Preparation of structures in liquid crystal polymer systems (PBLG) with spin coating

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Different macroscopic structures in poly(γ-benzyl-L-glutamate)(PBLG) films were prepared by spin coating using different preparation methods. These structures were analysed between two polarizers or using polarization microscopy. The main parameters for creating structures during the spin coating process have been determined. In particular, the influence of coriolis forces during the spin coating process and solution properties were studied and resulted in a proposal for the mechanism of the production of structures.

(Keywords: poly(γ-benzyl-L-glutamate); structure; spin coating)

INTRODUCTION

Poly(γ-benzyl-L-glutamate) (PBLG) in solution was studied by different research groups[1–4] with respect to the behaviour of the macromolecules on the surface. A summary has been given by Wada[5]. Enriquez *et al.*[6] studied the self-assembly of PBLG monolayers on a gold surface, and Elliot and Ambrose[2] showed orientation of PBLG drops stroked out by a razor blade. Robinson[4] has studied birefringent solutions. These showed parallel equidistant lines which were visible in natural light. The lines were separated by a distance of $\sim 10\ \mu$m, depending on the concentration of the solutions. Hence we can use this cholesteric polypeptide as an indicator of the influence of mechanical shear stress and/or other important parameters on the spin coating process.

The theory of the spin coating process was developed by Emslie *et al.*[7] who used a simple model (homogeneous film, only radial forces). The model was expanded by Meyenhofer[8], Lawrence[9] and Shimoji[10] by including the evaporation of the solvent. Bornside *et al.*[11] have simulated the influence of air turbulence. The aim of all these models was to provide a description of the parameters influencing the production of homogeneous thin films and did not describe the influence of shear stress on the orientation of the macromolecules. The aim of this paper is to provide a contribution to the understanding of the formation of structures in thin films produced by spin coating.

EXPERIMENTAL

Properties of the PBLG solutions

The PBLG (Poly Science) used in the experiments had a nominal molecular weight of 214 000. All solutions were prepared at least 24 h before use. Dioxane from Aldrich Chemical Company Ltd (Germany)[1] or dioxane from Apolda Laborchemie (Germany)[2] and a mixture of water and dioxane[1] were used as solvents.

Solutions prepared with dioxane[1] were gel-like at a concentration range of 12–16% [concentrations given as: PBLG/solution (w,w)] and colours became visible between crossed polarizers. Solutions prepared with a mixture of water and dioxane[1] or dioxane[2] showed a different behaviour. The solutions became less viscous. Temperatures above 25°C in the laboratories were critical the solution became inhomogeneous, due to the birefringent properties (phase separation). The solvent condensed on top of the cap and thus the concentration of the solutions became indefinite.

The differences of the dioxanes[1,2] could be explained in terms of a time-dependent destruction of the solvent. Stumpf[12] described the autoxidation of dioxane leading to the production of glycol aldehyde in the presence of water and, under the influence of u.v. light, to glyoxylic acid.

Experiments were conducted with different combinations of dioxane[1] (checked by i.r.), acids (HCl 0–0.5%, acetic acid 0–0.5%), acetaldehyde (0–0.5%) and water (0–4%) at different temperatures (20–26°C) using different preparation regimes.

To summarize, it could be shown that the solutions with water showed nearly the same behaviour as the dioxane[2] solutions. Also, it was observed that the aldehyde and acid tended to stabilize the behaviour of the solutions with regard to the evaporation rate which is understandable as they reduce the vapour pressure.

The solution became completely phase separated at $\sim 6\%$ water. The PBLG could be extracted and was dried for 2 days at 35°C. Then it was dissolved in dioxane[1]. The properties of the solution were different to the solution with pure PBLG. It required much more time to redissolve the PBLG (at 13.5% it was not possible to dissolve it completely) and the viscosities of 2% PBLG (extracted) and 13.5% PBLG with dioxane[1] were almost

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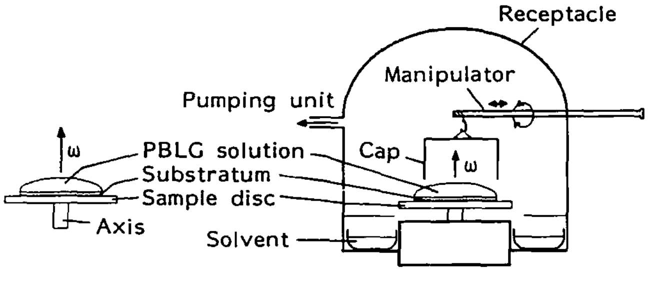

Figure 1 Main equipment for spin coating in air and with the receptacle system

identical. This result indicated a destruction of the hydrogen bonds of the PBLG α-helices by water and a transition between rod-like molecules to coils and/or a building of networks.

