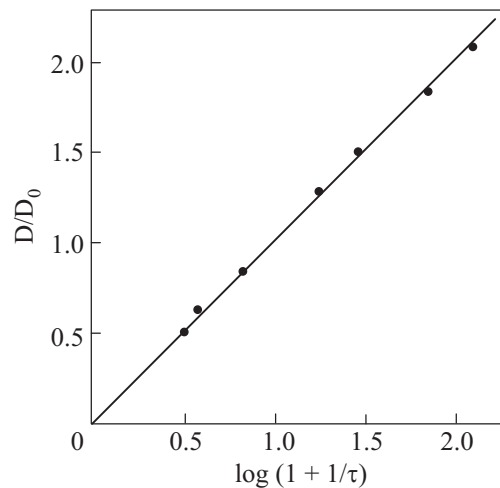
Fig. 5. Checking of interpolation formula $D = 0.43 D_0 \times \times \ln(1 + t/\tau)$ for polymer optical density at DEB crystal ($L = 1$ μm, 300 K) irradiation by light with λ = 253.7 nm. $D_0 = 0.23$, $\tau = 15$ s.

λ = 253.7 nm in the range from shortest to longest time (Fig. 5).

For open light of DRSH-1000 lamp, the picture of process is more sophisticated, since in this case one has to deal with the whole (230–340 nm) spectral range of UV irradiation action on DEB. At that, the action of light in the range of monomer own absorption (230–290 nm) is superimposed on action of light with spectral range (300–340 nm) which is weakly absorbed by monomer but notably absorbed by polymer. Therefore, the curve in the coordinate (D, log t) displays two parts with different inclination (Fig. 4,*d*). Polymer absorption efficiency was found by the comparison of irradiated sample absorption value and gravimetrically determined amount of polymer in it. One should take into account that gravimetrical method gives good results only in the case of low conversions. It means that correct determination is possible for gamma-irradiated samples where one can investigate a sample of any thickness which allows of an amount of polymer that can be suitable for correct results. The values of absorption cross-section and efficiency were found as follows: σ_p (400 nm) $\approx 3.0\cdot 10^{-17}$ cm^2 and ε_p (400 nm) $\approx 1.4\cdot 10^5$ cm^{-1} (monomer density was $N_m = 4.8\cdot 10^{21}$). Since the absorption characteristics for polymers obtained by different irradiation ways (Fig. 1,*d*) are close, and there is independence of absorption spectrum on conversion level, the values of polymer absorption cross-section and efficiency obtained for gamma-irradiated samples can be used for photo-irradiated ones. Results accounted on the base of the experimental data are summarized in Table 1.

Making an interpretation for the samples irradiated by light with λ > 300 nm (beyond the monomer absorption

Fig. 4. Dependence of polymer optical density D on logarithm of DEB crystals irradiation time by light with: *a*) λ = 253.7 nm (irradiation conditions the same like in Fig. 2,*b*). At λ = 360 (curve *1*), 450 (*2*), 500 (*3*) nm; *b*) 300 nm < λ < 340 nm (irradiation conditions like in Fig. 3,*a*). At λ = 360 (curve *1*), 400 (*2*), 450 (*3*), and 500 (*4*) nm; *c*) λ = 253.7 nm. Sample thickness: 50 μm (curve *1*); 1 μm (*2, 3*). Intensities: $I_0 = 1\cdot 10^{16}$ quant/cm^2·s (*1, 2*); 10^{15} quant/cm^2·s (*3*). At λ = 400 nm; *d*) λ = 230–340 nm (irradiation conditions the same like in Fig. 2,*a*). At λ = 400 nm.

