

## Effect of Nucleating Agents upon the Kinetics of Poly(ethylene Terephthalate) Crystallization

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### Synopsis

Experiments have been conducted to examine the effect of the following agents:  $\text{TiO}_2$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{BaSO}_4$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$  as modifiers on the poly(ethylene terephthalate) crystallization kinetics. Modifier concentration in the polymer varied from 0.5% to 3%. Crystallization rate measurements at a temperature of  $237^\circ\text{C}$  were performed by dilatometric method and measurements of spherulitic growth rate, by microscopic method. It has been stated that the addition of a modifier affects the crystallization rate, dimension, and homogeneity of spherulitic sizes. The spherulitic growth rate, with the exception of that modified by  $\text{CaO}$ , does not depend on the kind and the concentration of a modifier. Heterogeneous nucleating agents exert an effect, then, mainly on the heterogeneous nucleation process. In the presence of the agents, the nucleation in the poly(ethylene terephthalate) is of athermal character. The kind of a modifier applied exerts also an effect on the final crystallization degree.

### INTRODUCTION

The kinetics of poly(ethylene terephthalate) (PET) isothermal crystallization has been the research subject conducted by many authors.<sup>1-9</sup> Various experimental methods have been adapted to this end. These works have contributed to a great extent to the elucidation of the characteristic regularities of this phenomenon and also to the assignation of its mathematical description.

The course of the crystallization process depends on many physicochemical parameters. Recently, the research work of the effect of nucleating agents upon poly(ethylene terephthalate) crystallization process has acquired a great meaning. The agents influence the rate of the crystallization process, its morphology, the spherulite size and its distribution and so the physical properties of final product. This problem is related to the problem of polymers properties modification by physical methods.<sup>10</sup> A number of patent suggestions have been offered<sup>11</sup> to add different substances as nucleating agents to PET in order to improve its applied or processing properties. The results published so far<sup>12-14</sup> have not yet brought the elucidation of the mechanism of the effect of nucleating agents on the PET crystallization process. They indicate an urgent need of systematic research to be undertaken on this

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problem. The effect of some nucleating agents on the PET crystallization kinetics at a temperature of 237°C is reported in this work.

## EXPERIMENTAL

The following substances were selected as modifiers: titanium dioxide,  $\text{TiO}_2$ ; silicon dioxide,  $\text{SiO}_2$ ; aluminum oxide,  $\text{Al}_2\text{O}_3$ ; barium sulfate,  $\text{BaSO}_4$ ; calcium oxide,  $\text{CaO}$ ; and magnesium oxide,  $\text{MgO}$ . They were applied in powder form. These substances were chosen mainly because in the patent literature they are generally suggested as agents for PET. Some of them,  $\text{TiO}_2$ , for instance, are applied in industry as agents for mat. The research object was poly(ethylene terephthalate) produced by "ELANA" at Toruń in Poland, free from  $\text{TiO}_2$ . After preliminary purification of the polymer, the dried powder of PET was extracted by dioxane in a Soxhlet apparatus during 30 hr according to the method described in the literature.<sup>15,16</sup> After the extraction, the polymer was dissolved in a mixture of phenol-tetrachloroethane (1:1) and next precipitated by ethanol. The purpose of the extraction was to remove oligomers.<sup>15,16</sup>

PET samples containing specified percentage of the agents were prepared in the following way: purified PET was dissolved in the phenol-tetrachloroethane mixture (1:1). Gradually, a weighed amount of the agent was added to the solution without interruption of stirring. Next, the polymer was precipitated by ethanol and filtered by G-4. The samples to be studied (0.2 g) were molten at 280°C under vacuum of  $10^{-4}$ – $10^{-5}$  mm Hg and next placed in the dilatometer.

Dilatometric measurements were carried out according to the method described by Gordon and Hillier.<sup>17</sup> After degasification of the dilatometer, the given sample was submerged in mercury, Hg. Before remelting from the vacuum, free space over the Hg was filled with nitrogen at atmospheric pressure. Crystallization kinetics was carried out in an ultrathermostat filled with silicon oil. The temperature stability was maintained with an accuracy of  $\pm 0.05^\circ\text{C}$ . Before crystallization, the samples were molten in another ultrathermostat at a temperature of  $300^\circ \pm 1^\circ\text{C}$ . The change of the mercury column level in the dilatometer capillary was read on a cathetometer with an accuracy of  $\pm 0.01$  mm. Crystallization kinetics was measured at 237°C, because it is at this temperature that the time of induction is longer than that needed to even temperatures of dilatometer inside and thermostating liquid. Independently of crystallization kinetics research, spherulitic growth rate measurements in thin foils by microscopic method were performed for all PET samples. Crystallization temperature as well as melting conditions were identical as for dilatometer measurements.

Roentgenographic measurements were performed on an x-ray diffractometer of the DRON-1 type produced in the USSR, at an accelerating voltage of 35 kV, anode current intensity 16 mA, scintillation meter count range 500 imp/sec, time constant 4 meter, and angular velocity  $2^\circ/\text{min}$ . The preparations for roentgenographic measurements were prepared in the form of samples containing 0.2 g of the powder examined, placed in special developing dishes made of poly(methylmethacrylate). All the measurements were performed under equal conditions. Crystallinity indicator informing of rela-

tive change of crystalline phase content in the sample volume was found from the ratio of total surface pointing out the maximum value of the field between the diffractometer curve for the sample examined and the one for the model amorphous sample to the value of the same remaining sample surfaces. The samples for the roentgenographic measurements were crystallized during 5 hr.