Equipment

Spin coating equipment was developed. The engines were purchased from PORTESESCAP GmbH (Germany). Parameters involved: velocity, 200–26000 rev min^{-1} (200–6000 rev min^{-1} with cap); acceleration, 0.4–3 s to maximum velocity as a function of the sample weight (>3 s with cap); velocity error $<0.5\%$.

A PC with an AD/DA card (MEILHAUS GmbH, Germany) was used to control the engine. It was possible to program different run profiles. The substratum diameter was 20–30 mm and the sample disc diameter was 20–60 mm. Glass slides, float glass and silicon wafers (001) (Lot no. 5.17-5/1, HEK GmbH, Germany) were used as substratum.

Receptacle system. A receptacle system was developed to minimize evaporation before and during spin coating. The receptacle was filled with methylene chloride or dioxane[2]. The solution was placed in a cylindrical cap on the substratum. It was possible to insert the whole unit into the receptacle. A manipulator system enabled the removal of the cap from the sample disc in the receptacle (*Figure 1*).

System with rotating cap. A spin coating system with rotating cap was developed to reduce the air turbulence above the sample (*Figure 2*). The geometry of the cap determined the preparation technique.

Polarization microscope. To examine the thin films produced, a polarization microscope or two polarizers were used. Using this method it was possible to study the behaviour of the solution and the visible structures, occurring as a consequence of the birefringent state of the solution or film. The optical behaviour of the film is correlated with the orientation of the macromolecules as shown by Eliott[2], Robinson[4], Elias[13] and Basset[14]. Black areas between crossed polarizers were the result of oriented macromolecules with their optical axes parallel to the axes of the polarizers as shown by Elias[12]. Photographs were obtained with a camera using a polarization microscope (Amplival Pol-D, Carl Zeiss Jena) or macro resolution and two polarizers.

Preparation

Cleaning the substratum. Float glass was cleaned in HCl (10%) and H_2SO_4 (10%) for 2 h at 50°C. Then it was stored in distilled water for 10 min and finally it was put into a mixture of acetone and isopropyl alcohol (50/50). A few seconds before spinning it was wiped with precision wipers (Kimberly Clark, EEC) and methylene chloride. Sometimes a special cleaner (NEURO-80, VEB Selfama Magdeburg) was used (the main component was chromic acid) instead of the above acids.

The silicon wafers were cleaned only with acetone.

A more complicated cleaning procedure such as ion bombardment and annealing in an ultra high vacuum chamber or cleaning under inert gas conditions is of course possible but the use of soap and water and cleaning with distilled water has been shown to be sufficient for our purposes and gave the same results as the procedures described above.

The spin-coated films could be floated onto other substrata or prepared as self-supporting films which were removed from the water with a metal ring. This made it possible to compare the influence of various substrata like float glass or silicon wafers (001).

In air. Concentrations between 0.25% and 1% PBLG/dioxane[1,2] were used. The solution was placed on the disc before or during the spinning process.

With a receptacle. To reduce evaporation before and during preparation a receptacle system was developed. Solvent (methylene chloride or dioxane) was added to caps which were placed on the ground and air was removed for 10 min to create a pure solvent atmosphere. The engine-sample unit was inserted before starting the evacuation. After obtaining thermal equilibrium (~ 2 h), the cap was removed from the substratum with the manipulator system and spin coating was started. The samples were spun for ~ 20–60 s. Then the engine–disc unit was removed from the receptacle.

