Morphological changes during anisotropic photopolymerization

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Photosensitive materials that consist of photopolymerizable monomeric components (sensitizer, initiator, monomer, chain-transfer agents, etc.) dissolved in a solid plasticized polymeric matrix are called 'photopolymers'. We investigated structural changes occurring upon exposure to light in DuPont holographic, proofing and electrostatic photopolymers. In most cases, exposure of photopolymer films and coatings is unidirectional through some type of mask or target. Patterned exposure to light leads to concentration gradients between illuminated regions of photopolymer film and unexposed regions. Similarly, due to the high optical density of these materials, photopolymerization occurs faster near the illuminated surface creating a depthwise gradient in reactant and product concentration. High molecular weight products have lower diffusivity than low molecular weight reactants. Slow product outflow from the reaction zone and a difference in mobility of reactants migrating towards reaction regions in plasticized polymer upon unidirectional exposure lead to a variety of unusual structural changes. We report observation of swelling of the film regions exposed to light, and alignment of the polymeric molecules perpendicular to the illuminated surface. This observation is in agreement with the predictions of our previous model computations. Liquid crystalline mixtures or dichroic dyes added to the formulation align during film exposure to light perpendicular to the surface, parallel to the direction of light incidence. The direction of alignment is parallel to that of the forming polymeric molecules. This directly confirms the migratory mechanism of photopolymerization in films.

(Keywords: photopolymerization; morphology; films)

INTRODUCTION

It is well known that during photopolymerization 'solid' and liquid polymer systems shrink, and undergo other structural changes[1–3]. In many photoresist and photocurable coating systems, unsaturated oligomers or crosslinkable polymers are the major reactive components of the formulation. Such photocurable coatings, operating predominantly by cross-polymerization, exhibit noticeable shrinking (see ref. 2, p. 263). In these systems the reactive monomers present in the formulation are considered as 'diluents'[3] added to homogenize the formulation and to reduce its viscosity. However, in a growing number of applications, especially in imaging, photosensitive materials based entirely on monomer polymerization are used[2,4,5]. These composite materials, which consist of plasticized polymer matrix with the active polymerizable monomeric mixture (photosensitizer, initiator, monomer, chain-transfer agents, etc.) dissolved in plasticizer, are called 'photopolymers'[4]. Since research and development of photopolymers were often closely associated with materials based on oligomer and polymer crosslinking, it was generally assumed that photopolymers also shrink upon exposure to light. However, we failed to find any experimental proof of photopolymers shrinking upon exposure to light. Therefore, we decided to examine in more detail the question of structural changes in photopolymers caused by polymerization.

Photosensitive systems based on crosslinking of existing polymeric molecules or on further polymerization of long-chain oligomers constituting a major portion of the composition would, naturally, behave differently from systems based entirely on monomer polymerization, such as photopolymers. During photopolymerization, monomer and other components are consumed in the illuminated regions. This creates concentration gradients resulting in migration of reactive components towards the illuminated areas of the film. Growing polymer chains and oligomers migrate within the matrix much more slowly than low molecular weight reactants. Therefore, on the time-scale of the photopolymerization reaction very little, if any, outflow of forming polymer and polymer concentration equilibration occurs[6]. Naturally, this unbalanced transport process increases the total amount of matter in the illuminated areas of photoactive films, while depleting it in the shadowed regions adjacent to the exposed areas. In addition to such lateral mass transport, there is transport towards the illuminated surface, where the light intensity is higher and consequently, the reagent consumption is

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faster. In oligomer-containing photocurable coatings with, in some instances, as much as 70% oligomer, the relative displacement of crosslinking monomeric molecules is small and photoexposure results mostly in free-volume reduction. On the other hand, in a photopolymer system based entirely on monomer immobilization, no oligomer moieties are present prior to the reaction and photopolymerization will result in more significant molecular relocation and anisotropy in product distribution. In earlier publications we reported on our technique of monitoring molecular migration by the increase of fluorescence due to movement of fluorescent monomer towards the illuminated surface and its consequent conversion into stationary fluorescent polymer[7–9]. Our extensive numerical modelling of photopolymerization kinetics supported the experimental observations indicating that, indeed, the polymerized monomer will move into and accumulate in the illuminated regions[7,8]. Predictions of the model were confirmed experimentally: we observed swelling of the illuminated regions of photopolymer films[9]. The shape of the swelling of the exposed regions of photopolymer film corresponded to that which was computed using a model based on the assumption that the components diffuse from the shadowed to the illuminated regions[9].

