Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Effect of D-, L-Phenylalanine on Growth Rate and Morphology of α L-Glutamic Acid

Mitsutaka Kitamura [a] & Takeshi Yamanami [a]
[a] Dep. Chem. Eng., Hiroshima University, 1-4-1, Kagamiyama, Higashi-Hiroshima, 724, Japan
Version of record first published: 04 Oct 2006.

To cite this article: Mitsutaka Kitamura & Takeshi Yamanami (1996): Effect of D-, L-Phenylalanine on Growth Rate and Morphology of α L-Glutamic Acid, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 276:1-2, 213-220

To link to this article: http://dx.doi.org/10.1080/10587259608039379

Mol. Cryst. Liq. Cryst., 1996, Vol. 276, pp. 213–220
Reprints available directly from the publisher
Photocopying permitted by license only

EFFECT OF D-, L-PHENYLALANINE ON GROWTH RATE AND MORPHOLOGY OF α L-GLUTAMIC ACID

MITSUTAKA KITAMURA AND TAKESHI YAMANAMI
Dep.Chem.Eng., Hiroshima University,
1-4-1, Kagamiyama, Higashi-Hiroshima 724, Japan

Abstract The effect of L-and D-Phenylalanine(Phen) on the growth kinetics and morphology change of α L-Glutamic acid(L-Glu) was investigated using the method of single crystal in the flow system. With L-Phen the growth rate of L-Glu crystals in the direction parallel to the main plane decreased and the growth became to be irregular. However, no influence was observed in the direction of thickness. New face determined as (110), indicating that L-Phen adsorbs on that face. From crystallographic data the effect of L-Phen could be explained. However, more complicated mechanism for the morphology change was suggested. No effect of D-Phen means that the additive effect is highly stereo-selective.

INTRODUCTION

Some special additives influence on the precipitation and transformation behaviors of polymorphs. This is due to that the nucleation and growth rates of the polymorphs are changed by the additives differently. Furthermore, since the growth rates of each face of a crystal are differently influenced, the morphology change occurs. However, these behaviors are usually not treated quantitatively and the mechanisms are not known.

Recently, the effect of additive on crystal growth is frequently discussed using crystallographic data and structures of additive molecule[1,2]. An additive molecule, which has a similar molecular structure with the solute, adsorbs on a crystal surface through a common part with the solute, however, the substituted bulky group of the

additive molecule is excluded on the surface and it inhibits the growth.

L-aminoacids are composed of the common part including a chiral carbon(α-carbon) and the other substituted part. We reported previously[3,4] that L-phenylalanine (Phen) influences on the precipitation behavior of L-glutamic acid(L-Glu) polymorphs(α and β). In the crystallization at 25 °C, although only α L-Glu (Orthorhombic; $P2_12_12_1$[5]) tends to precipitate[4], L-Phen retards the precipitation rate and effects on the morphology of α L-Glu crystals, depending on the crystallization conditions.

In this paper the effect of L-Phen on the growth kinetics and morphology change mechanism of L-Glu is investigated using the method of single crystal in the flow system. Furthermore, stereo selectivity of the additive effect is examined using D-phenylalanine(D-Phen).

EXPERIMENTAL

A single crystal of α L-Glu (seed) was fixed on the end of steel wire in the growth cell. Solution of L-Glu containing L-Phen was circulated with a pump from a dissolving tank to the growth cell through a heat exchanger. The size of the crystals were measured by the microscopic measuring gauge and video-TV system. Temperature in the growth cell was controlled to be 25 °C and the solution velocity was varied between 0.05-0.25 m/s. Seed crystals of α L-Glu were prepared by batch crystallization. The shape and face index of them are shown in Fig.1. The seed crystal was set in the growth cell as shown in Fig.2(flow direction is shown with an arrow). The crystal size change (ΔL) in the directions of parallel to the main plane (A1,A2,A3) and thickness(D1,D2) were measured with elapsed time. The growth rates(G) were estimated from the relationship between ΔL vs time. The measurement was carried out in solutions without additives and in solutions including D- or L-Phen.

