CHAPTER III

DISCUSSION

III.1 General Theoretical Considerations

As pointed out by Zocher[1], even the smallest perturb-
ations due to impurities, foreign particles, surface inhomo-
geneities, or weak external forces can have profound and
long-range effects on the molecular orientation. Molecular
structure also plays an important role on the formation of a
mesomorphic texture.

The intermolecular attractions between the rod-like
molecules of nematic liquid crystals may be divided into the
following three types[2] of contributions:

1. Dipole-dipole attractions, the direct interactions
between permanent dipoles in the molecules.

2. Induced dipole attraction, arising from the mutual
polarization of the molecules by their permanent dipole
moments.

3. Dispersion forces, the attraction between the instan-
taneous dipoles produced by spontaneous oscillations of the
electron clouds of the molecules.

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[1] H. Zocher, Topics of Liquid Crystals Yet to be
Discussed, Mol.Cryst.Liquid Cryst., 7, (1969) 165.

[2] G.W. Gray, Molecular Structure and the Properties of
Liquid Crystals, Academic Press, London, (1968) pp.17-54.

In liquid crystals, these interactions must be strong enough to hold the molecules in parallel order. What is really of direct relevance in this case is not the total dipole moments but their positions and orientations with respect to the molecular axes. The mesomorphic behaviours, in fact, are determined primarily by the balance between the terminal and lateral dipole moments. If lateral attractions are stronger than terminal attractions, the molecules cannot slip past each other along the molecular axes. The molecules are then arranged in strata, and thus smectic phases are formed. If terminal attractions are dominant, then nematic phases are formed.

The geometry of the liquid crystalline molecules also plays an important part on the mesomorphic properties. Usually, an increase in breadth of the molecules effects a decrease of lateral interactions. Similarly, chain lengths also have important effects on the terminal interactions.

Growth kinetics

The crystallization of any crystals comprises the following three main steps[3]:

1. Degree of supersaturation or supercooling.
2. Nucleation of growth sites.
3. Growth of the crystals.

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[3] J.W. Mullin, Crystallization, Butterworths & Co. (Publishers) Ltd., London, (1961) pp.101-117.

An ideal crystallization operates strictly by these three steps. Generally these three operations may occur simultaneously at different positions of the growth sample.

It has been suggested that nucleation in liquids can arise when regions of ordered structure are present. These clusters are the results of random fluctuations and are sparse througout the liquid volume[4]. Homogeneous and heterogeneous nucleations may both be operating, however, and in general it is difficult to form truly homogeneous nuclei. From the calculation and experiments the rate of nucleation depends on the supercooling and interfacial energy.

However, even at low supercooling nucleation is always observed. It is proposed that strain is important and that the growth is enabled by a dislocation in such a process. The dislocation will reduce the strain energy, and thus will increase the activation to the nucleation. A high effectiveness of a dislocation to lower strain energy is expected, if the nucleus can be formed by dissociation into two partial dislocations. The nucleation process proceeds by the following steps[5]:

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[4] A.G. Walton, Nucleation in Liquids and Solutions, in Nucleation, A.C. Zettlemoyer, ed., Marcel Dekker, Inc., New York, (1969) pp.225-227.

[5] E. Hornbogen, Nucleation of Precipitates in Defect Solid Solutions, in Nucleation, A.C. Zettlemoyer, ed., Marcel Dekker, Inc., New York, (1969) p 343.

a) Attachment of the atoms at the steps by elastic interaction.

b) The two partial dislocations move apart by the seggregation.

c) The growth of the two-dimensional nucleus is changed into that in three dimensions by the formation of a screw dislocation and this leads to the spiral growth of the plane. Thus a three dimensional nucleus can be formed by the motion of the partial dislocations.

When a stable nucleus is formed, the crystal begins to grow. The growth rate is determined by the effects of surface energy, adsorption layer and diffusion.

Surface energy theories[6]

According to Gibbs the crystal will grow in such a way that its total surface free energy is minimum for a given volume at constant temperature. That is

$$\sum_i^n a_i g_i = minimum$$

where a_i is the area of the ith face of a crystal bounded by n faces.

g_i is the surface free energy per unit area of the ith face.

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[6] See Reference 3.

