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Measurement of the Domain Growth Kinetics in Multidomain Nematic Liquid Crystal Polymers by Means of the Worm Like Path Model for Multiple Scattering

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MEASUREMENT OF THE DOMAIN GROWTH KINETICS IN MULTIDOMAIN NEMATIC LIQUID CRYSTAL POLYMERS BY MEANS OF THE WORM LIKE PATH MODEL FOR MULTIPLE SCATTERING.

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Abstract The rate of domain growth in nematic side chain polymer samples is measured using the worm like path model for multiple scattering of light. The worm like path model which describes multiple scattering in terms of the optical persistence length is found to apply both to multiple scattering in liquid crystal polymer films as well as to model polystyrene dispersions. The required value of the optical persistence length can be calculated from the single scattering process so that there are no adjustable parameters in this model. The rate of domain growth in liquid crystal polymer samples is found to obey a scaling law where the growth exponent is about 0.85, contrary to the expected value of ½. In addition, an unexpected effect of the layer thickness on the rate of growth is observed, even for layer thicknesses much larger than the domain size.

INTRODUCTION

In order to investigate the rate of domain growth in a nematic side chain liquid crystal polymer (SCLCP) film use is made of a three stage approach:

1 describe the multiple scattering of a multidomain nematic texture using the worm like path model (WLP model),

2 relate the characteristic length scale for scattering, the optical persistence length L_p, to the "domain size",

3 model the kinetics of the "domain growth" (= director relaxation) by balancing a viscous torque (from the rotation viscosity) to an elastic torque (from Frank elasticity).

To quantitatively evaluate the multiple scattering behaviour, use is made of a set-up where the aperture of detection can be adjusted, see figure 1.

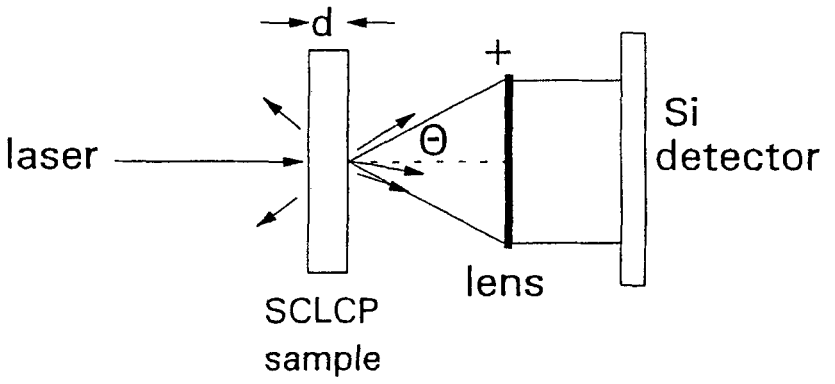

FIGURE 1 Schematic set-up to measure the scattering.

The numerical aperture of detection is given by:

$$NA = n \sin(\theta_{max}) \quad (1)$$

Where n is the index of refraction of the surrounding medium (in this case 1 for air) and θ_{max} is the maximum angle of detection. Using another set-up, the scattering distribution function of the multiple scattering samples was measured. To test the validity of the worm like path model, measurements on polystyrene (PS) dispersions also are reported.

I THEORETICAL

I.1 The worm like path model for multiple scattering

To model the behaviour of a multiple scattering film use is made of a method that we call the worm like path (WLP) model. In this model the trajectories of the photons are assumed to be directionally correlated for small photon displacements and to become random for larger displacements. The rate at which the photon loses it's directional information is described by a length scale, the "optical persistence length" L_p.

Analogous to the statistics of a polymer chain, the optical persistence

length is defined for the photon trajectories by (see fig.2):

$$\langle u_0 . u_s \rangle = \langle \cos(\theta) \rangle_s = \exp(-s/L_p) \qquad (2)$$

Here s is the traversed distance along the contour.

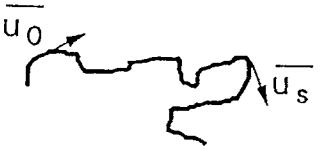

FIGURE 2 Worm like trajectory for the photons in a scattering medium.

