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Mass transport phenomena during lithographic polymerization of nematic monomers monitored with interferometry

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Photopolymerization of liquid-crystalline diacrylates is a versatile tool to make optical films for liquid-crystal display (LCD) enhancement. The constant drive towards LCD's having an improved front-of-screen performance demands optical films with properties that can be adjusted on (sub) pixel level. Birefringent films made from liquid-crystalline diacrylates allow for the required adjustment of the optical property on (sub) pixel level. In this paper we report on the composition of the acrylate mixture that results in planarly aligned nematic films usable as optical retarder in transmissive LCD's as well as the mass transport phenomena that take place during heating of a mask-exposed birefringent film of liquid-crystalline diacrylates. The mass transport phenomena are studied by interferometry as a function of temperature and time. Upon heating a pronounced surface corrugation arises from the latent image formed during the mask exposure. The surface profile largely depends on lateral feature sizes. For $1 \times 1\text{-mm}^2$ areas the exposed areas rise compared to the nonexposed areas, whereas the opposite is observed for $100 \times 100\text{-}\mu\text{m}^2$ areas. Finally, the direction of the mass transport depends on the molecular orientation of the liquid-crystalline diacrylate. The protrusion formed by lengthwise diffusion is 1.7 times higher than that formed by sideways diffusion. © 2005 American Institute of Physics. [DOI: 10.1063/1.1935129]

INTRODUCTION

Functional optical films such as cholesteric color filters, wide viewing angle foils, polarizers, antireflective coatings,^{1,2} and diffraction gratings³ are crucial for improving the optical performance of liquid-crystal displays (LCD's). One route to make these functional optical films is by photopolymerization of liquid-crystalline diacrylates.⁴ The advantage of using these compounds for the fabrication of optical films is the dependence of the light modulation on the order of the liquid-crystal monomers. This order can be manipulated before photopolymerization, enabling optimization per pixel or even per subpixel level.^{1,5} For instance, for an optimum front-of-screen performance in transmissive LCD's, films have to be used of which the retardation of the transmissive part is preferred to be zero, whereas the retardation of the reflective part of the pixel equals $\frac{1}{4}\lambda$.^{6,7} This can be achieved in polymeric films made from liquid-crystalline diacrylates. Isotropic domains can be created in a birefringent film by conducting in succession a mask exposure to cross-link the film locally in its nematic state and a flood exposure at a temperature exceeding the nematic to isotropic transition temperature of the liquid-crystalline monomers to fix the remaining isotropic areas.

A mask exposure of a mixture of monomers is, however, known to induce a flux of material into the exposed areas,

possibly accompanied by a counterflux of other material to the dark regions.^{8–11} In this way complex surface relief structures were obtained in *isotropic* films.¹¹ These surface relief structures are useful for the application of diffusive reflectors in a LCD, but highly undesired in patterned retardation foils. In this study we report on a material flux induced by a mask exposure of a film consisting of a mixture of reactive liquid-crystalline diacrylates being aligned on an alignment layer in their *nematic* phase followed by heating. Upon mask exposure at room temperature a latent image is formed where the exposed areas consist of partly cross-linked polymer network that may contain captured free radical species. In this paper we describe the study of transport phenomena occurring in birefringent films being exposed through a checkerboard mask with $100 \times 100\text{-}\mu\text{m}^2$ and $1 \times 1\text{-mm}^2$ squares. The formation of the surface profile from the latent image is monitored as function of time and temperature by interferometry. Apart from the transport phenomena we also report on a mixture composition of reactive liquid-crystalline molecules that form uniaxially and planarly aligned birefringent films before polymerization and that are thermally, photo-, and chemically stable after polymerization.

EXPERIMENT

Materials

RM82: [4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylphenyl 4-(6-acryloyloxyhexyloxy)benzoate, RM257: [4-(3-acryloyloxypropyloxy)benzoyloxy]-2-methylphenyl 4-

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(3-acryloyloxypropyloxy)benzoate, and RM522 were obtained from Merck. Irgacure 184 (1-hydroxycyclohexyl phenylketone) photoinitiator was obtained from Ciba Specialty Chemicals. All the other chemicals were obtained from Aldrich. Precursor OPTMER A11051 used for the alignment layer was purchased by Japan Synthetic Rubber Co.