Recently, a substantial amount of research has been devoted to macroscopic structural changes observed in solid polymers due to stresses[10,11] or microscopic inhomogeneity in the formation of polymer[12,13]. However, the subject of localized volume changes resulting from diffusion-controlled photopolymerization in such composite materials as photopolymer films was not considered in detail, although swelling upon illumination was utilized recently in optical recording with photopolymer[14]. Below we describe the continuation of our work on the mechanism and results of diffusion-controlled photopolymerization in films. We describe our observation of the local swelling of photopolymer due to reagent migration, swelling dependence on the size of exposed regions and, most importantly, the formation of anisotropic structures within the photopolymer film due to non-uniform exposure to light.

EXPERIMENTAL

Materials

The DuPont holographic and proofing photopolymers and DuPont–Xerox Imaging Company photopolymer used as a master in electrostatic printing were studied. The average formulation consisted of 46% monomer, 1.7% initiator. The detailed description of these materials is presented elsewhere[15,16]. Generally, the photopolymer composition used here contained *N*-vinyl carbazole and phenoxyethylacrylate monomers, *ortho*-chlorohexaarylbiimidazole initiator, merocyanine sensitizing dyes and 2-mercaptobenzoxazole chain-transfer agent.

Dichroic dyes used as dichroism-enhancing additives were Acridine Orange base, Direct Yellow 50, and Dispersed Red 1 (Aldrich Chemical Co., Inc.). The mesomorphic liquid crystalline phases also used as dichroism-promoting additives to the formulations were T733 TK-LQ 1019, and T735 TK-LQ 2028 mixtures with a nematic range between 10 and 80°C (Tokyo Kasei Kogyo Co., Ltd). All of the above additives were used in concentrations of 0.1% by weight.

Coating, exposure, observation

The photopolymer films were coated from dichloromethylene solution onto optical quartz slides by spin-coating or doctor knife methods. Average film thickness was $25 \pm 1\,\mu$m, similar to those used in most commercial products.

No cover was used with the film. Electron-beam-etched chromium on optical quartz photomask was used in the experiments. Square patterns, 5 mm × 5 mm in size, were etched on the photomask chromium-covered surface. Each pattern on the photomask consisted of equally spaced lines with covered and open areas of identical thickness. During the imaging the metallized part of the photomask, separated from the photopolymer film by a thin Mylar® gasket, was resting on the photopolymer surface. The gasket was placed between the photopolymer film and the photomask prior to exposure to avoid embossing. Small windows corresponding to the patterns were cut out of the Mylar® gasket before placing it under the mask.

The imaging was done using conventional unfiltered light from a 150 W xenon arc lamp. The average dose was $\sim 20\,\mathrm{mJ\,cm^{-2}}$. The initial experiments with the photopolymer designed for electrostatic proofing (DuPont–Xerox Imaging Co.) were done using an argon ion laser beam.

The images were analysed using an Olympus BH-2 microscope equipped with objectives containing a Nomarski prism for differential interference contrast observations. The image was captured by Polaroid camera or digitized into a Hewlett Packard RS/25C computer using BioScan Optimas software.

RESULTS AND DISCUSSION

The films are always illuminated from one direction thus creating anisotropic photopolymerization conditions. Monomer and other reacting molecules migrate towards the regions with higher light intensity where these small molecules are converted to relatively immobile polymer. The unidirectional migration of reagents creates within the film an unusual anisotropic distribution of forming polymer, as discussed previously[7–9]. In addition to product distribution anisotropy, diffusion of monomer towards the illuminated surface and absence of the forming polymer outflow leads to the accumulation of matter in the illuminated regions. This accumulation of polymerizing monomer should lead to swelling of the polymerized regions. For the first time the swelling was observed on the surface of the laser-imaged electrostatic photopolymers used by the DuPont–Xerox electrostatic proofing process. At the time the observation was not correlated with the diffusion of the monomer and other experimental results[7–9]. This observation, however, has led to more extensive analysis of the phenomenon. The swelling was concurrently observed in all of the photopolymers we have studied[9]. To ensure that we were dealing with swelling of the polymer surface, we also analysed the punctures and cross-sections of the swollen regions. The swelling of the exposed regions was confirmed by comparison of the microscopic image of the exposed photopolymer film with that of the punctures in the film, and the image of particulate matter placed on the film surface.

