Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

The Growth of Stilbene Single Crystals with High Structural Perfection

Sergei Budakovsky [a] , Nikolai Galunov [a] & Igor Krainov [a]
[a] Institute for Single Crystals, Kharkov, USSR
Version of record first published: 22 Sep 2006.

To cite this article: Sergei Budakovsky , Nikolai Galunov & Igor Krainov (1990): The Growth of Stilbene Single Crystals with High Structural Perfection, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 186:1, 159-166

To link to this article: http://dx.doi.org/10.1080/00268949008037206

Mol. Cryst. Liq. Cryst., 1990, vol. 186, pp. 159–166
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

THE GROWTH OF STILBENE SINGLE CRYSTALS WITH HIGH STRUCTURAL PERFECTION

SERGEI BUDAKOVSKY, NIKOLAI GALUNOV, IGOR KRAINOV
Institute for Single Crystals, Kharkov, USSR

Abstract The peculiarities of the growth of stilbene single crystals from melt doped with electron-seeking addition agents (ESAA) are discussed.

INTRODUCTION

As was shown earlier[1-3], radioluminescence of stilbene single crystals is essentially determined by the degree of structural perfection. Doping stilbene melt with ESAA such as benzol and benzophenone halogen derivatives allowed us to influence structural perfection by changing the root-mean-square random orientation (σ_c) of the single crystal mosaic structure and increase the maximal possible rate of perfect structure crystal growth. Adding 0.1 mol.% ESAA to the melt resulted in the highest structural perfection of the grown crystals. This was manifested by minimizing σ_c (Fig.1). It also reduced the concentration of deep traps of charge carriers ($\sim$ 1.2 - 1.4 eV) and singlet excitons ($\sim$0.24 eV) formed at aggregations and ensembles of dislocations. Doping the melt with very high ESAA concentrations deteriorated structural perfection, caused ESAA entry into the single crystal and emergence of another phase.[1-4]

The present paper investigates the causes determining the growth of structurally perfect stilbene single crystals from melt doped with ESAA (chloranil molecules), and the causes determining their radioluminescence processes as well.

EXPERIMENT

Figure 1 shows σ_c^3, the results of measuring melting heat capacity c_p, melting and crystallization heats Q and temperatures T, as well as the calculated variables

$$c_p/T = \partial S/\partial T \quad (1)$$

$$dQ/T = dW/T = dS \quad (2)$$

where S is entropy, W enthalpy. The measured values were

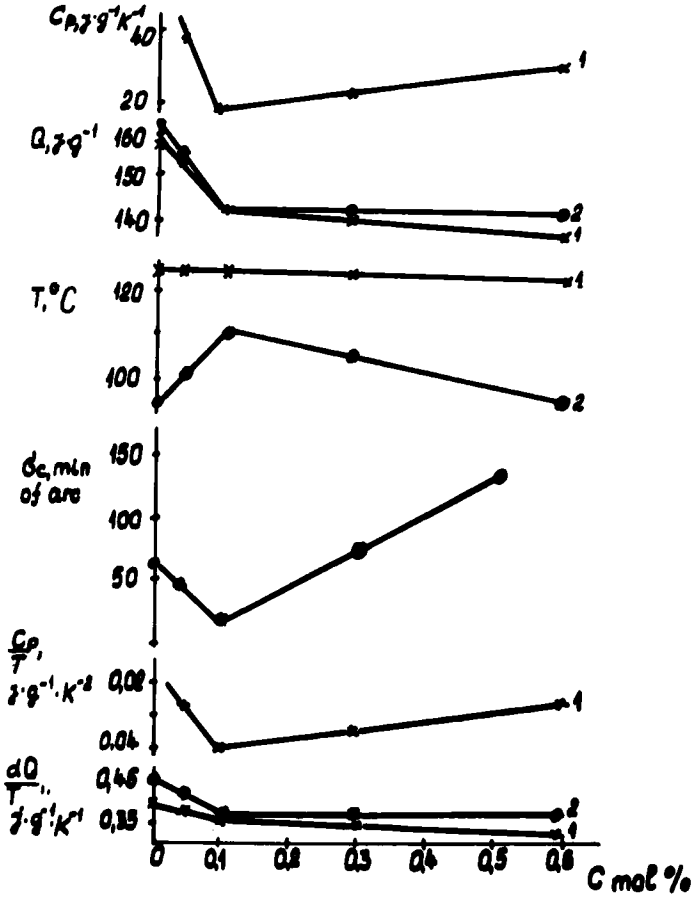

FIGURE 1 Measured and calculated values vs C for the cases of melting and crystallization processes (curves 1 and 2 respectively).

obtained, using a Mettler TA 3000 thermoanalytic system, by melting a uniform mixture of powdered stilbene and chloranil with the subsequent crystallization of the resulting melt. The process went on at constant pressure p, which determined the form of Equations (1) and (2).