Synthesis of 4-(6-acryloyloxyhexyloxy)phenyl 4-hexyloxybenzoate

4-(6-hydroxyhexyloxy)phenol

A solution of 40 g of sodium hydroxide in 200 ml of water was added dropwise to a refluxing mixture of 220 g of hydroquinone, 124 ml of 1-chloro-6-hydroxyhexane, 60 g of sodium iodide, and 800 ml of water. After refluxing for another 20 h, the mixture was cooled to room temperature and the precipitate was collected by filtration. After washing twice with 800 ml of water, the precipitate is mixed with a deaerated solution of 50 g of sodium hydroxide in 1000 ml of water. The solution obtained after filtration was cooled to 5 °C and 1.5N HCl solution was added until pH=2. The precipitate was collected on a filter. After washing with 500 ml of water it was dissolved in 400 ml of ethanol. 1 g of activated carbon was added, the mixture was heated to 60 °C and filtered over celite. To the clear solution 800 ml of boiling water was added and upon cooling the product crystallized in long needles. 84 g of the product (yield=40%) was obtained, mp=87 °C.

4-(6-acryloyloxyhexyloxy)phenol

A solution of 27 ml of acryloylchloride in 100 ml of tetrahydrofuran was added dropwise to a solution of 63 g of 4-(6-hydroxyhexyloxy)phenol and 42 ml of N,N-dimethylaniline in 300 ml of tetrahydrofuran, cooled in an

ice bath. After stirring for 20 h at room temperature 400 ml of diethyl ether was added and the mixture was extracted subsequently with 300 ml of water, 300 ml of 2.5N HCl solution, and 300 ml of brine. After drying over magnesium sulfate, the solvents were evaporated to leave 70 g of the product (yield=90%) as a yellow oil that slowly crystallized, with mp=55 °C.

4-(6-acryloyloxyhexyloxy)phenyl 4-hexyloxybenzoate

51 g of N, N'-dicyclohexyl carbodiimide was added to a mixture of 60 g of 4-(6-acryloyloxyhexyloxy)phenol, 50 g of 4-hexyloxybenzoic acid, 3 g of 4-N,N-dimethylaminopyridine, and 500 ml of dichloromethane cooled in an ice bath. After 1 h the ice bath was removed and the reaction was stirred for 16 h at room temperature. After filtering through a small layer of silica, the solvent was evaporated and the remaining solid was recrystallized from 500 ml of ethanol. 81 g of the product (yield=78%) was obtained as a white powder with mp=54 °C and cp =67 °C (nematic fluid).

IR (chloroform solution, ν in cm^{-1}): 2936 and 2861 (CH_2 and CH_3), 1734 ($\text{C}=\text{O}$, benzoate and acrylate), 1637 ($\text{C}=\text{C}$), 1608 and 1511 (aromatic rings), 1407 (CH_2 -acrylate), and 1253 (Ar-O). MS (MALDI): calculated for $\text{C}_{28}\text{H}_{36}\text{O}_6$: 468.25, found 468.27.

^1H -NMR (300 MHz in CDCl_3 , in ppm relative to tms, and J in Hz): 8.21 (d , 2H, $J=9.0, \text{H}^j$), 7.09 (d , 2H, $J=9.0, \text{H}^k$), 6.96 (d , 2H, $J=9.0, \text{H}^m$), 6.91 (d , 2H, $J=9.0, \text{H}^l$), 6.42 (dd , 1H, $J_1=17.3, J_2=1.5, \text{H}^a$), 6.13 (dd , 1H, $J_1=17.3, J_2=10.5, \text{H}^c$), 5.82 (dd , 1H, $J_1=10.5, J_2=1.5, \text{H}^b$), 4.17 (t , 2H, $J=6.4, \text{H}^d$), 4.02 (t , 2H, $J=6.4, \text{H}^e$), 3.95 (t , 2H, $J=6.4, \text{H}^f$), 1.82 (m , 4H, $\text{H}^g + \text{H}^h$), 1.71 (q , 2H, $J=6.4, \text{H}^i$), 1.49 (m , 6H, $\text{H}^j + \text{H}^k + \text{H}^l$), 1.35 (m , 4H, $\text{H}^m + \text{H}^n$), 0.91 (t , 3H, $J=6.4, \text{H}^o$).