Swelling was clearly observed in imaged areas of photopolymer used in holographic imaging[9,15,16]. Due

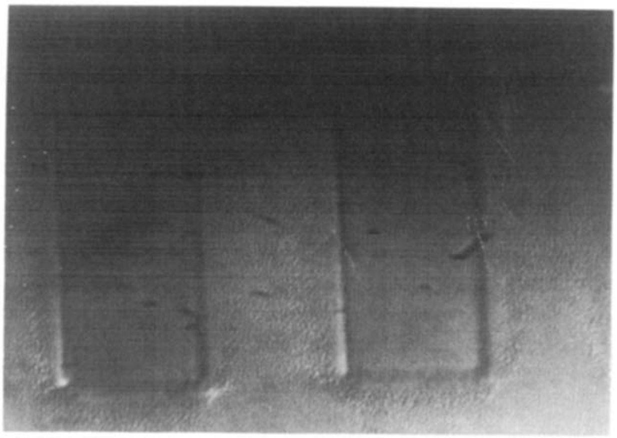

Figure 1 Swelling in photopolymer exhibiting 'orange peel' type vitrification. Differential interferometric contrast enhancement objective (Nomarski prism). Reflected light. Magnification 250 ×

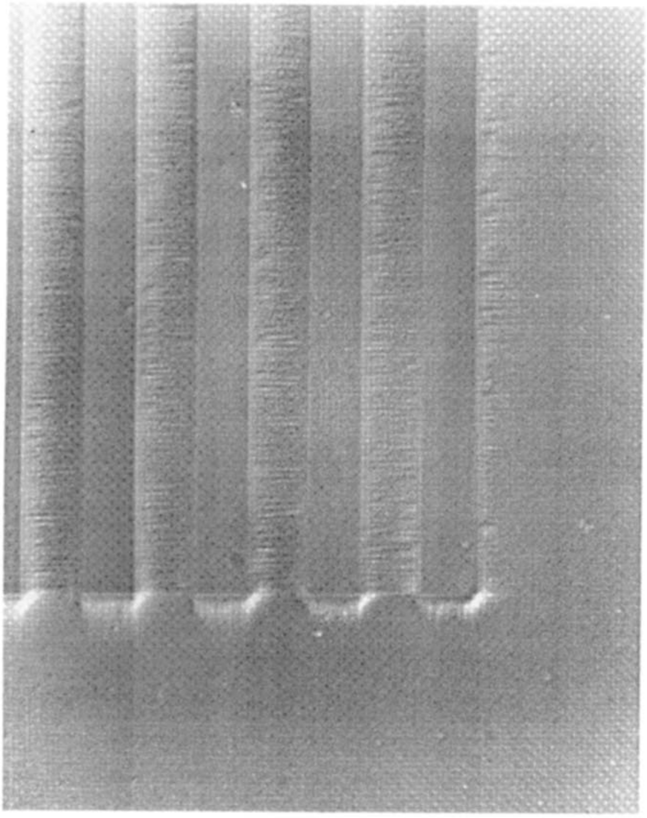

Figure 2 Swelling of the photopolymer film as seen under reflected light and external side illumination. The sample was placed between two crossed polarizers. Objective was equipped with Nomarski prism. Magnification 44 ×. The size of the exposed line is 50 μm

to the relative ease of handling this photopolymer formulation, we concentrated in the present work on the analysis of the photopolymer used in holographic imaging films[15,16]. The film imaged through a photomask with 50 μm lines displays swelling of the imaged regions, confirming migration of monomer towards the light and the resulting accumulation of the produced polymer in the illuminated zone of the film. The micrograph of the imaged holographic film is presented in *Figure 1*. The vitrification caused an 'orange peel' type[17] pattern clearly seen around the imaged areas. If the unidirectional diffusion towards the illuminated surface indeed accompanies this vitrification, then the vitrification should reflect the icicle-type anisotropic growth of polymer starting at the illuminated regions. Stress caused in the regions surrounding swollen portions of the film surface should also produce alignment of the polymeric molecules in the direction perpendicular to the boundary along which swelling occurs[10]. Indeed, when the film was placed between two crossed polarizers, we observed alignment (*Figures 2* and *3*).