### RESULTS AND DISCUSSION

Measurements were performed for the PET samples containing the nucleating agents the concentration of which changed from 0.2% to 3%. Figures

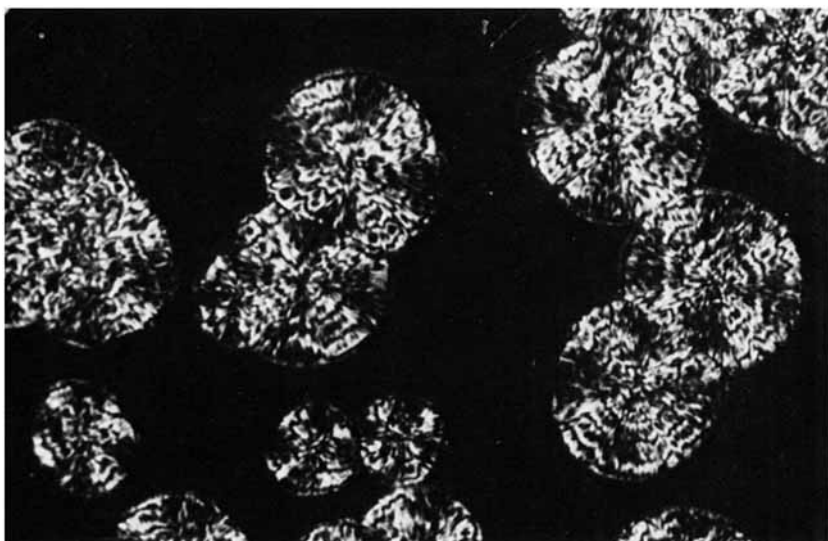


Fig. 1. Microphotography from polarizing microscope of spherulites taken for purified PET. Magnification 400X.

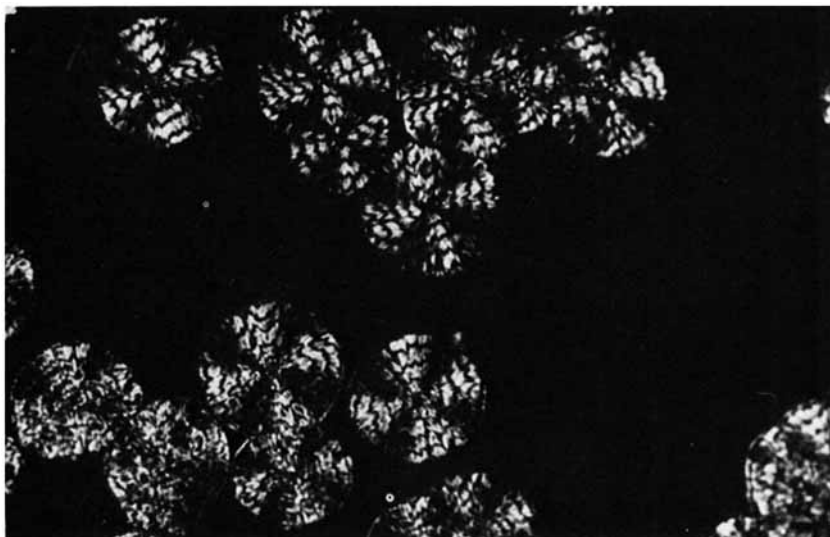


Fig. 2. Microphotography of spherulites in PET samples with 1.0% calcium oxide, CaO.

1 and 2 respectively show microphotographs from a polarizing microscope of the PET spherulites in the initial sample (without the agents) and those containing the modifier. Spherulitic growth rate by microscopic method was measured for all the dilatometrically measured PET samples. Table I shows

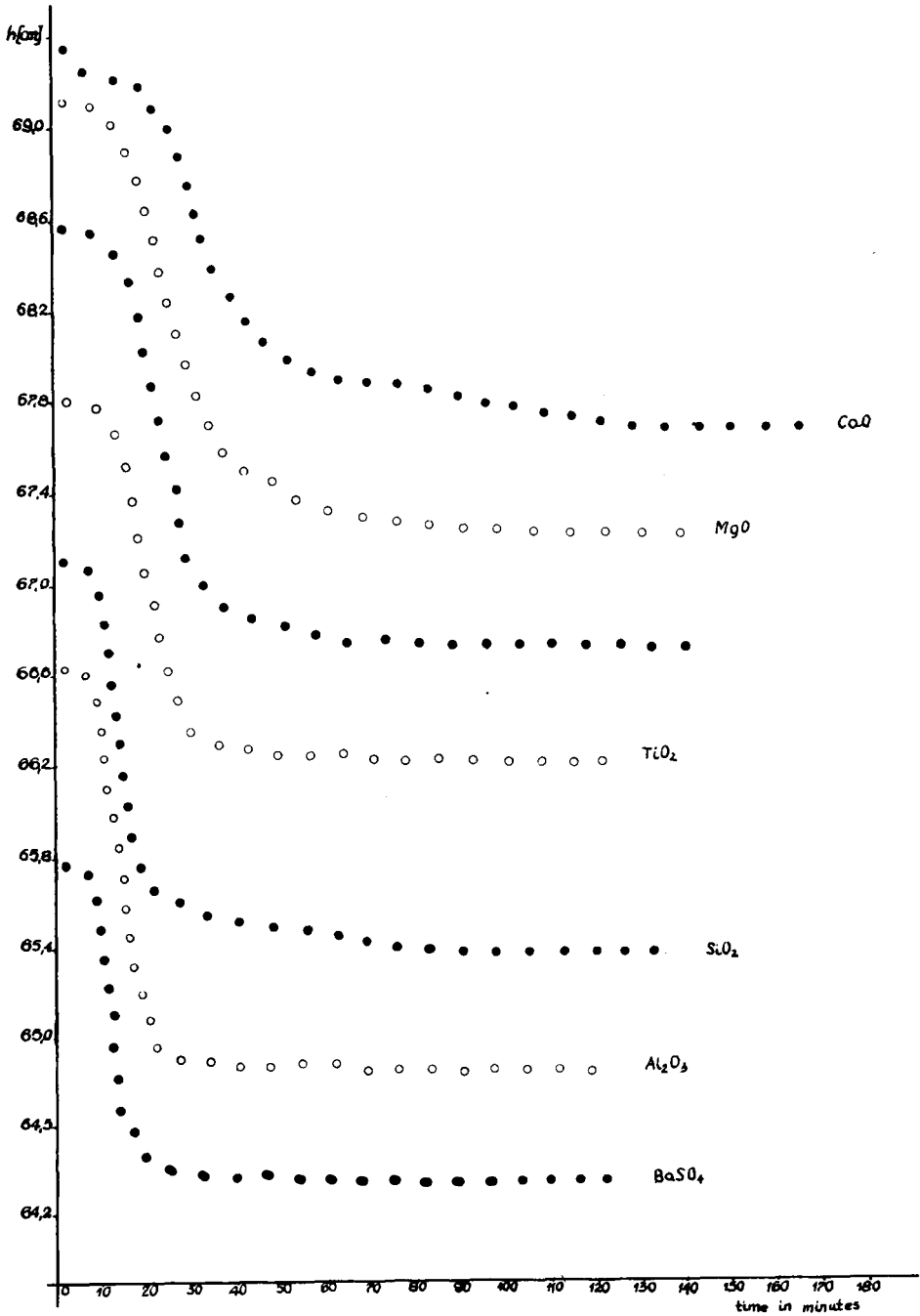


Fig. 3. Dilatometric curves for PET samples with 1.0% different nucleating agents. Crystallization temperature, 237°C. Curve 3, purified PET.