^{13}C -NMR (75 MHz in CDCl_3 , δ in ppm relative to tms, and J in Hz): 166.7 (C^3), 165.7 (C^{14}), 163.9 (C^{18}), 157.1 (C^{10}), 144.9 (C^{13}), 132.6 (C^{16}), 131.0 (C^1), 129.0 (C^2), 122.9 (C^{12}), 122.1 (C^{15}), 115.4 (C^{11}), 114.6 (C^{17}), 68.7 (C^{19}), 68.6 (C^9), 64.9 (C^4), 31.9 (C^{22}), 29.6 (C^{20}), 29.4 (C^8), 29.0 (C^5), 26.2 ($\text{C}^6 + \text{C}^7$), 26.0 (C^{21}), 22.9 (C^{23}), 14.4 (C^{24}).

Uniaxially and planarly aligned nematic films comprising isotropic areas

A solution was prepared by dissolving 2 g of RM257, 0.5 g of RM82, 0.5 g of 4-(6-acryloyloxyhexyloxy)phenyl

4-hexyloxybenzoate, 0.03-g Irgacure 184, and 0.015-g RM522 into 6-g xylene at 70 °C containing 0.07-mg/g *p*-methoxyphenol. This solution was spin coated on a substrate provided with an alignment layer being a rubbed polyimide. The spin conditions of the Convac spinner were 60 s at 2500 rpm yielding a birefringent film thickness of about 1.4 μm . The rubbed polyimide established nearly planar alignment of the liquid-crystalline monomers with its director parallel to the rubbing direction. The formation of the monodomain was facilitated by an anneal step on a hot plate at 70 °C for 30 s. The annealed film was subsequently mask

exposed for 0.1 s in N_2 using a Karl Suss MA8 exposure machine with an UV intensity of 9.5 mW/cm^2 . A checkerboard mask with feature sizes of $1 \times 1 \text{ mm}^2$, $100 \times 100 \text{ }\mu\text{m}^2$, $10 \times 10 \text{ }\mu\text{m}^2$, and $3 \times 3 \text{ }\mu\text{m}^2$ was used. The mask exposure step was followed by a flood exposure for 2 min at $120 \text{ }^\circ\text{C}$ using an Oriel lamp with an UV intensity of about 20 mW/cm^2 . The isotropic transition temperature of the liquid-crystal mixture was $103 \text{ }^\circ\text{C}$ when measured in a $5\text{-}\mu\text{m}$ cell in a hot stage. However, we found that complete isotropization of the nonexposed part in partly exposed films occurred at a hot plate temperature of $115 \text{ }^\circ\text{C}$.

Interferometry

The interferometry experiments were performed on a Wyko interferometer. The surface profiles were verified to those measured with the Tencor surface profiler. In addition, we checked whether the surface profile measured on a pure sample equaled the surface profile measured when the sample was covered with a thin gold film. No significant difference was found implying that the interferometer is a suitable method to study the surface profiles of birefringent films.

Surface profiles were measured as function of temperature and time. For both experiments the substrate provided with the liquid-crystalline mixture was partially cross-linked by an UV mask exposure. Subsequently, the sample was directly transported to the interferometer setup and measured. To estimate the influence of temperature, the temperature of the hot plate was incrementally increased from room temperature to $135 \text{ }^\circ\text{C}$. The inaccuracy of the film temperature was estimated to be $5 \text{ }^\circ\text{C}$ of the temperature set on the hot plate. The total measurement took about 30 min. As a consequence, some time effects were present in the surface profiles measured as function of temperature. However, the time-dependent experiments showed that time effects become important after 1 h (in the case of $105 \text{ }^\circ\text{C}$) implying that the effects seen as a function of temperature can be attributed to improved kinetics induced by viscosity and diffusivity changes rather than thermodynamics.