DISCUSSION

Since there is a high probability of ESAA-stilbene charge-transfer complex formation, ESAA molecules can exist in the melt only within complexes which it is possible to describe as electric dipoles with dipole moment[2,5] d = 2.5 D. Within a distance between complexes, $r < r_1$, dipoles can be attracted to one another forming "supercomplexes". At $r > r_1$ they will very probably drift apart due to thermal diffusion. When a crystal layer is being formed, the complexes can break down. This may be connected with structural obstacles to their entry into the single crystal. In such a case the ESAA molecules will return to the melt. If the diffusion in the melt is great enough and complex concentration in different melt regions evens out during the growth of one crystal layer, increase of C in the melt volume will be observed, otherwise considerable near-surface (i.e. near the crystal-melt boundary) increase of C will take place. In case of the break-down of complexes, a certain amount of energy is needed which will result in partial crystallization heat, q, absorbtion. Let us estimate these values.

Assuming the binding energy of complexes[5] is $E \sim 0.75$ eV

$$q = E N_A C/m, \qquad (3)$$

where C is the concentration of chloranil, N_A is Avogadro's constant, m = 244 g/mol. For C = 0.1 mol%, q = 0.3 J/g. With $C < C_1 = 0.1$ mol% and $C > C_1$ the va-

lues discussed behave differently (Fig.1). Assuming the complexes to be distributed uniformly within the melt, the average distance between them for $C = C_1$ is $R_1 = 63$ A. For the melt temperature, $T = 124^{\circ}C$ (Fig.1), the value $r_1 \simeq 4.6$ A can be obtained from the equality of the dipole attraction energy and kT.

Let us consider some processes in the melt during the crystal layer formation (thickness $x_0 = 1.475\ 10^{-7}$ cm). The values to be used are: growth rate $V = 3.778\ 10^{-5}$ cm/s and diffusion coefficient $D \sim 10^{-5} - 10^{-7}$ cm^2/s (for non-viscous liquids[6] $D \sim 10^{-5}$ cm^2/s). The problem describing the solid variation in C caused by complex "generation" on the melt-crystal boundary is an equation of diffusion with convection (moving boundary). The introduction of a moving coordinate y connected with x (crystal growth direction) by condition (4) and difference in concentration $u = C - C_0$ will result in partial differential equation (5) with initial (6) and boundary (7) conditions, i.e.

$$y = x - V t \tag{4}$$

$$\partial u(y,t)/\partial t = D\ \partial^2 u(y,t)/\partial y^2 \tag{5}$$

$$u(y,0) = 0 \tag{6}$$

$$\begin{cases} u(0,t) = f(t) \\ u(1,t) = 0 \end{cases} \tag{7}$$

where C_0 is complex concentration at time $t = 0$. The $f(t)$ function determines the source characteristics at the coordinate $y = 0$, i.e. on the crystal-melt boundary. It is not difficult to conclude that, during the growth of every crystal layer with frequency $w = V/x_0 = 2.56\ 10^2\ s^{-1}$, C_0 additional complexes appear at $y = 0$, and if N layers grow during the time t then $N = wt$ or

$$f(t) = C_0\ w\ t \tag{8}$$

Applying the Duhamel principle and solving Eq.(5) for a function $g(y,t)$ with the initial and boundary condi-

tions (6) and (7), but with $f(t) = 1$, it is possible to define $u(y,t)$ from the corresponding convolution equation for $g(y,t)$ and $f(t)$ (8).[7] Using the Laplace transform, we obtained a solution for Eq.(5) containing $g(y,t)$, then (according to the Duhamel principle) $u(y,t)$ and, finally,

$$C(y,t) = u(y,t) + C_0 = C_0 \, w \int_0^t \mathrm{Erfc}\left(\frac{y}{\sqrt{4D\,z}}\right)dz + C_0 \quad (9)$$

Selecting $D \sim 10^{-5}$ cm^2/s, it can be shown that the number of layers $n = y/x_0$, for which the diffusion shift occurs within the average time necessary for growth of one crystal layer, i.e. $\mathrm{Erfc}(y/\sqrt{4D/w}) \simeq 1$, is $n = 2.3\ 10^3$ layers. As follows from Eq.(9), the case for very low D, when complexes have accumulated in the layer close to the crystal-melt boundary, is only possible for $D \lesssim 10^{-11}$ cm^2/s. Above that, D was considered constant. Strictly speaking, to justify (9), D must also remain constant for a volume containing $m \gg n$ layers. If $m = 100n$, then the x-dimension of the corresponding melt volume is $l \lesssim 3\ 10^{-2}$ cm.

Thus, supercomplex formation only occurs upon direct collision. In other words, it is a diffusion-controlled process. During the growth period of one crystal layer diffusion shift can "shuffle" the molecules located in the $10^2 - 10^3$ layers of the melt. Hence the possibility of supercomplex formation exists for $C \geqslant 4.3\ 10^{-2}$ mol%. On their entry into the crystal layer, complexes normally break down [1,3-5]. This, however, is not necessarily the case with supercomplexes, since their complete break down requires a great deal of energy. The latter is confirmed by ESAA entry into crystals observable for $C >$ 0.1 mol%.

