

# Crystals of Linear Oligophenyls: Surface Properties, Nucleation and Growth

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**Abstract:** Crystals of linear oligophenylys  $p$ - $n$ P ( $n$  is the number of phenyl groups) are of interest for organic electronics and photonics as effective blue emitters and scintillators. The surface properties and external conditions of the growth medium are the determining factors in the nucleation and formation of crystals. However, the crystallization processes of conjugated linear molecules are still understudied and there is practically no experimental data on the surface properties of solutions and crystals. At the same time, there are few studies in the literature on modeling the surface energy of the crystal faces of these substances [1].

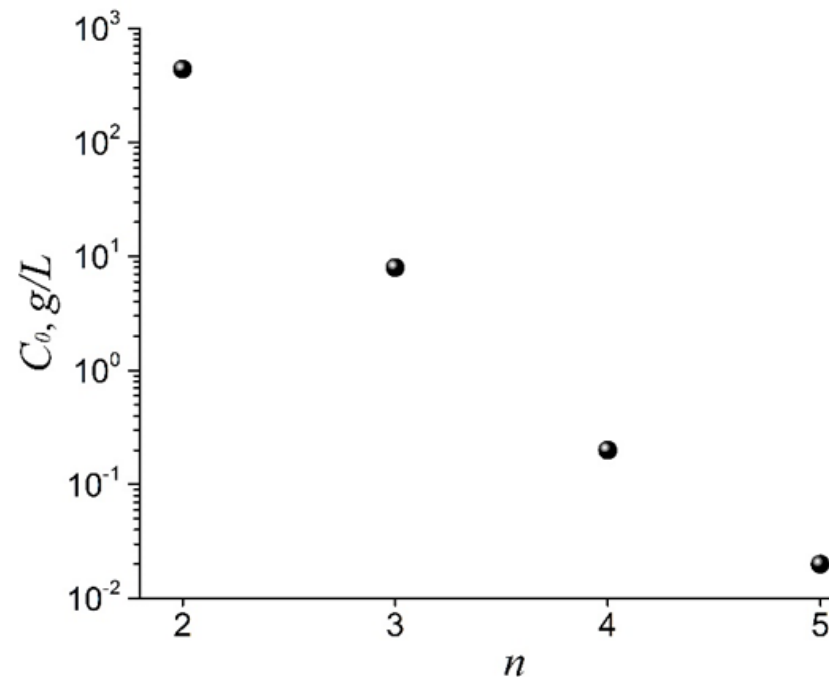
This work presents the results of studying of the linear oligophenylys ( $n = 2..6$ ) crystals growth from solutions and the vapor phase. In the approximation of the OPLS atomic force field method, the values of the surface energy of the (100), (010), (110), and (001) faces of the crystals are determined. Based on the data on the crystal structure and the obtained values of the surface energy of the faces, the morphology of the crystals is analyzed and their equilibrium shapes are predicted. Within the framework of the classical nucleation theory, the parameters of crystal nucleation under experimental conditions of growth from solutions and physical vapor transport are studied.

**Keywords:** linear oligophenylys, crystal structure, crystal growth, surface properties, crystal nucleation

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# Growth of linear oligophenyls crystals

To obtain relatively large single-crystal samples, the methods of crystal growth from solutions are most attractive from the point of view of simplicity and low cost. However, the significant decrease in solubility with an increase in the number  $n$  of  $\pi$ -conjugate units (phenyl rings) in the linear structure of an oligomer molecule (Fig.1) limits the applicability of this methods for growing large single crystalline films for long molecules ( $n \geq 4$ ).



**Figure 1.** Solubility in toluene (20°C) of nP depending on the conjugation number  $n$  [2].

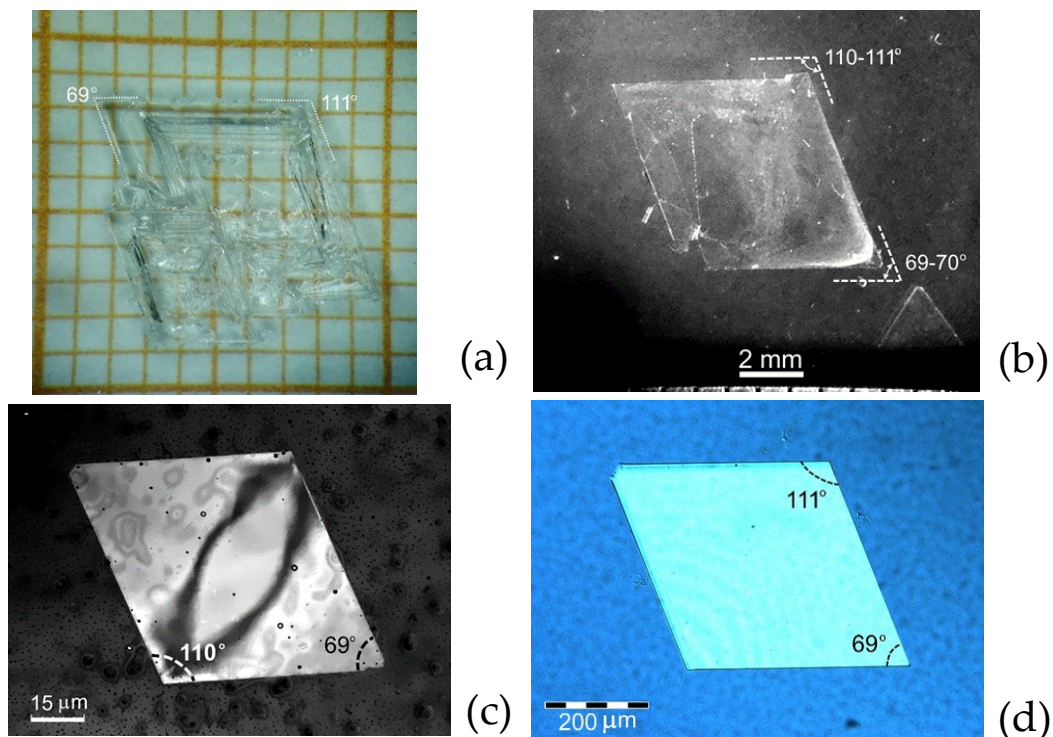
# Growth from Solutions

## Growth Methods [3-7]:

- 1) slow isothermal solvent evaporation,  $n=2\div 4$ , growth period – 7÷30 days;
- 2) “solvent-precipitant” method,  $n=2\div 4$ , growth period – 3÷8 days;
- 3) Slow isochoric hot solvent cooling,  $n\geq 3$ , growth period – 20÷30 days;