RESULTS AND DISCUSSION

Materials for uniaxially and planarly aligned birefringent films comprising isotropic areas

The chosen mixture composition is a result of accommodating the number of optical characteristics necessary for the application as optical foil in transfective LCD's. The films of liquid-crystalline diacrylates have to be made by a spin coat process at room temperature demanding the liquid-crystalline molecules to exhibit a nematic phase at room temperature, while after UV curing the film has to be thermally, photo-, and chemically stable. Furthermore, the nematic to isotropic transition should not be too high to avoid unwanted thermal polymerization upon heating the material to the isotropic state. In addition to the processing ability, the alignment of the photopolymerizable liquid-crystalline molecules has to be uniaxial and planar for application as optical retarder in transfective LCD's. A combination of diacrylates with a C3 spacer and a C6 spacer, compounds 1 and 2, re-

FIG. 1. Structures of [4-(3-acryloyloxypropyloxy)benzoyloxy]-2-methylphenyl 4-(3-acryloyloxypropyloxy)benzoate (1, RM257), [4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylphenyl 4-(6-acryloyloxyhexyloxy)benzoate (2, RM82), 4-hexyloxyphenyl 4-(6-acryloyloxyhexyloxy)benzoate (3), and 4-(6-acryloyloxyhexyloxy)phenyl 4-hexyloxybenzoate (4).

spectively, in scheme 1 allows for a high conversion necessary to meet the stability demands. However, a mixture of only diacrylates crystallizes during or shortly after the spin coat process and exhibits a relatively high nematic to isotropic transition. To prevent crystallization of the spin-coated film and to decrease the transition temperature, a monoacrylate can be added to the diacrylate mixture. Addition of 16 wt % of 4-hexyloxyphenyl 4-(6-acryloyloxyhexyloxy)benzoate (3 in Fig. 1) to the diacrylate mixture showed a stable supercooled nematic film after spin coating and the isotropic transition decreased from 125 to approximately $115 \text{ }^\circ\text{C}$. However, this monoacrylate induces a splayed orientation due to its tendency to orient homeotropic at the film-air interface even if a surfactant was added to the mixture. This known monoacrylate¹² is relatively simple to make but exhibits a smectic-A phase only $11 \text{ }^\circ\text{C}$ below its nematic-isotropic transition at $65 \text{ }^\circ\text{C}$. It is possible that this smectic behavior influences the orientation knowing that smectic materials often show a tendency to orient homeotropic. To avoid this effect of smectic behavior, an isomeric compound was used, namely, 4-(6-acryloyloxyhexyloxy)phenyl 4-hexyloxybenzoate (4 in Fig. 1). This compound was synthesized according to Fig. 2.

It was made by esterification of 4-(6-acryloyloxyhexyloxy)phenol and the commercially available 4-hexyloxybenzoic acid. The former compound was prepared from hydroquinone that was alkylated by chlorohexanol followed by acrylation of the so-formed 4-(6-hydroxyhexyloxy)phenol. The last-mentioned compound could be separated rather easily from the dialkylated hydroquinone, the most important side product of its formation. By using *N,N*-dimethylaniline as a base, the reaction with acryloyl chloride occurred exclusively at the alcoholic group; the phenolic did not react. This way of forming 4-(6-acryloyloxyhexyloxy)phenol is much more simple than the previously described method using protecting groups.¹³ Compound 4 is a nematic monoacrylate with a thermotropic range of $13 \text{ }^\circ\text{C}$ above its melting point of $54 \text{ }^\circ\text{C}$. Even upon

FIG. 2. Synthesis of 4-(6-(6-acryloyloxyhexyloxy)phenyl) 4-hexyloxybenzoate (4).

cooling below its melting point no transition to a smectic phase was observed before crystallization at around room temperature occurred. In this respect the compound is more useful for application in nematic mixtures than its isomer 3 (reversed ester group) that exhibits a smectic-A phase.

Indeed, mixtures with 16 wt % of compound 4 did result in planar alignment of the liquid-crystalline mixture. Thus, this mixture was used further in this study. In addition to the monoacrylate choice, the choice of surfactant is crucial for creating and maintaining planar orientation. Although surfactants such as RM502 and FC171 all induce planar alignment at room temperature, it was found that FC171 and RM502 evaporated during the anneal step. As a result splayed, uniaxial films were obtained. RM522, on the other hand, did not evaporate during the anneal step resulting in uniaxially planar aligned films of photopolymerized liquid-crystalline molecules.

