Polymer Vol. 38 No. 12, pp. 3069–3083, 1997
© 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/97/$17.00 + 0.00

PII: S0032-3861(96)00873-7

Macroscopic structures in liquid crystal systems prepared with spin coating

A. Schreckenbach*
Fachbereich Werstoffwissenshaften, Martin-Luther-Universität Halle-Wittenberg, Geusaer Strasse, 06217 Merseburg, Germany
Revised 14 August 1996)

Macroscopic structures have been created in poly(γ-benzyl-L-glutamate) films, OM-20 films, poly(hexyl-isocyanate) films and 4′-pentyl-4-cyanobiphenyl using spin-coating equipment with rotating cap. The orientation of the molecules in the films has been determined using crossed polarizers. The visible macroscopic maltese crosses were the result of a radial symmetrical orientation of the molecules in the film plane. The development of the macroscopic structures during the spin coating process has been studied. The late development of the structures at low flow velocity explain the none appearance of Coriolis effects on the structure. An asymmetrical growth of the structure in the film plane has been observed during the spin-coating process independent of the polymer used. The experimental results led to a theoretical model of a flow-induced spherulite growth. © 1997 Elsevier Science Ltd.

(Keywords: PBLG; PHIC; OM-20)

INTRODUCTION

Spin coating is a common technique for the preparation of polymer films. The spin-coating process has been studied experimentally and theoretically by different groups[1–7]. The common spin coating equipment was essentially modified for the creation of poly(γ-benzyl-L-glutamate) (PBLG) films with macroscopic structure[8,9]. Air turbulences and the evaporation of the solvent during spin coating were suppressed by a rotating cap. Therefore, the equipment made it possible to prepare films over minutes or hours in the liquid state, which is necessary for the production of structures. In this work[9], the parameters which influence the preparation of macroscopic structures have been classified. Rheological effects and the self-organization of a spherulite have been discussed as possible reasons for the structures, but it was impossible to experimentally specify the mechanism more precisely[9].

The aim of this work was generalization of the macroscopic effects by using different liquid crystal systems and the identification of the physical mechanism which cause the orientation of the macromolecules. For this, three polymers and a low molecular weight system were used.

The cholesteric PBLG was used to determine the influence of water on the viscosity of the solution as a possible reason for the water-dependent macroscopic structures, poly(γ-benzyl-L-glutamate)-*co*-(γ-*n*-octadecyl-L-glutamate) (OM-20) was used to determine the influence of a higher viscosity of the solution on the growth of the structure, and the nematic poly(hexyl-isocyanate) (PHIC) was used to determine the influence of the crystallization type of the system on the macroscopic structure.

The pure 4′-pentyl-4-cyanobiphenyl was used to exclude possible phase separation effects in binary solutions as primary reason for the growth of macroscopic structures.

EXPERIMENTAL

Investigations by polarized light

To examine the thin films during spin coating, two polarizes were used[10]. The optical behaviour of the film is correlated with the orientation of the macromolecules[11,12]; black areas between crossed polarizers were the result of macromolecules orientated with their optical axes parallel to the axes of the polarizers. A program was developed to calculate the macroscopic structure for a given field of orientated macromolecules. The rod-like macromolecules were represented by directors (x, y, e_x, e_y), where x, y were the coordinates of the director in the film plane and e_x, e_y the components of the unit vector of the orientation of the director. The program checks the orientation of the directors with regard to the crossed polarizers, which were represented by unit vectors $\boldsymbol{p}_1$, $\boldsymbol{p}_2$. Directors which were orientated parallel to the polarizers with a maximum deviation from d degrees resulted in a black area of the calculated macroscopic structure. The deviation d corresponds to the statistical deviation of an ideal structure of the macromolecules in the film. A total of 30 000 directors were used for the calculation, but only a few were used to create a clearly arranged figure, and were represented by flags.

A radial symmetrical orientation of the directors/molecules corresponds to a maltese cross structure (*Figure 1*). A radial symmetrical orientation with linear increase of the angle α between radius and molecules dependent on the distance to the centre corresponds to a

---

* Present address: Blumenstrasse 7, 25557 Hanerau-Hademarschen, Germany

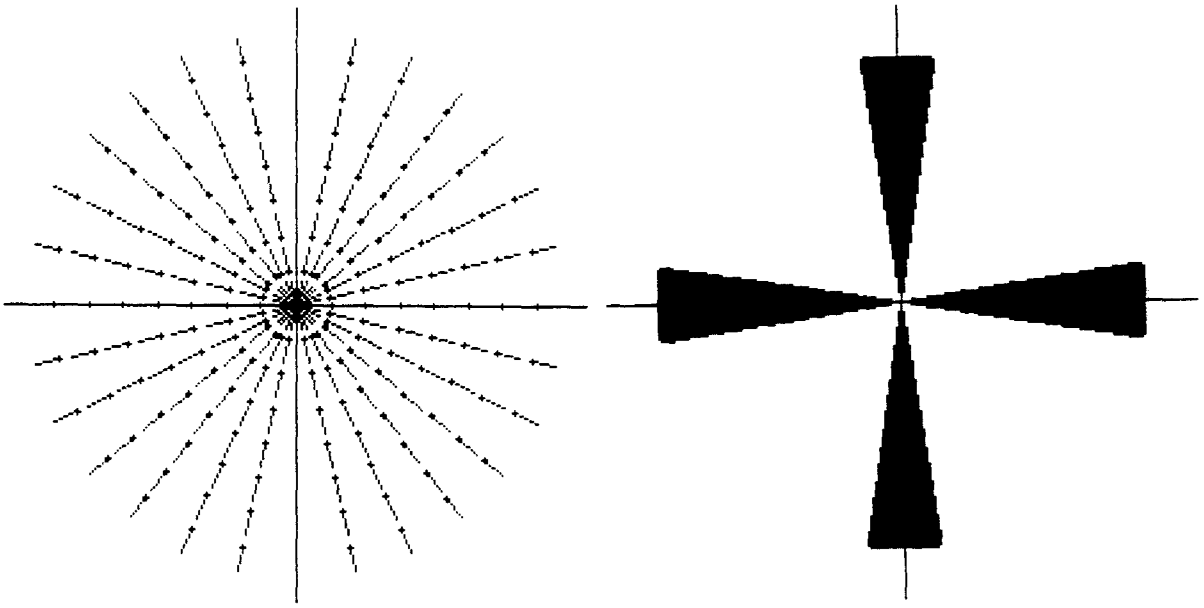


Figure 1 Maltese cross structure visible between crossed polarizers (right) caused by radial orientation of macromolecules/directors represented by flags (left); maximum deviation *d* between polarizers and directors, 9°; orientation of the crossed polarizers, 0°, 90°. A total of 30 000 directors, which arranged homogeneously in the film plane, were used for calculation, but only 200 were used to create a clearly arranged figure

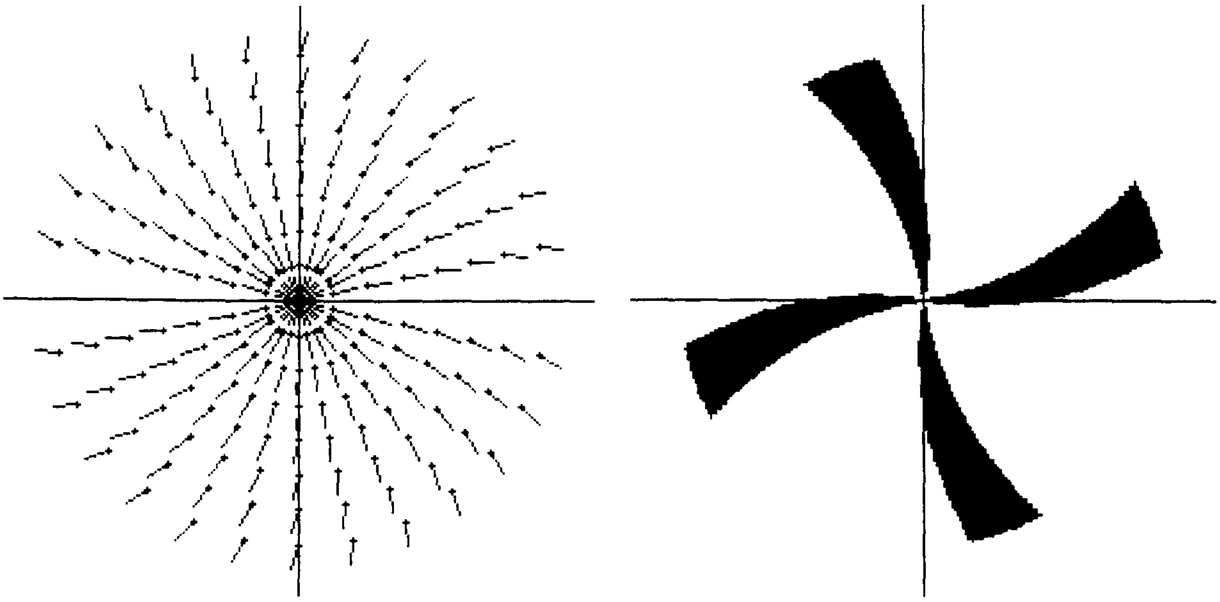


Figure 2 Spiral structure visible between crossed polarizers (right) caused by radial orientation of macromolecules/directors (left) with increasing angle α between the radius and the directors ($r = 0, \alpha = 0° \rightarrow r = 1, \alpha = 20°$); maximum deviation *d* between polarizers and directors 9°; orientation of the crossed polarizers, 0°, 90°

spiral structure. The direction of the curves was dependent on the orientation of the molecules (*Figures 2* and *3*), and the curve of the spiral arms was dependent on the increase of the angle between the radius and the molecules (*Figure 4*).

In contrast to radial symmetrical structures, radial asymmetrical structures resulted in different images of the macroscopic structure depending on the orientation of the crossed polarizers. A radial asymmetrical structure like a spherulite[12] is represented in *Figures 5* and *6*, where the distance $c = 0$ describes radial symmetrical arranged molecules.