Solvents: alcohols (2P); n-hexane, acetone (3P); benzene, toluene, xylene, chlorobenzene ( $n\geq 3$ ).

Precipitants (solvatophobic solvents): Water (2P), alcohols ( $n=3\div 4$ ).



**Figure 2.** Solutions grown crystals of linear oligophenyls: 2P (a), 3P (b), 4P (c) and 5P (d).

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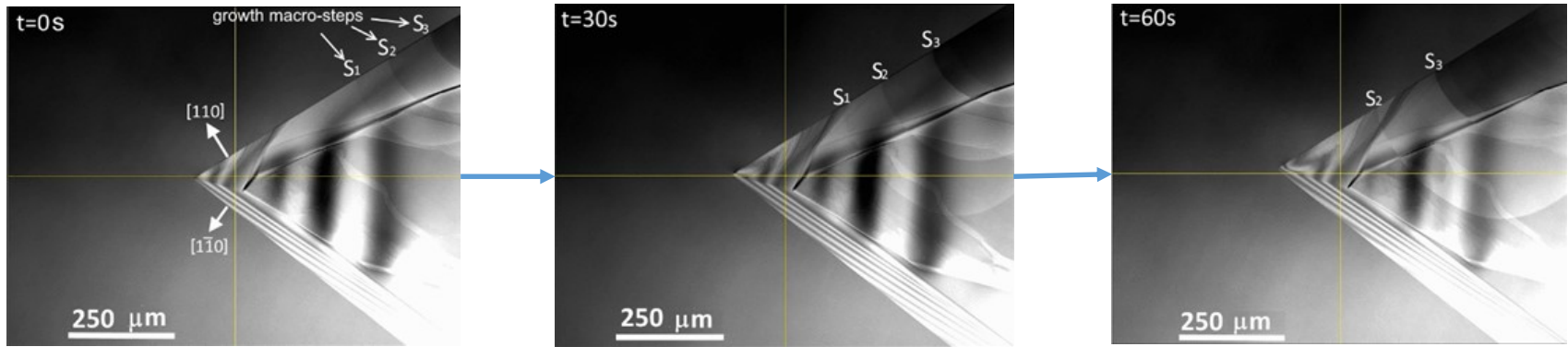
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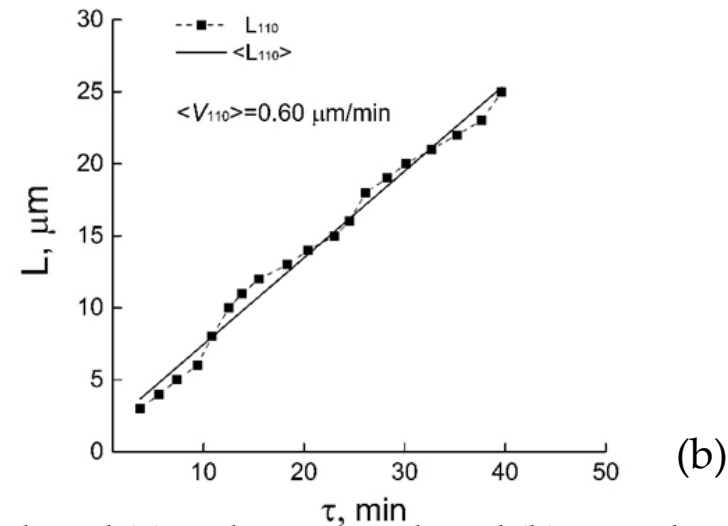
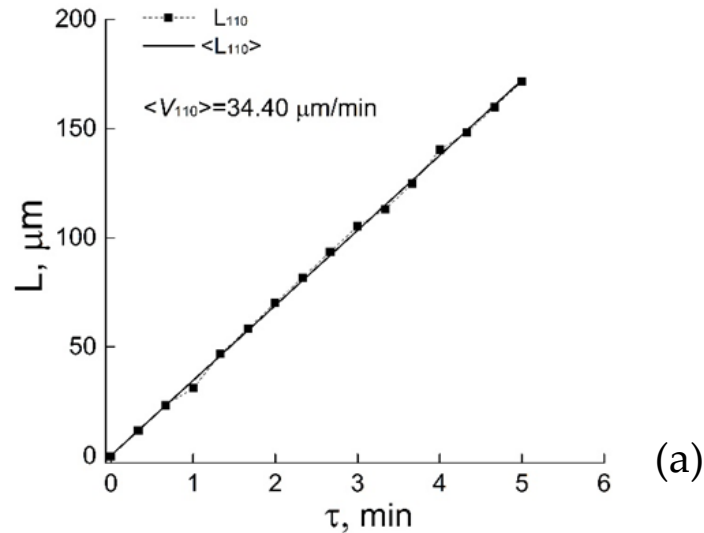
[7] Postnikov, V.A.; Sorokina, N.I.; Lyasnikova, M.S. et. al. *Crystals* **2020**, 10, 363.