Formation of polymerized films

Figure 3 shows a typical picture of a thermally patterned film taken by a polarizing microscope with the sample in between crossed polarizers consisting of birefringent (bright) and isotropic (dark) domains made by an UV exposure through a mask while the monomer is in its nematic phase and a post-UV exposure, while the sample was heated above the nematic to isotropic transition in the unexposed areas. The orientation of the director in the birefringent domains is 45° with respect to the transmission axis of the polarizer. As is shown in Fig. 3, isotropic domains are created next to birefringent domains with a resolution down to $10\ \mu\text{m}$. Hence, thermal patterning is a useful tool for the manufacturing of patterned optical retarders. However, examination of the surface profile revealed a corrugated surface. Figure 4 shows the cross section of the surface profile for both $1\times 1\text{-mm}^2$ and $100\times 100\text{-}\mu\text{m}^2$ squares. The exact nature (i.e., shape and height difference) of the surface profile varies from sample to sample. This is found to be a result of the strong dependency on exposure dose, mixture composition, and process times (e.g., waiting times between the mask exposure and the flood exposure). However, the surface profile appears to be also a function of the mask feature size. For the applied process conditions, the height of the birefringent part

FIG. 3. Polarization microscopy picture of thermally patterned retardation foil. The orientation of the director in the birefringent domain (bright) is 45° with respect to the transmissive axes of the crossed polarizers. The bright areas have been photopolymerized in the nematic state. The dark domains correspond to the nontransmissive area of the mask (10×10 and $100\times 100\ \mu\text{m}^2$, respectively) and have been polymerized in the isotropic state.

(polymerized in the nematic phase) is always lower than that polymerized in the isotropic phase for the $1\times 1\text{-mm}^2$ squares, while for the $100\times 100\text{-}\mu\text{m}^2$ squares the opposite is found (i.e., the birefringent part was higher than the isotropic part). In addition, the birefringent part contains a protrusion

FIG. 4. Surface profiles of the $1\times 1\text{-mm}^2$ (a) and $100\times 100\text{-}\mu\text{m}^2$ (b) squares of a thermally patterned retardation foil made according to the process conditions given in the experimental section and measured by interferometry.

FIG. 5. (a) Surface profiles as a function of the temperature for $1 \times 1\text{-mm}^2$ squares of a mask-exposed birefringent film. (b) Detail of the interface between the exposed and nonexposed areas.

at the edge and the isotropic part shows an indentation independent of the mask feature size. The level differences cannot be explained by density differences between the birefringent and the isotropic sites and therefore must be the result of mass transport during heating or UV illumination. In order to gain insight in the mechanism of mass transport upon localized exposure of nematic films followed by a heating step at a temperature higher than the transition temperature, the development of the surface profiles is monitored with interferometry as function of time and temperature keeping the mixture composition and exposure dose constant.

The formation of the surface corrugation as a function of temperature

Figure 5(a) shows how the surface profile of a $1 \times 1\text{-mm}^2$ square develops with temperature. Upon mask exposure at room temperature, a latent image is formed where the exposed areas consist of partly cross-linked polymer network. The surface relief structure is absent directly after the mask exposure, presumably due to the high viscosity of the mixture at room temperature and related low monomer mobility towards diffusion.¹¹ The exposed part is about 40–70 nm lower than the nonexposed part. This decrease in height is attributed to polymerization shrinkage, which in the case of a layer thickness of $1.4\text{ }\mu\text{m}$ corresponds to 3–5 vol %, assuming no change in lateral dimensions. This value is reasonable, because the volume shrinkage for liquid-crystalline diacrylates with similar structure is known to be in the order of 7%–10% in the case of complete conversion.¹⁴ In this case