the results of these measurements. The dilatometric curves obtained for the samples containing the agents of different content are shown in Figures 3-5. Dilatometric curves are similar for the PET with the remaining agents. Figure 6 shows an example of the diffractograms from which a crystallization de-

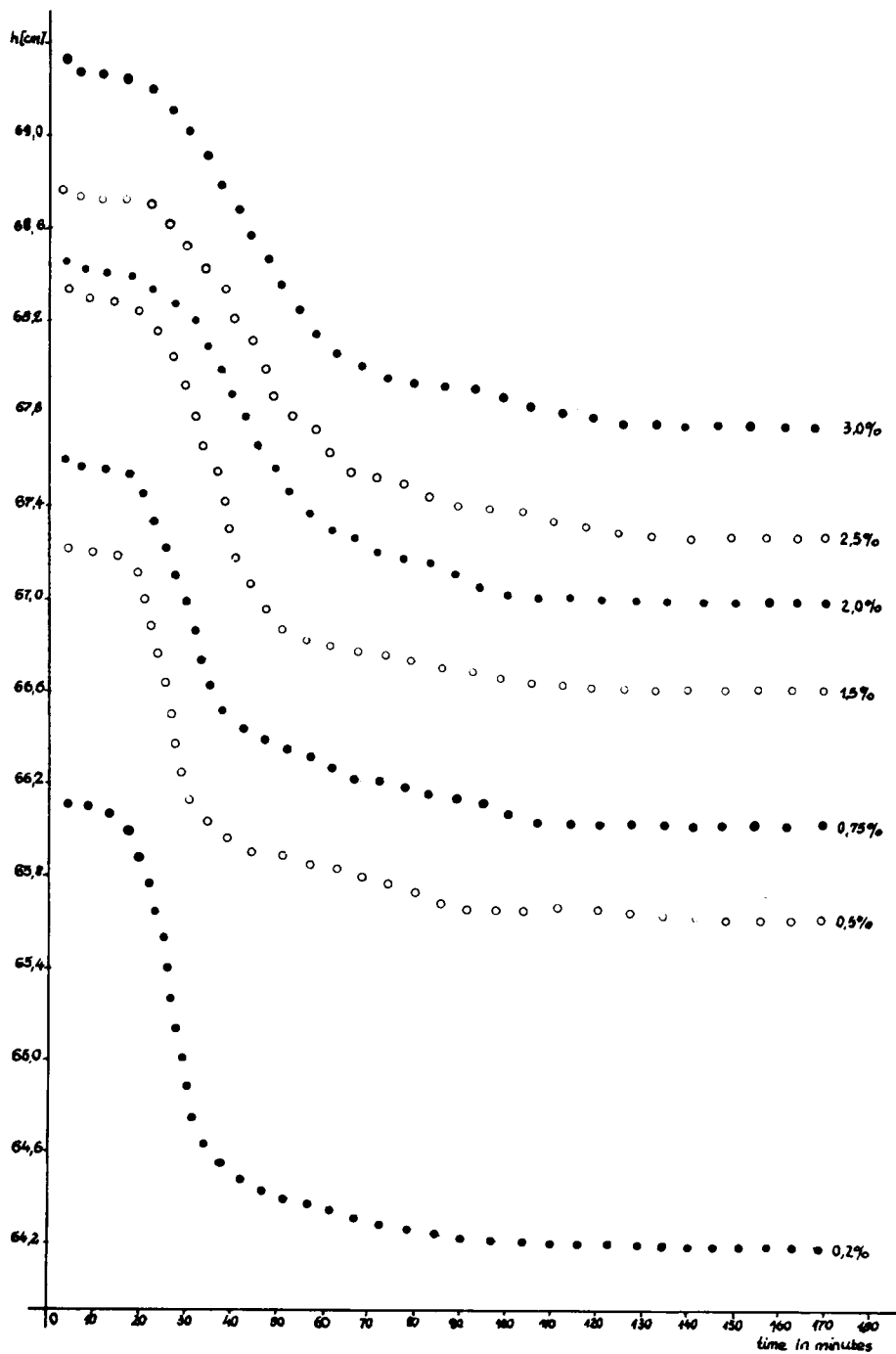


Fig. 4. Dilatometric curves for PET samples with various concentrations of silicon oxide, SiO<sub>2</sub>.

gree was calculated. Table II shows the numerical value of crystallization half-time calculated from kinetic measurements. The measurements of particle dimension in the agents were performed on a projection microscope. The results of these are collected in Table III. The agent  $\text{BaSO}_4$  contains particles smaller than  $1 \mu\text{m}$ . Within microscope shot, they constituted an average