# In situ Study of Crystal Growth Kinetics



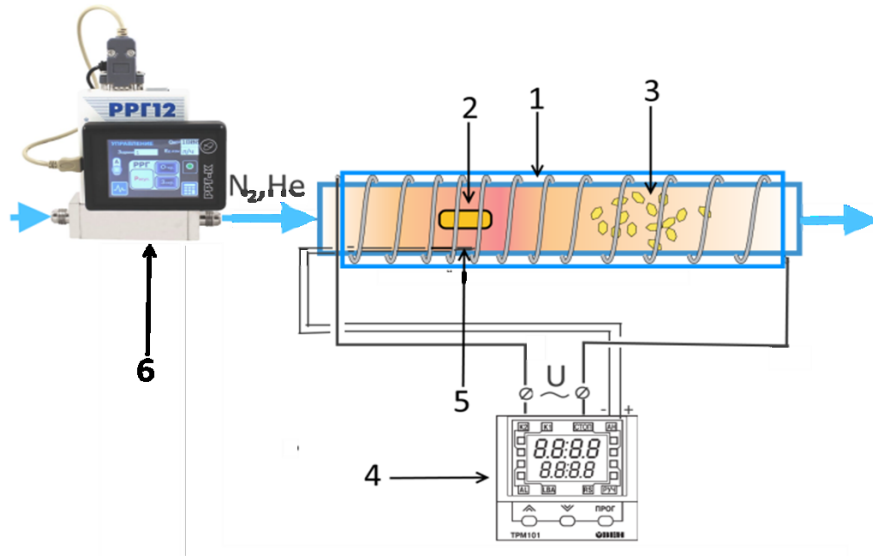
**Figure 3.** Storyboarded confocal images of growth kinetics of faces (110) and macro-steps on the surface of the face p-terphenyl crystal (001) in a drying drop of chlorobenzene solution on a glass substrate (298 K).

$\langle V_S \rangle = 340 \text{ } \mu\text{m}/\text{min}$  - average velocity of growth macro-steps  $S_i$  of over the surface of the (001) face of a 3P crystal (Fig.3)

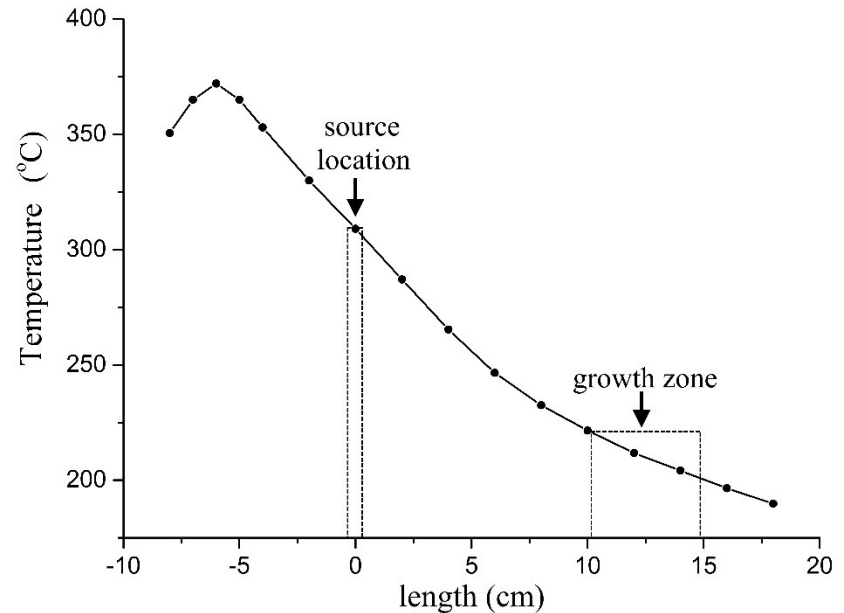


**Figure 4.** Kinetics of growth of the face (110) of a p-terphenyl (a) and p-quaterphenyl (b) crystals from a drop of a chlorobenzene solution under the same normal conditions.

# Crystal Growth with Physical Vapor Transport (PVT) Method

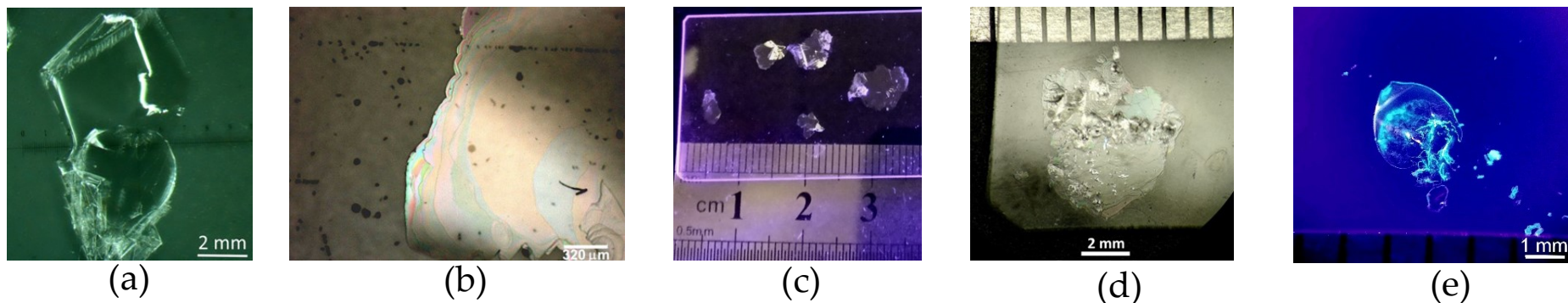


**Figure 5.** PVT growth setup scheme with a gradient temperature field: 1 - quartz growth furnace, 2 - source of organic material, 3 - crystal growth zone, 4 - temperature controller, 5 - temperature sensor, 6 - controller - inert gas flow meter.



**Figure 6.** Temperature profile inside the quartz growth tube with the specified positions of the substance source and the p-quinquephenyl crystals growth zone [7].