Wulff[6] has suggested that the equilibrium shape of a crystal is related to the surface free energies and the crystal will grow at the rate proportional to its surface energies. Up to now, there is still no general acceptance of the surface energy theories of crystal growth.

Adsorption layer theories[6]

The atoms try to attach themselves to the growing crystal, towards the positions where there is maximum attractive interaction or where the greatest number of bonds are formed. When steps are built up, it is obvious that the atoms will attach at these steps. The process is repeated until the whole surface is completed. Before further layers will be built up again, a monolayer island must be nucleated. This process is possible only at high supersaturation or supercooling.

However, crystal growth is also observed at low supersaturation, and Frank suggested that growth might be catalyzed by the presence of screw dislocations. One end of the dislocation line is fixed at an emergence point. The atoms are attached to this step which tends to displace in " a spiral staircase". Thus steps are always present and the growth continues until maximum curvature is reached.

The shape of the growth spirals is given approximately by[7]

7 S. Amelinckx, The Direct Observation of Dislocations, Academic Press, New York, (1964) pp.3-6.

$$\rho = 2\rho_c \theta$$

where (ρ, θ) are polar coordinates.

ρ_c is the radius of curvature of the critical nucleus. The rate of growth of the spiral form is determined by

$$v(\rho) = v_\infty (1 - \frac{\rho}{\rho}) \tag{1}$$

where v_∞ is the velocity of a straight growth front.

Diffusion Theories[6]

The diffusion theory of crystal growth was proposed by Berthoud and Valeton.. The mass deposition is caused by the transportation of molecules from the fluid to the solid surface, followed by a first-order reaction when the molecules arrange themselves into the crystal lattice.. The rate of mass change in the solid surface is

$$\frac{dm}{dt} = KA (c - c^*) \tag{2}$$

where

$$\frac{1}{K} = \frac{1}{K_d} + \frac{1}{K_r}$$

A = surface area of the crystal

K_d = the coefficient of mass transfer by diffusion

K_r = the rate constant for the surface reaction

c = concentration of the bulk

c^* = concentration of the growing crystal

thus $c - c^*$ = driving force resulting from the concentration gradient..

Many investigations indicated that the reaction rate was slightly different from that of first order, while some indicated a second-order reaction. The diffusion constant as well as the rate constant also vary from face to face. From the refractive index measurements, it is surprising that the concentration was highest at the corners and lowest at the centre of the face. It is not known whether this condition was a result of the mode of crystal growth or it was caused by a particular mode of growth.

III.2 Discussion of Experimental Results

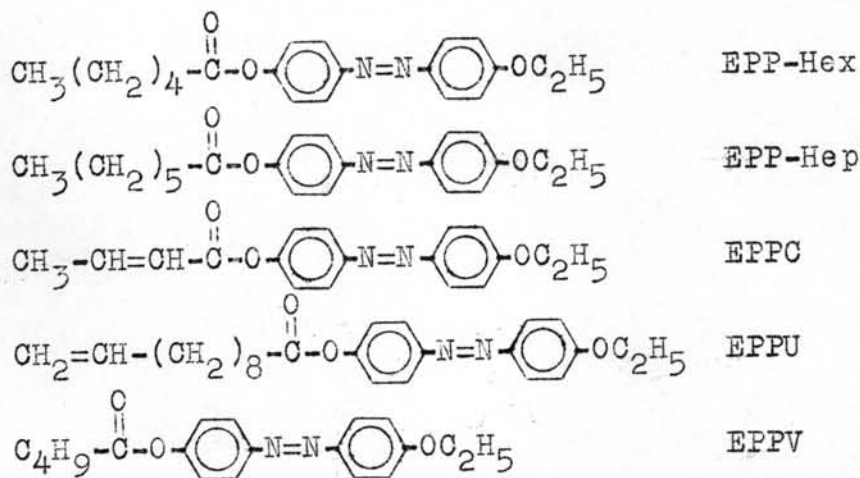III.2.1 Formation of schlieren texture in nematic liquid crystals.