The time scale of the processes discussed:

- the time for complex formation (with stilbene - ESAA molecules in direct contact) $\lesssim 10^{-11}$ s;
- the time of supercomplex formation (diffusion-controlled process of two complexes coming together at inter-

action distance ~ 4.4 A) $\sim 10^{-8} - 10^{-7}$ s;
- the time for single layer growth is $2.5\ 10^{-3}$ s.

Let us consider the melting process. It is accompanied by the complex-formation process. Beginning with a definite C_1 concentration, with the intercomplex distance small enough, i.e. about R_1, their diffusion shift will cause active supercomplex formation in the shape of stacks. Further increase in C should not result in a noticeable change in the total sum of the complexes and supercomplexes in the melt since R_1 has already been reached. The number of supercomplexes will possibly grow. For supercomplexes with a very great number of links, k, a break down effect must be observed due to the increasing thermal effect. In the case of "regulated" melt region formation, the number of orientated stilbene molecules, K, per ESAA molecule will be higher for complexes than for supercomplexes; for the latter K will decrease with the growing k, since the inter-stack complex field in a supercomplex will be partially shielded by the top and bottom complex fields. Consequently, with the growing C, the melt "regulation" effect will increase more rapidly for $C < C_1$, than for $C > C_1$, which, in fact, was observed in the experiment (Fig.1). The kinetic energy of stilbene molecules, complexes and supercomplexes grows during the melting process. Since supercomplexes are large enough, molecules of different molecular layers will take part in their movement. This will require additional energy, and for that reason, for $C > C_1$, the C increase causes $\partial S/\partial T$ increase and the slowing down of the dS decrease for "solid solution - partially regulated melt" transition (Fig.1).

Let us consider the crystallization process. At most, it is defined by:
- melt "regulation";
- energy gain from complex break down in the crystallization process;

- *supercomplexes or their break down product entry into the single crystal.*

The strengthening of the first two (positive) factors is connected with the C increase for $C < C_1$. The strengthening of the third (negative) factor is caused by the C increase for $C > C_1$. It should be stressed that complex concentration in the melt (the above C) will increase in direct proportion to the time of growth or inversely to the remaining melt volume until the average distance between complex molecules approximates R_1. It follows that even if $C < C_1$ at the beginning of the growth, the final value of C may already be more than C_1.

CONCLUSIONS

Melt formation is simultaneous with complex (ESAA - stilbene) formation. When their concentration C is large enough, diffusion- controlled supercomplex formation takes place. During the growth of one crystal layer a levelling in C values in the melt and near the melt-crystal boundary should be observed. Therefore the properties of the grown single crystals are consequently determined by initial ESAA concentration. It is possible to present complexes as electric dipoles. It causes the "regulated" melt region formation. The number of orientated stilbene molecules per ESAA molecule will be higher for complexes than for supercomplexes.

The factors contributing to a more rapid growth and higher structure perfection of single crystals are: "regulation" of the melt regions at distances of several molecular diameters from charge-transfer complexes (ESAA - stilbene), and a gain in the value and, consequently, rate of the heat withdrawal due to the process of complex break down in which some of the heat, instead of being used for agitating the crystal lattice, is directed to destroying complexes at the moment of their entering

the single crystal. With the C increase the said effects intensify for $C < C_1$, and decrease for $C > C_1$. It is necessary to note that the analysis of the experimental data discussed enables us to estimate only the processes taking place in the melt. Apparently, on entering the growing crystal layer, complexes with their polarization environments can essentially affect the kinetics of crystal growth.

REFERENCES

1. S. V. Budakovsky, N. Z. Galunov, I. P. Krainov, T. R. Mnatsakanova, Zh. Prikl. Spektr. (USSR), 44, 1012 (1986)
2. S. V. Budakovsky, N. Z. Galunov, I. P. Krainov, V. P. Seminozhenko, Dokladi Akademii Nauk UkSSR (USSR), Ser. A, No. 1, 44 (1989).
3. I. P. Krainov, N. Z. Galunov, S. V. Budakovsky, Cryst. Res. Technol., 24, 193 (1989).
4. E. A. Silinsh, Organic Molecular Crystals. Their Electronic States (Springer - Verl., Heidelberg, 1980), p. 406.
5. F. Gutmann, L. E. Lyons, Organic Semiconductors (John Wiley and Sons, Inc., New York-London-Sydney, 1967), p. 858.
6. L. Sh. Afanasiadi, N. Z. Galunov, B. M. Krasovitsky, et al. Zh. Prikl. Spektr. (USSR), 49, 994 (1988).
7. S. J. Farlow, Partial Differential Equations (John Wiley and Sons, Inc., New York-London-Sydney, 1982), p. 472.