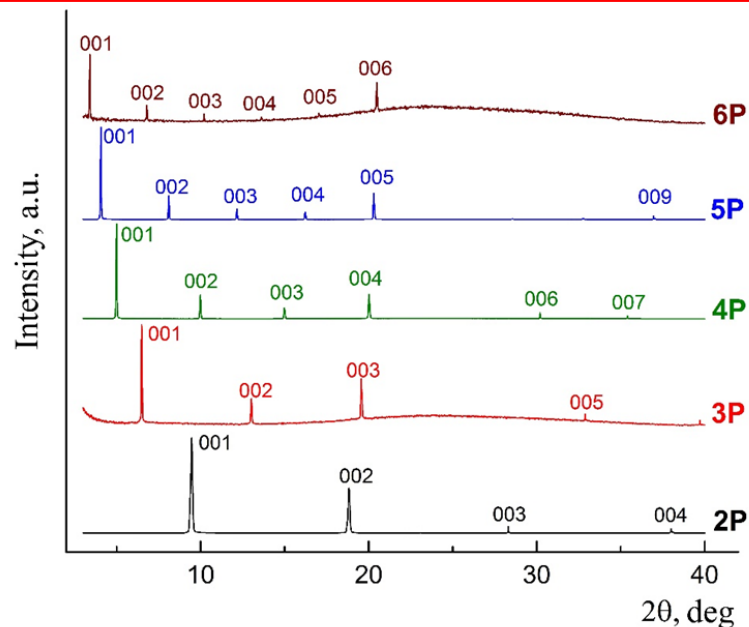
# Crystal Growth with PVT Method



**Figure 7.** Vapor grown single crystalline films of nP: 2P (a), edge fragment of a 3P crystal in reflected light (b), 4P (c), 5P (d), 6P under UV light (e).

**Table 1.** Growth parameters of linear oligophenyls crystals under PVT conditions.

nP	Formula	$T_0$ , K	$\tau$ , hour	$L_m$ , mm	$H_m$ , μm	$V_L$ , μm/ hour
2P	$C_{12}H_{10}$	318	48	22	205	458
3P	$C_{18}H_{14}$	438	22	18	43	818
4P	$C_{24}H_{18}$	523	48	18	83	375
5P	$C_{30}H_{22}$	583	64	8	1.4	125
6P	$C_{36}H_{26}$	618	3	18	21	



**Figure 8.** X-Ray diffraction patterns of vapor-grown single crystalline films of nP.

\*Note:  $T_0$  - source temperature,  $\tau$  - growth period,  $L_m$  and  $H_m$  - maximum length and thickness of crystalline films, respectively,  $V_L$  - average growth rate of crystals in length.

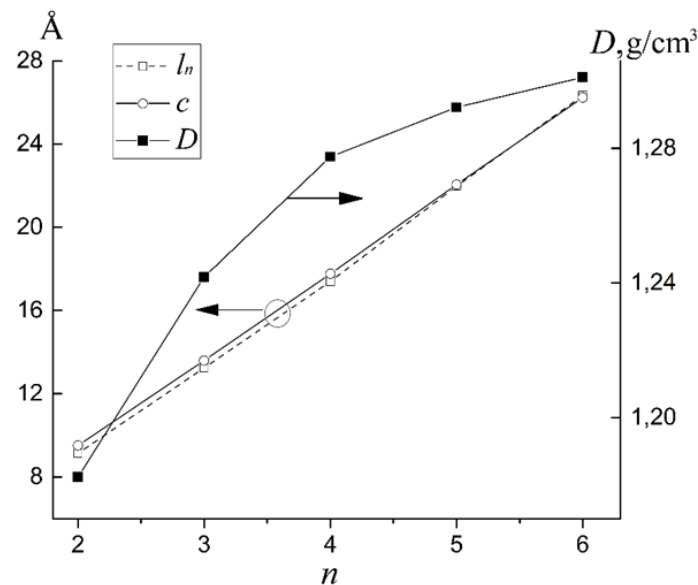
# Crystal Structure of Linear Oligophenylys

For the initial members of the homologous series of linear oligophenylys, there is a similarity in the crystal structure.

**Table 2.** Crystal structure parameters of nP at 295 K [4-8].

nP	Sym.	a, Å	b, Å	c, Å	$\beta$ , deg	Z	$V_0$ , Å <sup>3</sup>	$d_{001}$ , Å	$l_n$ , Å
2P	P 2 <sub>1</sub> /a	8.12(2)	5.63(1)	9.51(2)	95.1(3)	2	433.0	9.34	9.14
3P	P 2 <sub>1</sub> /a	8.089	5.603	13.592	91.973	2	615.7	13.63	13.24
4P	P 2 <sub>1</sub> /a	8.071	5.580	17.770	95.73	2	796.3	17.74	17.40
5P	P 2 <sub>1</sub> /a	8.070	5.581	22.056	97.91(1)	2	983.5	21.88	21.98
6P	P 2 <sub>1</sub> /a	8.091	5.568	26.241	98.17(2)	2	1170.2	25.98	26.33

\*Note:  $V_0$  - unit cell volume;  $d_{001}$  - interplanar distance in [001] direction (monolayer thickness);  $l_n$  - calculated molecule length.