In air using a cap before spinning. One method used was spinning in air using a cap to reduce evaporation before spinning. The depth of the solution before spinning

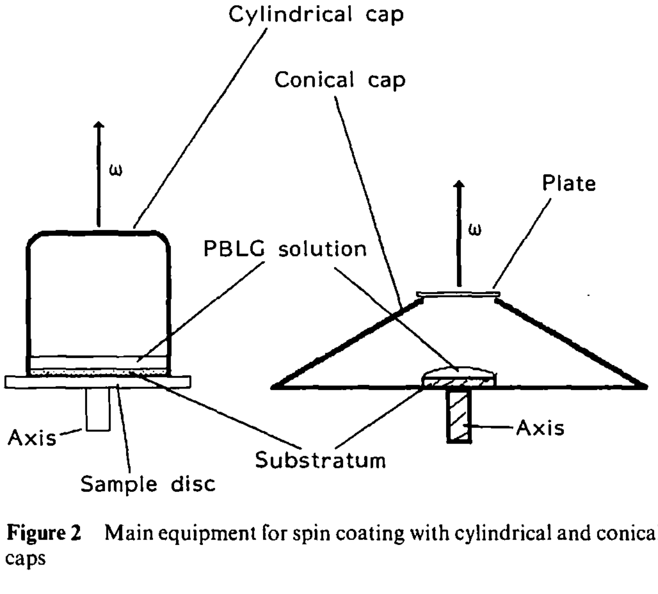

Figure 2 Main equipment for spin coating with cylindrical and conical caps

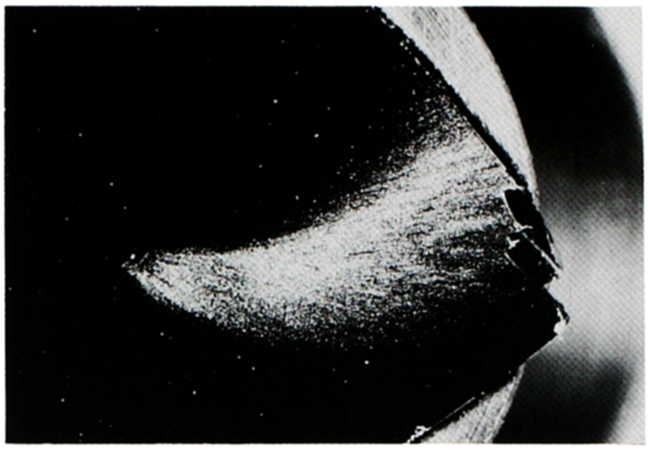

Figure 3 Test with a marker and PVAc/toluene solution on silicon (001). Length of curve ~12 mm

was ~1 mm and almost homogeneous. As spin coating was started the cap was removed.

With rotating cap. To produce films with a rotating cylindrical cap the following procedure was used:

1. fill the cap with PBLG solution;
2. cement the sample and cap together with PBLG solution;
3. turn the engine-disc unit to get the solution onto the substratum;
4. start the spinning process;
5. turn the engine–disc unit back to the original position. This allows the solution to flow down to the bottom of the cap whilst the film remains attached to the substratum.

The disadvantage of the spin coating process with a cylindrical cap was the drifting of the solution to the substratum. At higher velocities the structure of the film was destroyed. With a rotating conical cap it was possible to produce samples without turning the engine–disc unit (*Figure 2*). In contrast to preparation with a cylindrical cap the polymer solution was placed on the substratum and then the cap was closed. This resulted in much higher evaporation before and during spin coating.

Measurements and observations

Tests with a marker. Poly(vinyl acetate)/(PVAc) with toluene as solvent was used in the first experiments in air. We took a marker (dye dissolved in toluene) to set a point on the substratum near the centre. The engine started to rotate when the solution was poured onto the substratum. The result was a curve as shown in *Figure 3*. Experiments using powder produced the same results. It has to be stressed that the curves change their direction if the direction of rotation is changed.

Experiments in air. Experiments with dioxane^2 and methylene chloride as solvent were carried out. The method whereby solution was placed on the disc during spinning gave poor results with respect to the production of homogeneous films. Structures between the polarizers were not visible after spin coating (velocity 1000–22 000 rev min^{-1}). Solutions with concentrations above 11.5% resulted in a skin on the surface of the solution. The remains of this skin destroyed all structures that could have existed.

Experiments in the receptacle. In a receptacle it was possible to spin solutions with concentrations above 11.5%. Experiments with such high concentrations using the method where the solution was placed on the disc during spinning failed because the drop left the substratum without spreading out. The samples showed macroscopic structures between the polarizers over a small range (<5 mm) but the films were not homogeneous. The air movement in the receptacle was high, as indicated by the movement of a paper strip. The result was a chaotic evaporation of the solvent and an opaque and rough film. Therefore it must be concluded that it is impossible to obtain homogeneous films using the 'classical' spin coating. Even more important is the fact that air turbulence destroys all structures during the spin coating process. In summary, 'classical' spin coating does not lead to definite and reproducible conditions during the spin coating process.