By D.S.C.(Differential Scanning Calorimeter) method, Barrall et.al.[8] observed a small pre-transition peak in the heat capacity curve of PAA. The temperature range of this small peak is very small. This should be compared with the temperature range of the schlieren texture shown in Table II. For PAA it is only $0.1^{\circ}C$ just above the nematic-isotropic transition. The purity of PAA used by Barrall et.al. was 99.9%. It is not likely that this pre-transition peak arose from the impurity effect, but a similar peak was not observed

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8 E.M. Barrall,II, R.S. Porter, and J.F. Johnson, Specific Heats of Nematic, Smectic, and Cholesteric Liquid Crystals by Differential Scanning Calorimetry., J.Phys.Chem., 71, (1967) 895.
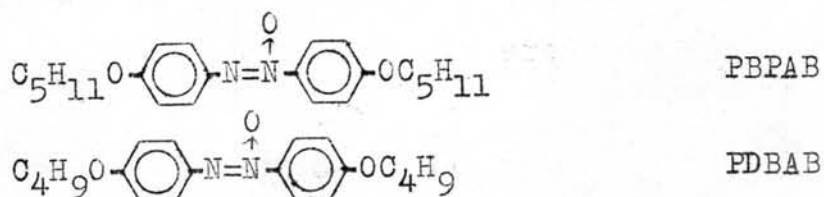
in   PASA.   There was no evidence of two nematic mesophases
in PASA.   But schlieren texture was observed in this compound.
It is not yet clear whether the schlieren texture is a real
phase of the nematic state or its presence is due to the
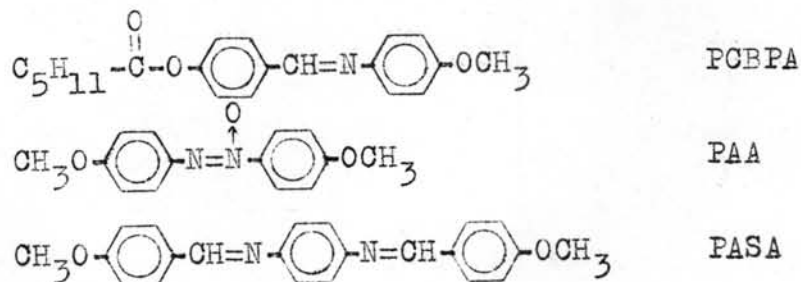effects of impurities.

From the observation of more than twenty organic com-
pounds which showed the nematic phase, only seven compounds
did not show the schlieren texture.   It is surprising that
six of these seven compounds belong to the azo group.   The
purity of the substance is determined by the temperature
range of melting.   These azo compounds seem to have wide temp-
erature ranges of melting, thus they are not absolutely pure.

Consider the molecular structures of these compounds

$CH_3(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-\bigcirc-N=N-\bigcirc-OC_2H_5$ EPP-Hex

$CH_3(CH_2)_5-\overset{O}{\overset{\|}{C}}-O-\bigcirc-N=N-\bigcirc-OC_2H_5$ EPP-Hep

$CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-O-\bigcirc-N=N-\bigcirc-OC_2H_5$ EPPC

$CH_2=CH-(CH_2)_8-\overset{O}{\overset{\|}{C}}-O-\bigcirc-N=N-\bigcirc-OC_2H_5$ EPPU

$C_4H_9-\overset{O}{\overset{\|}{C}}-O-\bigcirc-N=N-\bigcirc-OC_2H_5$ EPPV

Compare these with the molecular structures of those
which show the schlieren texture

$C_5H_{11}O-\bigcirc-N=\overset{O}{\overset{\uparrow}{N}}-\bigcirc-OC_5H_{11}$ PBPAB

$C_4H_9O-\bigcirc-N=\overset{O}{\overset{\uparrow}{N}}-\bigcirc-OC_4H_9$ PDBAB

$C_5H_{11}-\overset{\overset{O}{\|}}{C}-O-\bigcirc-CH=N-\bigcirc-OCH_3$ PCBPA

$CH_3O-\bigcirc-\overset{\overset{O}{\uparrow}}{N}=N-\bigcirc-OCH_3$ PAA

$CH_3O-\bigcirc-CH=N-\bigcirc-N=CH-\bigcirc-OCH_3$ PASA

There is no exact difference between these two types of liquid crystals. However, it is noticeable that all compounds containing the azoxy group exhibit the schlieren texture, and from TableII PAA possesses the smallest temperature range of schlieren texture.

