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# Photopolymerized self-assembly microlens arrays based on phase separation

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In the past decades, there has been much effort in developing and improving new techniques for the production of microlens arrays. Here a low-temperature self-assembly method using phase separation is demonstrated for the first time for the fabrication of polymer microlens arrays. In this paper, we present a simple method for producing microlens arrays based on liquid crystal/photopolymer blends *via* phase separation. The morphology of the microlens arrays has been measured by SEM, AFM and scanning white light interferometry. Our results show that the microlens arrays obtained from our experiments have a comparable light-gathering capability and can be applied in optical systems.

# 1. Introduction

The ability to develop micro-optics for use in devices, such as communication performance, display technologies, and photovoltaic devices, has been of considerable interest over the past few decades.1 Making the fabrication technique faster and more efficient requires that optical systems be produced simply and parallel, and as a result the low-cost fabrication of microlenses is becoming necessarily and even plays an important role in many optics-based applications. Several fabrication techniques for microlens array have been demonstrated such as the photo-resist reflow method,<sup>2</sup> the gray-scale photolithography,<sup>3</sup> the micro-jet fabrication,4 the LIGA process,5 and so on. However, the reflow method has many drawbacks. For example, the high processing temperature and the need for an etch-transfer process, to produce stable optical components, is not convenient in microlens production. As for the gray-scale photolithography, it is difficult to fit the desired shape precisely and distinguish the gray levels in a sharp edge so that the lens surface is also rough. In addition, micro-jet fabrication suffers from limitations in the minimum lens size and alignment accuracy. Similarly, the modified LIGA method is also quite complex, especially given its time-consuming processes using expensive facilities. Although these above-mentioned techniques can produce micro-optic devices, their fabrication requires multiple sophisticated processes and long timescales for mass production.

To date, many techniques have been developed for making arrayed microlenses with a variety of materials. For example, swellable polymer microlenses upon exposure to solvents create a tunable range of focal lengths.<sup>6</sup> Due to the hydrophobic effect in this technique, the well-defined boundary of the microlenses in the solvent vapors would either expand or contract, resulting in a variation of the focal lengths. In addition, the stimuli-

responsive hydrogel aperture undergoes reversible volume change in response to environmental stimuli by absorbing and releasing water in order to function as an adjustable focusing lenses.7 Herein, this paper describes a novel technique for fabricating polymeric microlens arrays based on liquid crystal (LC)/photopolymer blend phase separation and self-assembled process owning to the surface tension. First, the sample cell is irradiated through a holes-patterned photomask by UV light and then the photocurable polymer, under the exposure area, is polymerized which leads to the formation of the polymer pillar arrays. In forming a pillar structure, several factors, such as UV light intensity, exposure time, and material can influence the morphologies simultaneously in the phase separation process. Second, the uncured polymer around the polymer pillars is gradually accumulated on the exposed area which exhibits lower surface energy, and then self-assembled to form a hemisphere shape covering each polymer pillar at room temperature. Finally, the plano-convex lens arrays are formed and cured by the second UV irradiation. Our method does not need heating or cooling treatment, and possesses a simple production process for the fabrication of microlens arrays. To the best of our knowledge, this low-temperature self-assembly method is demonstrated for the first time to fabricate polymeric microlens arrays. We also show that the microlens arrays fabricated by this method have a comparable light-gathering capability and can be applied in optical systems.

# 2. Experiments and discussion

A schematic diagram of the fabrication process of this study is shown in Fig. 1, which comprises of several steps. In Fig. 1(a), a mixture of LC, a photocurable polymer and a photo-initiator was confined within a packing cell which is composed of two glass substrates, and its cell gap was controlled by a  $\sim 13 \mu m$  aluminium spacer. In this procedure, UV light was irradiated onto the photopolymer in areas that are not covered with a chrome-on-quartz photomask.

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**Fig. 1** A schematic representation of the formation of self-assembled microlens arrays using photopolymerization based on phase separation. (a) A cross-sectional view of the packing cell that was injected with the mixture of LCs, photo-curable polymer and photo-initiator. (b) The cell was exposed to UV light through the photo mask which is patterned with circular-hole arrays. The polymer is polymerized under the radiation area and the polymer pillar structure is connected to the top and bottom substrates. "t" means the thickness of the non-reactive polymer layer. (c) Peeling off the top substrate induces the broken columns which are affixed to the bottom substrate. (d) The uncured polymer around the short columns gradually accumulates to form the plano-convex lens. The microlens arrays are completely polymerized after another UV treatment.