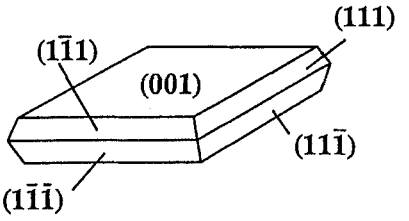


Fig. 1 Seed crystal

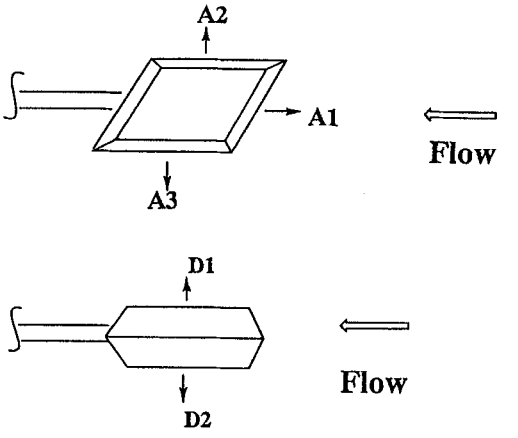
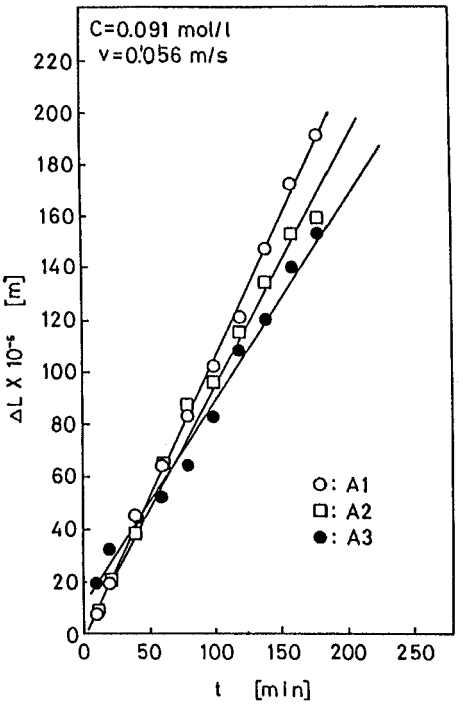


Fig.2 Set of crystal in growth cell

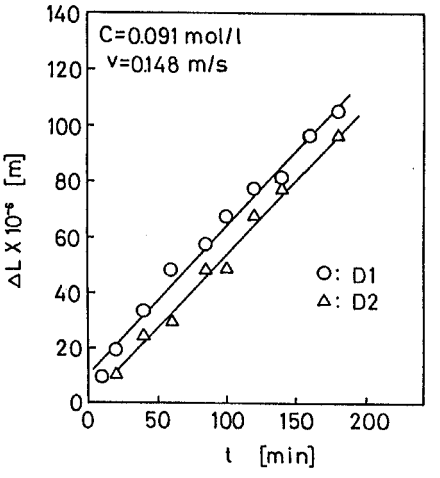
RESULTS AND DISCUSSION

Growth rate in solutions without additive

In Figs.3 (a) and (b), typical results of relationships between crystal size change (ΔL) and time(t) for A and D directions are shown, respectively (concentration of L-Glu(c)=0.091 mol/l; solution velocity(v)=0.056 and o.148 m/s). The good linear relationships between ΔL and time were observed in all cases and from these results the growth rates were estimated. In A direction almost the same inclinations i.e. the same growth rates, were obtained for A1, A2, A3. This seems to correspond to the same face structure as the space group of α L-Glu is $P2_12_12_1$. The growth rate in D direction is about 2/3 of that in A direction. The crystal size was measured in different solution velocity for the same L-Glu concentration (c=0.091mol/l). In the velocity range of 0.05-0.25 m/s in our experimental little influence was observed on the growth rates in both directions. The results suggests that the growth process is mainly controlled by the surface reaction process and the contribution of diffusion in solutions is small.



(a) A direction



(b) D direction

Fig.3 Relationships between crystal size(ΔL) and time(t)

Growth rate in solutions including L-Phen

The growth rate of L-Glu crystals in A direction decreased by adding L-Phen in the solution. When L-Phen concentration exceeded 7.7×10^{-4} mol/l the plots deviated from the linear relationship of ΔL and time(t). In Fig.4 the result at L-Phen concentration(c_p) of 1.3×10^{-3} mol/l is shown. The growth became to be irregular, i.e. temporarily the growth stopped and after some interval it grew again.