the conversion has not been completed yet and as a consequence the shrinkage will be lower than the reported 7%–10%. Upon heating an indentation at the edges of the nonexposed part evolves while simultaneously a protrusion is formed at the edge of the cross-linked part. Figure 5(b) zooms into the transition area from exposed to nonexposed to illustrate the development of the protrusion and indentation as a function of temperature. The protrusion clearly grows continuously in width and height at the expense of the nonexposed part. At 107 °C, just before the isotropic-nematic transition, the height and the width of the protrusion are 230 nm and 100 μm , respectively, and the depth and width of the indentation are 380 nm and 63 μm , respectively. Transport of monomer to the exposed area is believed to cause the protrusion formation enforced by polymer network swelling. In the literature^{8,15} corrugation phenomena have been described for isotropic systems, where monomer diffusion to the exposed areas was modeled in terms of chemical potential of the reacting and the formed species. When the monomer conversion proceeds fast compared to the diffusion, the migrating species cannot reach the center of the exposed regions because of immobilization by polymerization. Consequently, thicker protrusions at the edges of the exposed areas were observed. It was also found that this phenomenon is more pronounced for larger feature sizes, because of larger diffusion lengths. Under our conditions, the protrusion remains virtually unaffected at the moment that the nonexposed part becomes isotropic. Material transport probably still occurs because the center surface of the nonexposed part, now being isotropic, forms a parabolic interface upon further heating. As we will see later this parabolic surface disappears again in favor of the birefringent part. After ruling out volume changes and dewetting phenomena as a plausible cause, we have attributed the parabolic surface to migration of material in combination with the difference in surface tension between the birefringent and isotropic state.

In the previously mentioned two-dimensional (2D) reaction-migration model,¹⁵ other effects than concentration gradients, i.e., monomer size, cross-linking degree, and surface tension, are also driving forces for material transport, although nematic effects and a composition-dependent surface tension are not incorporated. Similar differences between 1-mm and the 100- μm structures are observed when this model is applied to a system of a mono- and a diacrylate assuming a diffusion coefficient in the order of $10^{-10}\text{ m}^2\text{ s}^{-1}$, and the migration for the monoacrylate is chosen more efficient (e.g., ten times) than for the diacrylate. In both cases, mainly the diacrylate migrates from the peripheral region of the nonexposed regions to the exposed regions. For the 100- μm case, the diacrylate from the center of the nonexposed regions can easily reach the exposed regions, resulting in a net mass migration towards the exposed regions. For the 1-mm structure, however, a concentration gradient of the monoacrylate within the nonexposed region arises. As a result, migration of the monoacrylate from the peripheral region to the center of the nonexposed regions is observed resulting in mass buildup in the center region. This region

FIG. 6. A thermal sequence of nonexposed parts viewed in between crossed polarizers showing the gradient in transition temperature. The orientation of the director in the exposed part is 45° with respect to the transmissive axis of the polarizer. In this orientation the nematic parts appear bright, while the isotropic parts appear black.

minimizes its surface energy by forming a parabolic surface. The Marangoni effect, which was not incorporated in the model, can enhance this effect.

The Marangoni effect explains that a gradient in surface tension may lead to contraction of the higher energetic central area, giving it a spherical shape and expansion of the lower energetic peripheral area.¹⁶ Because of density reasons the nematic state has a higher surface tension than the isotropic state of the same material. If the transition from nematic to isotropic occurs later in the central part because mass transport induced a gradient in mixture composition and consequently in transition temperature, the center will temporarily have a higher surface tension, establishing the parabolic surface profile. Figure 6 shows a thermal sequence of microscopic pictures taken on the nonexposed $1 \times 1\text{-mm}^2$ pattern in between two crossed polarizers with a microscope equipped with a Mettler Toledo FP5 hot stage. At $T = 105^\circ\text{C}$ the nonexposed part is nematic and appears white. The sequence distinctly demonstrates that isotropization of the 1-mm^2 pattern starts at the edges at $T = 106.5^\circ\text{C}$ and grows towards the center (the image appears black). At $T = 115^\circ\text{C}$ the entire nonexposed part is isotropic, taking away the driving force for surface deformation and the effect will diminish again.