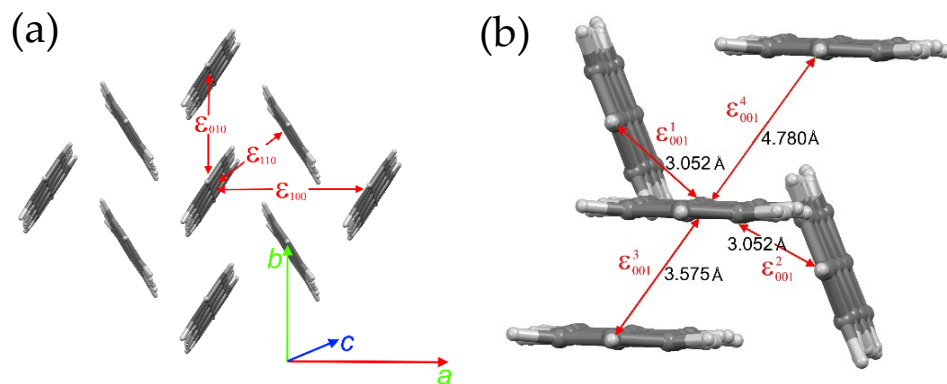


**Figure 9.** Graphs of the change in molecule length  $l_n$ , c parameter of the unit cell (left axis) and the x-ray density of crystals (right axis) of nP at 295 K depending on the number n of phenyl groups.



# Modeling the Surface Energy of Crystals

The surface energy of faces of the nP crystals was calculated with OPLS atomic force field method [9]. In the calculations, X-ray diffraction structural data [4-8] on the relative positions of molecules in the crystal, as well as on the position of atoms in the molecule, were used and parallel molecular bilayers that lie in either of the main crystallographic planes ((001), (010), (110), (100) ) containing several tens of molecules were constructed on their basis. The total van der Waals energy of the  $U_{hkl}$  oriented bilayer was determined. Then, the energy of identical monolayers constituting the  $U_{1hkl}$  bilayer was calculated in a similar fashion. The binding energy of the bilayers is  $\Delta U_{hkl} = U_{hkl} - 2U_{1hkl}$ . It is assumed in the model that the positively determined cohesion energy is  $\Delta U_{hkl}$  and the surface energy is equal to the ratio of the cohesion energy to the doubled monolayer area, i.e.,  $\sigma_{hkl} = -\Delta U_{hkl}/(2S_{1hkl})$ .



**Figure 10.** Scheme of intermolecular interactions in crystals of linear oligophenyls: (a) - lateral contacts, (b) - end contacts.

**Table 3.** The intermolecular potential energies  $\epsilon_{hkl}$  between molecules in a crystal calculated with OPLS method.

n	$-\epsilon_{100}$ kcal/mol	$-\epsilon_{010}$ kcal/mol	$-\epsilon_{110}$ kcal/mol	$-\epsilon^1_{001}$ kcal/mol	$-\epsilon^2_{001}$ kcal/mol	$-\epsilon^3_{001}$ kcal/mol	$-\epsilon^4_{001}$ kcal/mol
2	0.363	3.137	3.928	0.980	0.980	1.198	1.198
3	0.667	5.165	6.586	1.054	1.054	1.337	0.218
4	0.769	4.858	8.950	0.964	0.964	1.202	0.102
5	1.223	9.23	11.61	0.814	0.814	1.099	0.220
6	1.543	11.42	14.60	1.617	1.406	1.467	0.520

# Modeling the Surface Energy of Crystals

**Table 4.** Binding energy  $E_{hkl}$  between molecules and surface energy  $\sigma_{hkl}^V$  of nP crystal faces and total lattice energy  $\Delta H_S$  (sublimation enthalpy) calculated with OPLS method.

n	- $E_{100}$ kJ/mol	- $E_{010}$ kJ/mol	- $E_{110}$ kJ/mol	- $E_{001}$ kJ/mol	$\sigma_{100}^V$ mJ/m <sup>2</sup>	$\sigma_{010}^V$ mJ/m <sup>2</sup>	$\sigma_{110}^V$ mJ/m <sup>2</sup>	$\sigma_{001}^V$ mJ/m <sup>2</sup>	$\Delta H_S$ , kJ/mol		
									calc.	experiment	corr. *
2	27.9	25.5	17.6	9.1	72.5 122 <sup>[10]</sup>	81.9 129 <sup>[10]</sup>	65.9 118 <sup>[10]</sup>	78.0 97 <sup>[10]</sup>	69.1	80.4 <sup>[11]</sup>	78
3	35.0	56.9	28.2	9.2	92.1 124 <sup>[10]</sup>	91.5 136 <sup>[10]</sup>	75.6 123 <sup>[10]</sup>	72.0 99 <sup>[10]</sup>	106.8	116.2 <sup>[12]</sup>	121
4	48.0	78.0	38.7	9.0	81.7 124 <sup>[10]</sup>	92.0 140 <sup>[10]</sup>	79.2 124 <sup>[10]</sup>	71.0 96 <sup>[10]</sup>	140.4	168 <sup>[13]</sup>	166
5	60.0	83.7	46.5	9.5	75.9 -	85.5 -	63.0 -	70.9 -	171.8	-	209
6	80.9	123.9	54.0	8.2	86.6 142 <sup>[10]</sup>	99.4 142 <sup>[10]</sup>	72.5 135 <sup>[10]</sup>	67.9 107 <sup>[10]</sup>	211.6	-	253

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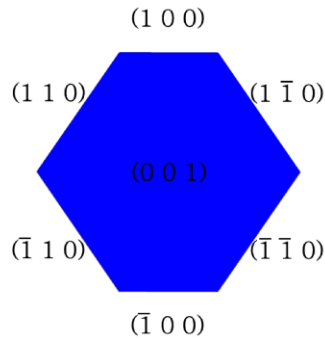
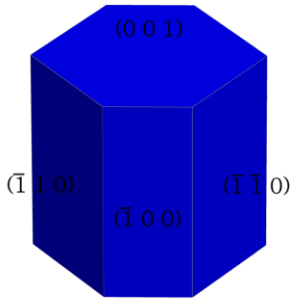
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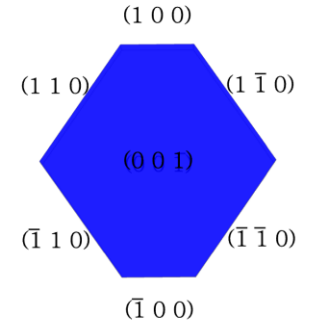
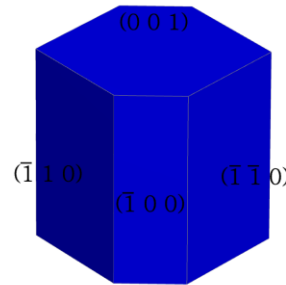
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# Equilibrium Shape of nP Crystals Predicted on the Basis of the Gibbs - Curie - Wolfe principle