Employing a combination of cross polarization and objective equipped with Nomarski prism (differential interference contrast), we observed alignment in the expected direction, i.e. almost perpendicular to the surface

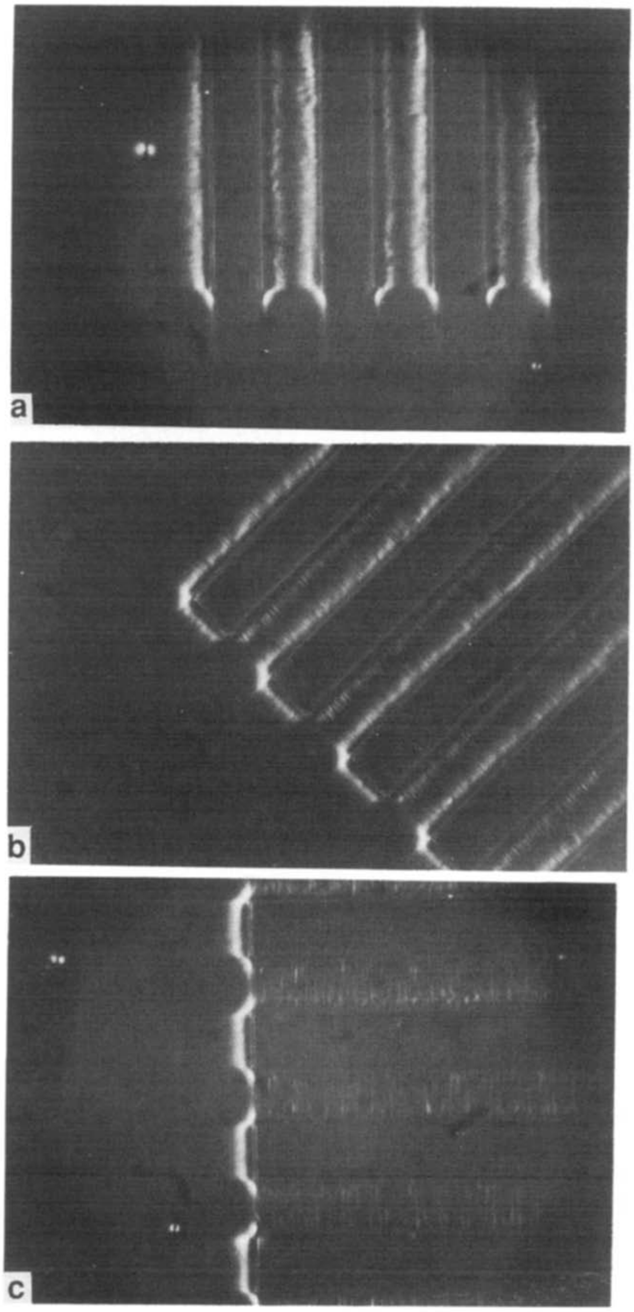

Figure 3 Swelling of the exposed region of the photopolymer as seen in reflected light through objective equipped with Nomarski prism when the sample is placed between two crossed polarizers. Line pattern period is 50 μm. Alignment of the polymer in the regions surrounding the exposed pattern is visible. Magnification 100 ×. (a) Lines in the pattern are perpendicular to the polarization plane of the first polarizer; (b) lines in the pattern are at 45° to the planes of polarization; (c) lines in the pattern turned 90° relative to those of (a)

of the film and perpendicular to the boundary of the exposed regions (*Figures 2* and *3*). When the polymer was exposed through the 50 μm line pattern, the observations in reflected and transmitted light were almost identical. The orientation takes place primarily within the swollen region rather than around it, since without the Nomarski prism the alignment around the sides of the pattern was not as obvious.

It is known that mechanical stretching of polymer films containing mesomorphic phases forces alignment of the dopant mesomorphic molecules along the stress direction[18,19]. Similarly, flow of slowly cooling polymer during production of fibres or thin film coatings results in alignment of liquid crystal or dichroic dye dopants[20]. We concluded that formation of the oriented polymer chains during anisotropic photopolymerization and stretching due to swelling of the exposed regions should force alignment of the long rigid molecules within the photopolymer formulation as well. The alignment of mesomorphic phases is usually easy to detect visually by an increased dichroism of the sample, manifested in the increase of the brightness of the aligned regions observed when the film is placed between two crossed polarizers. We introduced dichroic dyes (0.1%) into our plasticized matrix. Acridine Orange base, Direct Yellow 50 and Dispersed Red 1 were tested. In every case we observed a spectacular increase in dichroism around the swollen regions of the photopolymer film.