Tests where the cap is removed before spinning. The concentration of the solution with dioxane^2 was ~14%. After spin coating the film was transparent but evaporation made it opaque within 20 s. Weak macroscopic structures (Maltese crosses, diameter 20 mm) were visible at the end of the experiment but no microscopic structures were observed due to the opacity of the film.

Experiments with rotating cap. With a rotating cap system it was possible to create transparent and optically homogeneous polymer films with a microscopic and macroscopic structure.

Experiments with dioxane^1. Experiments were carried out at temperatures between 20°C and 25°C and a concentration range of 12–15.5% PBLG/dioxane with cylindrical and conical caps. The results were macroscopic Maltese crosses observed between crossed polarizers and their appearance was independent of the angular velocity (1000–4000 rev min^{-1}).

Experiments with dioxane^1 and water. Below concentrations of 11.5% (limit of birefringent behaviour of the solution) we could not prepare films with visible structures between crossed polarizers. This result was also obtained for preparation in air. At a concentration of 11.5% it was possible to prepare a structure. The structure improved at concentrations above 11.5% (*Figure 4*). The concentration range between 12% and 16% is the most interesting. The samples were spin coated for ~10 min. The following four macroscopic structures (diameter 20 mm, the whole sample) were able to be produced. These structures were visible with crossed polarizers without a microscope.

1. Maltese cross. The concentration of the solution (polymer/solvent) was 13.5%. With 0–3% water in combination with dioxane^1 using the cylindrical cap it was possible to create Maltese crosses at a temperature between 20°C and 22°C (*Figure 5*).
2. Spiral arms right curved. The direction is defined by the right hand rule. From a 13.5% solution of PBLG in aqueous dioxane (4% water) using a cylindrical

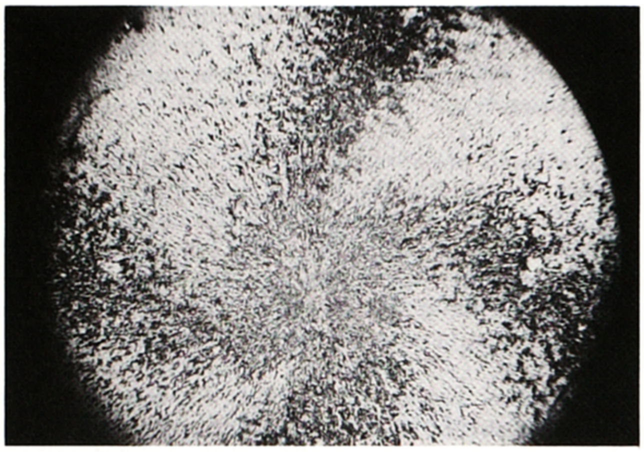

Figure 4 Macroscopic structure prepared with cylindrical rotating cap. Concentration of the PBLG/dioxane² solution ~ 11.5%; diameter 2.5 mm; 4000 rev min⁻¹ anticlockwise

Figure 5 PBLG film prepared with cylindrical rotating cap. Concentration 13.5%; solvent dioxane¹; diameter 20 mm; 2000 rev min⁻¹ clockwise; crossed polarizers; angle of the polarizer axes 12 h, 3 h

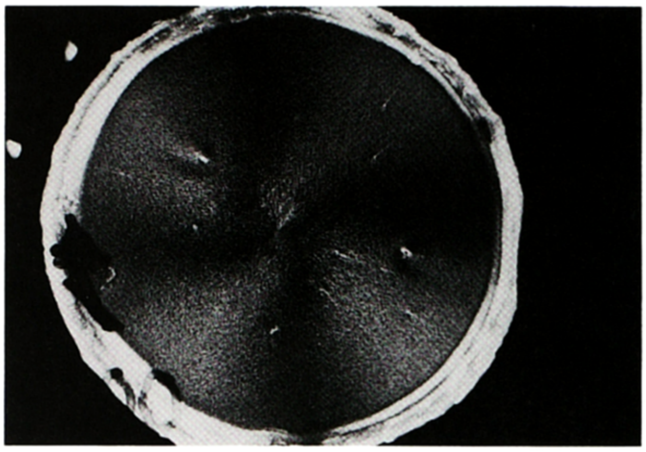

Figure 6 PBLG film prepared with cylindrical rotating cap. Concentration 13.5%; solvent dioxane²; diameter 20 mm; 900 rev min⁻¹ clockwise; crossed polarizers; angle of the polarizer axes 2 h 40′, 11 h 40′