It is shown in Section II.5.2 that the schlieren texture can be exhibited by all nematogenic substances on dirty slides. For example, EPP-Hep (recryst.), EPP-Hex (recryst.) and EPPU, which do not give the schlieren texture in their pure state can be induced to do so by the presence of impurities. Thus it is appropriate to state that the schlieren texture is "easily" or "hardly" formed by a particular substance.

It appears that the formation of the schlieren texture arises from the combined effects of the molecular structure (in particular, as regards its dipole moments and terminal chain lengths), surface effects and impurities.

a) The influence from the molecular structure.

1. The dipole moments. The ratios of lateral dipole moment to terminal dipole moment in the nematogenic molecules are roughly equal. It has been shown that most of the compounds containing the azoxy group readily exhibit the schlieren

PAA
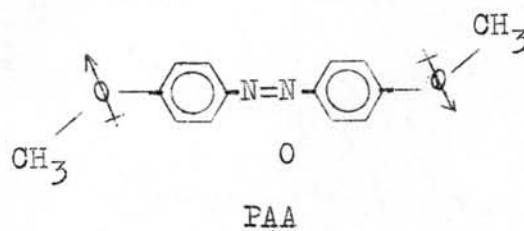
texture. The azoxy group causes strong lateral dipole moments, while the terminal dipole moments are approximately cancelled by the symmetry of the terminal groups. It seems that the schlieren texture is readily formed by the molecules with a lateral dipole moment crossing the molecular axis. However, the schlieren texture is hardly formed in PAA, though it contains the azoxy group.

Although PAA possesses a lateral dipole moment arising from the azoxy group, its terminal chains are short and symmetrical. If total terminal dipoles exist, the ratio of the lateral dipole to the terminal dipole is low compared with those in molecules with long alkyl groups.

Consider the molecular structure of the nematic compounds that do not readily exhibit the schlieren texture. Although they possess the strong dipole moment of the double bonds in the lateral position, they are not symmetric. Their strong lateral dipole moments are reduced by their terminal dipole moments, resulting in a low ratio of lateral to terminal dipole moments.

From this consideration, the molecules should be aligned in cybotactic groups. The cybotactic groups show a strong tendency to form pseudo-isotropic textures. It is evident

that the pseudo-isotropic texture has a strong tendency to show the schlieren texture (Fig.13b), and some substances shown in Table II have great tendency to show the isotropic texture, for example, PCBPA. Another evidence supporting this this conclusion is that the schlieren texture is also formed by smectic-C such as terephthal-bis-(p-amino-n-butylbenzoate) which also possesses strong lateral dipole moments.

It has been proposed that the isotropic-nematic phase transition displays typical features of a second-order phase transition[9]. The existence of short-range order above the transition temperature has been confirmed by Cabane and Clark[10] by NMR method, and by Stinson and Litster[11] by applying magnetic field to MBBA. This implies that the molecular arrangement does not change drastically when passing from the mesophase to the isotropic phase.

2. Geometrical effects. The chain length also has an important effect on the mesomorphic properties. At the

[9] H. Bässler, Liquid Crystals, in FestkörperproblemeXI: Advances in Solid State Physics, O. Madelung, ed., Pergamon, Oxford, (1971) pp.118-119.

[10] B. Cabane and W.G. Clark, Effects of Order and Fluctuations on the N^{14} NMR in a Liquid Crystal., Phys.Rev.Lett. 25, (1970) 91.

[11] T.W. Stinson III and J.D. Litster, Pretransitional Phenomena in the Isotropic Phase of a Nematic Liquid Crystal, Phys.Rev.Lett., 25, (1970) 503.

nematic-isotropic transition, rotation and translation of molecules occur. These movements are resisted by the mass of the molecules: the higher the molecular weight, the more difficult the molecules move. Another combined effect arises from the flexibility of the molecules. The flexibility of a long molecular chain linked by single bonds is usually higher than that of the shorter one with multiple bonds. At some certain modes, the polarization of the molecules is distorted and the molecules may be rearranged in such a way as to give a new texture.

III.2.2 Observation of the mesomorphic textures.

An interesting investigation is on the detailed features of the nematic textures near the nematic-isotropic transition temperature. As shown in Fig.6b and Fig.7b, the texture of a rather pure nematogenic compound is usually different from those found in impure substances. As the temperature increases the refractive index of the extraordinary ray decreases while that of the ordinary ray increases. At sufficiently near the transition temperature, the two rays travel almost in the same direction. Concentric rings are observed due to the phase difference between the ordinary and extraordinary rays[12].

