

## OPTICAL METHODS IN RHEOLOGY: POLARIZED LIGHT IMAGING

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## 1. Introduction

Knowledge about crystallization processes and crystal orientation is essential for material, process and product development as they strongly influence the product's final properties. Utilizing polarized light, the Polarized Light Imaging Option allows observation of effects like flow induced crystallization processes of polymers or local shear induced effects as they may occur in liquid crystals.

The wave model of light describes light waves oscillating at right angles to the direction of propagation with all directions being equally probable, see Fig. 1. This is referred to as "common" or "non-polarized" white light. A polarizing filter selects a single component of polarized light to pass through while absorbing all other components of incoming waves. If a second polarizing filter is placed above the first one, but with its polarization axis rotated by 90°, no light can pass through because the polarization passed by the first filter is blocked by the second filter.

When optically active materials (birefringent materials), such as liquid crystals, are placed between polarizing filters crossed in this way, some light may get through, because the material changes the polarization of the light. Thus, when light enters a birefringent material, the ray of light is split by polarization into two rays, a fast one (called the ordinary ray) and a slow one (called the extraordinary ray) components, taking slightly different paths. Because the two components travel at different velocities, the waves get out of phase. When the rays are recombined as they exit the birefringent material, the polarization state has changed because of this phase difference. Investigations of birefringent materials are mostly performed with polarized light, as it strongly interacts with

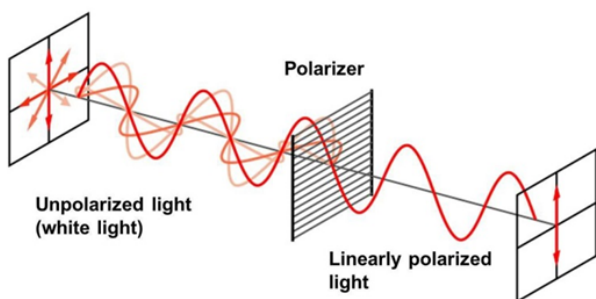


Fig. 1 Wave model of light: using a polarizer, unpolarized light is transformed to linearly polarized light

the sample generating contrast with the background, allowing focusing on details not visible with unpolarized light. Polarized light is capable of providing information on optical path boundaries between sample structures of differing refractive indices and can also distinguish between isotropic and anisotropic materials.

Both polarized light microscopy and polarized light imaging take advantage of using polarized light. Nevertheless there is a considerable difference between these two methods.

## Microscopy

Using microscopy, there is an image magnification and therefore single elements (particles, droplets, polymer chains, crystallites) can be observed and identified. The image that is retrieved is a local information from a small part of the sample only. Therefore, when investigating samples under shear the information actually gained is not coming from the same element but from some other elements, occurring at the same location in a parallel plate or cone-plate system, passing at a later time point through the field of view.

- Small details are visible.
- Average values over large samples are not easy to obtain.
- The results are not representative for the whole sample.
- With the polarized microscopy only a small part of the sample, as a local area, can be seen and therefore it is difficult to detect a spatial phase difference in the sample.

## Polarized Light Imaging

Polarized light imaging has no magnification option and therefore single elements cannot be observed. Differently from microscopy, the polarized light imaging is an integrative method, where the whole sample can be observed (25 mm diameter). The structure of the sample itself cannot be directly seen but it can be made visible using polarized light imaging. The phase difference of light passing through different regions of the sample is detected and visualized as a color mapping. Therefore it is possible to identify changes in the structure over the whole sample area.



- Small details are not visible.
- Integrative information on the whole sample can be obtained.
- The results are representative but difficult to interpret quantitatively.
- Having the whole sample in the field of view it is possible to obtain a space-resolved information about the strain distribution in the investigated material by color mapping induced by phase differences.

### 1.1. Sample

Liquid crystals are materials having properties between conventionally flowing liquids and solid crystalline materials showing molecules which are orientated like in crystals. The liquid crystal materials might show different phases, each phase having different optical properties. Thus, by using polarized light it is possible to distinguish between various states, resulting in distinct textures.