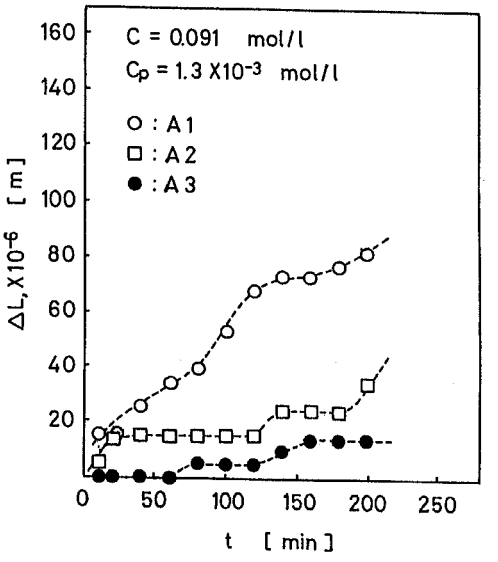


Fig.4 ΔL versus time(t) in the presence of L-Phen

Dependence of growth rate in A direction (G(A)) on the concentration of L-Phen(cp) is shown in Fig.5. Disperse in the growth rate was observed among seed crystals as shown by vertical bars in Fig.5. The growth rate completely stopped at the value (cp) of 1.8×10^{-3} mol/l.

On the other hand, in D direction the growth rate did not decrease by adding L-Phen, even when the concentration

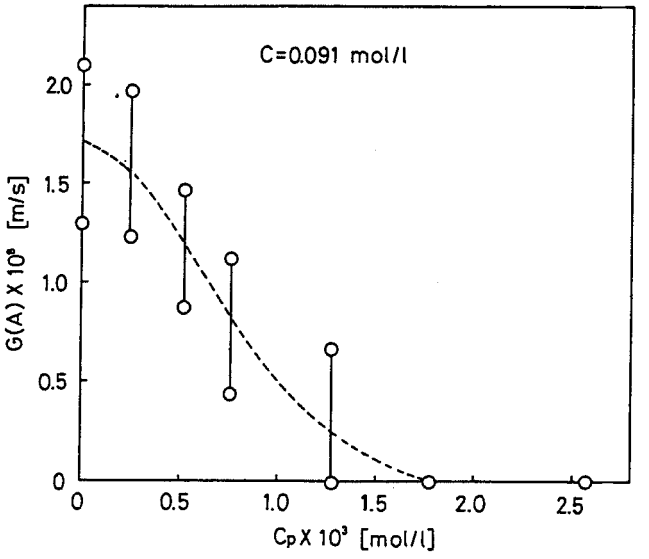


Fig.5 Relationship between the growth rate and L-Phen concentration in A direction

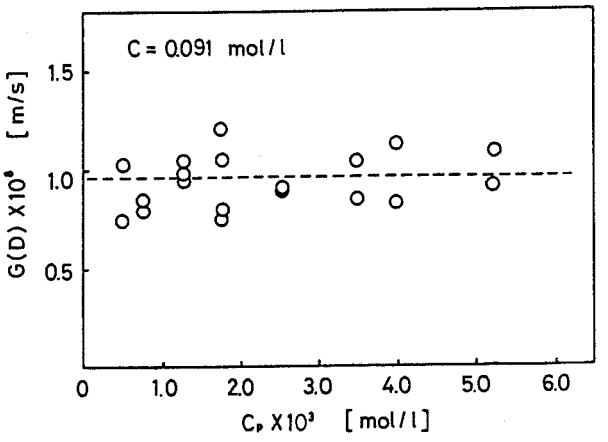


Fig.6 Relationship between the growth rate and L-Phen concentration in D direction

of L-Phen(c_p) was increased up to 1.8 x10^{-3} mol/l(Fig.6).

These results indicate that the shape of L-Glu crystal becomes thicker with L-Phen concentration.

Morphology change and the mechanism

It was expected from the results that L-Phen adsorbs on (111) face and disturbs its growth. However, from the microscopic observation it was confirmed that in the growing process new face appeared as shown in Fig.7. With X-ray diffraction analysis, the new face was decided to be (110). These results indicate that L-Phen adsorbs on (110) face selectively and not adsorbs on (001) face.

Crystallographic data shows that (001) face is very rich in carboxylic acid group (Fig.8). Accordingly phenyl