Figure 7 shows the two-dimensional surface profiles taken at different temperatures for a $100 \times 100\text{-}\mu\text{m}^2$ patterns. As with the larger patterns, just after cross-linking at room temperature, the cross-linked part is slightly lower than the nonexposed part. However, the protrusion and indentation are already distinctly present at room temperature. A situa-

FIG. 7. Surface profiles of the $100 \times 100\text{-}\mu\text{m}^2$ squares of a mask-exposed birefringent film monitored by interferometry for various temperatures.

tion that does not change upon heating until 90°C . Beyond this temperature, the partly cross-linked nematic material swells at the expense of the nonexposed part. Above $T = 120^\circ\text{C}$ no change in the surface profile is measured upon further heating. Apparently, for the $100 \times 100\text{-}\mu\text{m}^2$ squares the diffusion rate is fast enough to allow for monomer migration to the center of the cross-linked part at the time scale the measurements took place. This $100 \times 100\text{-}\mu\text{m}^2$ dimension corresponds to the dimensions in which the protrusion and indentation formation took place as observed in the $1 \times 1\text{-mm}^2$ experiments shown in Fig. 5(b), i.e., $200\text{ }\mu\text{m}$. Hence, the difference between $1 \times 1\text{-mm}^2$ and $100 \times 100\text{-}\mu\text{m}^2$ patterns can be attributed to the diffusion rate.

In correspondence with the $1 \times 1\text{-mm}^2$ structures, the $100 \times 100\text{-}\mu\text{m}^2$ structures show a temporary parabolic structure in agreement with our explanation on a gradient of transition temperature and the transition-driven Marangoni effect. The thermal sequence of microscopic pictures of the nonexposed $100 \times 100\text{-}\mu\text{m}^2$ squares taken in between two crossed polarizers with a microscope equipped with a hot stage underpins the observed parabolic surface. Indeed the onset of isotropization starts around 90° , while the nonexposed part is isotropic at 106°C . That is, the temperature at which isotropization starts for the $1 \times 1\text{-mm}^2$ nonexposed squares implies that the mixture composition of the nonexposed $100 \times 100\text{-}\mu\text{m}^2$ square is different to the nonexposed $1 \times 1\text{-mm}^2$ square as a result of mass transport.

The formation of the surface corrugation as a function of time

In order to distinguish between kinetically or thermodynamically controlled transport phenomena, experiments were performed as function of time at a constant temperature. At room temperature the evolvement of the protrusion and indentation is observed. However, because the sample is in its supercooled state at room temperature, crystallization of the nonexposed part hindered observation of changes at prolonged times. The timed surface profiles measured at 105°C show a combination of the phenomena observed at the temperature-dependent experiments for the $1 \times 1\text{-mm}^2$ and $100 \times 100\text{-}\mu\text{m}^2$ patterns. Figure 8 shows the surface profiles

FIG. 8. Surface profiles of $1 \times 1\text{-mm}^2$ squares of a mask-exposed birefringent film monitored by interferometry at 105°C as a function of time.

as a function of time at a constant temperature of 105°C measured by interferometry. At relatively short times the parabolic surface and the protrusion are formed which is consistent with the observations for 1-mm squares at elevated temperatures. However, prolonged heating at the same temperature revealed that the monomers in the nonexposed parts diffuse towards the center of the cross-linked part. As a consequence, the cross-linked part swells. The swelling process continues for about 116 h after which the surface profile remains unaltered, presumably by advancing polymerization in the exposed and unexposed areas. A similar time sequence of surface profiles is measured at $T = 120^\circ\text{C}$ with the difference that within 15 min a parabolic interface is formed on the nonexposed part which height is about 500 nm higher than that exposed. In addition, the time scale in which the exposed part swells at the expense of the nonexposed part is shorter. The shorter time scale is attributed to thermally enhanced diffusion processes.

In conclusion, the observed surface profiles in thermally patterned films comprising birefringent and isotropic regions are caused by material transport from the nonexposed parts to the cross-linked exposed parts in combination with surface tension phenomena. However, the diffusion is kinetically hampered. As a consequence, the obtained surface profile depends on the feature sizes of the mask, time, and temperature. The monomers are able to travel $50\text{--}100\text{ }\mu\text{m}$ in about $30\text{--}60\text{ min}$ at an elevated temperature, which is a reasonable distance for these kinds of monomers, also confirmed by the modeling results assuming a diffusion coefficient of $10^{-10}\text{ m}^2/\text{s}$ at room temperature. Therefore, the exposed parts rise as compared to the nonexposed parts for the $100 \times 100\text{-}\mu\text{m}^2$ squares. In the case of the $1 \times 1\text{-mm}^2$ squares, the distance to the center of the exposed part is too long in the experimental time scale. The monomers accumulate on the protrusion and a parabolic surface may occur.