A particularly strong increase in observed dichroism (brightness of the aligned regions observed in the imaged film placed between two crossed polarizers) was detected when mesomorphic phases consisting of nematic liquid crystals were introduced (0.1%) into the photopolymer formulation. (The nematic liquid crystals used were T733 TK-LQ 1019 or T735 TK-LQ 2028 mixtures with the nematic range between 10 and 80°C, Tokyo Kasei Kogyo Co., Ltd.) The observed substantial increase in dichroism was an indication of the alignment of liquid crystalline moieties along the direction in which the sample was exposed to light (*Figure 4*).

When the photopolymer film was exposed through the grating with the period 5 μm, the lines were not swollen so distinctly as in the case of 50 μm grating; however, the image of the entire pattern was raised over the film surface (*Figure 5*). The exposure through the 0.5 μm mask did not produce any individual swelling of the exposed lines, but swelling of the entire pattern became more pronounced than in the case of exposure through the mask with 5 μm line width (*Figures 6a* and *b*). The line pattern could not be clearly observed in reflected light; however, in transmitted light the pattern was clearly visible. This indicates that optical effects distorting the resolution, such as interference, diffraction, etc., were relatively small. We measured the line spacing and size to make sure that the pattern was indeed a result of the 0.5 μm mask imaging. The line size was regular and equal to 0.5 μm within the experimental error (*Figure 6*); however, no swelling was detected. Apparently, the elasticity of the photopolymer film matrix was not sufficient to allow individual swelling of the exposed regions with size less than 5 μm. In addition, when pattern spacing is narrow (< 5 μm) the amount of monomer in the shadowed regions is small and molecular migration from the unexposed regions of the film towards the illuminated regions is likely to contribute less to photopolymerization and swelling than migration from the depth of the film towards the illuminated surface. Migration from the depth of the film is likely to result in less differentiation in the amount of material attracted by the light and shadowed regions of the pattern. Nevertheless, the entire exposed region swells, and the alignment of the added mesomorphic phases is clearly visible along the outside edge of the pattern (*Figure 6*). This indicates an overall influx of material to the reaction zone. The absence of individual swelling of the exposed 0.5 μm lines explains why in holographic application the image is not distorted: no individual swelling of the holographic fringes positioned less than 5 μm from each