Table 1. Characteristics of DEB crystals polymerization

Initiation method	T, K	Sample's thickness, L, μm	Light beam intensity, I_0, quant/cm²·s	D_0	τ, s	ε_p, 10^5 cm^{-1} ($\lambda = 400$ nm)	Polymerization quantum and radiation yield, η, ($\lambda = 400$ nm)	N_p^c / N_m, %	Quantum and radiation yield of radicals, G_R	Kinetic length of chain, υ
λ = 230–340 nm	300	1.0±0.2	(4.2±1.0)·10^{17}	0.42	0.67	1.3±0.4	(2±4)·10^{-2}	10	(1.1±0.2)·10^{-4}	200
λ = 253.7 nm	300	1.0±0.2	(1.0±0.3)·10^{16}	0.23	15	1.3±0.4	5.68·10^{-2}	7.0±2.0	(1.2±0.2)·10^{-4}	(4.7±2.0)·10^2
γ-irradiation ^{60}Co	300	1.0±0.2	(12±1.2) kGy/h			1.3±0.4	8.1	10	(5.0±1.0)·10^{-2}	(1.6±0.6)·10^2
λ = 300–340 nm	300	1.0±0.2	(2.4±0.6)·10^{17}	1.4		1.3±0.4	3.0·10^{-4}	37±10	(3.0±0.6)·10^{-4}	1.0±0.5
				1.25	2.1·10^2		0.88·10^{-3}	32±8		3±2
λ = 230–340 nm	77	2.0±0.4	(6.0±1.5)·10^{16}	0.175	37.8	1.3±0.4	3.00·10^{-3}	7.0±2.0	(1.1±0.2)·10^{-4}	30±15

range) is more difficult. In this case autocatalytic character of kinetic data at low conversions (Fig. 3,*a*) points to possibility that polymerization occurs due to light absorption by polymer molecules. The connection of kinetic curves autocatalytic character with light absorption by polymer formed during irradiation by this light is supported by experiments on irradiation of DEB crystals which already contain polymer (Fig. 3,*b*). In turn, it means that in this case, contrary to considered above other cases, the amount of absorbed light and depth of its penetration are changing during irradiation. However, these results have basic importance to understanding polymerization mechanism of acetylene monomers. Therefore, we tried to gather even broad quantitative information for this case too. Experiments with samples of large thickness ($L = 50$ μm instead $L = 1$ μm) have shown that the absorption of light with $\lambda > 300$ nm in DEB molecules is negligibly small, and that all indicated absorption is connected with polymer thermally formed in the process of monomer crystals growing (Table 1).

The comparison of polymerization quantum and/or radiation yields of DEB crystals with those of radicals determined by ESR method (which initiate polymerization) has shown:

1. At low conversions polymerization kinetic length of chain both for DEB crystals gamma-irradiation and/or photo-irradiation (in monomer-own absorption range) is rather large and equal to $2\cdot10^2$. It is worth to note that for γ-irradiation, when it was possible to define polymerization yield by gravimetrical method, the value of chain kinetic length has appeared to be close to that value (see Table 1), which confirmed corrections of optical investigations interpretation.

2. Photo-irradiation of polymer molecules which were obtained in one way or another leads to nonchain polymerization (chain kinetic length is equal to 2±1).

3. It is necessary to take in consideration that long kinetic chains appear only at low conversion. By all types of irradiation, there is the polymer molecules critical concentration (about the same) starting with which the polymerization kinetic lengths decrease. Such a «kinetic stop» comes at conversions around of 7%. And at conversions about of 30–40%, the rates of «monomer» (chain) and «polymer» (nonchain) polymerizations are closely related.

Thus, DEB crystals polymerization at 300 K has a chain character.

3.3. Low-temperature investigations

As it was mentioned above, the polymerization takes place both at 77 and 4.2 K. Similarly as at 300 K, the irradiation by open light of DRSH-1000 lamp at 77 K leads to red shift in absorption spectra (Fig. 6,*a*). The character of spectra shows that there is a set of polymer molecules of different length. If such molecule is a dimmer, its absorption spectrum would have a red shift but the edge of absorption band would be as sharp as monomers one. Processed data showed that dependence (D versus log t) has a logarithmic character at already very small conversions. For correct definition of quantum and/or radiation yields and critical concentration of polymer formed, an interpolation formula (2) was used as it was done at 300 K. The determined quantum yield has appeared to be around $3\cdot10^{-3}$. The kinetic length of chain is equal to 30±15 (Table 1). The same kinetic length of chain determined by another way — as a ratio of gravimetrically found polymer yield to concentration of radicals leading a chain — appeared to be near and equal to 20 (this experiment was carried out for gamma-irradiated sample). Post-polymerization was observed during sample heating (Fig. 6,*b*). Its amount depends on initial portion of polymer formed during irradiation at 77 K: the more initial polymer fraction the less post-polymerization fraction.