Using this statistics of the photon trajectories, which should apply to all cases where the scattering entities are not small compared to the wavelength of light, the multiple scattering behavior has been simulated for various values of nd/L_p, the relative layer thickness. This is shown in figure 3 for several values of nd/L_p.

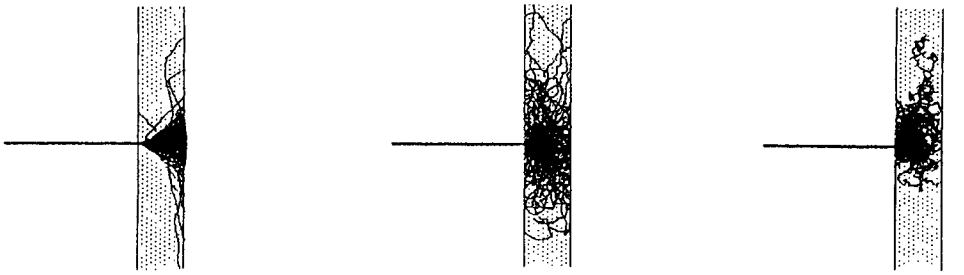

FIGURE 3 Image of worm like path simulations for three values of nd/L_p, respectively 0.2, 2, and 20 (left to right).

For an optically thin layer, e.g. $nd/L_p = 0.2$, the multiple scattering leads to mainly forward scattering with a Gaussian broadening of the intensity distribution. For an intermediate layer thickness ($nd/L_p = 2$) more or less symmetric foreward and back-scatter occurs as might have been expected for a layer thickness equal to the optical Kuhn length

(L_k-$2L_p$). Finally, for thick layers (nd/L_p = 20) mainly backscatter occurs. This behaviour as a function of layer thickness is in qualitative agreement with common experience of multiple scattering media.

Using the WLP model, the apparent optical density of a multiple scattering layer as a function of the relative layer thickness (nd/Lp) and the numerical aperture of detection is calculated. This is shown in figure 4.

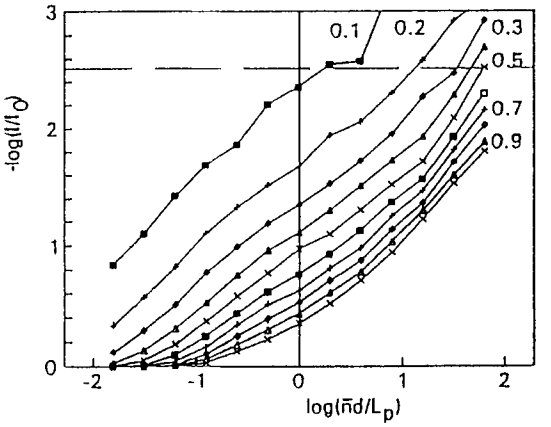

FIGURE 4 Apparent optical density from the worm like path simulations as a function the relative optical layer thickness nd/L_p, for several values of NA.

The curves show that the apparent optical density increases with increasing layer thickness and with decreasing numerical aperture of detection. Using these curves, experimental data measured at various values of NA can be converted to the single dimensionless parameter nd/L_p, which then allows the calculation of L_p (assuming n and d are known).

A more complete description of the worm like path model, together with a comparison with existing theories of multiple scattering[1,2] and experimental data, is being prepared[3].

I.2 Relation of L_p with the domain size in the nematic phase

To allow comparison with domain sizes from microscopic inspection of nematic multidomain samples, it is neccesary to convert the measured L_p value (as obtained from the WLP model) to the actual domain size D of

the nematic texture. As the local structure in a multidomain texture is random, and is not known a priori, this problem cannot be solved in an exact way. Here we will use an approximate relation that can be derived assuming a lattice for the director field, where the possible orientations of the director and polarisation of the incident light are limited to discrete values along x, y, or z. Two adjacent cells of the texture each have three possible orientations and there are two polarisation states so that in all 18 combinations have to be considered. Some of these will cause a phase shift of the incident light leading to a deviation of the direction of the wavefront over an angle θ, where:

$$n\ D\ \sin(\theta) = \Delta n\ D \qquad (3)$$

Here D is the size of the domains, Δn is the birefringence, n is the average index of refraction and θ is the angle over which the wavefront deviates from its initial direction, see figure 5.