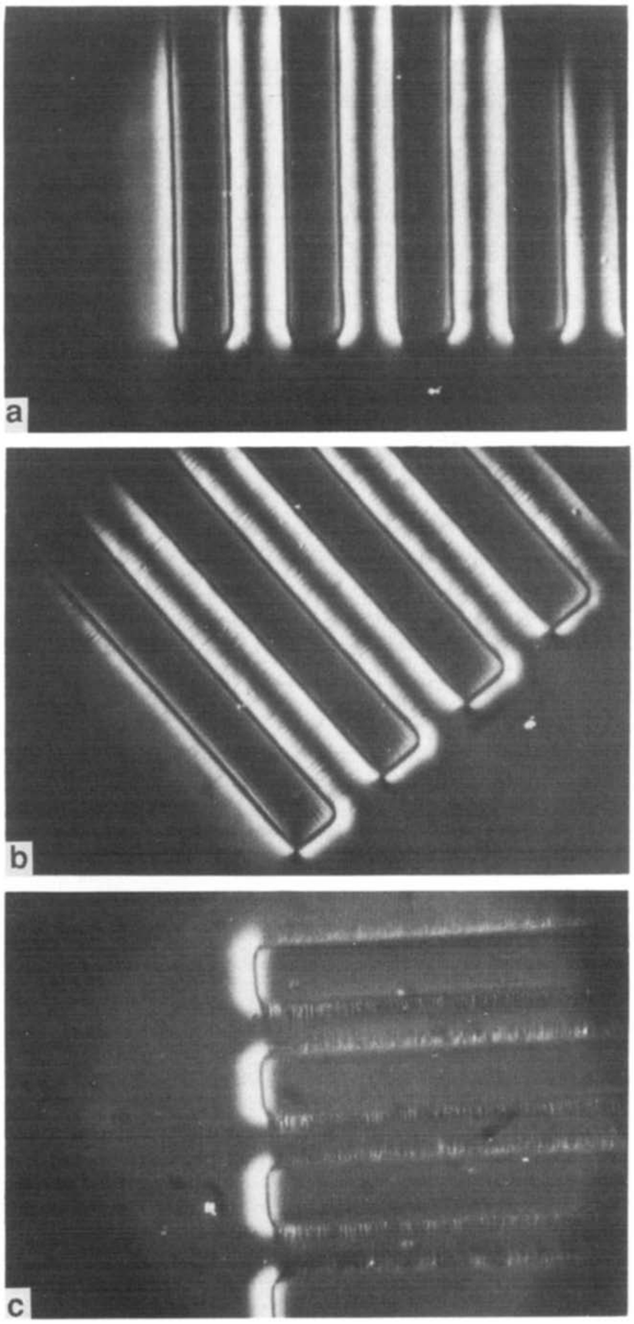

Figure 4 Swelling of the exposed photopolymer containing 0.1% of inert liquid crystal phase in formulation. Pattern period is 50 μm. The sample is placed between two crossed polarizers and is viewed through objective equipped with Nomarski prism in reflected light. Magnification 100 ×. (a) Lines in the pattern are perpendicular to polarization plane of the first polarizer; (b) lines in the pattern are at 45° to the planes of polarization; (c) lines in the pattern turned 90° relative to those of (a)

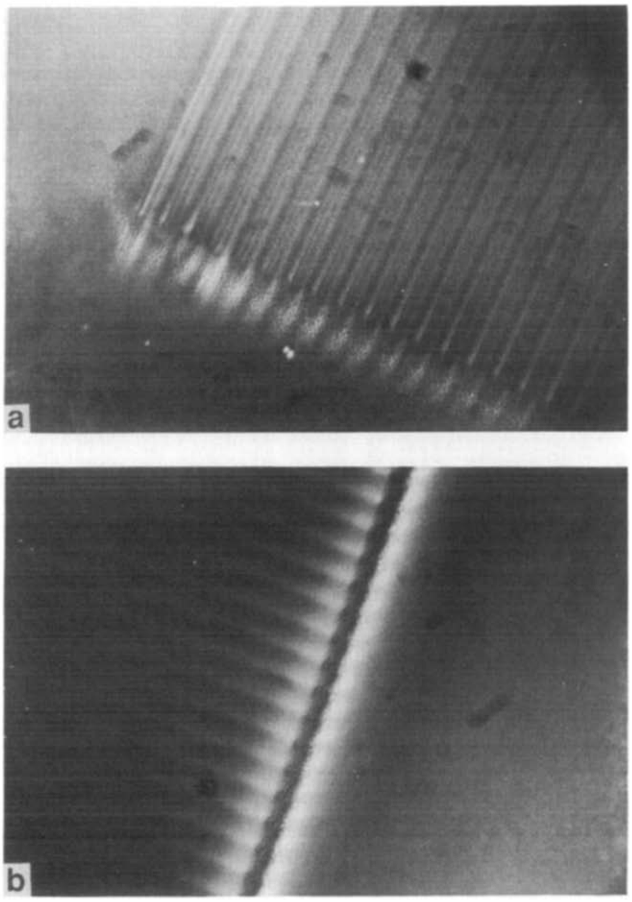

Figure 5 Photopolymer exposed through 5 μm mask. Sample is viewed as in *Figures 3* and *4*. Reduction in swelling of the individual lines is observed. Swelling of the entire pattern is visible. (a) Photopolymer film contained no liquid crystals; (b) photopolymer film contained 0.1% of liquid crystal mixture added to the formulation

other occurs. It was reported recently that post-photopolymerization introduction of the mesomorphic phases into exposed holographic photopolymer resulted in alignment of these phases within the photopolymer, even in the case of relatively narrow line size[19]. The reported observation supports our data and is in agreement with the monomer-diffusion-controlled mechanism of image formation in photopolymer.