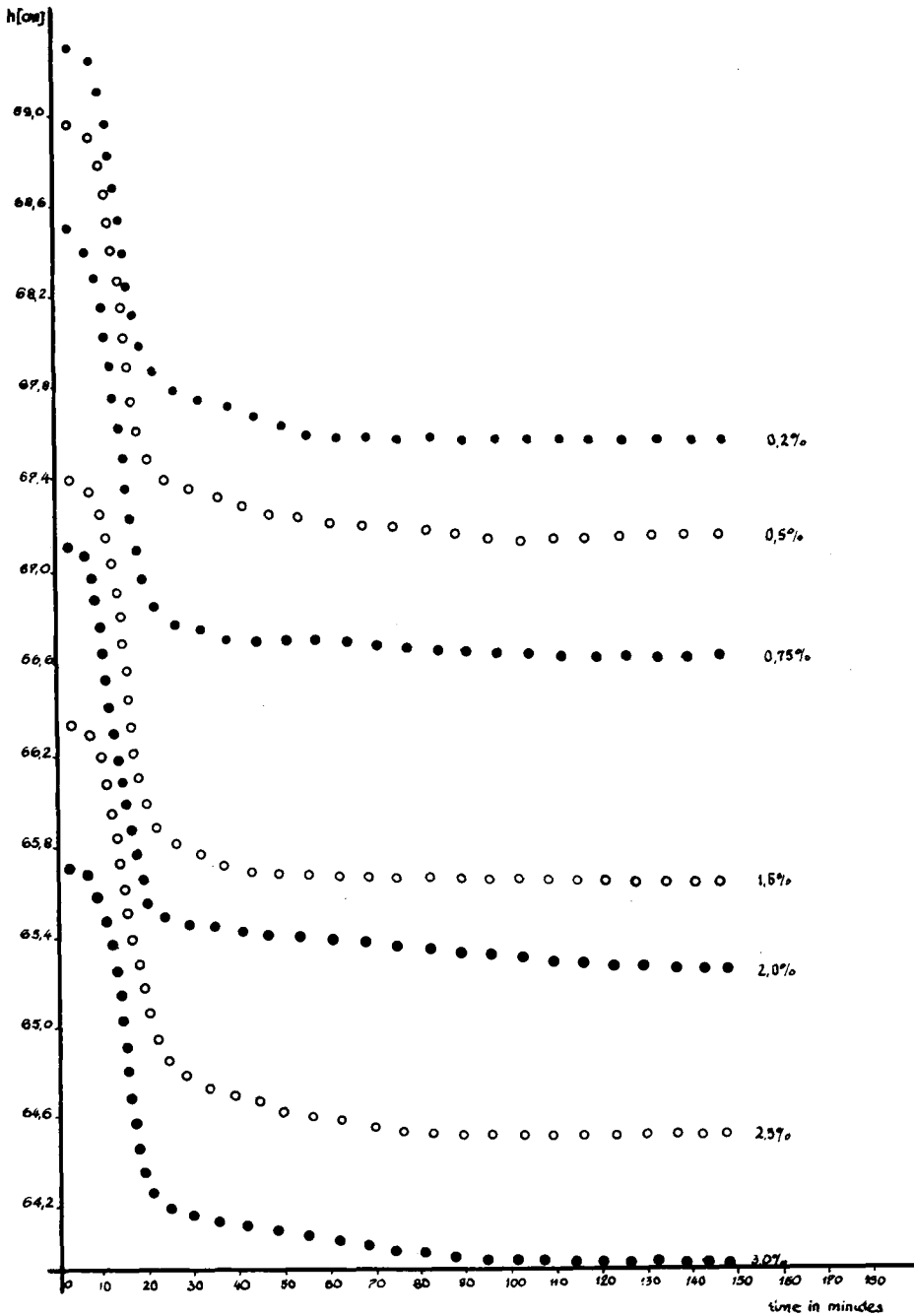


Fig. 5. Dilatometric curves for PET samples with various concentrations of calcium oxide,  $\text{CaO}$ .

TABLE I  
Results of Measurements of Spherulitic Growth Rate in PET Samples Containing Nucleating Agents (2G in  $\mu\text{m}/\text{min}$ )

Concentration of solid admixtures in sample, %	Particle fraction $n/\Sigma n^a$						Purified PET
	CaO	TiO <sub>2</sub>	MgO	BaSO <sub>4</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	
0.2	2.7 ± 0.6	3.4 ± 0.4	2.9 ± 0.5	4.1 ± 0.5	4.3 ± 0.5	4.2 ± 0.4	—
0.5	2.8 ± 0.6	4.0 ± 0.4	3.6 ± 0.5	3.6 ± 0.5	3.0 ± 0.5	3.7 ± 0.4	—
0.75	2.6 ± 0.6	3.7 ± 0.4	3.9 ± 0.5	4.0 ± 0.5	3.7 ± 0.5	4.1 ± 0.4	—
1.0	2.3 ± 0.6	4.2 ± 0.4	3.8 ± 0.5	4.2 ± 0.5	3.7 ± 0.5	4.0 ± 0.4	—
1.5	2.1 ± 0.6	4.2 ± 0.4	4.4 ± 0.5	4.2 ± 0.5	3.6 ± 0.5	4.2 ± 0.4	—
2.0	2.1 ± 0.6	4.3 ± 0.4	3.2 ± 0.5	3.5 ± 0.5	3.7 ± 0.5	4.2 ± 0.4	—
2.5	1.9 ± 0.6	4.1 ± 0.4	4.0 ± 0.5	3.7 ± 0.5	4.1 ± 0.5	3.6 ± 0.4	—
3.0	2.0 ± 0.6	3.7 ± 0.4	4.1 ± 0.5	3.5 ± 0.5	3.3 ± 0.5	3.8 ± 0.4	—
—	—	—	—	—	—	—	3.9 ± 0.3

TABLE II  
Half-time of Crystallization  $t_{1/2}$  (in min)

Concentration of nucleating agents in sample, %	Particle fraction $n/\Sigma n^a$						Purified PET
	CaO	TiO <sub>2</sub>	MgO	BaSO <sub>4</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	
0.2	18	19 <sup>30</sup>	20 <sup>30</sup>	17	9 <sup>45</sup>	12 <sup>45</sup>	—
0.5	18	17 <sup>30</sup>	20 <sup>15</sup>	11 <sup>45</sup>	10 <sup>15</sup>	11 <sup>15</sup>	—
0.75	22	16 <sup>45</sup>	17 <sup>30</sup>	11 <sup>30</sup>	10	9 <sup>45</sup>	—
1.0	25 <sup>30</sup>	16	20	9 <sup>45</sup>	10 <sup>15</sup>	9 <sup>30</sup>	—
1.5	27	16 <sup>45</sup>	21	10 <sup>45</sup>	10 <sup>45</sup>	9 <sup>45</sup>	—
2.0	36	16	20 <sup>30</sup>	8 <sup>15</sup>	9 <sup>45</sup>	12 <sup>45</sup>	—
2.5	36	15 <sup>30</sup>	20 <sup>45</sup>	6 <sup>15</sup>	10 <sup>30</sup>	13 <sup>45</sup>	—
3.0	35	15 <sup>30</sup>	22	6 <sup>15</sup>	10 <sup>45</sup>	13 <sup>45</sup>	—
—	—	—	—	—	—	—	19