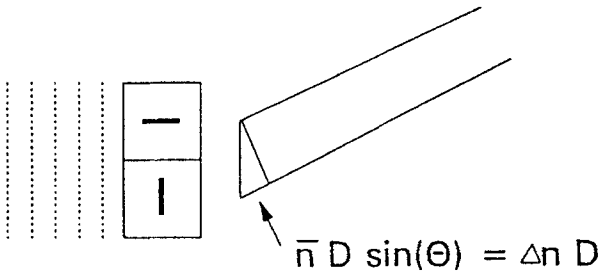

FIGURE 5 Deviation of the incident wavefront on the multidomain lattice due to a difference in optical path length.

Considering all 18 combinations and averaging then leads to the following expression for the relation between the domain size and the optical persistence length:

$$L_p = 9/4\ n\ D\ /\ (1 - \cos(\sin^{-1}(\Delta n/n)) \qquad (4)$$

It is expected that, despite the used approximations, this expression will provide a good first order estimate for the actual value of the

domain size. At the 15th ILCC (Budapest) we disovered that our construction for calculating the deflection of the incident light, based on the collected phase difference, appears to be similar to "anomalous diffraction" models being used for the description of single scattering in polymer dispersed liquid crystal displays[4], this will be discussed in more detail in the future publication[3].

I.3 Domain growth kinetics

To describe the growth of the nematic domains a model is used where an elastic torque from Frank elasticity is balanced by a viscous torque. Assuming for simplicity that we may use a single Frank elastic constant, that no material flow occurs during the relaxation process, and using a 1-D model, it is derived[5] that the director orientation obeys the following equation:

$$\gamma_1 \frac{d\Phi}{dt} = K \frac{d^2\Phi}{dz^2} \qquad (5)$$

Where Φ is the orientation angle of the director at time t and position z, γ_1 is the rotation viscosity, and K is the Frank elastic constant. Solving by separation of variables leads to the following scaling behavior of the domain size: $D \sim t^{1/2}$. This result can also be derived from the observation that we are dealing with a Fick type equation, i.e. that director relaxation can be viewed as a "diffusion process".

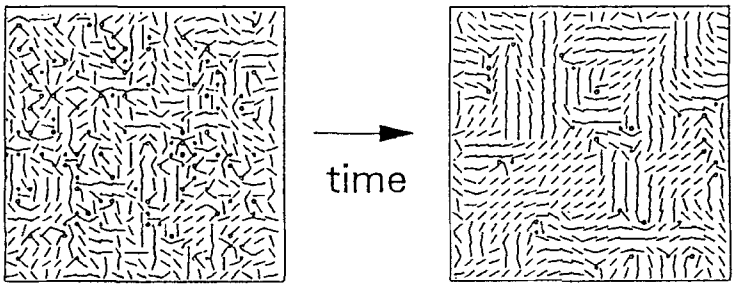

FIGURE 6 Result of the 2-D lattice model showing the increasing domain size as a function of anneal time[5].

This scaling behaviour is not specific for the 1-D case but holds for director relaxation in 2 and 3-D space as well, as may be derived using the full Frank free energy expression.

The 2-D case mentioned above has also been calculated using a lattice model[5] that allows visualisation of the disclinations in the director field, this is shown in figure 6.

From these figures, a sensible definition of the domain size is argued to be the square root of the area per disclination[5,6]. Similarly, for the 3-D case one should use the cube root of the volume per disclination.

II EXPERIMENTAL RESULTS

II.1 Measurements on PS disperions

To test the validity of the WLP model, experiments were performed on model polystyrene dispersions in water. The particle size was large (e.g. 821.9 nm) so that a single scattering process will on average only slightly perturb the trajectory of a photon.

Several concentrations and layer thicknesses were measured for numerical apertures of detection ranging from 0.1 to 0.4. In figure 7 some results are shown for NA = 0.3.