Properties of the PBLG solutions

The PBLG[13] (Poly Science, lot 436200) used in the experiments had a nominal molecular weight of 214 000. 1,4-Dioxane (Aldrich GmbH, Germany) was used as the solvent. The solutions were prepared at least 8 h before use at room temperature and were in the liquid crystal state at a concentration of 14% (concentrations given as PBLG/solution (w/w)). Below a concentration of 12% the solutions were in the isotropic phase indicated between crossed polarizers (the solution became completely transparent). The phase diagram of the PBLG/dioxane solution[14] showed a two-phase region between the isotropic and liquid crystal phases. Therefore, to exclude unwanted phase effects during the preparation, only solutions with a concentration of 14% or more were used. The viscosity of the solution was measured with a cone plate viscosimeter (TA Instruments Ltd, UK)

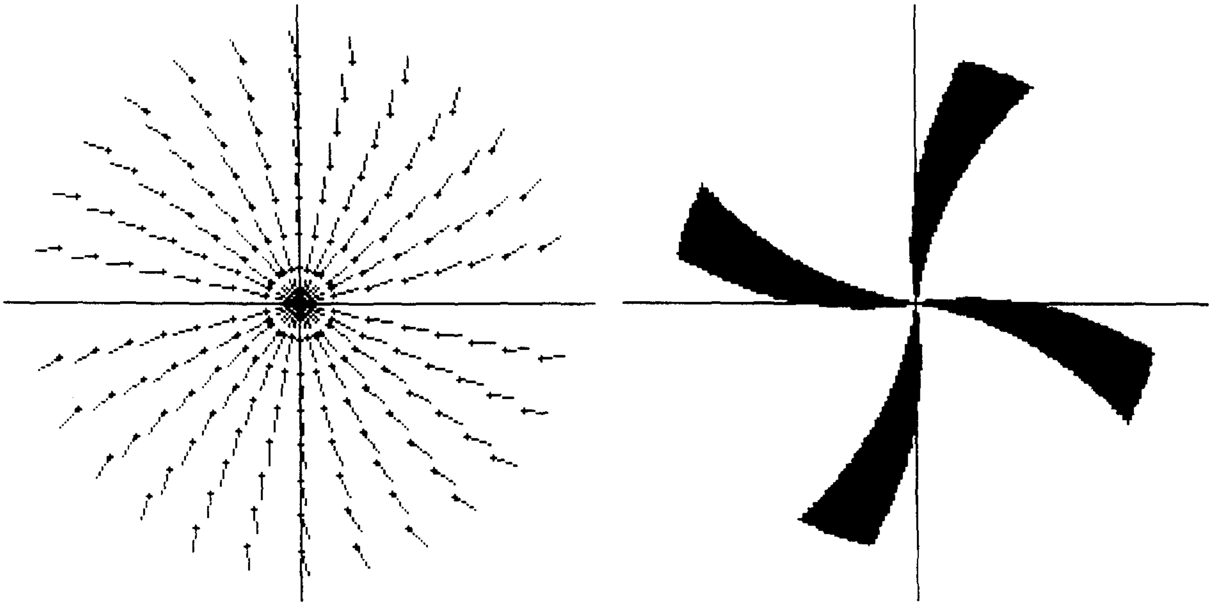


Figure 3 Spiral structure visible between crossed polarizers (right) caused by radial orientation of macromolecules/directors (left) with increasing angle α between the radius and the directors ($r = 0$, $\alpha = 0° \rightarrow r = 1$, $\alpha = -20°C$); maximum deviation d between polarizers and directors, 9°; orientation of the crossed polarizers, 0°, 90°

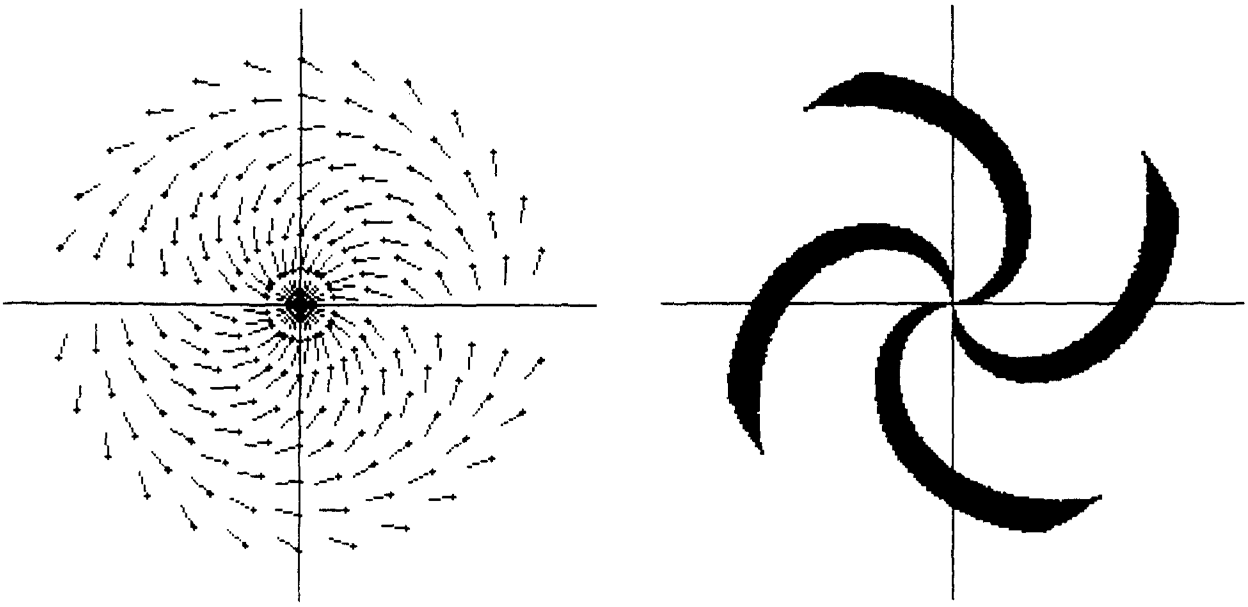


Figure 4 Spiral structure visible between crossed polarizers (right) caused by radial orientation of macromolecules/directors (left) with increasing angle α between the radius and the directors ($r = 0$, $\alpha = 0° \rightarrow r = 1$, $\alpha = 120$); maximum deviation d between polarizers and directors, 9°; orientation of the crossed polarizers, 0°, 90°

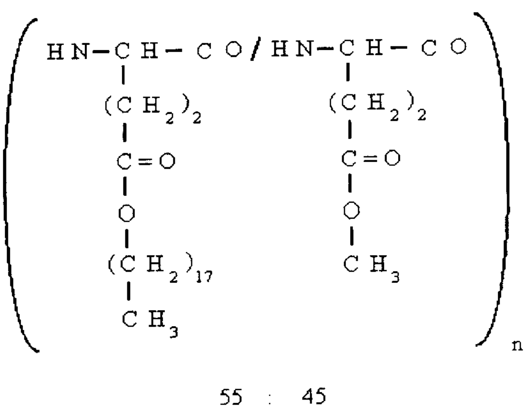
(*Figures 5–7*). To reduce the evaporation of the solvent during the measurement, silicon oil was poured onto the solution remaining outside the cone. The viscosity dependence on the shear velocity (*Figure 8*) became lower if 2% water was added to the solvent. An increase to 4% water in the solvent only caused a slight change of the viscosity (*Figure 9*). This is important because it has been shown that a transition from the macroscopic structure maltese cross to spiral arms is caused by an increase in the water content of the solvent to 4%[9].

Properties of the OM-20 solutions

The OM-20 with 20% octadecyl and 80% methyl side-chains was synthesized[15] (MPI for Polymer Research, Mainz, Germany). 1,4-Dioxane was experimentally found to be an appropriate solvent for the spin-on process. Methylene chloride was inappropriate for the preparation because of the high evaporation rate. The OM-20/dioxane solution was in the liquid crystal phase and birefringent (visible between crossed polarizers) above a concentration of 13%, and in the isotropic phase below 13% (transparent solution between crossed polarizers). It was prepared 14 h before use. In contrast to PBLG solutions the viscosity was higher (*Figure 10*), and the consistency of the solution was similar to a paste.

Properties of the PHIC solutions

PHIC (Poly Science, lot 423750)[16] with a nominal molecular weight of 65 000 is a lyotropic–nematic rod-like liquid crystal polymer, in contrast to the cholesteric



PBLG. Toluol was used as the solvent, and the solution was in the lyotropic–nematic phase at a concentration of 40%^{17}. The solution was prepared 6 h before use.

Properties of a 4′-pentyl-4-biphenyl-carbonnitrile

4′-Pentyl-4-cyanobiphenyl ($CH_3(CH_2)_4C_6H_4C_6H_4CN$) was purchased from Aldrich GmbH, Germany. It is a thermotropic system which becomes birefringent at room temperature. The crystallization point is at 22.5%°C, and the nematic–isotropic transition temperature is at 35°C^{18}. Therefore, the laboratory temperature was 26°C during preparation. 4′-Pentyl-4-cyanobiphenyl was extremely sensitive to scratches at the substratum.

Equipment

Spin coating equipment (*Figure 11*) was developed to observe the production of the liquid films *in situ*. The disadvantages of the existing spin-coating equipment is that it is impossible to observe the sample with optical methods in the transmission direction because the component cap, sample disc, engine and axis are not transparent and the engine and the axis are necessarily in the optical path. The general problem was overcome by using a cap, a sample disc and a substratum which were transparent in the area of the transparent film. A transparent rotation body (in the direction of the

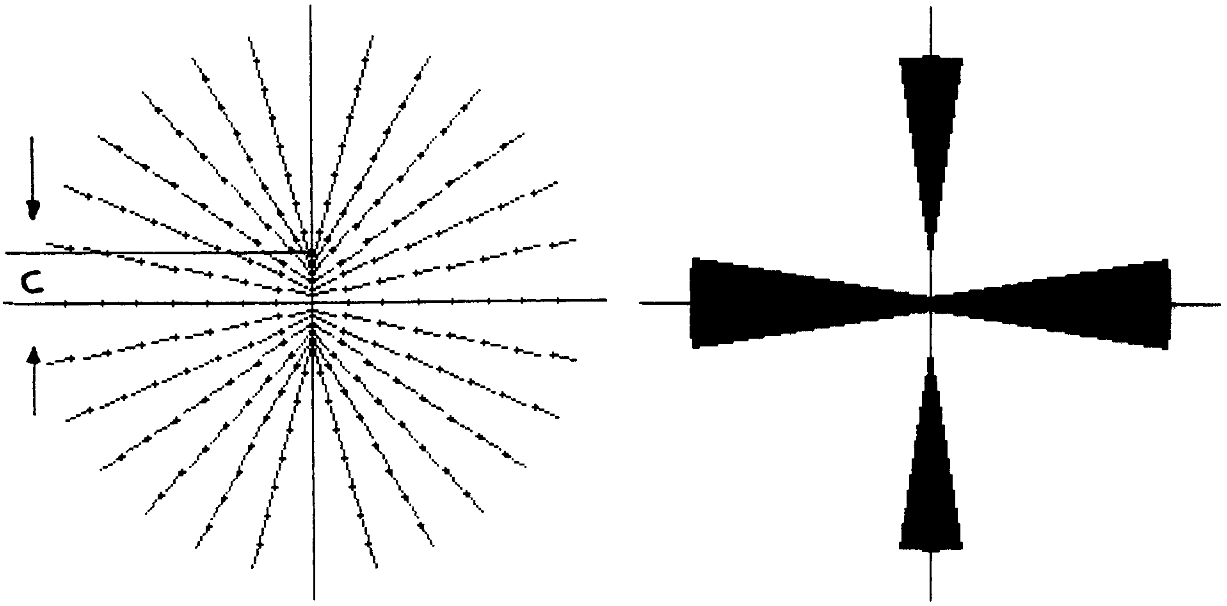


Figure 5 Spherulite structure visible between crossed polarizers (right) caused by radial asymmetrical orientation of macromolecules/directors (left); distance $c = 0.2$; maximum deviation d between polarizers and directors, 0°; orientation of the crossed polarizers, 0°, 90°