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[12] N.H. Hartshorne and A. Stuart, Crystals and the Polarising Microscope, 4[th]ed., Edward Arnold (Publishers) Ltd., London (1969) pp.503-538.

The colour rings arise from the dichroism of the substance. The number of rings increase with the thickness of the specimen.

It is evident that the major effects on the formation of the schlieren texture are from the impurities. Experimentally, the schlieren texture is always formed on a dirty slide by all compounds, and the amount of the impurities present can be so low that the melting point is not significantly shifted. In fact the principal contribution to the formation of the schlieren texture is dust particles or particles which do not melt in the mesomorphic temperature range of the substances.

When foreign particles exist in the mesomorphic substance, the molecular arrangements are disturbed, depending on the size and number of the foreign particles. Disclination lines are created in order to reduce the strain in the specimen with the impurities behaving as origins of the stress field. It has been shown in Fig.7c that the impurities can act as multiple singularities. Another interesting evidence has been given by Meyer[13] that air-bubbles existing in the nematic sample also behave as point singularities. The conclusion can thus be drawn that point singularities are centres of the stress fields.

The schlieren texture generally looks more smooth than the marbled texture in which sharp disclination lines are always observed. Near the nematic-isotropic transition, these sharp lines are enlarged in width and begin to rotate as the rotating polarizer. The stress field in the schlieren

texture also looks more smooth than in the marbled texture. The stress field present in the bulk seems to cause ordering effects near the nematic-isotropic transition of longer range and to decay smoothly at longer distance than in the marbled phase. Far from the transition, the stress field caused by the impurities or any strain may be resisted by the strong attraction between the parallel molecules. The molecular orientation can change drastically only in the misfit regions. At higher temperatures, the attractive forces between the molecules are reduced by thermal vibrations. The stress field is then much influenced by thermal motion and it can have an important effect in aligning the molecules in such a way that the elastic energy is minimized. The molecular alignments have already been considered in Section I.1.

As shown in Fig.11, the mixture of EPP-Hep and EPP-Hex shows the same texture as in the cases of the pure substances. This is reasonable because EPP-Hep and EPP-Hex belong to the same homologous series; they have almost the same structure and properties, and their refractive indices are almost equal. When these compounds are mixed together, their molecules are mixed almost homogeneously and not so much strain is produced in the mixture. On the other hand, when compounds with different chemical groups such as EPP-Hep and PAA, are mixed, distorted disclination lines are observed (as shown in Figs. 12a,b). Presumably, this may be a result of the inhomogeneous packing of the molecular clusters, and the resulting stress field is very much distorted.

III.2.3 Growth of nematic droplets.

In the present discussion, the kinetics of growth of nematic droplets have been based on the standard nucleation theory and on the modification of Frank's[13] theory of crystal growth. It has been shown in the previous section that in pure substances the nematic droplets are not so round and that they tend to stick to the glass surface. In impure substances the droplets are usually round, can float almost freely, and contain dark brushes inside them. It is possible that the formation of the nematic droplets in these two cases may result from two different mechanisms.

The growth mechanisms of the nematic droplets should occur in two steps, viz., the nucleation of the embryos, followed by the actual growth process, which is probably similar in its essential nature to the Frank-Read[14] mechanism that is usually operative in the case of growth of normal solid crystals. The nucleation is presumably heterogeneous, since it is influenced by the glass surface and by the impurities or dust particles. In a pure substance, the nucleus is formed at the glass surface by virtue of thermal fluctuation

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[13] F.C. Frank, The Influence of Dislocations on Crystal Growth, Disc.Faraday Soc., 5, (1949) 48.

[14] W.T. Read, Jr., Dislocations in Crystals, McGraw-Hill Book Company, Inc., New York, (1953) pp. 139-154.

and supercooling. The number of nuclei depends on the degree of supercooling. At small cooling rate, the molecules are slowly aligned by the cohesive forces between the glass surface and the molecules and by the attraction between the sites and the molecules. A planar alignment should result. The molecules are arranged over the whole surface as soon as nucleation in the next layer occurs. Such a process is evident from the non-uniform growth rate in PAP. At high cooling rate, non-uniform temperature distributions and differential contraction between the liquid crystal droplet and the glass surface in contact with it may give rise to a dislocation. Indeed it has been observed that disclination lines are always present in such a case.