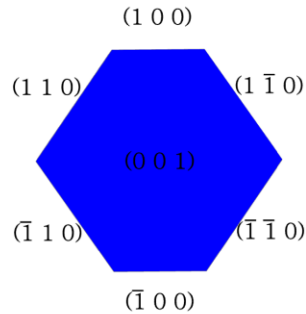
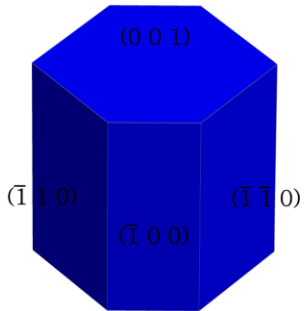
*p-2P*



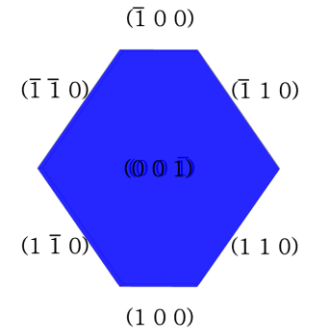
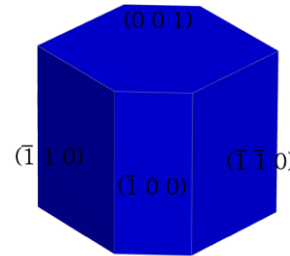
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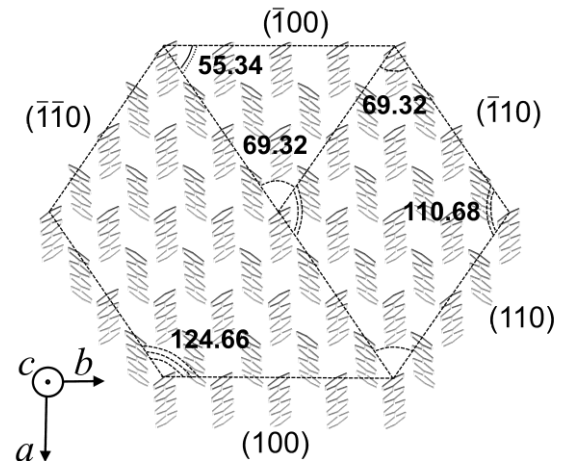
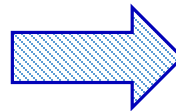
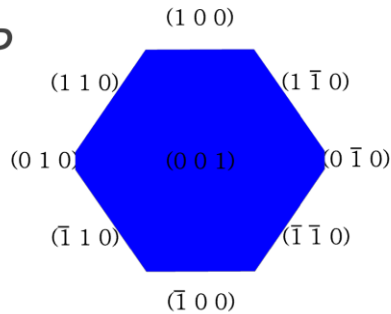
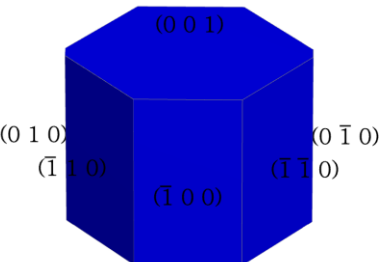
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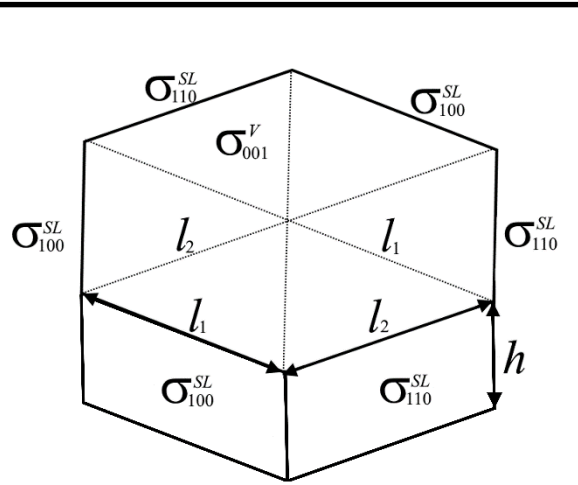
*p-6P*



*p-4P*



# Analysis of the nP Crystal Nucleation Parameters Based on the Classical Thermodynamic Model



**Figure 11.** Schematic model of a crystal nucleus.

In the chosen nucleus geometry, the opposite sides at the base are parallel and equal, and the sides  $l_1$  and  $l_2$  are connected by the ratio:

$$l_2 = \frac{l_1}{2} \left( \frac{a^2}{b^2} + 1 \right)^{1/2} = A \cdot l_1, \quad (1)$$

where  $a$  and  $b$  are lattice parameters. The nucleus base area  $S$  is determined as follows :

$$S = \frac{3}{2} l_1^2 \left( \left( \frac{l_2}{l_1} \right)^2 - \frac{1}{4} \right)^{1/2} = \frac{3}{2} l_1^2 \left( A^2 - \frac{1}{4} \right)^{1/2} = B \cdot l_1^2 \quad (2)$$