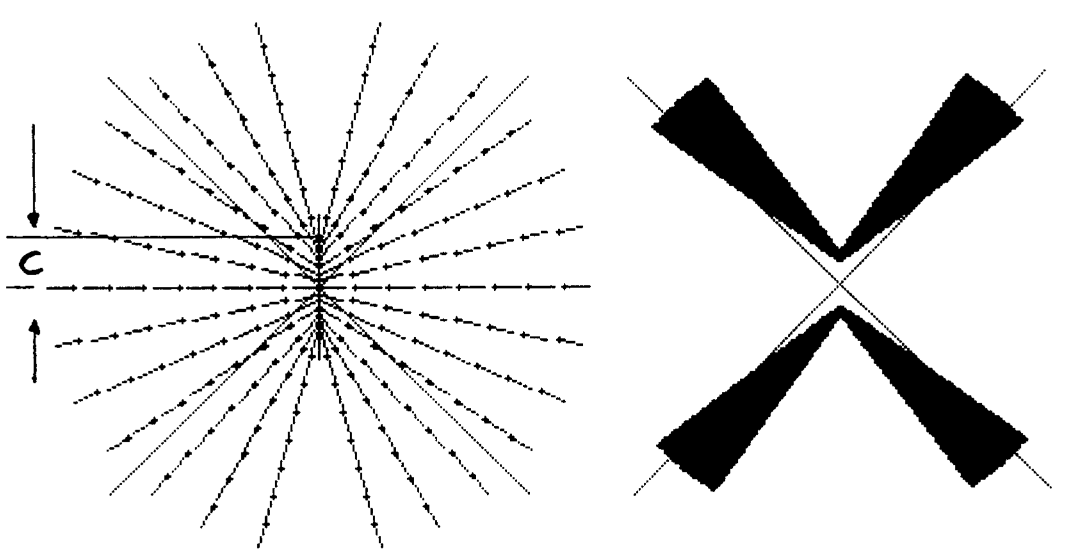


Figure 6 Spherulite structure visible between crossed polarizers (right) caused by the radial asymmetrical orientation of macromolecules/directors of *Figure 5* (left); orientation of the crossed polarizers, 45°, 135°

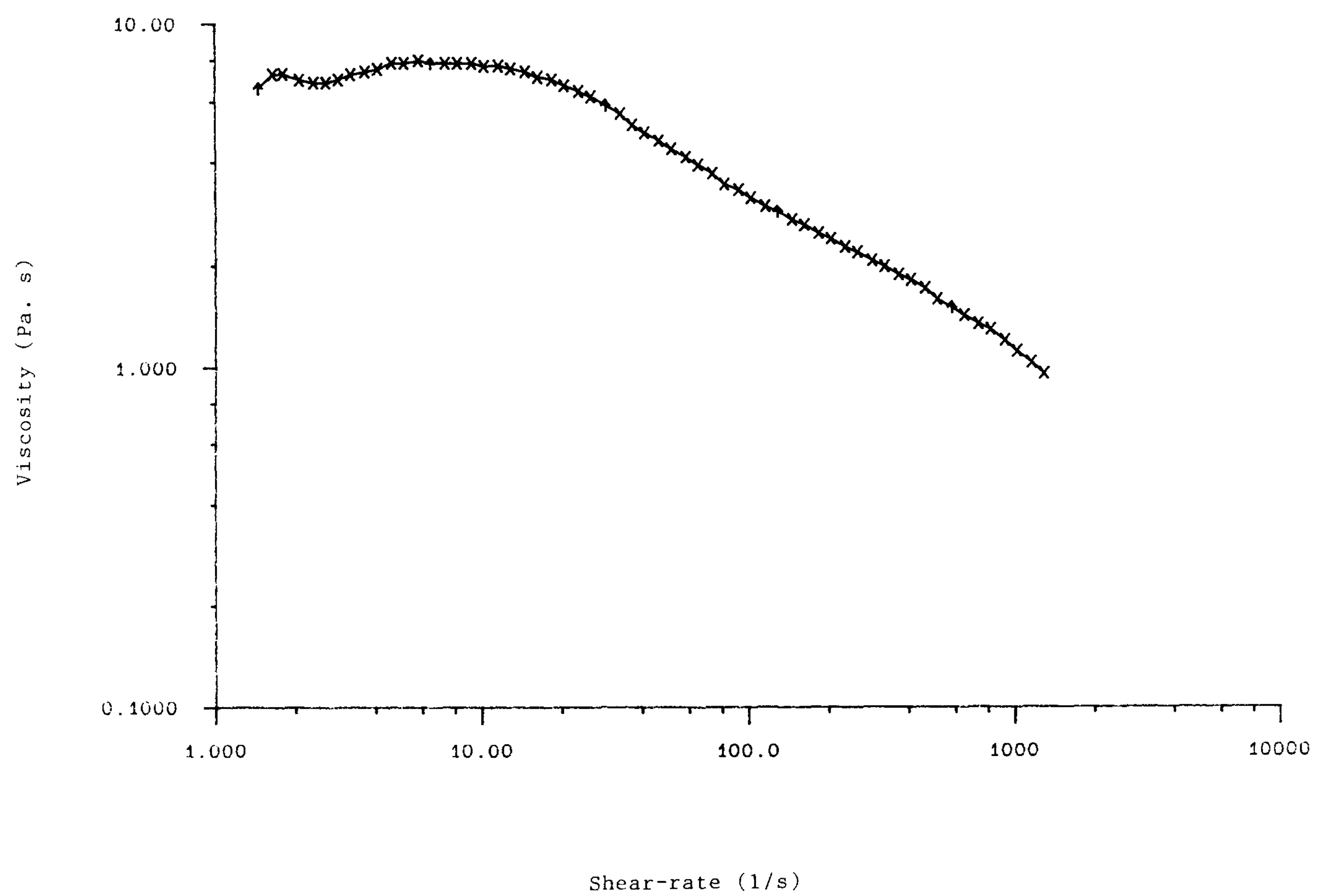


Figure 7 Viscosity of a PBLG solution depending on the shear velocity measured with a cone plate viscosimeter; PBLG/dioxane solution, 15% (w/w); 0% water in the solvent; temperature, 23°C

rotation axis) was constructed by connecting these components with a hollow axis (in the area of the film, diameter 20 mm) and a cog-wheel. The rotation body was fixed with two ball bearings in a block of brass which was cooled by air because of the friction of the dust caps at the ball bearings and the belt drive. The drive was indirect using an external engine (PORTESCAP GmBH, parameters: 200–10 000 rev min^{-1}, 200–8000 rev min^{-1} with rotation body, velocity error ± 1%) and a belt drive. Vibrations were suppressed by using two ball bearings and the heavy block of metal in combination with a belt drive. Magnets at the sample disc and a coil at the block were used to measure the angle velocity, which was controlled by a PC. The whole system was placed, using rubber sockets, on a small aluminium table with a hole in the area of the sample. The engine was fixed separate from the table to reduce vibrations. To increase the reproducibility of spiral arm structures in PBLG films, a ring could be placed onto substratum, which caused a homogeneous and flat solution profile.

Using two crossed polarizers attached to the rotation body it was possible to observe each point of the sample under the same optical conditions By fixing the polarizers to the laboratory system, it was possible to observe each point with different directions of polarized light, as the direction was changed dependent on time during spinning.

With direct sight or a video system only a diffuse macroscopic structure would be visible because of the poor time resolution. Therefore, the investigations were realized by using a camera (Contax 167 MT) with electronic release and an electronic flash (Metz 32 CT, t_{Flash} 0.001 s to 25 μs). Furthermore, a macro resolution lens was used (Novoflex automatic bellows + 60 mm objective). The position of the camera and flash were above and below the rotation body, respectively. The camera was controlled by a PC, and photographs were taken with time intervals above 0.3 s (resolution of the winder).

Cleaning the substratum

The float glass (Flachglas AG, 25 × 25 mm, thickness 2 mm) was cleaned with soap and water and rinsed with distilled water[9]. For the experiments with 4′-pentyl-4-cyanobiphenyl the float glass was cleaned with aqueous HCl 30% before cleaning with distilled water.