Thus, under photo- or gamma-irradiation of DEB crystals at 77 K, the chain-type polymerization occurs with kinetic length around 20, which is an order of magnitude
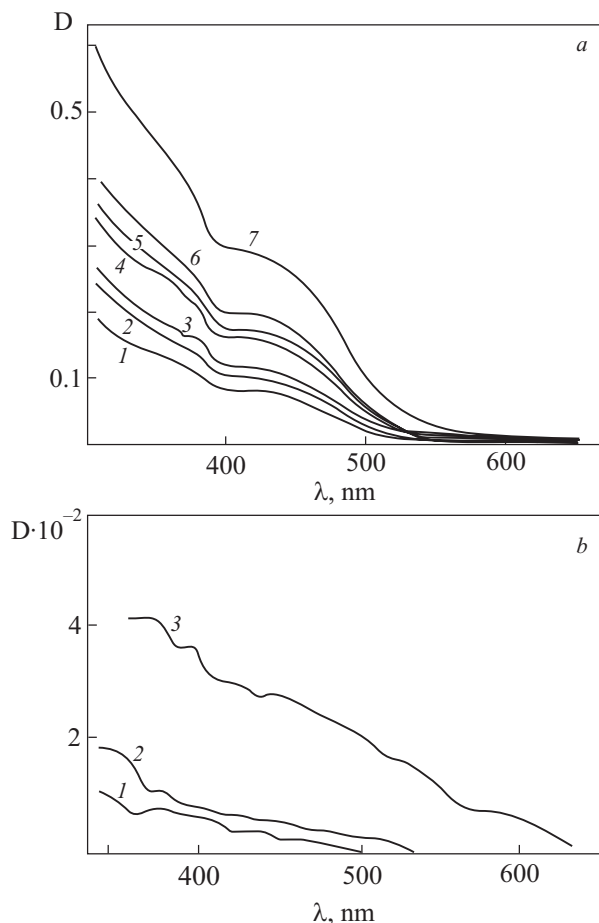
Fig. 6. a — Absorption spectra of DEB crystal (*L* = 2 μm) irradiated by light (λ = 230–340 nm, $I_0 = 6 \cdot 10^{16}$ quant/cm²·s) at 77 K. Time (min): 2 (*1*); 2.5 (*2*); 4 (*3*); 6 (*4*); 8 (*5*); 10 (*6*); 40 (*7*). *b* — Absorption spectra changes at heating of the irradiated at 77 K DEB crystal: absorption spectrum of DEB crystal irradiated at 77 K by light with λ = 230–340 nm, $I_0 = 6 \cdot 10^{16}$ quant/cm²·s (curve *1*); an increase of *D* after heating (2.5 grad/min) of this sample up to 230 (*2*) and 300 (*3*) K. Spectra were recorded at 77 K.

less than that for polymerization at 300 K. It is interesting to note that the critical concentration has appeared to be the same as for polymerization at 300 K. It means that polymer chains interlock each other just geometrically and the temperature governs kinetic length of chain, in other words, the rate of critical concentration approach.

In case of polymerization at 4.2 K, all observations were carried out only qualitatively. It has appeared that with ratio like that at 77 K, photo- and gamma-irradiation lead to red shift responsible for polymer formation. Poly-

mer formed thus shows a dichroism. Post-polymerization process takes place during heating of the samples and polymer obtained in such a way has the same absorption spectra as polymer formed at higher temperatures.

To resolve if the chain process makes a contribution to polymerization at 4.2 K, one should carry out further experiments. Anyway the mechanism of monomer molecules addition to polymer ones (even in succession) at temperatures, at which the processes with activation energy of 0.1 kcal/mol cannot be performed, is of great interest.

Conclusion

1. It was shown that the kinetics of polymer accumulation is in a good agreement with the phenomenological model

$$D = 0.43 D_0 \ln\left(1 + \frac{t}{\tau}\right).$$

2. Polymer absorption efficiency, polymerization quantum yield, and critical polymer concentration, beginning with which the effect of «kinetic stop» has appeared, have been determined.

3. The polymerization kinetic chain length (ν) was determined at low conversions by comparison of polymerization quantum or radiation yields with yields of free radicals initiating polymerization process. It is shown that for γ- or UV irradiation (in the range of monomer-own absorption) the values of ν are equal to 200 at 300 K and 20 at 77 K.

4. Nonchain (ν = 1) polymerization takes place in the course of light absorption by polymer formed.

The most plausible hypothesis is that the polymerization at 4.2 K (contrary to that at 300 or 77 K) is nonchain (ν = 1) and, for polymerization, every act of monomer addition to polymer needs extra quantum of light.

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