All the tests shown here have been performed with a *N*-(4-Methoxybenzylidene)-4-butaniline 98 %, thermotropic liquid crystal with rod-like molecules, also called MBBA, from Sigma Aldrich.

## 2. Experimental Setup

The Polarized Imaging Option consists of a color CCD camera, an optical tube which transfers the image telecentrically onto the CCD chip and an inlet for light.

A light source emits light which is transferred by the light guide into the optics. This white light travels through

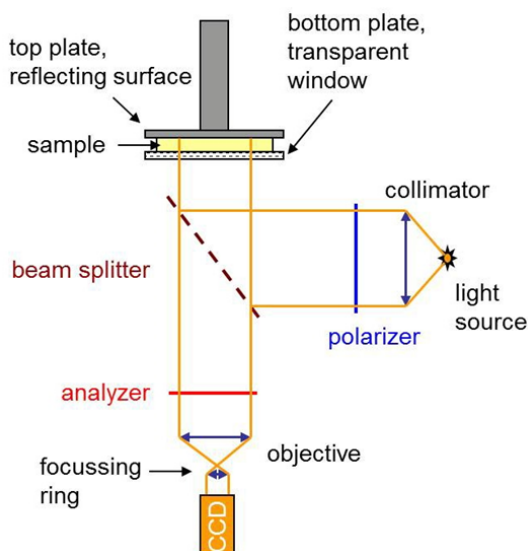


Fig. 2. The polarized imaging option enables to monitor the sample using polarized light, a telecentric optics module and a CCD camera

a polarization filter to the beam splitter where it is deflected towards the sample so that the sample is illuminated with polarized light. Different polarization states can be generated by rotating the second built-in polarization filter (called analyzer). Additionally to the linear polarized light, circular polarized light can be used as well by changing the polarization filters. The image of the illuminated sample is transferred telecentrically to the CCD chip, allowing the recording of changes in sample structures induced by the shear forces of the rheometer leading to e.g. birefringence.

As measuring systems, parallel-plates and cone-plates up to 50 mm in diameter can be used. As 25 mm of the shear area are monitored, also local effects can be studied. The temperature control of the system is ensured either by the Peltier-heated or the electrically heated universal optical device (P-PTD 200/GL or P-ETD 300/GL) and the corresponding hood (H-PTD 200 or H-ETD 400) in a temperature range from -20 °C to 200 °C or from room temperature up to 300 °C, respectively.

For the measurements shown here a Peltier-heated universal optical device, P-PTD 200/GL and the corresponding hood, H-PTD 200, have been used. All the tests have been performed at the constant temperature of 25 °C.

## 3. Results and Discussion

Liquid crystals are anisotropic materials, and the physical properties of the system vary with the average alignment (molecular director). In a typical liquid crystal, the birefringence (difference in the indices of refraction from the ordinary and extraordinary rays) is not constant over the entire sample. Thus, when a liquid crystal is placed in the measuring cell with polarizer and analyzer cross aligned (with polarization axis rotated by 90°) some areas appear dark and some appear light, see Fig. 3 representing the liquid crystal sample placed in a parallel plate system at rest, with a gap of 0.3 mm.

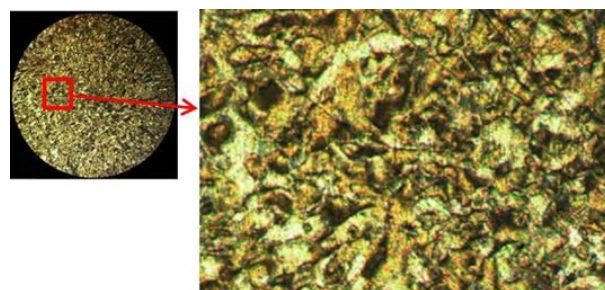


Fig. 3. Liquid crystal at rest: the light and dark areas correspond to domains where the liquid crystal molecules are oriented in different directions, i.e. regions with differing molecular director orientation

In order to investigate the structural changes of the sample during rheological tests, an amplitude sweep has been performed. The strain has been varied from 10 % to 1000 % logarithmically, with 6 points per decade. The measuring point duration has been set to 15 s. In order to observe the orientation changes of the liquid crystals domains during oscillation, a low frequency of  $f = 0.1$  Hz has been set.