Preparation

The solution was poured onto the substratum before spin coating started. In the case of PBLG solutions including 4% water, a ring was placed onto the substratum. OM-20 solution was spread out on the substratum with a spatula. The cap was fixed on the sample disc, forming a closed system. A few seconds after fixing the cap the engine was accelerated. There was no substantial loss of solvent through evaporation after closing the system. During the spin-coating process the sample was photographed by the camera system using a logarithmic time-scale. After spinning, the cap was lifted, and the solution on the substratum dried in a few seconds, depending on the thickness of the film. As

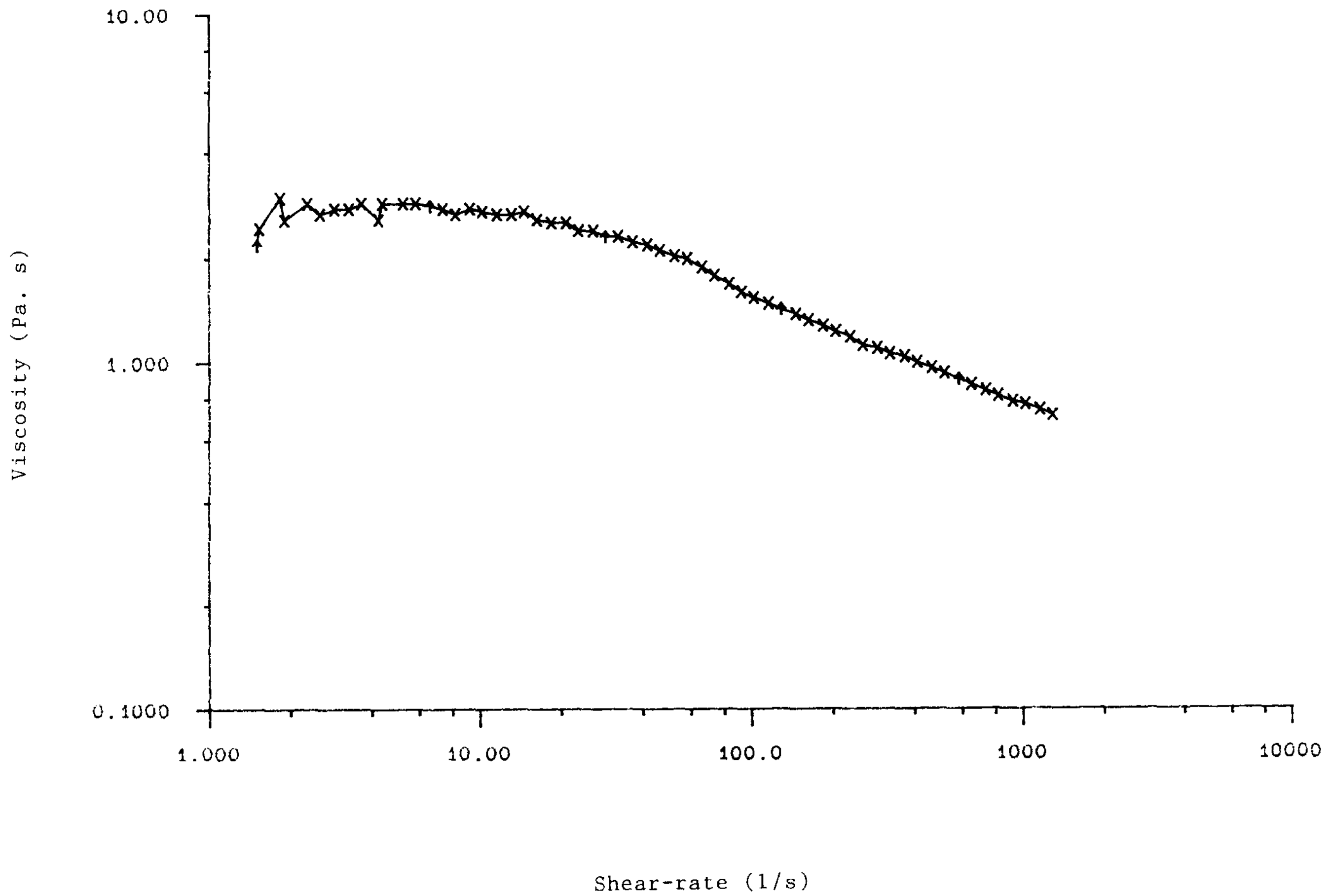


Figure 8 Viscosity of a PBLG solution depending on the shear velocity measured with a cone plate viscosimeter; PBLG/dioxane solution, 15% (w/w); 2% water in the solvent; temperature, 23°C

expected, 4′-pentyl-4-cyanobiphenyl retained its liquid consistency.

Measurements and results

In general, all provided structures were independent of the direction of rotation, in agreement with earlier results[9].

Estimation of shear rate during the spin-coating process

The PBLG and PHIC solutions described above were used to estimate the velocity of the solution and shear rate during the spin-coating process. The velocity of the solutions which span off the substratum immediately after starting spin-coating into the receptacle[9] was determined by the distance travelled by the solution before striking on the base of the receptacle and the distance between the base and the substratum. The velocity was of the order 1–10 $\mathrm{ms^{-1}}$. The velocity during the production of the structures was measured by using a marker (dye dissolved in dioxane or toluene[9]) or air-bladders which were created by pouring the solution onto the substratum. As expected, the velocity of the solution during the production of the structure was lower than in the starting phase of spin-coating, with values of the order of 10^{-3}–$10^{-4}\,\mathrm{ms^{-1}}$. The thickness of the liquid films before starting the spin-coating process was 1 mm, and the final thickness of the dried films of the order of 1 μm (measured mechanically with an alpha step 200, MPI Mainz). The thickness of the films during the phase of the structure growth was estimated to be 100–1 μm. The estimation of the shear rate dv/dz follows from these results:

After starting the spin-coating process ($\ll$2 s):	10 000–2000 $\mathrm{s^{-1}}$
During growth of the structures (>10 s):	300–3 $\mathrm{s^{-1}}$

From these values and the obtained viscosity measurements dependent on the shear rate in the most interesting range between 0 and 1400 $\mathrm{s^{-1}}$ (limit of the viscosimeter), the viscosity at spin-coating conditions could be determined approximately.

PBLG film with maltese cross structure

PBLG/dioxane solutions always produced a maltese cross visible between crossed polarizers for angular velocities between 1000 and 8000 rev $\mathrm{min^{-1}}$, in agreement with earlier results[11]. The preparation time was 10 min. A series of photographs of the first minute of preparation (*Figure 12*) shows two ‘boomerangs’ which grew together and built a maltese cross. The double boomerang represented a radial asymmetrical orientation of the molecules in the film plane as described before (*Figures 5* and *6*). Therefore, the flow of the liquid is not a sufficient explanation for the production of macroscopic structures because there is no obvious explanation for an asymmetrical flow under symmetrical conditions in the preparation chamber. Furthermore, the photographs showed that the macroscopic structure started to penetrate the primary domain structure caused by pouring the solution onto the substratum after a few

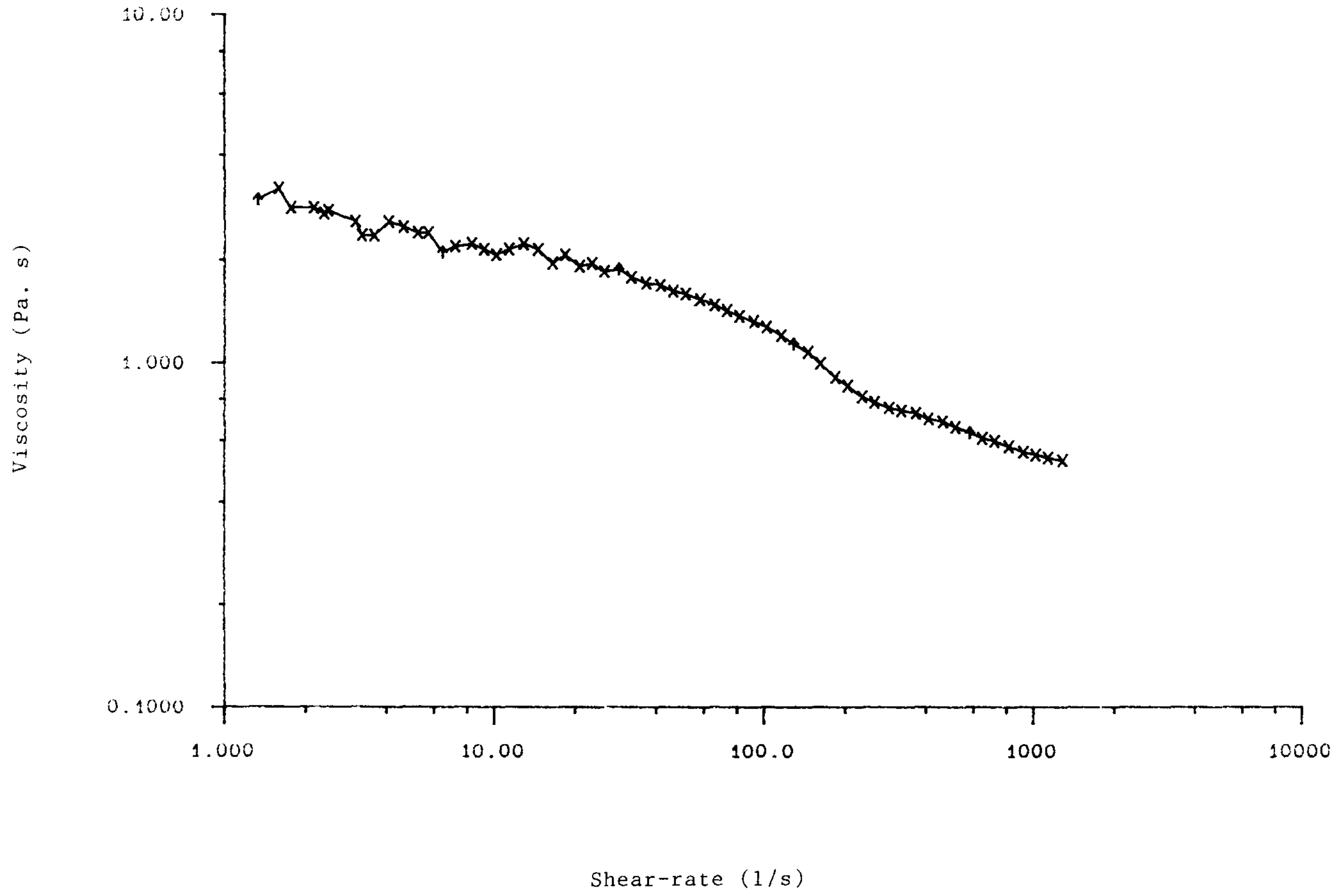


Figure 9 Viscosity of a PBLG solution depending on the shear velocity measured with a cone plate viscosimeter; PBLG/dioxane, 15% (w/w); 4% water in the solvent; temperature, 23°C

seconds. The late development of the structure in combination with the low velocity of the solution provides the explanation for the non-effect of Coriolis forces on the macroscopic structure. This result was independent of the macroscopic structure (maltese cross, spiral structure).

Two simple experiments were carried out to study the behaviour of the liquid PBLG film. As expected, there was no macroscopic structure produced without rotation of the sample disc. Therefore, the flow of the liquid is necessary for the production of macroscopic structured films.

After spin-coating the cap was left on the sample disc for an hour, which prevented the evaporation of the solvent. The cap was then removed, and there was no macroscopic structure visible, in contrast to the case where the cap had been lifted immediately after spinning. The experiment showed that the structure was destroyed by thermodynamic movement, in contrast to ordinary spherulites grown in solution.