TABLE III  
Distribution of Particle Size Solid Admixtures

Particle size, $\mu\text{m}$	Particle fraction $n/\Sigma n^a$				
	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	CaO	SiO <sub>2</sub>
do 4	0.375	0.380	0.074	0.348	0.416
4-8	0.253	0.252	0.125	0.252	0.275
8-12	0.123	0.131	0.165	0.135	0.121
12-16	0.071	0.090	0.151	0.087	0.053
16-20	0.086	0.048	0.171	0.039	0.027
20-24	0.034	0.025	0.116	0.025	0.027
24-28	0.030	0.025	0.060	0.025	0.018
28-32	0.011	0.016	0.048	0.016	0.018
32-36	0.008	0.010	0.037	0.018	0.009
36-40	0.012 <sup>b</sup>	0.027 <sup>b</sup>	0.014	0.046 <sup>b</sup>	0.034 <sup>b</sup>
40-44			0.014		
44-48			0.08		
above 48			0.015		

<sup>a</sup>  $n$  = Number of particles in particular range of dimensions;  $\Sigma n$  = total number of particles.

<sup>b</sup> The fraction of particles of dimensions greater than 36  $\mu\text{m}$ .

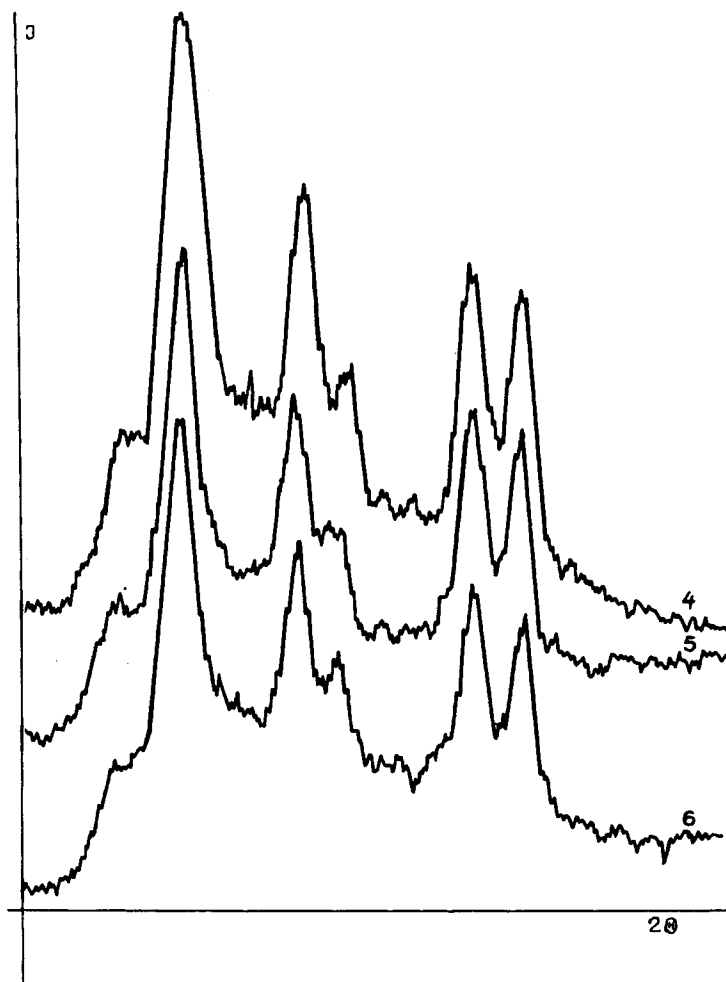


Fig. 6. Wide-angle x-ray diffraction curves for PET samples with 1.0% different nucleating agents: (4) CaO; (5) purified PET; (6) SiO<sub>2</sub>. Intensity of x-ray radiation denoted on ordinate; Bragg's angle  $2\theta$ , on abscissa.

of 80%. The rest, that is 20%, was occupied by particle aggregates to  $45\ \mu\text{m}$  in size. About 70% of aggregates ranged  $18\text{--}25\ \mu\text{m}$  in size. Dilatometric results were worked out on the basis of the Avrami-Mandelkern crystallization kinetics theory.<sup>19-22</sup> The essence of this theory is contained in the following equation:

$$\theta = \frac{h - h_{\infty}}{h_0 - h_{\infty}} = \exp \{-k \cdot t^n\} \quad (1)$$

where  $\theta$  = content of amorphous phase in a sample at time  $t$ ;  $h_0$ ,  $h$ ,  $h_{\infty}$  = respectively mercury column levels in the dilatometer capillary at the time of induction, at time  $t$ , and after the completion of the crystallization process (that is, at time  $t = \infty$ );  $k$  = constant crystallization rate, directly proportional to crystal growth rate as well as to the nucleation rate; and  $n$  = exponent of time, the value dependent on the geometry of the growing crystals and also on a function describing dependence of nucleation rate on time. The experi-



TABLE IV  
Values of Avrami's Exponent  $n \pm 0.04$

Concentration of nucleating agents, %	CaO	TiO <sub>2</sub>	MgO	BaSO <sub>4</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Purified PET
0.2	3.05	3.24	3.18	3.37	3.06	3.25	
0.5	3.22	3.19	3.93	2.91	3.18	3.29	
0.75	3.24	2.99	3.33	2.88	2.90	3.21	
1.0	2.91	3.17	2.95	3.41	3.17	3.16	
1.5	2.69	3.17	3.16	2.83	3.23	2.90	
2.0	2.51	3.17	3.03	2.95	3.03	2.89	
2.5	2.69	3.05	2.95	3.21	2.99	3.15	
3.0	2.65	2.98	3.28	3.08	3.16	3.24	
—	—	—	—	—	—	—	3.41

mental results obtained, after indispensable calculations basing on eq. (1) were presented in the Avrami bilogarithmic system (Figs. 7-9).