Swelling of the exposed regions of the film as a result of anisotropic photopolymerization caused by unidirectional pattern-wise exposure of photopolymer to light is only one of the unusual aspects of chemistry in viscous media. Another anisotropic effect — formation during photopolymerization of oriented polymer chains — was shown in our observations and could be deduced from the results of Ingwall and Adams[19]. Both effects, swelling and orientation, may have to be taken into account in photopolymer imaging applications. In high resolution applications, such as holography and optical wave-guide production, orientation of polymer within the exposed region may be beneficial, enhancing the difference in optical properties between the exposed and unexposed regions of the film. However, swelling of the exposed regions of photopolymers should not be neglected in lower resolution applications. For example, when imaged photopolymer is used to deliver ink or toner from the reservoir to receptive paper, as is the case in most of the printing/proofing applications, the non-uniform swelling of the photopolymer surface can cause an unexpected change in the size of the half-tone dot on paper. Indeed, the size of the swollen area which will receive most of the toner (positive working photopolymer) will not coincide with the size of the aerial image used for photopolymer exposure. Moreover, the dot-gain from the printing with protruding regions of the photopolymer master will not be the same as that produced by the flat inked surface. In general, when unexpected ink-transfer and dot-gain problems are encountered in photopolymer applications in printing and proofing, it is possible that a change of the photopolymer surface due to monomer migration is involved.

CONCLUSIONS

We observed swelling of the exposed regions of photopolymer films. Using polarization microscopy we confirmed our earlier conclusions[9,14] that the swelling is consistent with molecular migration during photopolymerization. Indeed, the observed linear alignment around and within the exposed regions is consistent with the unidirectional migration of the monomer towards the illuminated regions of the film where polymerization takes place. Such migration

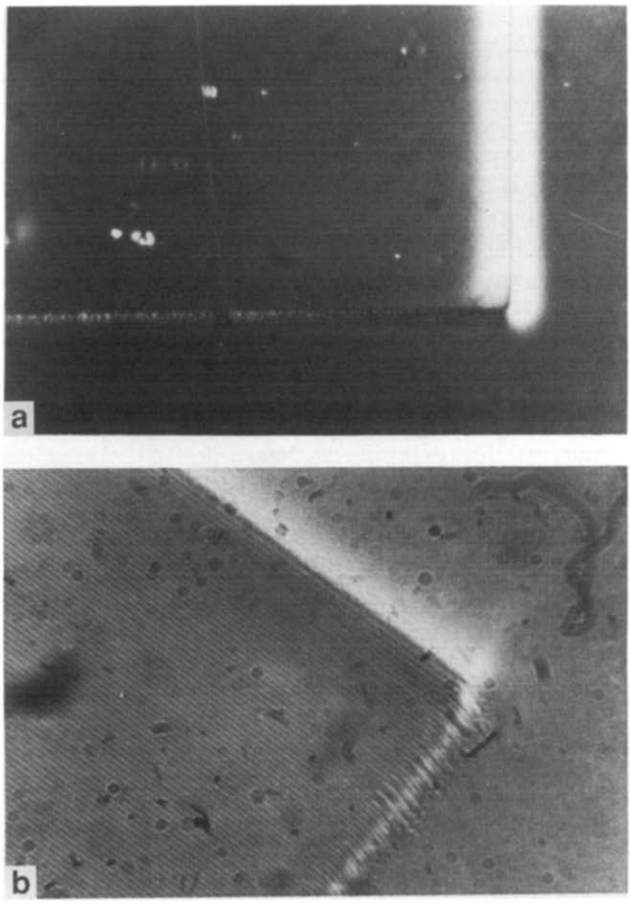

Figure 6 Photopolymer containing 0.1% of liquid crystal mixture exposed through the 0.5 μm mask. Magnification 500 ×. (a) The exposed film viewed as in *Figure 5b* in reflected light. No swelling of the individual lines in the pattern is detected. Overall swelling of the exposed region is visible. (b) The same exposed film placed between two crossed polarizers viewed in transmitted light using objective equipped with Nomarski prism. Recorded 0.5 μm pattern is visible

should force the inert mesomorphic phases added to the formulations to align in the direction of the monomer 'flow' and polymer growth parallel to the incident light[20]. This expected alignment of the mesomorphic phases was, indeed, observed by us. To the best of our knowledge, this is the first reported observation of polymer molecule alignment due to anisotropic photopolymerization in a plasticized matrix. In previous work[9] we demonstrated that the observed extent and shape of swollen regions coincide with those derived from computations based on the monomer-diffusion-controlled photopolymerization mechanism. We supported the earlier conclusions by actually observing the 'flow' pattern in formation of orientation within the polymerized regions.