PBLG film with spiral structure

PBLG films with a spiral structure were produced with 4% water in the solvent (water/dioxane, w/w) at angular velocities between 1000 and 4000 rev min^{-1}. To achieve more reproducible conditions in contrast to ordinary conical caps[9] a ring was placed onto the substratum. By using the equipment with and without a ring under the same conditions it was found that the spiral structures were dependent on the solution profile and independent of the height of the solution in the range of 0.5–3 mm. Therefore, the equipment with a conical cap[9] with a droplet profile of the solution produce more different directions of curves than the cylindrical cap with a flat profile[9].

The experiments *in situ* showed the same double boomerang structure as described above, but it was impossible to discriminate the double boomerang structure which resulted in spiral arms or a maltese cross. The differences which were expected could not be distinguished.

PHIC film with maltese cross structure

The experiments were carried out with PHIC/toluol solutions with a concentration of 43% at room temperature and angular velocities between 1000 and 7000 rev min^{-1}. Observation *in situ* by a camera showed a double boomerang structure which grew together to a maltese cross (*Figure 13*). The behaviour of PHIC is identical to PBLG, although it is a nematic liquid polymer in contrast to the cholesteric PBLG. Experiments with a mixture of water and toluol as solvents resulted in inhomogeneous solutions due to the immiscibility of toluol and water.

OM-20 film with maltese cross structure

OM-20 films with maltese cross structure were produced within 2 h at 8000 rev min^{-1}. The long preparation time was caused by the high viscosity of the solution. As a consequence, it was possible to stop the spin-coating process at an early stage of the development of the structure. (It must be remarked that the study of the development of a structure using different samples which

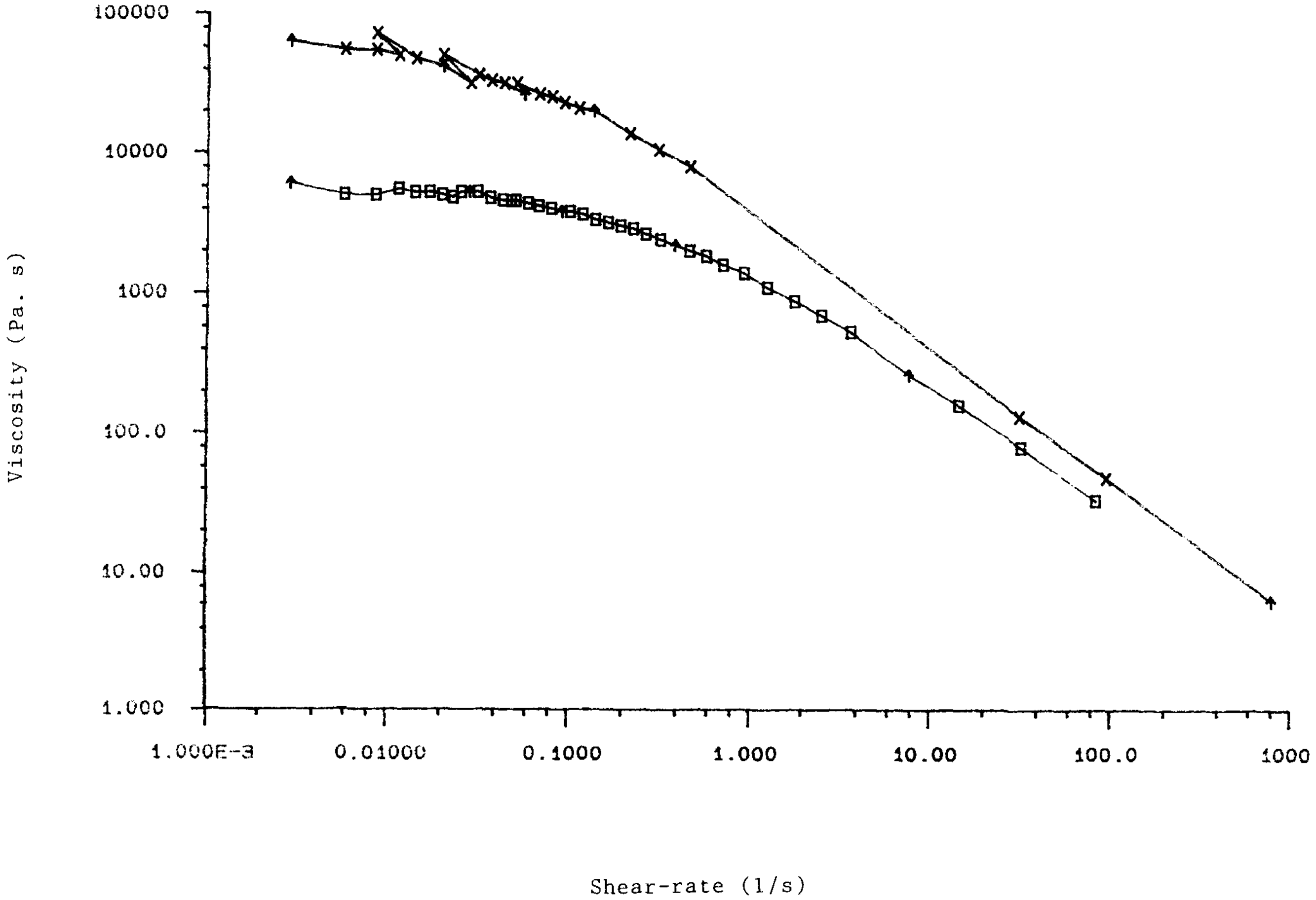


Figure 10 Viscosity of a OM-20 solution depending on the shear velocity measured with a cone plate viscosimeter; OM-20/dioxane solution, 14% (w/w); temperature, 23°C. (×), Without silicon oil to reduce the evaporation of the solvent; (O), with silicon oil at the edge of the cone

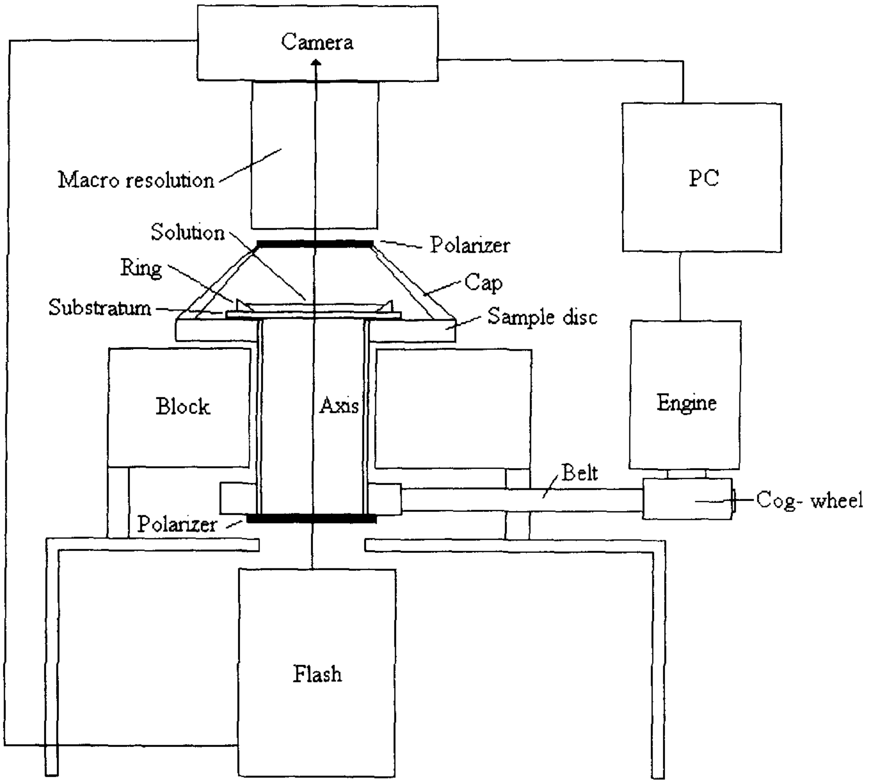
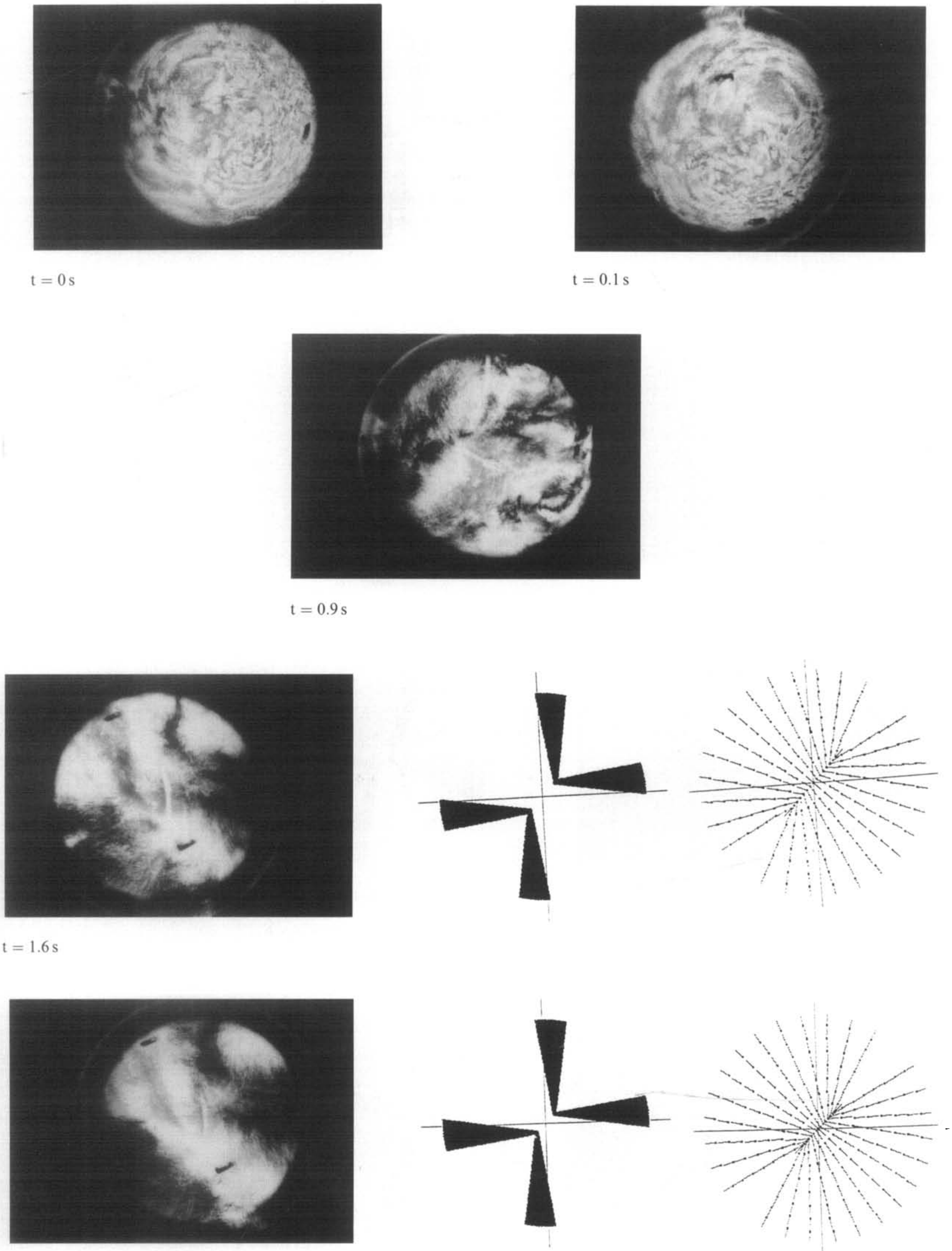