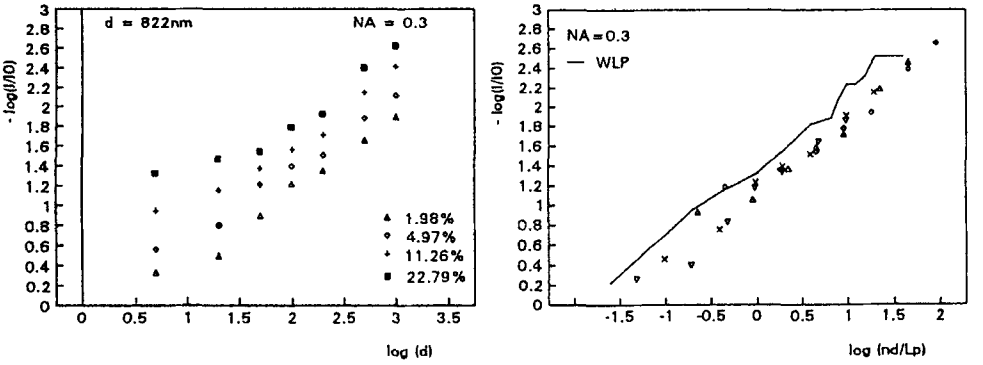

FIGURE 7 Left: measured optical densities of a polystyrene dispersion as a function of layer thickness for NA = 0.3 and various concentrations. Right: Replotted results as a function of the WLP parameter nd/L_p, using L_p from Mie theory, drawn curve WLP model.

Also, these results are shown as a function of $\log(nd/L_p)$ using the L_p value calculated from Mie theory (see below). It is observed that by using this procedure all the results fall onto a single curve and that this curve is in reasonable agreement with the calculated curve from the WLP model.

The value of the optical persistence length used here is calculated from Mie theory that provides the single scattering distribution function and the scattering cross section σ_s.
The scattering cross section allows the calculation of the mean free path L_s for a single scattering event to occur: $L_s = 1/N\sigma_s$. The single scatttering (Mie) distribution allows the calculation of the first scattering moment $\langle\cos\theta\rangle_{ss}$ where: $\langle\cos\theta\rangle_{ss} \equiv \exp(-L_s/L_p)$. This equation allows L_p to be calculated from Mie theory without any adjustable parameters.

As a further test of the WLP model the scattering distribution function was measured directly by scanning a detector over the angle θ. To reduce the effect of refraction and internal reflection at the interface the planar sample was immersed in water in a cylindrical cuvet. The measured intensity distribution functions are shown in figure 8 for three values of the relative layer thickness together with the simulated distribution functions from the WLP model. Obviously, the extension of the WLP model to include the effect of refraction and internal reflection would be straightforward. However, for the purpose of verification, it seems useful to test the WLP model without such embellishments.

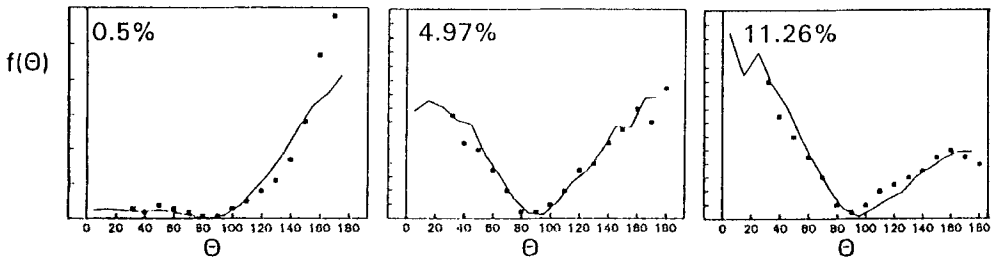

FIGURE 8 Some measured distribution functions compared with those from the WLP theory using the Mie value for L_p.

From the observed agreement between experiment and theory it is concluded that the worm like path model succesfully describes the multiple scattering in this system. Moreover, the parameter of the WLP model (L_p) is in quantitative agreement with Mie theory.