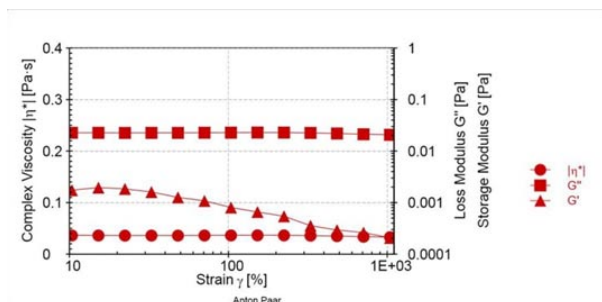
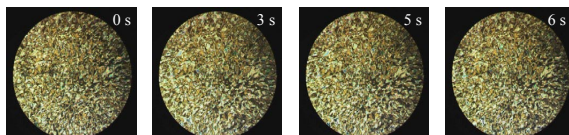


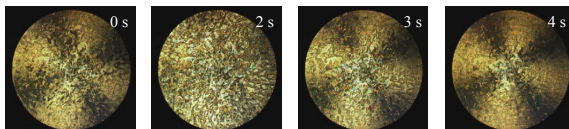
Fig. 4. Amplitude sweep performed with the liquid crystal sample (gap 0.3 mm)

At a low strain, here displayed for 10 %, no change of the images during oscillation could be observed. At higher strains, here at 100 %, 485 % and 1000 %, see Fig. 5, dark sectors disposed perpendicularly, the so called birefringent

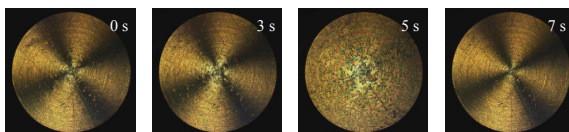
Strain 10%



Strain 100%



Strain 485%



Strain 1000%

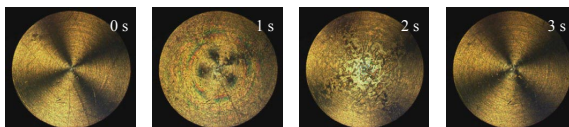


Fig. 5. Images taken during an amplitude sweep. The measuring point duration for each preset strain was 15 s. Taken at the same strain, the time points of the pictures are specified relatively to the first image (gap 0.3 mm)

Maltese cross zone, can be observed. The Maltese cross, a set of four symmetrically disposed sectors, corresponds to the transparent area of the sample. The liquid crystals are anisotropic, optically active materials. Thus, the refractive indexes of such materials are not constant, as they depend on the orientation of the domains. The orientations and magnitudes of the refractive indices are depicted by an index ellipsoid, also called optical indicatrix.

The appearance of the Maltese cross indicates a parallel orientation of one of the main axes of the optical indicatrices (polarizability ellipsoids) of a birefringent structure in the plane of polarization of the incident light. Thus, the linearly polarized light passing through will not change its polarization, resulting in dark regions, see Fig. 6a. If the nematic director is not aligned with either of the polarizing filters, polarized light passing through the first filter becomes partially polarized along the nematic director.