Figure 11 Spin coating equipment for the observation *in situ*. The optical path is marked by an arrow



t = 0 s

t = 0.1 s

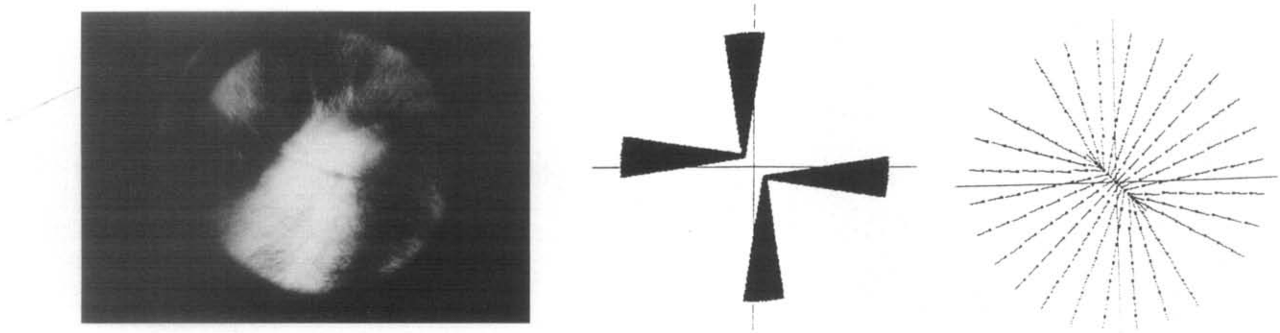
t = 0.9 s

t = 1.6 s

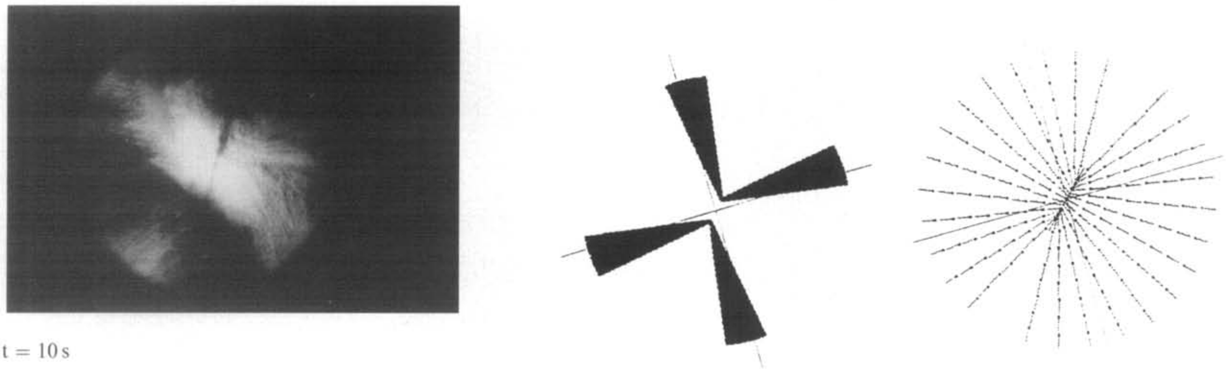
t = 3 s

Figure 12 Development of a maltese cross structure; theoretical polarizer figure and orientation of the molecules: PBLG/solvent, 14% solvent, water/dioxide 3%; 4000 rev min^{-1} clockwise; fixed polarizers; distance of the marks on the back side of the substratum, 1 cm; time of the observation, 1 min

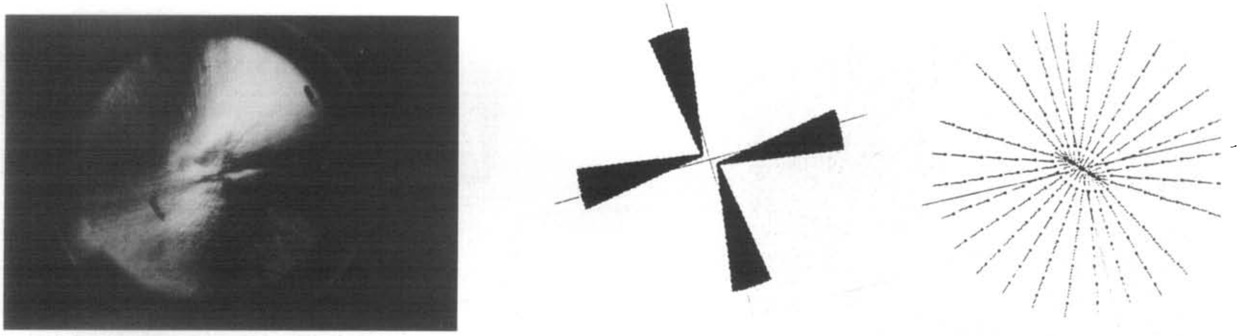
were stopped at different times at the same angle velocity is not striking evidence for the growth of a structure because parameters such as the stopping of the sample disc and different filling times of the chamber were uncontrolled.) *Figures 14* and *15* showed the behaviour of a radial asymmetrical structure described above. Furthermore, the structure was influenced by the surface roughness of the solution. As expected, the experiments *in situ* showed the development of the double boomerang structure into a maltese cross.



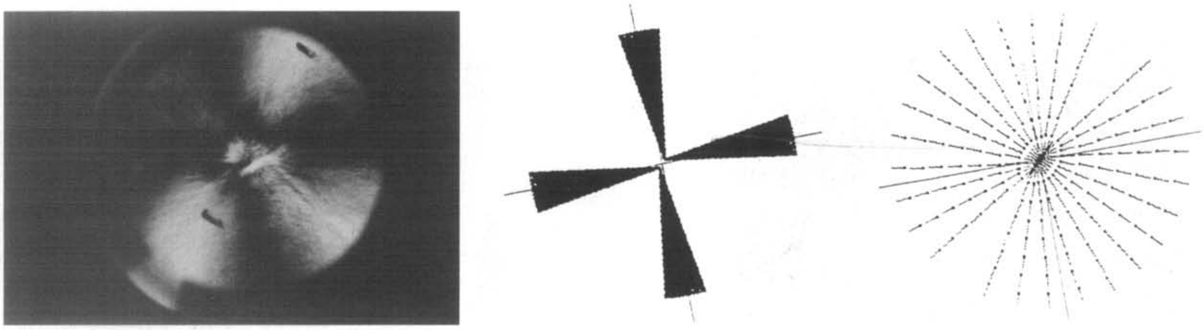
t = 5.5 s



t = 10 s



t = 18.2 s

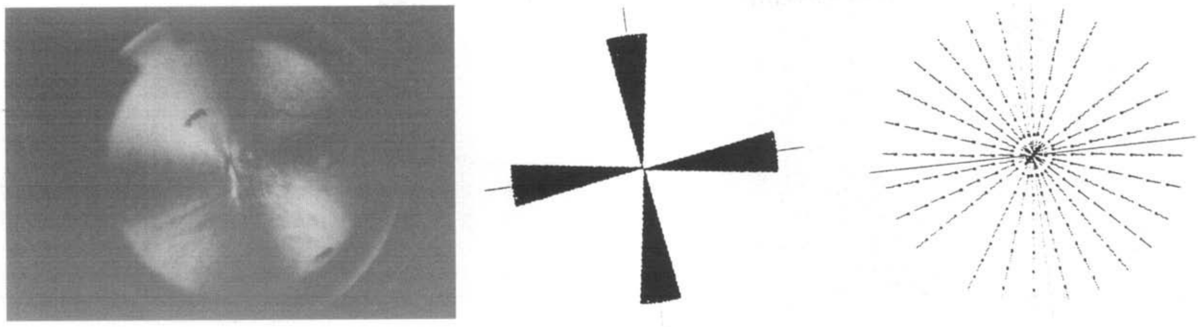


t = 33.1 s

Figure 12 (*Continued*)