II.2 Measurements on nematic side-chain polymer layers

To study the domain growth in side chain polymer layers, a variety of measurements were performed for various temperatures, layer thicknesses and numerical apertures of detection. An example of such a set of measurements is shown in figure 9.

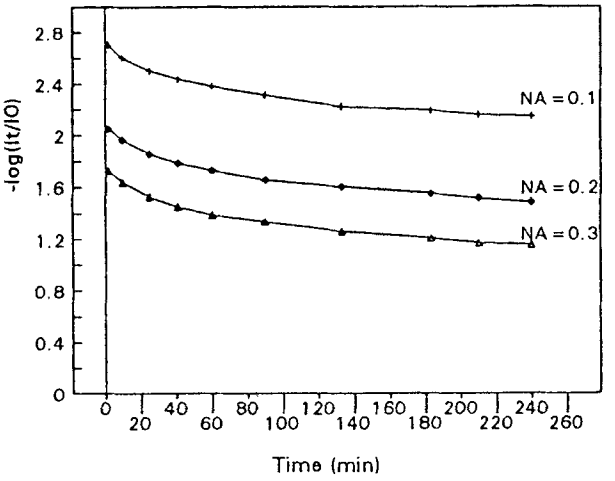

FIGURE 9 Apparent optical density of a SCLCP film as a function of anneal time.

Using the WLP model the effect of the numerical aperture can be eliminated giving a single curve in terms of the parameter nd/L_p. This is shown in figure 10.

Next, using the simple interference model described in section I.2, the domain size can be estimated from L_p. This is shown in figure 11 both on a linear and a log-log scale versus the annealing time. From the latter curve a rate exponent of about 0.85 is found for the domain growth kinetics.

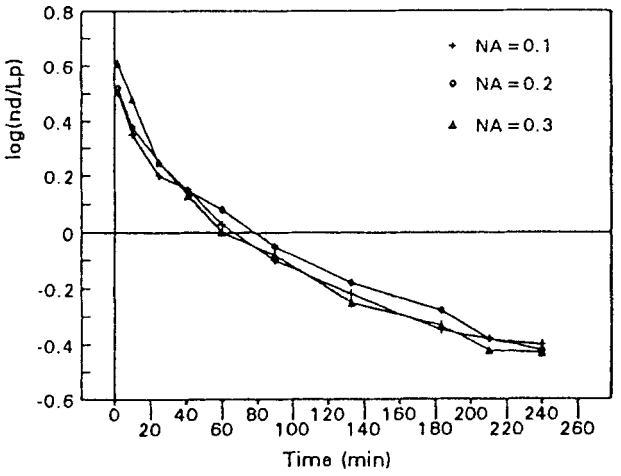

FIGURE 10 Relative optical layer thickness nd/L_p as a function of annealing time, obtained by applying the WLP model to the measurements in figure 9.

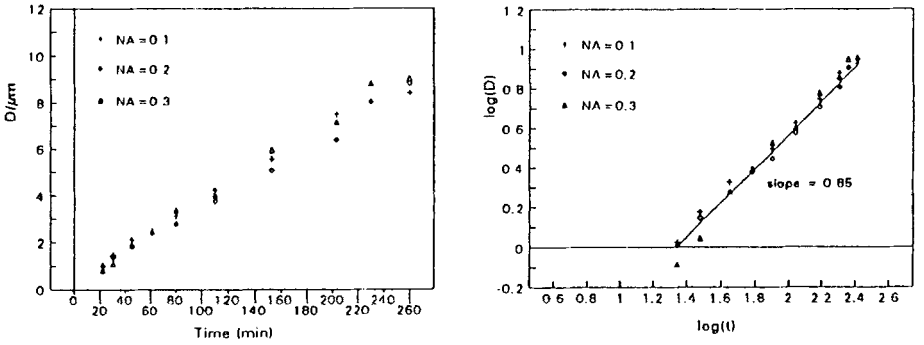

FIGURE 11 Domain size as a function of annealing time on a linear (left) and a log-log scale (right).