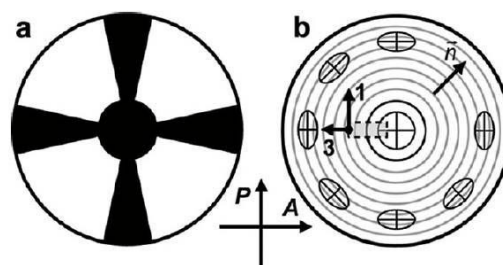


Fig. 6. (a) Schematic extinction pattern (Maltese cross) observed in Polarized Light Imaging of a sheared sample, here a block copolymer. (b) Projections of optical indicatrices (polarizability ellipsoids) on a surface of the samples sheared in a parallel-plate geometry<sup>1</sup>

Comparing the images taken at different strains during the amplitude sweep (Fig. 5) it can be seen that at low strains there are some light and dark areas, i.e. regions with differing director orientation, similar to the static situation. Increasing the strain, the domains are becoming more orientated within the flow, the so called Schlieren texture cannot be visualized any more. When the flow direction is changed within one oscillation, such mixed dark-light regions are appearing, but less pronounced as for the static case.

In a parallel-plate system, the shear rate and the resulting stress in the sample increases with the increasing radius. Stress-induced birefringence of the material, increasing towards the edge, can result in a colorful pattern<sup>2</sup>. Rings of alternating interference colors can be observed only during high amplitude oscillations. An example of such a colorful pattern can be seen in Fig. 5 for the images taken at a strain of 485 %, here after 5 s from the beginning, as well as at strain 1000 %, here after 1 s.

The changes in the birefringence of the sample depend on few factors, for example on the strain or shear rate as well as on the sample thickness. While performing the same test as above, the measuring gap has been reduced to 0.2 mm. Additionally, the frame rate of the camera has

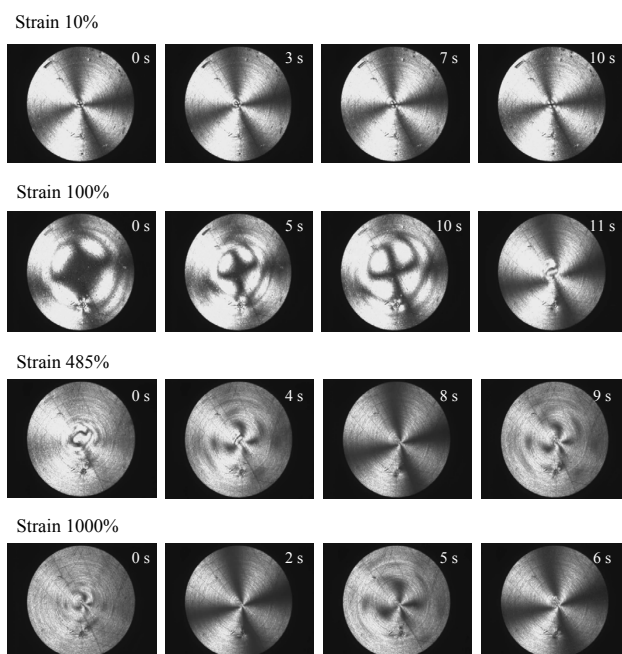


Fig. 7. **Amplitude sweep, performed at a gap of 0.2 mm.** The measuring point duration for each strain was 15 s. Taken at the same strain, the time points of the pictures are specified relatively to the first image

been increased from 15.9 fps (frames per second) for the maximum output size of the camera, no binning, to 26.13 fps (binning 2). As a result, only black and white pictures can be taken, see Fig. 7.

When recording a movie during oscillatory tests it can be seen how the nematic director follows the oscillatory motion. Dark and light areas with well-defined pattern are changing periodically during each single oscillation. The shape of such pattern depends on the frequency used for the oscillatory testing (which is not presented here) as well as on the applied strain values. To exemplify this, screen shots taken at different particular time points during the oscillation (at a frequency of  $f = 0.1$  Hz) are shown in Fig. 7.

#### 4. Summary

By using the Polarized Light Imaging technique, a connection between the macroscopical properties of a sample under shear and the corresponding microstructure can be established. Changes in the birefringent properties of the materials under shear are monitored over the complete sheared sample, enabling visualization of the flow field. The method can be successfully used not only to investigate orientation phenomena in liquid crystals but also for corresponding shear induced structural transitions based on orientation of the super-structures in polymer solutions or melts.

#### REFERENCES

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2. Mykhaylyk O. O.: *Soft Matter* 6, 4430 (2010).