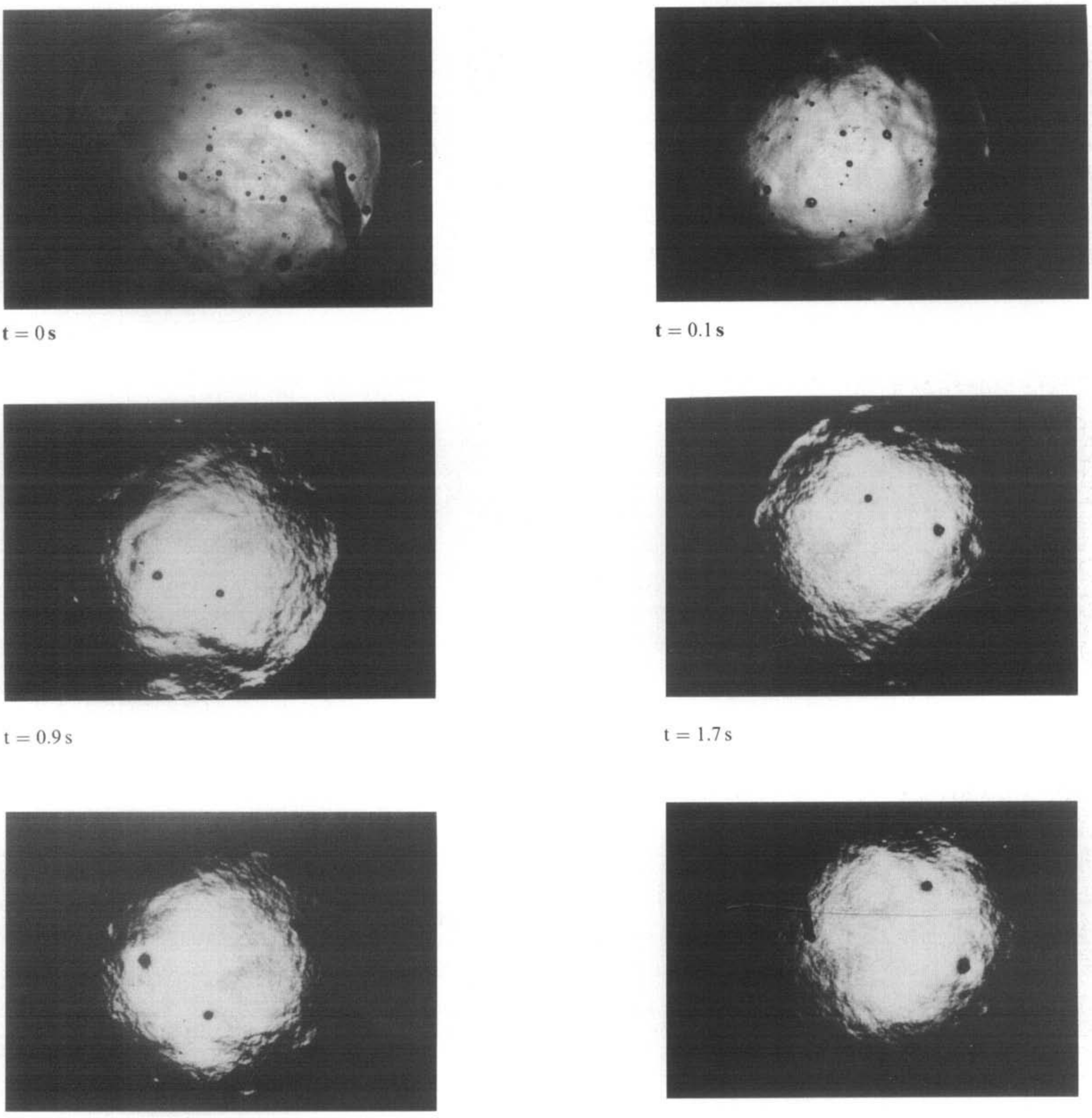
4′-pentyl-4-cyanobiphenyl with irregular maltese cross structure

Experiments with 4′-pentyl-4-cyanobiphenyl resulted in predominantly irregular maltese crosses (*Figure 16*) independent of the angular velocity (2000–4000 rev min^{-1}) at temperatures between 23 and 28°C. The preparation time was 10 min. The irregularity was sometimes too strong to define a structure as a maltese cross, spiral structure or a mixture of both. No changes of the produced structure were observed within 25 h in air at 23–28°C. However, the structures were destroyed completely after 3 days.



t = 60.3 s

Figure 12 (*Continued*)



t = 0 s

t = 0.1 s

t = 0.9 s

t = 1.7 s

t = 2.2 s

t = 2.7 s

Figure 13 Development of a maltese cross structure (diameter 20 mm); PHIC/toluol, 14%; 3000 rev $\min^{-1}$ clockwise; rotating polarizers; time of observation 150 s

The reproduction of macroscopic structures (<5% of all samples) was difficult, in contrast to PBLG, PHIC and OM-20 (100%) due to the strong interaction of 4′-pentyl-4-cyanobiphenyl with the glass surface. Scratches on the glass surface and the traces of precession wipes became visible between crossed polarizers due to the orientation of the macromolecules along such discontinuities of the surface. Therefore, the experiments carried out *in situ* led

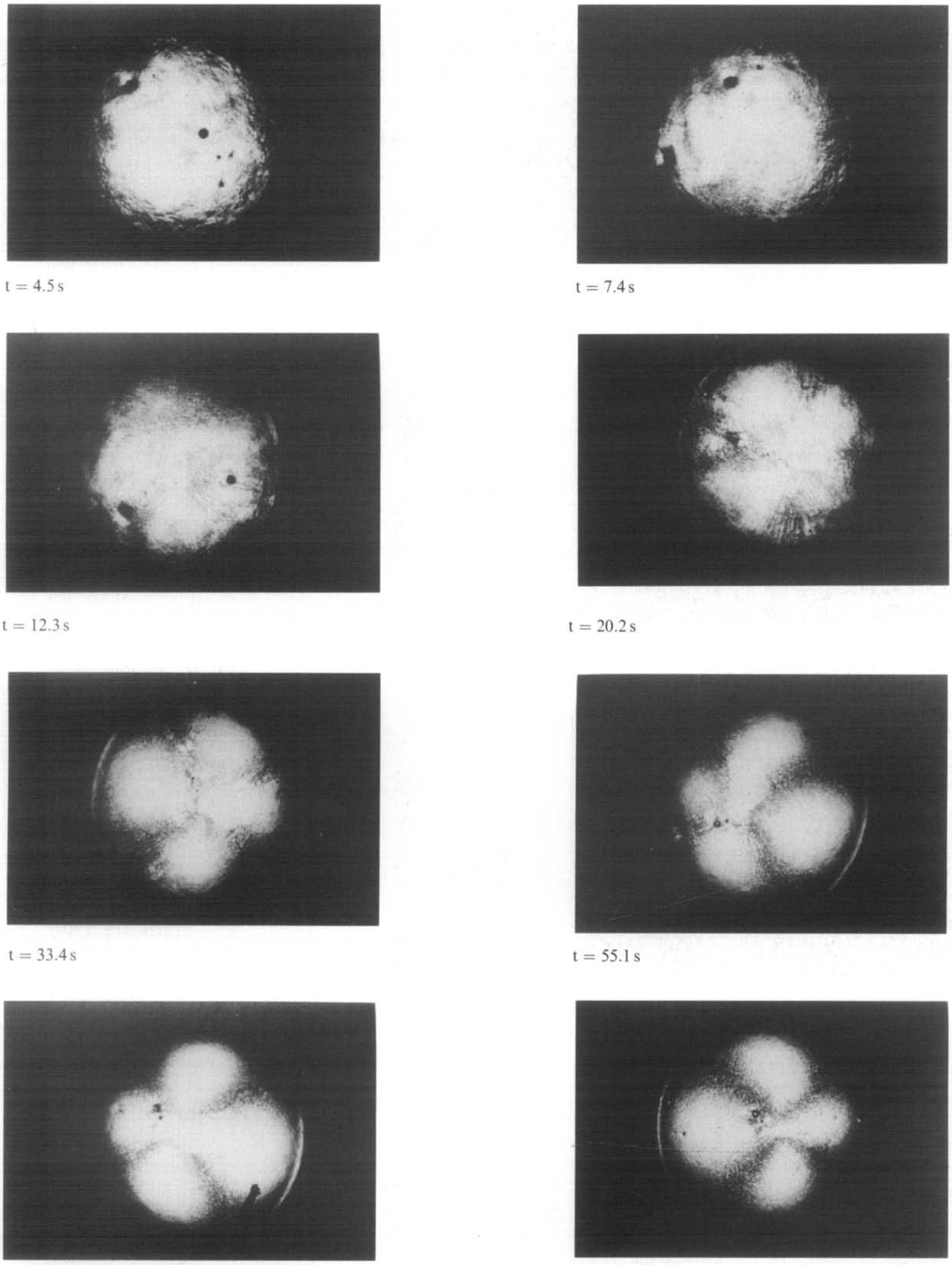
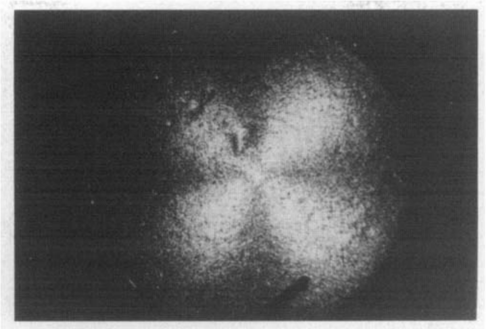

t = 4.5 s
t = 7.4 s
t = 12.3 s
t = 20.2 s
t = 33.4 s
t = 55.1 s
t = 90.0 s
t = 150 s

Figure 13 (*Continued*)

to no clear determination of the development of the structures.

DISCUSSION

This work demonstrates the production of macroscopic cross structures in different systems such as PBLG, OM-20, PHIC and 4′-pentyl-4-cyanobiphenyl. Furthermore, the development of these structures was studied *in situ* using new spin-coating equipment. As a first result it was found that the production of macroscopic maltese cross structures is not only confined to PBLG but is also possible with nematic systems such as PHIC and thermotropic systems such as 4′-pentyl-4-cyanobiphenyl. Therefore, the production of macroscopic structures



t = 640 s dried film after spin coating

Figure 13 (*Continued*)

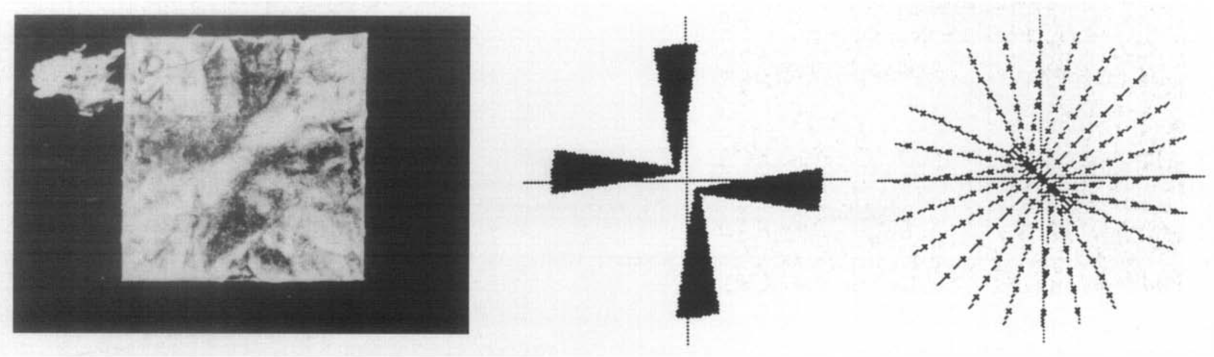


Figure 14 OM-20 film between crossed polarizers (after spinning), theoretical figure between crossed polarizers and orientation of the molecules; 3500 rev min^{-1} clockwise; OM-20/dioxane, 14%; time of preparation, 47 min