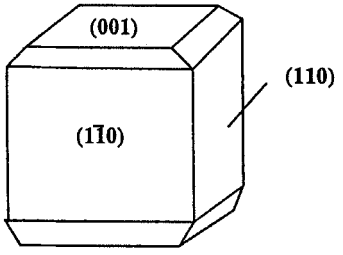


Fig.7 Morphology obtained after growth

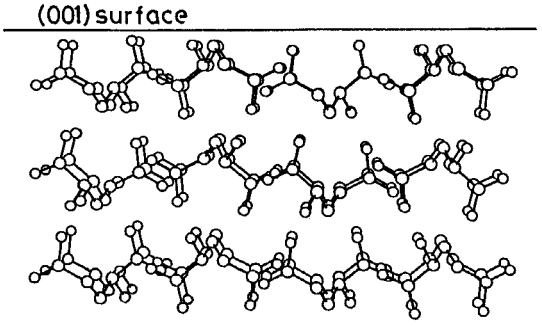


Fig.8 Packing arrangement in (001) surface

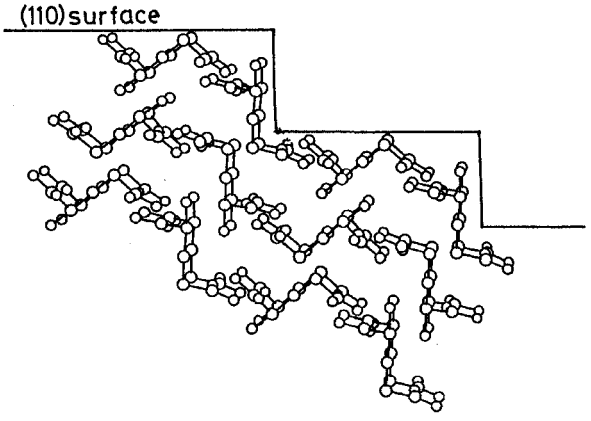


Fig. 9 Packing arrangement in (110) surface.

group of L-Phen may be repulsed in (001) face and so L-Phen molecule can not adsorb on (001) face. On the other hand in (110) face molecular arrangement of L-Glu seems to be partly suitable for the adsorption of L-Phen(Fig.9), i.e. L-Phen can adsorb on the surface of (110) through the common part of amino acid including chiral carbon.

On the other hand, in the batch crystallization other morphologies of L-Glu were observed[6], i.e. the morphology changed dynamically with crystallization conditions containing L-Phen concentration. This means that the mechanism of morphology decision is more complicated and the morphology depends on the competitive growth rates of individual face and characteristic interaction between the mother crystals and additives. The morphology shown in Fig.7 was scarcely appeared in the batch crystallization, suggesting that the morphology in Fig.7 can be obtained only in the narrow condition. Under this experimental condition, the growth rate of (110) face may be slower than the other faces as (111) face.

Effect of D-Phen

When D-Phen is added in the solutions, no effect on the

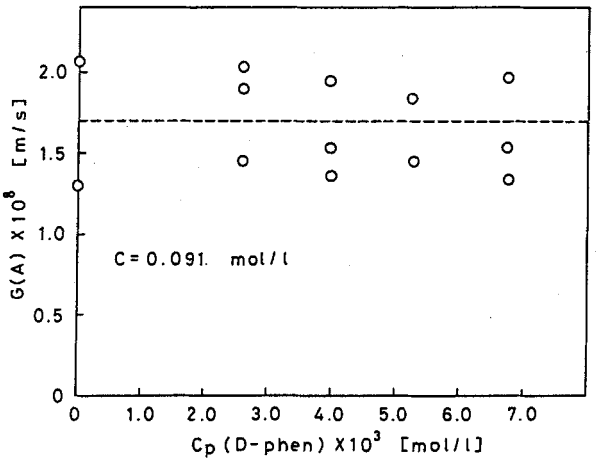


Fig.10 Dependence of the growth rate on D-Phen concentration

growth rates was observed in both directions of A and D at least up to D-Phen concentration of 7×10^{-3} mol/l. In Fig.10 the results for A direction is shown. These results indicates that the additive effect in this case is highly stereo-selective.

CONCLUSION

The growth rate of α L-Glu crystals in A direction (parallel to the main plane) decreased with L-Phen concentration and the growth became to be irregular. On the other hand, no influence was observed in D-direction. New face appeared and the face index was determined as (110). From crystallographic data the effect of L-Phen on (110) was explained in comparison with (001) face. However, more complicated mechanism for the morphology change was suggested. No effect of D-Phen on the growth rates means that the additive effect is highly stereo-selective.

REFERENCES

1. L.Addadi,Z.Berkovitch-Yellin, I.Weissbuch, J.V.Mil, L.J.W.Shimon, M.Lahav and L.Leiserowitz, Angew. Chem. Int. Ed. Engl. 24,466(1985)
2. S.G.Wolf, Z.Berkovitch-Yellin, M.Lahav and L.Leiserowitz, Mol.Cryst.Liq.Cryst., 186, 3(1990)
3. M.Kitamura and H.Funahara, J. Chem. Eng. Japan, 27, 124(1994)
4. M.Kitamura, J.Crystal Growth, 96, 541(1989)
5. N.Hirayama, K.Shirahata, Y.Ohashi and Y.Sasada, Bull. Chem. Soc. Jpn., 53, 30(1980)
6 M.Kitamura and H.Hashimoto, submitted to Mol. Cryst. Liq. Cryst.