Anisotropic diffusion

A difference in lengthwise and sidewise diffusion is found in both fluid nematic liquid crystals^{17–20} and birefringent films made from single-component reactive mesogens.³ Translational motion in nematic liquid crystals has been studied experimentally and theoretically in the 1970s and

FIG. 9. The solid and dashed lines represent the surface profile attributed to lengthwise and sidewise diffusion, respectively.

1980s. However, the measurement of the diffusion constant of a liquid crystal involves difficulties not encountered for normal liquids or solids since in liquid crystals there are both anisotropy and viscous flow. As a consequence, data obtained with different techniques often differ. Bates and Luckhurst¹⁷ reported the anisotropy ratio (i.e., the quotient of the lengthwise and sidewise diffusion) calculated from the long-time behavior of the mean-square displacement for the nematics to be 4.66 (note that the anisotropy ratio for smectic A was calculated to be 1.74). Noack¹⁸ and Franklin¹⁹ reported measured anisotropy ratios of 1.6 and 1.4 for 4,4'-di-*n*-balkyloxyazooxybenzene at 119°C and *p*-azoxyanisole at 125°C , respectively, whereas the anisotropy ratio for 5-cyanobiphenyl is found to be 2.3.²⁰ In our case the quantification of the anisotropic diffusion constant is even more complicated because it will also depend on the conversion of our cross-linking reaction in the exposed area.

Hence, the anisotropic diffusion will be time and location dependent. A pragmatic approach is therefore to compare the protrusion heights parallel to the nematic director (i.e., formed by sidewise diffusion) with those perpendicular to the nematic director (i.e., formed by lengthwise diffusion). In order to verify anisotropic diffusion, two nematic films were exposed through a line mask with a $200\text{-}\mu\text{m}$ broad transmissive line and $100\text{-}\mu\text{m}$ broad dark line, followed by a flood exposure at 115°C . The orientation of the line mask was parallel to the rubbing direction for the first film and perpendicular to the rubbing direction for the second film. Figure 9 shows an example of the effect of anisotropic diffusion on the protrusion formation upon a line mask exposure. The ratio between the protrusion height perpendicular and parallel to the director shown in Fig. 9 is 1.7, whereas examination of a series of the block-patterned nematic films revealed ratios in the range of 1.4–2.1. This variation in the ratio of the protrusion height perpendicular and parallel to the director is attributed to the strong dependence on the process conditions and mixture composition. The found order in ratio in protrusion height corresponds to the anisotropic diffusion ratio found in Ref. 3 for reactive mesogens in a birefringent film at a temperature of 100°C (i.e., 1.78). This correspondence suggests that the difference in protrusion heights is indeed caused by the difference between

lengthwise and sidewise diffusion of the monomers. It also underpins that the formation of the protrusion and indentation can be explained by diffusion.

CONCLUSION

Isotropic domains are created in a birefringent film by a mask exposure followed by a flood exposure at a temperature exceeding the transition temperature of the mixture. Upon heating a pronounced surface corrugation arises from the latent image formed at the mask exposure. The surface corrugation is due to a flux of material towards the exposed areas and a temporarily gradient in surface tension caused by a phase transition from nematic to isotropic as a consequence of the gradient in composition. The material flux can be explained by changes in chemical potential of the reacting species. The surface tension gradient, here defined as a transition-driven Marangoni effect, amplifies the surface corrugations and can be utilized to control the shape of surface relief structures. As it is a temporary effect the deformed surfaces can be fixed by polymerization or can become minimized again by prolonged heating. The surface profile also depends on the feature size. For the $1 \times 1\text{-mm}^2$ areas the exposed areas are lower than the nonexposed areas, whereas the opposite is observed for $100 \times 100\text{-}\mu\text{m}^2$ areas, which is a result of the diffusion rate being too small to reach the center of the $1 \times 1\text{-mm}^2$ areas within the experimental time frame. Finally, anisotropic diffusion is observed. The protrusion formed by sidewise diffusion is 1.7 times lower than that formed by lengthwise diffusion.

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