The remaining experimental results present similar graphs in the Avrami system. Numerical values of the exponent of time  $n$  were calculated by the

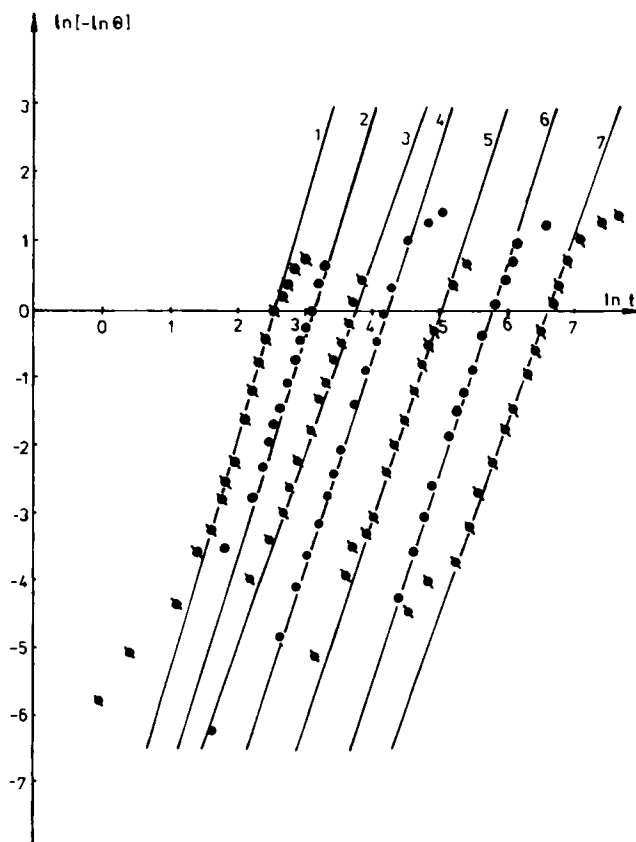


Fig. 7. Diagrams in Avrami coordinate system for PET samples with 1.0% different nucleating admixtures: (1) SiO<sub>2</sub>; (2) purified PET; (3) CaO; (4) TiO<sub>2</sub>; (5) MgO; (6) BaSO<sub>4</sub>; (7) Al<sub>2</sub>O<sub>3</sub>.

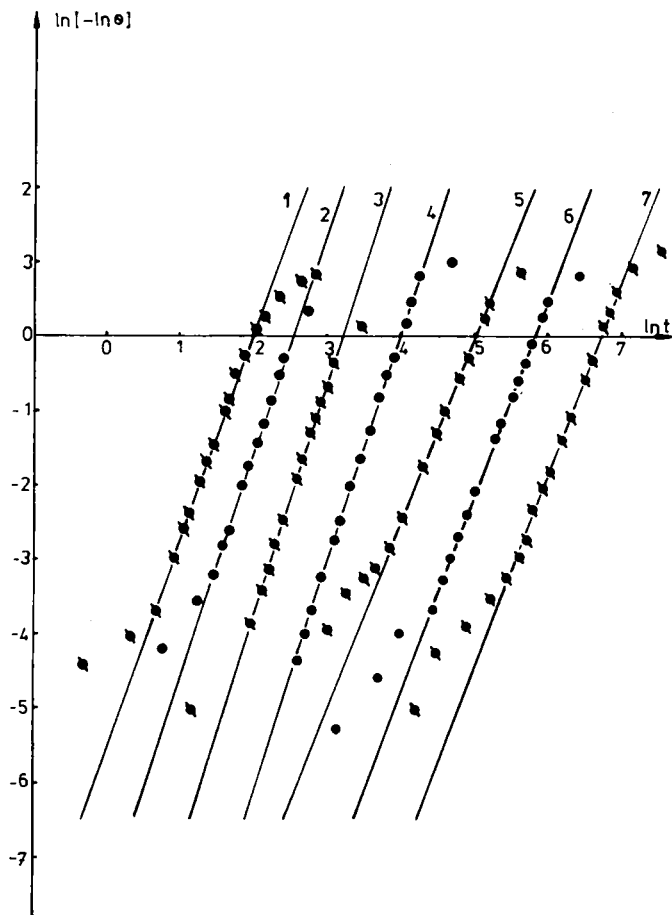


Fig. 8. Avrami plots for PET samples with various concentrations of CaO: (1) 0.2%; (2) 0.5%; (3) 0.75%; (4) 1.5%; (5) 2%; (6) 2.5%; (7) 3.0%.

least-squares method (Table IV). Constant crystallization rate  $k$  was calculated from the formula

$$k = \frac{\ln 2}{t_{1/2}^n} \quad (2)$$

where  $t_{1/2}$  = crystallization half-time. The following dependence among crystallization constant  $k$ , spherulitic growth rate, and the nucleation rate exists<sup>23</sup>

$$k = \frac{4}{3} \pi G^3 N \rho \quad (3)$$

where  $G$  = radial spherulitic growth rate;  $N$  = number of crystal nuclei originating in 1 cm<sup>3</sup> during 1 min; and  $\rho$  = polymer density. Table V exhibits numerical values of nucleation rate for the samples containing the agents. They were calculated from eq. (3).