If impurities are present in the bulk, nucleation will occur at the sites of the impurities and supercooling will be decreased. Screw dislocations are formed at the crystal surface and the molecules are attached parallel to the steps by means of van der Waal forces and dipole-dipole interactions. The growth then continues in a spiral form. Since the inner circumference is shorter, the outer ends of the molecules are far apart and the space inbetween may allow other molecules to fill in. The shape of a growing nematic droplet looks like a sea urchin and appears with dark distinct crosses under the crossed polarizers. The molecular orientation to be expected is the same as that observed by Meyer[13]. If high strength of dislocation is present; the screw dislocation

would dissociate into two partial dislocations. The growth then continues in opposite directions and two point singularities can be observed. This process should be the same as that occurring in the spherulite growth.

From equation (2), if the temperature is fixed and the rate of diffusion at the surface is constant, it follows that initially the increase in volume of the crystal with time should be described by the relation: $r^{3/2} \propto t$, where r is the radius of the spherical droplets and t is the time. Later on, when the growth of the nematic droplets in a thin layer of the liquid crystal becomes two-dimensional, it can be expected that the radius of the flat nematic droplets would increase with time according to the relation: $r^2 \propto t$. Generally, however, the diffusion rate is not constant. In the usual Frank-Read mechanism, the rate of growth is proportional to the square of the degree of supercooling at low supercooling, and varies linearly with it at high supercooling[15]. From the experiment, the rate of growth of the nematic droplets varies from one droplet to another. This may be an effect due to supercooling. If a droplet is formed at a certain temperature, and another droplet is subsequently formed in its neighbourhood, then the presence of the other droplet may significantly decrease the local degree of supercooling

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15 R.A. Laudise, The Growth of Single Crystals, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, (1970) p.98.

by virtue of the heat being transferred between the droplets and the growth rate of the former droplet is thus slowed down. Similarly, the latter droplet must also grow at a lower degree of supercooling, and thus at a different growth rate.

The cease of growth of the nematic droplets may also be influenced by another effect caused by the presence of the impurities in the bulk. There are two kinds of impurities present, the mobile and the immobile impurities[16]. The immobile impurities should not affect the rate of growth, but the mobile impurities can sometimes be adsorbed onto the steps and the growth layers are then blocked.

Another important effect arises from the short range attraction between the molecules. Thermal vibration will be comparatively large for large droplets. The combined effect is the higher diffusion rate of molecules from the growth surface. When the number of molecules diffusing from the surface is equal to the number of molecules arriving at the surface, the droplets cease to grow.

In the experiments, the growth rate of a binary system is not significantly different from that of a pure nematic liquid crystal when the nematogenic molecules are similar in shapes and properties. Thus the molecular arrangement in this case is only slightly distorted by the presence of the foreign molecules.

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16 N. Cabrera and R.V. Coleman, Theory of Crystal Growth from the Vapour, The Art and Science of Growing Crystals, J.J Gilman, ed., John Wiley&Sons, Inc., New York, (1963) pp.20,21.

III.3 Concluding Remarks.

The formation of textures in liquid crystals are governed by many factors, such as the molecular structures, the inter and intramolecular motions, molecular interactions, the mechanical stress, structural imperfections, and impurities. It has been established in the present investigation that the molecular structures and the presence of the impurities play important parts in the formation of the schlieren texture. However, the minimum amount and type of impurities required in each case have not yet been studied in detail, and the problem should be a challenge for further investigations. Also, the significance of the exact magnitudes and positions of the dipole moments in the nematogenic molecules that have great tendency to exhibit the schlieren texture should be an interesting subject for future studies.

Since the growth kinetics in liquid crystals can be influenced by so many factors, e.g., the presence of impurities, the degree of supercooling, thermal fluctuations, and disclinations, the growth rates of nematic droplets alone has not given much information concerning the details of the growth mechanisms. Thus, in future investigations on the formation of textures, the amounts and types of the impurities present in the liquid crystals should be controlled more precisely. Determination of the growth rates at various

degrees of supercooling may give further useful knowledge of
the growth mechanisms, since at a low degree of supercooling
the relation between the growth rate and the degree of super-
cooling should approximately satisfy the parabolic law.