The region irradiated by UV light was cured faster compared to the shaded region. This situation leads to a spatial distribution of the thickness of the cured polymer layer, and the polymer pillar arrays were thus formed between the top and bottom substrate, which can be seen in Fig. 1(b). It is better to use thinner glass substrates ( $\sim 100 \ \mu m$ ) in this procedure to reduce the diffraction effect of incident UV light. The diameter of the pillar is in a range of  $10 \sim 20 \,\mu\text{m}$ . After polymerization was performed with 356 nm UV light, the top substrate was subsequently removed and therefore the pillar arrays adhered to the substrate were broken into short column arrays which are shown in Fig. 1(c). The short columns are always surrounded by some uncured polymer because polymers under the shadow of the photomask are not completely polymerized. Then we placed the substrate patterned with flat columns in a moisture-proof box for few hours, and the uncured polymer would tend to accumulate within the boundaries where the flat columns had originally dwelt. Finally, the accumulating polymer was self-assembled into the plano-convex shape as shown in Fig. 1(d). We speculate the formation of a hemisphere shape was driven by the minimization of the surface free energy. After the second UV exposure, the microlens arrays that were made of uncured polymers became fully cured and stable. It is thus demonstrated that the microlens arrays are formed by self-assembled polymer and can be solidified by photopolymerization.

The photocurable polymer has been applied in many optical systems and is a malleable material that can be molded into various micro/nano shapes.<sup>8</sup> It was originally developed as a low-loss polymer material for optical wave-guide devices, because such material provide low optical absorption. Now, it is popularly applied to fabricate polymer structures and can produce nano-scale patterns at a much lower pressure and temperature.

In addition, the photocurable polymer is a good index-matching material, which has been utilized in display industries.<sup>9</sup> Here we tend to take the advantage of the photocurable materials to produce self-assembled polymeric microlenses without requiring complicated processes and expensive facilities.

The experiments were carried out with a 50/50 (wt/wt) mixture of LC E7 and a methacrylate-base polymer-forming material. The chemical structures of the compounds are shown in Fig. 2. The methacrylate polymer, i.e. isobornyl methacrylate, was selected because the monomers can uniformly dissolve in LC, but also phase separate well during polymerization. Moreover, isobornyl methacrylate was chosen as the main component because it combines many properties like high solubility and low viscosity before the experiment, high diffusion rates and controlled phase separation during polymerization, and is rigid after the process.<sup>9</sup> In order to get a better absorption, photoinitiator Irgacure 651 has been added in the mixture for ultraviolet radiation in the wavelength region around 360 nm. Excellent phase separation is achieved due to strong immiscibility of the acrylates with LC molecules.<sup>10</sup> Due to strong immiscibility of the polymerized monomers, a diffusion of monomers occurs so as to maintain the equilibrium of their relative concentration in the mixed solution.<sup>11</sup> During UV curing, an oxygen free environment is necessary since oxygen inhibits the radical polymerization of methacrylates. Therefore, the mixture enclosed within a glass cell to prevent the attack of oxygen from air. Through the holepatterned photomask, the ultraviolet-reactive material is cured via traditional photolithography. Then, the segregation of the material occurs effectively to form a polymer pillar which is functionalized as a settler for a polymer microlens.

#### 2.1 Sample preparation

The packing cell (1cm  $\times$  1cm) was constructed from two glass substrates which were separated by two aluminium strips (13 µm thick). Commercially available LCs E7 (from Merck), photocurable prepolymers, *e.g.*, Isobornyl-methacrylate (IBOMA), and photoinitiator Irgacure 651 (purchased from Ciba Company) were mixed in our experiments. Their mixing ratio was 50 : 49.5 : 0.5 by weight. The refractive index of cured IBOMA is 1.447 at visible light wavelengths. The mixture was injected into the empty cell by capillary action upon heating at 70 °C. This is preferably done at a temperature above the LC's clearing point (60 °C) because the mixture formulation is in the isotropic state.