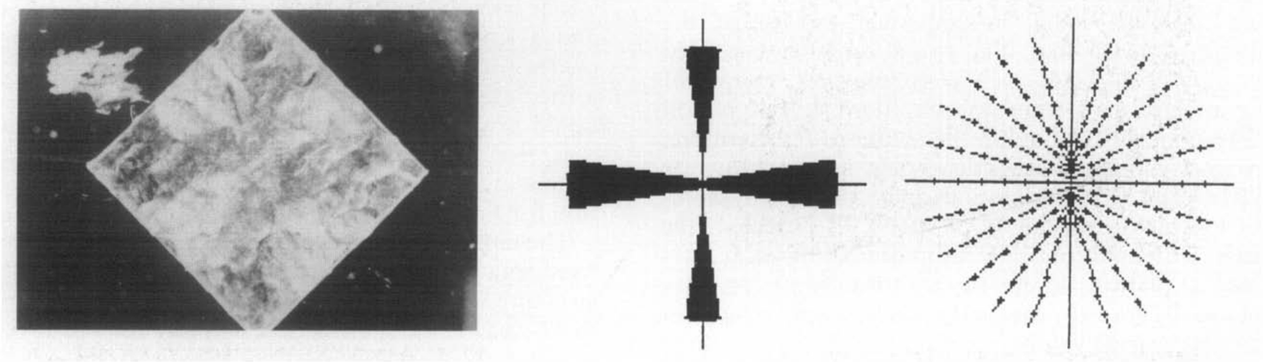


Figure 15 OM-20 film of *Figure 14* between crossed polarizers (after spinning), theoretical figure between crossed polarizers and orientation of the molecules; 3500 rev min^{-1} clockwise; OM-20/dioxane, 14%; time of preparation, 47 min

using the spin-coating equipment with a rotating cap[11] is a more general effect. Furthermore, the results showed that macroscopic structures were not the result of the cholesteric properties of PBLG.

Under these circumstances the spiral structure in PBLG solutions with 4% water must be regarded as a special case. The viscosity measurements showed that the spiral structure is not caused by the change in viscosity. There was no change of structure (maltese cross) between water concentration of 0–2% in the solvent, although the viscosity decreases. However, there was a change of structure (maltese cross to spiral structure) between 2 and 4% water in the solvent, although the viscosity decrease was unimportant. The experiments with a ring showed that the solution profile influences the development of a spiral structure. In combination with the viscosity dependency on the water concentration, the experiments with the ring exhibit a complicated effect which could not be explained using the present experimental results. Therefore, temperature stabilized and automatic equipment is necessary.

The experiments with PBLG using fixed equipment showed that the flow of the solution is necessary for the production of macroscopic structures.

The experiments with 4′-pentyl-4-cyanobiphenyl showed that phase separation is neither a necessary nor a sufficient condition for the production of macroscopic structures, as with the pure system (without any solvent) there is no reason for phase separating effects.

Following results were extracted from the experiments *in situ*: The macroscopic structure was created in the solution during spin-coating and not after the spin-coating process through evaporation of the solvent.

The structure grew from the outside to the inside, in contrast to ordinary spherulite growth.

The late development of the structure (in the case of PBLG after a few seconds) explains the non-effect of Coriolis forces on the structure because of the then low

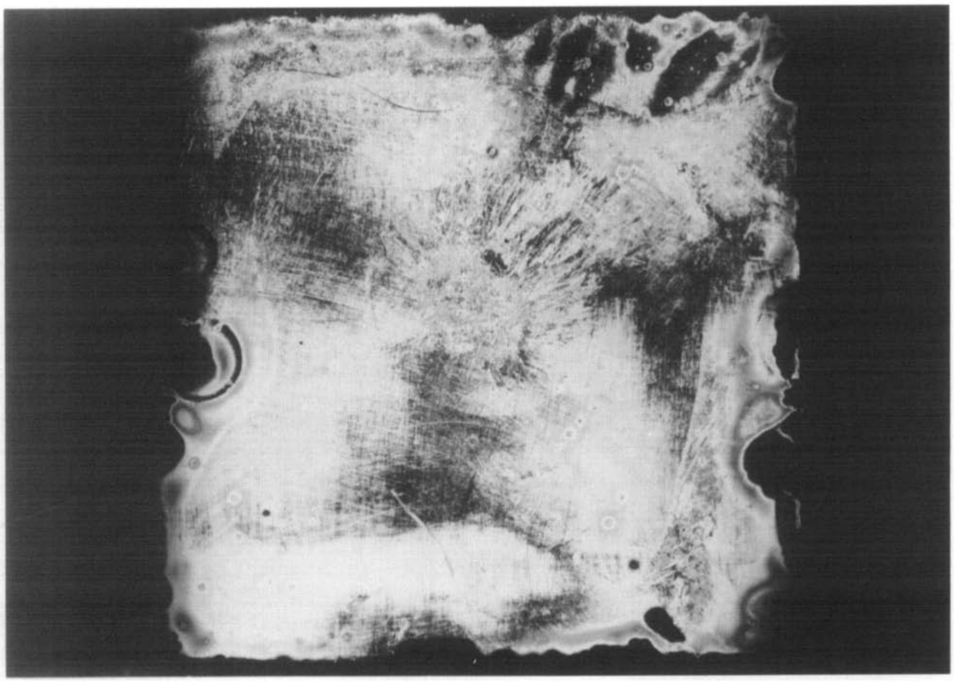


Figure 16 4′-Pentyl-4-cyanobiphenyl with irregular maltese cross structure; 1000 rev min^{-1}; 24°C; time or preparation, 10 min; crossed polarizers

velocity of the solution. In contrast to the observations of dried OM-20 films, the study *in situ* is striking evidence for the radial asymmetrical growth of the macroscopic structure in PBLG, PHIC and OM-20 films.

The observed radial asymmetrical growth of the structure showed that the structure is not caused primarily rheologically as the symmetrical equipment and symmetrical experimental conditions gave no reason for an asymmetrical flow of the solution. Furthermore, the viscosity measurements dependent on the shear rate of PBLG and OM-20 solutions have shown no anomalous loss at decreasing shear rates. As expected, the viscosity increased continuously at decreasing shear rates up to a plateau level. In contrast to a primary rheologically forced process the macroscopic structures grow at increasing viscosity and not in the starting phase of the spin-coating process at maximum shear rates. Only the different preparation times of PBLG and OM-20 films resulted from the different viscosity of the systems.

The observed asymmetrical growth is a strong argument against phase separation effects as sufficient reason for the production of macroscopic structures because the observed asymmetry could not generally be explained by an homogeneous effect in the solution.

The following model types could be excluded by the experimental results:

(1) Models which assume a production of a macroscopic structure primarily based on the cholesteric characteristic of the polymer system because of the successful experiments with the nematic PHIC and the short molecular system 4′-pentyl-4-biphenylcarbon nitrile.

(2) Models which assume a development of the macroscopic structure exclusively conditioned by rheological effects. In general, all models fail which were based on rheological arguments because of the radial asymmetrical growth of the structure under symmetrical flow conditions.

(3) Models which assume only self-organization (spherulite growth) fail because the structures do not grow without the flow of the solution.

The combination of the exclusively rheological model and a spherulite growth gives a successful model, in contrast to the models discussed above. In this model of a rheological induced spherulite growth the flow of the liquid is a necessary condition for the production of a macroscopic structure, and the spherulite growth as a characteristic of polymer systems is a sufficient explanation for the production of macroscopic structures.

The model could explain the absence of structures at a fixed rotation body and the asymmetrical growth of the structure. The spherulite growth of the structure resulted in it being independent angular velocity and the direction of rotation. The flow-induced growth of the structure caused the dependence of the preparation time on the viscosity of the solution and the angle velocity. The long starting time of the growth of the structure could be explained by spherulite growth, in contrast to a predominately rheological process which would show growth in the earliest phase of spin-coating because of the high shear rate in this phase[3]. The absence of the effects of Coriolis forces on the structure could be explained on the one hand by the low velocity of the solution during the phase of growth and on the other hand by the growth of a spherulite, which induces an asymmetrical growth of the structure. As expected, the rheological induced growth of a spherulite is influenced by the unstable conditions of the solution (especially in the case of water in PBLG solutions) and the preparation regime.

ACKNOWLEDGEMENTS

The author would like to thank Dipl. Chem. C. Bruhn for making available OM-20 synthesized at the MPI for Polymer Research, Mainz. Furthermore, I would like to thank Professor Dr R. Schnabel of Martin-Luther-Universität Halle-Wittenberg for his support and Professor Dr E. Straube for helpful discussions. This work was supported by the BMFT, Förderkennzeichen 05 50LAAI 0.

REFERENCES

1. Emslie, A. G., Bonner, F. T. and Peck, L. G., *J. Appl. Phys.*, 1957, **29**, 858.
2. Meyenhofer, D., *J. Appl. Phys.*, 1978, **49**, 3993.
3. Lawrence, C. J., *Phys. Fluids*, 1988, **31**(10), 2786.
4. Shimoji, S., *J. Appl. Phys.*, 1989, **66**(6), 2712.
5. Bornside, D. E., Brown, R. A., Ackmann, P. W., Frank, J. R., Tryba, A. A. and Geyling, F. T., *J. Appl. Phys.*, 1993, **73**(2), 585.
6. Stillwagon, L. E., Larson, R. G. and Taylor, G. N., *J. Electrochem. Soc.*, 1987, **134**(8), 2030.
7. Stillwagon, L. E., Larson, R. G. and Taylor, G. N., *SPIE Adv. Resist Technol. Processing IV*, 1987, **771**, 186.
8. Schreckenbach, A. D Patent 43 27 427, 1993.
9. Schreckenbach, A., Wünsche, P., *Polymer*, 1994, **35**(26), 5611.
10. Azzam, R. M. A. and Bashara, N. M. *Ellipsometry and Polarized Light*. Elsevier, Amsterdam, 1989.
11. Elias, H. G. *Makromoleküle*, 4th edn. Hüthig & Wepf, Basel, 1981, p. 155.
12. Basset, D. C., *CRC Crit. Rev. Solid State Mater, Sci.*, 1984, **12**, 97.
13. Robinson, C., *Trans. Faraday Soc.*, 1956, **52**, 571.
14. Sakamoto, R., *Colloid Polym. Sci.*, 1984, **262**, 788.
15. Wassermann, D., Garber, J. D. and Meigs, F. M. US Patent 3 285 953, 1966.
16. Moscicki, J. K., Williams, G. and Aharoni, S. M., *Polymer*, 1981, **22**, 1361.
17. Moscicki, J. K., Williams, G. and Aharoni, S. M., *Macromolecules*, 1982, **15**, 642.
18. Gray, G. W., Harrison, K. J. and Nash, J. A., *Liq. Cryst. a. Fluids*, 1973, **2**, 617.