Additional measurements at different temperatures give an increasing rate of domain growth with increasing temperature, while the same rate exponent is found. This is shown in figure 12 for three temperatures, again on a log-log scale.

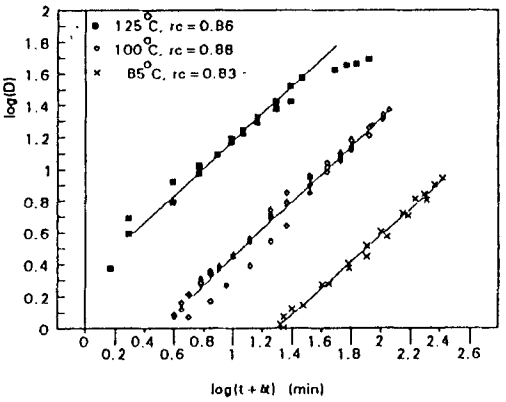

FIGURE 12 Domain size as a function of annealing time for various temperatures as indicated on a log-log scale.

One might speculate that the high value of the rate exponent, compared to the model of section I.3, is related to a non-Newtonian behavior of the rotation viscosity.

Considering the high domain growth rate exponent found from the experiments a possible effect of the layer thickness was also investigated. It was found that there is an effect of layer thickness on the rate of domain growth even for layer thicknesses substantially larger than the domain size. This is shown in figure 13, where we find that the rate of domain growth increases with 1/d.

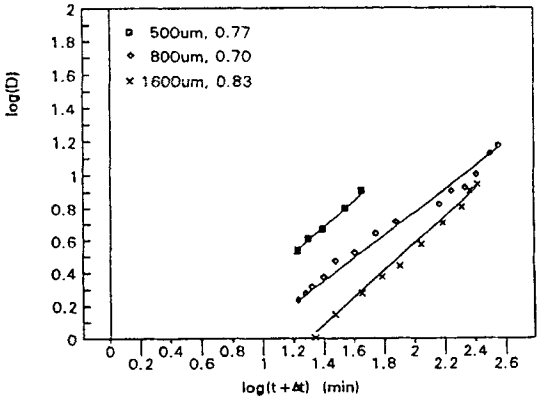

FIGURE 13 Domain size as a function of anneal time for various layer thicknesses (log-log scale).

From microscopic investigation of the samples, it was concluded that this effect is not an artefact from the worm like path model and does reflect an actual change in the domain size. Obviously, this remarkable result requires further analysis since the mechanism for this effect is not clear. One might speculate that it is related to a boundary effect from the glass substrates (which seems unlikely) or is due to the manner in which the samples are prepared by rapidly quenching from the isotropic phase (due to the low thermal conductivity of the polymer samples, the rate of cooling in the centre of the samples will be different for different values of d).

Summarising, the experimental results on the SCLCP layers yield the following scaling behavior for the rate of domain growth:

$$D.d \sim t^{0.85} \tag{6}$$

where D is the domain size, d is the layer thickness and t is the annealing time. The absolute rate of domain growth is strongly influenced by temperature as might have been expected.

III SUMMARY AND CONCLUSIONS

From the above results it appears that the worm like path model provides a useful and quantitative description of multiple scattering by random highly scatttering media. Both for polystyrene dispersions and nematic side chain LCP layers it appears that the multiple scattering results (giving the optical persistence length L_p) can be interpreted in terms of the (change in) local structure. The growth-rate exponents found for the SCLCP samples (about 0.85) are higher than expected from a simple model based on Frank elasticity and a Newtonian rotation viscosity (giving ½). Unexpectedly, even if the layer thickness is much larger than the domain size, the rate of domain growth increases with decreasing layer thickness.

From the experimental data the overall scaling relation for the domain growth is found to be: $D.d \sim t^{0.85}$. This result obviously requires further study. As a hypothesis we propose that this behavior is due to a combined effect of the initial quench (giving the unexpected

dependence on the layer thickness d) and a non-newtonian rotation viscosity (giving the high rate exponent).

A further, more detailed, description of the worm like path model and the experimental results summarised here is under preparation[3].

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