We observed that the extent of swelling is restricted by the distance between the exposed regions. Exposure of single lines separated by more than 50 μm results in a change of volume independent of the line size[9]. However, when the spacing between the lines is less than 5 μm, swelling of the individual exposed regions is not observed. These non-uniform volume change effects may cause the loss of quality in photopolymer-based proofing and printing, since uneven change in the proofing film surface morphology could result in problems with toning the photopolymer and consequent ink transfer to paper.

These observations of macroscopic and molecular changes may be taken into account in applications of photopolymer imaging. Our observations are still mostly phenomenological, and more quantitative characterization of swelling and molecular organization during anisotropic photopolymerization has to be performed. Work on the mechanism of structure formation in photopolymers is in progress. We can add that although the monomer-diffusion-controlled photopolymerization was correlated with the swelling of the exposed regions[9,14], other unusual effects occurring in photopolymer films upon anisotropic unidirectional photopolymerization, such as unexpectedly high depth of imaging and image resolution amplification, still await detailed mechanistic investigation and numerical modelling, which would allow correlation of molecular dynamics within the photopolymer and observed macroscopic changes in the 'pattern exposed' photopolymer films.

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REFERENCES

1 Oleinik, E. F. in 'Advances in Polymer Science' (Ed. K. Dusek), Springer-Verlag, Berlin, 1986
2 Roffey, C. G. 'Photopolymerization of Surface Coatings', John Wiley, Chichester, 1982
3 Tu, R. S. in 'UV Curing Science and Technology' (Ed. S. P. Papas), Vol. II, Technology Marketing Corporation, Stamford, 1985, p. 143
4 Sturge, J. M. (Ed.) 'Imaging Processes and Materials' 8th Edn, Van Nostrand Reinhold, New York, 1989
5 Reiser, A. 'Photoactive Polymers. The Science and Technology of Resists', John Wiley, New York, 1989
6 Sperling, L. H. 'Introduction to Physical Polymer Science', John Wiley, New York, 1986
7 Krongauz, V. V. and Yohannan, R. M. *Polymer* 1990, **31**, 1130
8 Krongauz, V. V., Schmelzer, E. R. and Yohannan, R. M. *Polymer* 1991, **32**, 1654
9 Krongauz, V. V. and Schmelzer, E. R. *SPIE Proc. Photopolym. Device Phys. Chem. Applic.* 1991, **1559**, 354
10 Plummer, C. J. G. and Donald, A. M. *Polymer* 1991, **32**, 3322
11 Ivanov, V. V. and Smirnov, B. R. *Vysokomol. Soedin., B* 1991, **33** (11), 807
12 Kloosterboer, J. G. and Lippits, G. J. M. *J. Imaging Sci.* 1986, **30**, 177
13 Kloosterboer, J. G., Van de Hei, G. M. M. and Boots, H. M. J. *Polym. Commun.* 1984, **25**, 332, 354
14 Suzuki, T., Todokoro, Y. and Komenou, K. US Patent No. 4,877,717, Fujitsu Limited Co., 1989
15 Howe, D. G., Thomas, H. T. and Wrobel, J. J. *Photogr. Sci. Eng.* 1979, **23**, 370
16 Smothers, W. K., Monroe, B. M., Weber, A. M. and Keys, D. E. *SPIE OE/Laser Conf. Proc.* 1990, **1212**, 20
17 Michell, J. S., Geener, J. and Contestable, B. A. *Macromolecules* 1990, **23**, 186
18 Broer, D. J. Doctoral Thesis, Rijksuniversitet te Groningen, 1990
19 Ingwall, R. T. and Adams, T. *Proc. SPIE Int. Soc.* (*Opt. Eng. Comput. Opt. Gener. Hologr. Opt.*) 1991, **1555**, 279
20 Tsvetkov, V. N., Rjumtsev, E. I. and Shtennikova, I. N. in 'Liquid Crystalline Order in Polymers' (Ed. A. Blumstein), Academic Press, New York, 1978, pp. 50–52