Then the change in the Gibbs free energy during the formation of a crystal nucleus at the liquid - air interface can be written in the form [9,14]:

$$\Delta G = - \left( \frac{B \cdot l_1^2 h}{\Omega} \right) \Delta \mu + B(\sigma_{001}^V + \sigma_{001}^L - \sigma_{LV}) l_1^2 + 2(\sigma_{100}^L + 4A \cdot \sigma_{110}^L) l_1 h \quad , \quad (3)$$

where  $\Omega = M/\rho$  is the molar volume,  $\Delta \mu = RT \cdot \ln(C/C_0) = RT \cdot \ln(1+\xi)$  - driving force of crystallization,  $C_0$  - saturated solution concentration,  $\xi = (C-C_0)/C_0$  - relative supersaturation of the solution at the phase boundary, surface energy of faces at crystal - air ( $\sigma_{001}^V$ ) and crystal - solution interfaces ( $\sigma_{100}^L, \sigma_{010}^L, \sigma_{110}^L, \sigma_{001}^L$ ),  $\sigma_{LV}$  - surface tension of the solution. The equilibrium condition for the crystal shape ( $\Delta G_S = \min, V_0 = S \cdot h = \text{const}$ ) implies the relationship between the length of the side face  $l_1$  and the thickness  $h$  of the crystal nucleus:

$$\frac{h}{l_1} = \frac{B(\sigma_{001}^V + \sigma_{001}^L - \sigma_{LV})}{\sigma_{100}^L + 4A \cdot \sigma_{110}^L} \quad (4)$$

Taking into account expression (4), from the condition of the extremum of the function  $\Delta G$  we obtain expressions for the sizes of the critical nucleus:

$$l_{1c} = \frac{2\Omega}{B \cdot \Delta \mu} (\sigma_{100}^L + 4A \sigma_{110}^L), \quad h_c = \frac{2\Omega}{\Delta \mu} (\sigma_{001}^V + \sigma_{001}^L - \sigma_{LV}) \quad (5)$$

# Analysis of the nP Crystal Nucleation Parameters Based on the Classical Thermodynamic Model

Using Young's equation, it is possible to establish a relationship between the surface energy of a face wetted with a solution and a dry one:

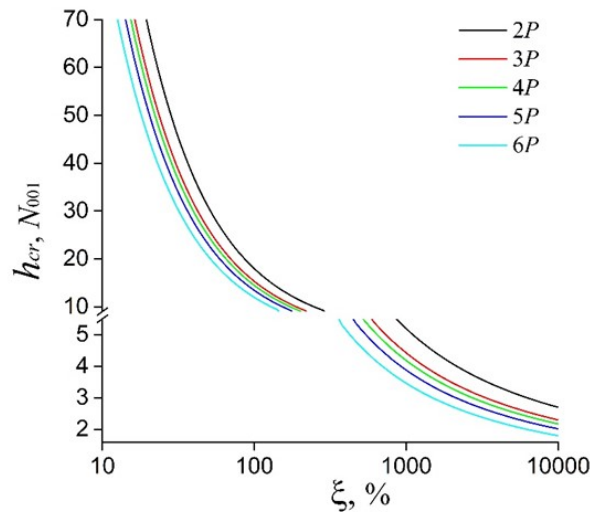
$$\sigma_{hkl}^L = \sigma_{hkl}^V - \sigma_{LV} \cdot \cos \theta_{hkl} \quad (6)$$

Taking into account that the saturated solution (toluene) completely wets the crystal surface (contact angle of crystal wetting with solution  $\theta_{hkl} \approx 0$ ), expressions (5), taking into account Young's equation, can be rewritten as follows:

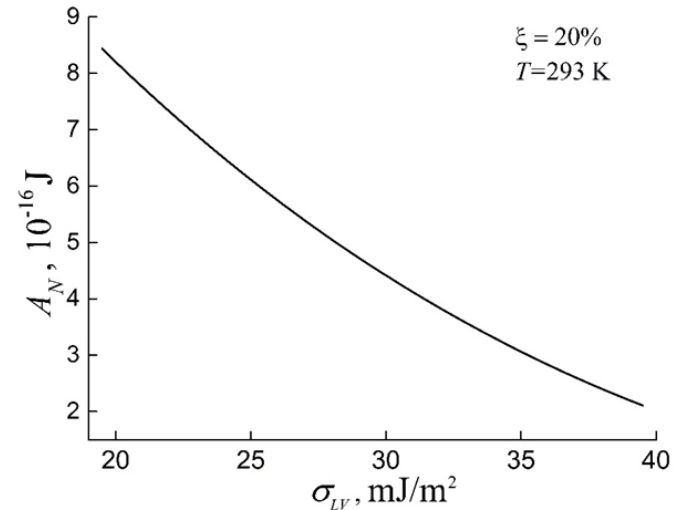
$$l_{1c} = \frac{2\Omega}{B \cdot \Delta\mu} (\sigma_{100}^V + 4A\sigma_{110}^V - \sigma_{LV}(1+4A)), \quad h_c = \frac{4\Omega}{\Delta\mu} (\sigma_{001}^V - \sigma_{LV}) \quad (7)$$

Function  $\Delta G$  has a maximum, the value of which determines the work of formation of the critical nucleus  $A_N$ :

$$A_N = \left( \frac{2\Omega}{\Delta\mu} \right)^2 (\sigma_{100}^V + 4A\sigma_{110}^V - \sigma_{LV}(1+4A)) \cdot (\sigma_{001}^V - \sigma_{LV})^2 \quad (8)$$



**Figure 12.** Dependence of the nP critical crystal nuclei thickness on the relative supersaturation of a toluene solution at 293 K.  $N_{001}$  - number of monolayers with thickness  $d_{001}$  (table 2).



**Figure 13.** Dependence of the formation work of the crystal nucleus of a p-quaterphenyl on the value of the surface tension of the solution.