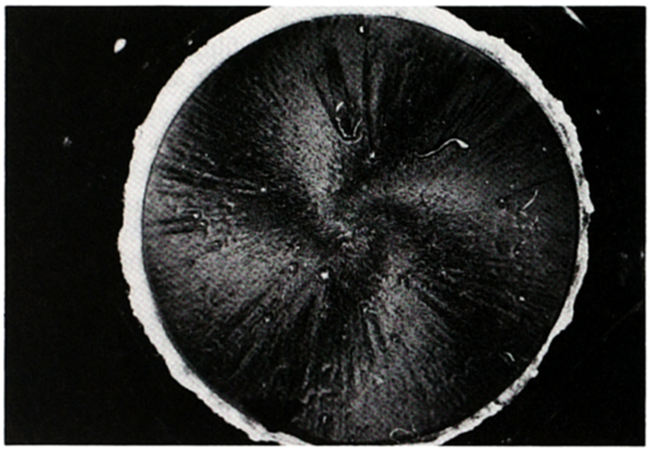

Figure 7 PBLG film prepared with cylindrical rotating cap. Concentration 13.5%; solvent dioxane²; diameter 20 mm; 2300 rev min⁻¹; crossed polarizers; angle of the polarizer axes 2 h 40′, 11 h 40′

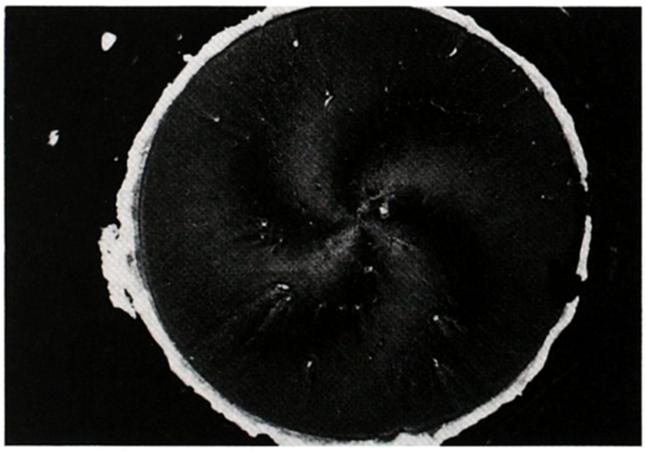

Figure 8 PBLG film prepared with cylindrical rotating cap. Concentration 13.5%; solvent dioxane²; diameter 20 mm; 3300 rev min⁻¹ clockwise; crossed polarizers; angle of the polarizer axes 2 h 40′, 11 h 40′

cap it was possible to create right curved spiral arms at temperatures between 20°C and 22°C. At greater angular velocities the curvature of the visible spiral arms became greater (*Figures 6–10*). The same results were obtained using dioxane².

3. Spiral arms left curved. Using a 14.5% polymer solution in aqueous dioxane (3.5% water) and a conical cap it was possible to create left curved spiral arms in a temperature range of 24.3–24.7°C.
4. Spiral arms left and right curved. Spiral arms changing the direction of curves in the arms were produced at approximately the same conditions (concentration, temperature) as left or right curved spiral arms. However, preparation with a conical cap showed much more of these structures than the preparation with a cylindrical cap (*Figures 11* and *12*). The shape of the cap does not influence the type of structure as it was possible to produce all different curves (left, right, mixture) with the conical cap. The difference between using the conical or cylindrical cap was the evaporation before and during spin coating in the preparation technique.