The experiments and their analysis on the basis of Avrami theory indicate that the effect of nucleating agents on the course of the crystallization process

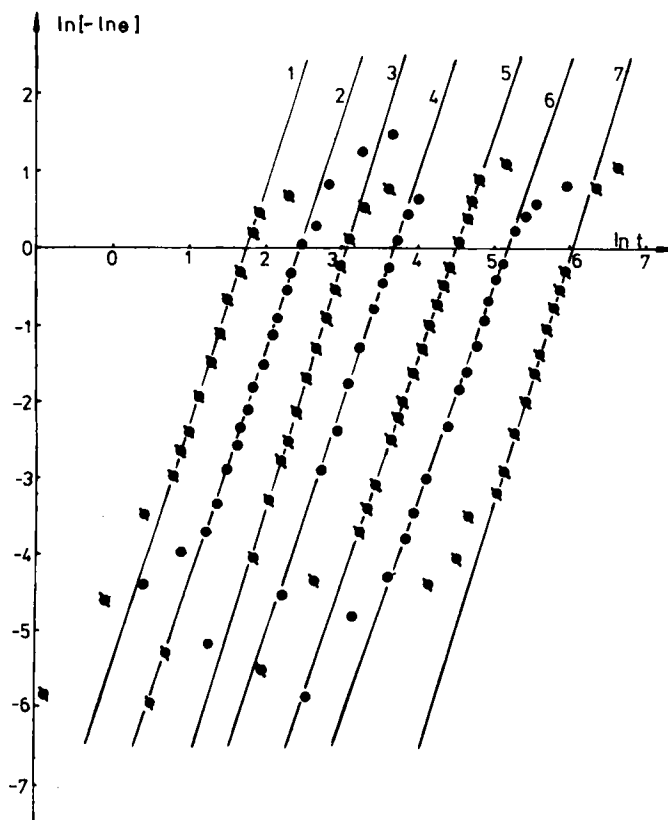


Fig. 9. Diagrams in Avrami coordinate system of dilatometric data obtained for PET samples with various concentrations of SiO<sub>2</sub>: (1) 0.2%; (2) 0.5%; (3) 0.75%; (4) 1.5%; (5) 2.0%; (6) 2.5%; (7) 3.0%.

varies considerably. Some modifiers, calcium oxide, CaO, for instance, cause the crystallization half-time to lengthen, which appears quite clearly especially with growth of percentage. Calcium oxide also affects spherulitic growth rate causing it to decrease (Table I). PET samples with CaO also showed clearly longer induction times (about 10 min). So crystallization rate and spherulitic growth rate in the PET with the CaO modifier are reduced. This effect can be caused by molecular processes rate reduction, for instance, be-

TABLE V  
Values of Nucleation Rate *N* (Number of Nuclei Developing in 1 cm<sup>3</sup> During 1 min)

Concentration of nucleating agents, %	CaO	TiO <sub>2</sub>	MgO	BaSO <sub>4</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Purified PET
0.2	9.2 × 10 <sup>4</sup>	1.6 × 10 <sup>5</sup>	2.3 × 10 <sup>4</sup>	2.1 × 10 <sup>5</sup>	2.8 × 10 <sup>6</sup>	7.7 × 10 <sup>5</sup>	
0.5	6.3 × 10 <sup>5</sup>	2.1 × 10 <sup>5</sup>	5.0 × 10 <sup>5</sup>	2.6 × 10 <sup>6</sup>	2.0 × 10 <sup>6</sup>	1.0 × 10 <sup>6</sup>	
0.75	5.9 × 10 <sup>5</sup>	1.5 × 10 <sup>6</sup>	2.3 × 10 <sup>5</sup>	3.0 × 10 <sup>6</sup>	3.8 × 10 <sup>6</sup>	2.1 × 10 <sup>6</sup>	
1.0	8.4 × 10 <sup>5</sup>	3.8 × 10 <sup>5</sup>	4.2 × 10 <sup>5</sup>	1.2 × 10 <sup>6</sup>	2.1 × 10 <sup>6</sup>	2.5 × 10 <sup>6</sup>	
1.5	2.9 × 10 <sup>6</sup>	4.4 × 10 <sup>5</sup>	1.6 × 10 <sup>5</sup>	4.0 × 10 <sup>6</sup>	1.5 × 10 <sup>6</sup>	2.5 × 10 <sup>6</sup>	
2.0	2.3 × 10 <sup>6</sup>	4.0 × 10 <sup>5</sup>	3.2 × 10 <sup>5</sup>	6.8 × 10 <sup>6</sup>	3.0 × 10 <sup>6</sup>	2.1 × 10 <sup>6</sup>	
2.5	1.8 × 10 <sup>6</sup>	1.4 × 10 <sup>6</sup>	3.8 × 10 <sup>5</sup>	9.5 × 10 <sup>6</sup>	2.4 × 10 <sup>6</sup>	7.8 × 10 <sup>5</sup>	
3.0	1.7 × 10 <sup>6</sup>	1.6 × 10 <sup>6</sup>	1.3 × 10 <sup>5</sup>	1.1 × 10 <sup>7</sup>	1.8 × 10 <sup>6</sup>	7.8 × 10 <sup>5</sup>	
0.0	—	—	—	—	—	—	1.2 × 10 <sup>5</sup>

cause of viscosity growth. In the PET samples containing CaO, the number of crystal nuclei is greater than in the initial sample, and it is only to a small degree that it grows with percentage growth of the agent (Table V). In spite of spherulitic growth rate reduction, calcium oxide is an efficient catalyzer of nucleation, causing an increase in the number of crystal nuclei. Some agents affect PET crystallization to a minimal degree: so does magnesium oxide, MgO (Table II). However, the remaining agents hasten the PET crystallization process.

Spherulitic growth rate within the bounds of experimental error is in fact independent on the kind of agent and its percentage for PET samples containing different substances as agents (with the exception of MgO). This is shown in Table I. In Table V, calculations were made with  $G = 1.9 \mu\text{m}/\text{min}$ . On the basis of these measurements, it can be accepted that the particles of the agents affect PET nucleation process causing the growth of crystal nuclei. Table V supports this conclusion. Thus, it has been stated that  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{BaSO}_4$  quicken PET crystallization.

The time exponent  $n$  in the Avrami equation receives usually values of approximately 3. Systematic variation observed for the CaO is connected most probably with an earlier overlapping of the second crystallization occurrence on the primary crystallization process. Values calculated for  $n$  are mostly fractional. The results of the experiments on the spherulitic growth in a polarizing microscope suggest that also in samples crystallized in a dilatometer the main morphologic form of crystal growth are spherulites. Then, according to the accepted interpretation of the Avrami equation, values of the exponent  $n$  should be 3 or 4, according to the kind of nucleation. It has been proved<sup>24</sup> that nucleation in a poly(ethylene terephthalate) is complex and appears to be an overlapping of two processes: athermal nucleation and nucleation sporadic in time. This explains fractional values of  $n$  for the initial PET sample. Observations made in a polarizing microscope at the time of spherulitic growth rate measurements in PET samples containing nucleating agents showed that the nucleation sporadic in time is minimal. Nucleation in PET in the presence of the agents, then, is athermal. Fractional values for  $n$  can be caused by great local fluctuations in a distribution of particles of agents. It can be accepted, then, that numerical values for  $n$  approximate 3 (Table IV), and generally accepted interpretation points to three-dimensional crystal growth and athermal nucleation. This conclusion is in agreement with the results of observations in a polarizing microscope made on the PET films containing nucleating agents.