# Analysis of the nP Crystal Nucleation Parameters Based on the Classical Thermodynamic Model

For homogeneous formation of a crystal nucleus from the vapor phase:

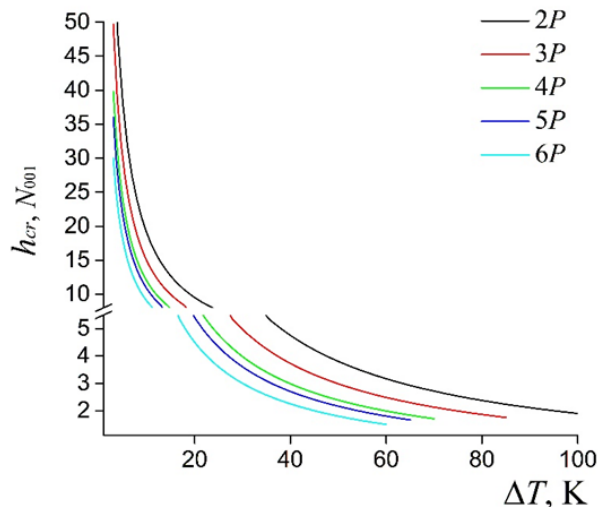
$$\Delta G_{vap} = -\left(\frac{B \cdot l_1^2 h}{\Omega}\right) \Delta \mu_{vap} + 2B \cdot \sigma_{001}^V \cdot l_1^2 + 2(\sigma_{100}^V + 4A \cdot \sigma_{110}^V) l_1 h \quad (9)$$

Under the condition of a weak change in the pressure of saturated vapors in the interval between the source of substance sublimation and the zone of deposition of crystals, the magnitude of the driving force of crystallization can be written in an approximate:

$$\Delta \mu_{vap} \approx \frac{\Delta H_S \cdot \Delta T}{T_0} \quad (10)$$

where  $\Delta H_S$  is the enthalpy of sublimation (table 4),  $T_0$  is the temperature of the source of the substance,  $\Delta T$  is the temperature difference between the source and the point of formation of the crystal nucleus. The critical sizes of the crystal nucleus in this case are determined by the following expressions:

$$l_{1c} = \frac{2\Omega}{B \cdot \Delta \mu} (\sigma_{100}^V + 4A \sigma_{110}^V), \quad h_c = \frac{4\Omega}{\Delta \mu} \sigma_{001}^V \quad (11)$$



**Figure 14.** Dependence of the nP critical crystal nuclei thickness on the vapor supercooling at the corresponding source temperature  $T_0$  (Table 5).

**Table 5.** Parameters of nP crystals nucleation from a solution of toluene (293 K) and vapor phase.

nP	$l_c/h_c$		$C_{cr}$ g/L	$T_0$ K	$\Delta T_{cr}$ K
	solution	vapor			
2P	1.67	1.80	-	318	95
3P	2.40	2.29	-	438	74
4P	2.49	1.93	30	523	60
5P	1.84	1.93	5	583	54
6P	2.48	2.31	$\leq 0.5$	618	44

Note:  $l_c/h_c$  is the ratio of the length to the thickness of the critical nucleus,  $C_{cr}$  is the critical concentration of the supersaturated solution at which  $h_c \leq 2d_{001}$ ,  $T_0$  - source temperature at PVT growth,  $\Delta T_{cr}$  is the critical vapor supercooling, at which  $h_c \leq 2d_{001}$ .

# Conclusions

1. In this report, we presented the results of studies of the linear oligophenyl crystals growth from solutions and vapor phase under conditions of PVT method. Due to the low solubility of linear oligophenylys under normal conditions at the conjugation length of the molecule  $n \geq 4$ , the growth of their crystals from solution has serious difficulties. In particular, for  $n \geq 5$ , it is necessary to use methods with significant heating of solutions ( $T > 100^\circ\text{C}$ ) to increase solubility. The most favorable materials for growing crystals from solutions are diphenyl and p-terphenyl. Their high solubility is favorable for *in situ* studies of the crystal growth kinetics (Fig.3,4). On the other side, linear oligophenylys with low solubility under PVT conditions crystallize rather quickly (2-6 days) in the form of thin large single crystalline films (up to 8 mm long for 5P), although with a coarser surface morphology than those grown from solutions.

2. On the basis of the Gibbs - Curie - Wolfe principle using the values of the surface energy of the crystal faces calculated with OPLS method and taking into account the crystal structure, the equilibrium shape of the crystals of linear oligophenylys is predicted.

3. Based on the values of the surface energy of the main low-index faces, calculated with OPLS method, a thermodynamic analysis of the parameters of linear oligophenylys crystals nucleation from a solution of toluene and the vapor phase was carried out. The considered anisotropic classical model of nucleation gives an idea of the scale and shape of the formed crystal nuclei in solution and in the vapor phase under the experimental conditions of crystal growth, depending on the degree of supersaturation of the solution or the value of supercooling of the vapor relative to the temperature of the substance source, respectively. In particular, the critical sizes of crystal nuclei are almost an order of magnitude higher under experimental conditions of growth from solutions than under conditions of physical vapor transport (Fig.12, 14). According to the results obtained, the surface tension of the solution has a significant effect on the critical size and work of the formation of a crystal nucleus at the liquid - air interface, which is also confirmed by experimental observations using the example of 4P crystals (Fig.13).

## Acknowledgments

Studies in part on crystals growth from solution and modeling the surface energy of crystal faces were made with financial support from the Ministry of Science and Higher Education of the Russian Federation within the State assignment FSRC “Crystallography and Photonics” RAS using the equipment of Collaborative Access Center “Structural diagnostics of materials” (project # RFMEF162119X0035); studies in part on crystals growth by the PVT method, their crystal structure and nucleation thermodynamic analysis were made under the support of the Russian Foundation for Basic Research (grant no. 19-32-90145); development of the approaches to purification of the conjugated oligomers was supported by the Russian Science Foundation (grant no. 18-73-10182).