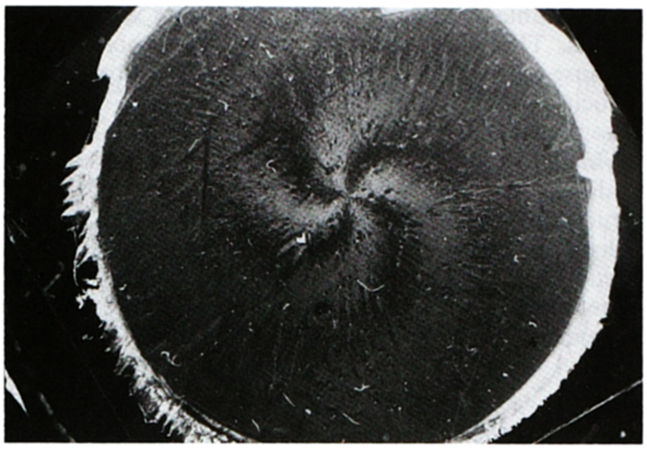

Figure 9 PBLG film prepared with cylindrical rotating cap. Concentration 13.5%; solvent dioxane^2; diameter 20 mm; 4300 rev min^{-1} clockwise; crossed polarizers; angle of the polarizer axes 2 h, 11 h

Figure 10 PBLG film prepared with cylindrical rotating cap. The same solution as in *Figure 8* was used; diameter 20 mm; 3300 rev min^{-1} anticlockwise; crossed polarizers; angle of the polarizer axes 2 h 40', 11 h 40'

General observations

A very interesting finding is that there was no change in the direction of the macroscopic curves if the direction of rotation was changed but it was possible to create both directions by changing the solution properties and by different film preparations.

Tests with silicon as the substratum showed no visible difference to experiments with float glass or glass.

The prepared structures were stable for at least 12 months at room temperature in air.

Mechanical disturbances like stopping the cap abruptly or vibrations during the rotation of the disc destroyed the structures.

All structures were created before the evaporation of the solvent which 'froze' the structures within 1–3 s.

Air movement during the evaporation phase destroyed the macroscopic structure.

RESULTS

This work demonstrates the production of macroscopic structures in PBLG films prepared by the spin coating process using different preparation regimes. The differences between these macroscopic structures and the typical polymer spherulites as shown by several research groups are the different size (factor of 200–20000) and the spiral arms. There was no indication that the size of the structures was limited.

The following parameters do not influence the preparation of structures during the spin coating process.

Air movement (in the rotating cap). Air movement in the cap could be excluded during spin coating because of the production of all types of curves (right, left) independent of the direction of rotation.

Geometry of the cap system. The geometry of the cap system could be excluded for the same reason as above.

Substratum and cleaning method. The substratum and the cleaning method could be excluded because of the

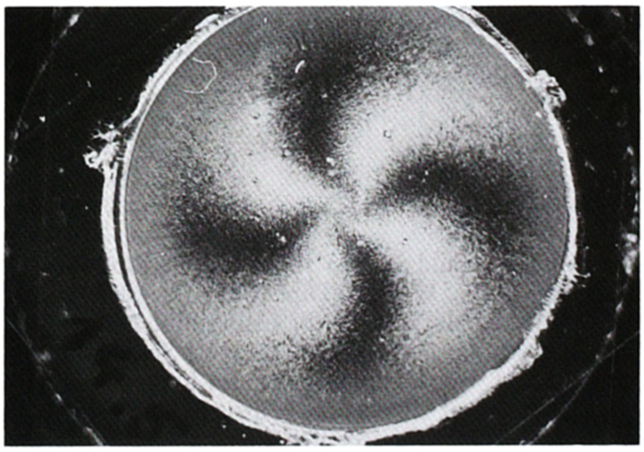

Figure 11 PBLG film prepared with conical rotating cap. Concentration 13.5%; solvent dioxane^2; diameter 20 mm; 4000 rev min^{-1} clockwise; crossed polarizers; angle of the polarizer axes 2 h 40', 11 h 40'

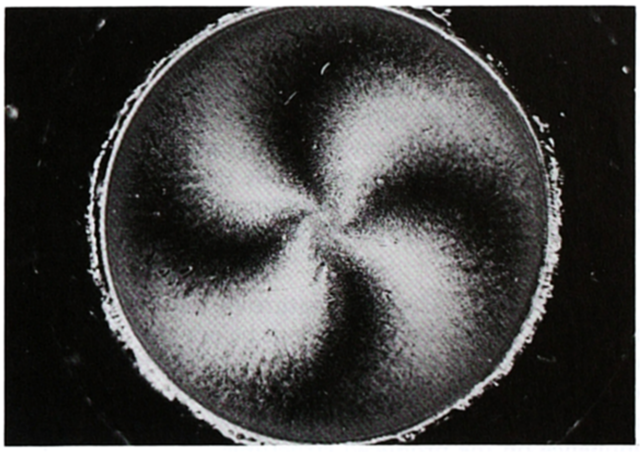

Figure 12 PBLG film prepared with conical rotating cap. Concentration 13.5%; solvent dioxane^2; diameter 20 mm; 4000 rev min^{-1} anticlockwise; crossed polarizers; angle of the polarizer axes 2 h 40', 11 h 40'