It has been stated that for some modifiers the number of crystal nuclei depends on their percentage in the PET only to a small degree. This phenomenon appears with MgO,  $\text{SiO}_2$ , CaO, and  $\text{Al}_2\text{O}_3$ . Experimental results point out, then, that not every particle of these agents added to the polymer as modifier exhibited properties hastening formation of crystal nuclei. This fact formed a base for a suggestion that not all the modifier particles take active part in the nucleation quickening. This effect can have essential connection with the nucleation mechanism. It can be a signal pointing out a fundamental role the surface structure of the particles plays in the nucleation process.<sup>25</sup> Such surface structure elements as grain boundaries, steps and folds of appropriate sizes, and also places of dislocation, and so on, are taken into

consideration here. Surface roughnesses of this kind can facilitate alignment of macromolecules segments on a surface of agent particle which in turn is conducive to formation of surface crystal nuclei. According to the nucleation phenomenological theory, surface roughnesses such as, for instance, steps or folds enlarge an interphase field between an agent particle and a polymer crystal, which in turn contributes to diminish free energy barrier for nucleation.

Compiled experimental material enables also to assume an attitude toward the role of crystallographic similarity in the nucleation occurrence.<sup>26,27</sup> Poly-(ethylene terephthalate) crystallizes in a triclinic system. Dimensions of its crystal cell have been pointed out.<sup>28</sup> The experiments conducted by Yamashita<sup>29</sup> on PET monocrystals received from dilute solutions prove that their morphology is very complicated. PET monocrystals appeared in the form of irregular lamellae. It has been shown by electron diffraction that chain axes were placed at angles of 25–35° to the normal to the base of the crystal lamella. Substances applied as modifiers crystallize in systems of high symmetry. Calcium and magnesium oxides form crystals of the NaCl type (regular system), SiO<sub>2</sub> crystallizes in a lattice of diamond type, and crystals of the remaining substances belong to the tetragonal system. The great difference in crystallographic lattice symmetry and their parameters values for the nucleating agent as well as for the PET and also complex morphology of crystals of this polymer do not give a proper base for expecting that crystallographic similarity would be fulfilled in the nucleation process.

According to this principle, a discrepancy parameter

$$\delta = \left| \frac{a_s - a_\beta}{a_\beta} \right|$$

[where  $a_s$ ,  $a_\beta$  = lattice distances of adjoining crystal faces respectively of the basis ( $s$ ) and of a crystallizing substance ( $\beta$ )] of crystallographic lattices of the basis and a substance crystallizing on it should be smaller than 0.15. A similar phenomenon of nucleation independence on parameter match degree of polymer crystallographic lattices and an agent substance has already been noted in scientific works.<sup>10</sup> Calcium and magnesium oxides, although both crystallize in a system of the NaCl type, exert a different effect on the PET crystallization rate. Most probably it is connected with interaction forces of crystal surface to which a thin layer of the polymer adheres. Comparing experimental material with the Turnbull nucleation theory,<sup>26,27</sup> it can be concluded that the formation of crystal nuclei on agent particles in the PET does not depend essentially on the polymer match degree of polymer crystallographic lattices and the modifier substance.

An important parameter affecting polymer applied properties is crystallization final degree. Numerical values of this parameter are shown in Table VI. Relative crystallization degree takes the highest value for the PET samples containing TiO<sub>2</sub> as the modifier, and it increases with increase of its content. However, for the remaining agents, it is little dependent on their content. It is smaller for the PET with BaSO<sub>4</sub> or MgO added than for the samples containing the remaining agents, and its value can be compared with that for the initial sample. The results given in Table VI are preliminary ones, and they serve as an argument to testify that the kind of modifier af-

TABLE VI  
Values of Relative Degree of Crystallinity Measured by X-Ray Diffraction Method

Concentration of nucleating agents, %	CaO	TiO <sub>2</sub>	MgO	BaSO <sub>4</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Purified PET
0.2	0.748	0.751	0.555	0.575	0.785	0.744	—
0.5	0.764	0.767	0.501	0.544	0.800	0.662	—
0.75	0.619	0.787	0.574	0.528	0.842	0.751	—
1.0	0.813	0.796	0.587	0.533	0.794	0.768	—
1.5	0.728	0.767	0.612	0.650	0.691	0.616	—
2.0	0.752	0.822	0.575	0.663	0.775	0.717	—
2.5	0.785	1.00 <sup>a</sup>	0.585	0.582	0.705	0.801	—
3.0	0.813	0.910	0.670	0.646	0.775	0.830	—
—	—	—	—	—	—	—	0.592

<sup>a</sup> We assume that in this sample the degree of crystallinity is 1.00.

fects not only the crystallization process course but also final crystallization degree of PET. Similar effects have been observed for other polymers.<sup>10</sup>

## CONCLUSIONS

The conducted experiments support the proposition about an essential effect of modifiers on the crystallization process in the PET. A change of crystallization rate takes place in the presence of the agents. The modifiers affect also crystalline structure, spherulitic sizes and their dimension distribution, and the final degree of crystallization. Physical properties of a product can be affected by changes caused by a modification in the PET crystalline structure. Foreign substances exert an effect on the nucleation process causing a change in its rate. Some agents can also affect the spherulitic growth process. Modifier effect mechanism is connected with a complex phenomenon of the effect of molten and solidified polymer on the surface of particle agents. Particle surface structure ought to play an important role in this process. However, nucleation seems not to depend on the parameter match degree of polymer crystallographic lattices and a modifier. The explanation of a mechanism of modifier catalytic influence on nucleation requires further research. In PET in the presence of nucleation agents, the nucleation is of athermal character.

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