production of all types of curves independent of the substratum (float glass, glass and silicon) and the cleaning method.

Coriolis force. It was shown experimentally that the influence of coriolis effects on the flow of a polymer solution cannot be neglected. In contrast to the experimental result with the marker, the direction of the macroscopic spiral arms (left, right) was independent of the direction of rotation in all cases. The experiments with pure dioxane[1] showed only Maltese crosses. Again, no influence of coriolis forces was visible.

Viscosity. The results obtained with dioxane[1] were independent of the angular velocity (Maltese crosses). The results with aqueous dioxane ($<3\%$ water) showed the same Maltese crosses, but the solutions were less viscous. This excluded the influence of viscosity and the resulting different flow of the polymer solutions as a main parameter for producing left and right spiral arms.

From the experimental results the main parameters influencing the production of structures on the film could be determined.

Solvent. With pure dioxane[1] it was possible to produce Maltese crosses. The influence of aqueous dioxane on the structures produced is evident. Aqueous dioxane (water 0–3%) reduced the viscosity of the solution without changing the Maltese crosses and led to spiral arms at 4% water.

Concentration of the solution. The production of visible structures from solutions with concentrations below 11.5% (below the birefringent state) was impossible independent of the preparation regime.

Air movement (without using a cap). Air turbulence destroyed structures during spin coating in air and using a receptacle. It can be concluded that the preparation of structures during the spin coating process cannot be achieved in air. The tests with a receptacle system led to inhomogeneous films.

Evaporation. The influence of evaporation could not be separated from the influence of air turbulence during spin coating in air and with a receptacle. Evaporation during spin coating with a cap is important to produce spiral arms with different direction curves. Evaporation after spin coating with a cap made the film opaque and in combination with air movement it destroyed the structures which were produced.

Temperature. The temperature of the solution is an important factor of the conditions before and during spin coating. It will be very interesting to study the behaviour of the solution at different temperatures more systematically because of phase separation effects and their influence on the produced structures.

Mechanical disturbances. The abrupt stop to rotation destroyed the structures. Furthermore, it is obvious that considerable vibrations of the equipment led to poor results. This effect must be taken into consideration because resonances of the system, dependent on angular velocity, could destroy the structures.

Angular velocity. At concentrations between 12% and 16% it was possible to produce a macroscopic structure which showed a dependence on the angular velocity if a mixture of water ($>3\%$) and dioxane[1] was used as solvent. The macroscopic spiral arms produced were more curved at higher velocity. There was no dependence if only pure dioxane[1] was used.

DISCUSSION

Provided that the curves and the orientation of the macromolecules are a direct result of the operator equation that describes the transformation of inertial systems, the curves or orientation of the macromolecules should change with the direction of rotation because of the coriolis forces. However, the experiments showed that the direction of the curves was independent of the direction of rotation. A process must exist which leads to an unsymmetrical orientation of the macromolecules with respect to the direction of rotation.

The self-organization of macroscopic spherulites which originates from the solution and/or the self-orientation of macromolecules in solution is a sensible assumption. A strong interaction between PBLG molecules in solution made it possible to explain the results with pure dioxane[1], especially the independence of angular velocity and viscosity whose influence is coupled with coriolis forces. The shear stress during the spin coating will only support the arrangement of the macromolecules in this assumption.

The flow of the liquid combined with phase separation effects is another sensible assumption. It was found that water changed the structure of PBLG. The weakening of the interaction of PBLG in solution could explain the dependence of the orientation of the macromolecules from the distance to the centre of rotation and the spiral form of the arms as the centrifugal force. The stronger evaporation during spin coating with a conical cap could change the degree of weakness of interaction/or phase separation and change the orientation properties (left/right). Further investigations are necessary to understand the system completely.

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