Fig. 2 The chemical structure of the LC E7, the reactive monomer isobornyl methacrylate, and the photoinitiator Irgacure 651. The relative amounts of these compounds in the mixture are shown in the parentheses.

Phase separation was initiated by exposing the cell to a UV exposure system (Karl Suss, 365 nm) through one of the substrates. During exposure, the cell was in proximity contact with the photomask which was previously patterned with circular holes, the diameter of which is 10 µm. The LC molecules absorb UV light more strongly than anything else in the mixture at wavelengths near 365 nm. As a result, an intensity gradient was produced in the sample cell. Thus, the polymerization process would first take place near the exposed area. The UV intensity is 5 mW cm<sup>-2</sup> and the irradiation time is 30 mins. After exposure was complete, the polymer pillars were formed between the upper and the bottom substrates. Then the upper substrate was peeled off to break the polymer pillars into half segments on either the upper or bottom substrate. The UV-zone treated area shows high wettability such that the uncured prepolymer can accumulate on the exposed area and then self-assemble to form a hemisphere shape covering each polymer pillar. A few hours later, an array of liquid plano-convex lenses was formed on the flat substrate due to the minimization of the surface tension of the photopolymer. Finally, the microlenses were hardened and stabilized by the second UV-light curing for 30 s. Generally, the successful area of self-assembled microlens arrays is around 4 mm<sup>2</sup> as the splitting force is not uniform across the whole surface.

The surface profile of the microlenses was measured using a scanning white light interferometer (BMT WLI). The lens diameter was determined using a SEM (JEOL JSM-6390LV). The sag height of the microlenses was obtained using an atomic force microscope (Veeco CP-R).

#### 2.2 Morphologies of self-assembled microlens arrays

Each process of the formation of the self-assembled microlens arrays was observed under an optical microscope (see Fig. 3). First, the small column arrays were broken into half segments



**Fig. 3** Optical microscope images of the polymer structure at each stage of the fabrication process. (a) The small column arrays after splitting the glass cell. (b) The uncured polymer around the column arrays are moving toward the columns. (c) The accumulated polymer gradually forms a hemisphere lens shape after a few hours in a moisture-proof environment. (d) The polymer-dispersed LC (PDLC) structure is formed without a photomask during the UV irradiation process.

during cell splitting and remained on the substrate after the top substrate was peeled off. The diameter of the small column arrays is around 30 µm and its pitch is 50 µm, as shown in Fig. 3(a). In the beginning, the uncured photopolymer was distributed randomly between the small column spacings, then slowly flowing into the small column patterns and finally selfaccumulating to form plano-convex structures. Fig. 3(b) depicts the intermediate process and Fig. 3(c) reveals the formation of the plano-convex microlens arrays. However, if a photomask is not exploited in this experiment, the polymer is not cured in the form of a pillar shape, but has instead a polymer-dispersed LC (PDLC) structure.<sup>12</sup> The structure of the polymer layer in this experiment is completely different from that of PDLC because the structures, such as polymer networks and LC droplets, are not seen in this polymer layer. On the contrary, in a PDLC system, LC usually forms micron-sized droplets which are randomly dispersed in the polymer matrix. The morphologies of a PDLC system are observed if we do not apply a photomask during the UV radiation process (see Fig. 3(d)).

The surface profile of the structure after the formation of the polymer microlens arrays has been visualized with the aid of a interferometric microscope. Shown in Fig. 4 is a top and side view of the microlens arrays. The average sag-height of the microlenses arrays is around 400 nm. The top view picture demonstrates that the profile of the microlens arrays is uniform and each microlens is equal in high. Fig. 5(a) reveals the top view scanning electron microscopy (SEM) image of a self-assembled microlens with diameter  $d = 12 \,\mu\text{m}$ , while that in Fig. 5(b) shows a lens profile obtained by an atomic force microscopy. The samples for the SEM measurement had been pre-treated as follows. The resultant polymer microlens arrays were first rinsed with ethanol to remove the LCs. Then the polymer surface was coated with a thin film of Au to avoid electron damage. It should



**Fig. 4** (a) The top view of a microlens array. (b) The side view of a microlens array. The resulting height variations could be observed with the aid of a white light interferometer.



**Fig. 5** (a) The SEM image of a microlens array that was self-assembled by an uncured photopolymer. The lens has a 425 nm height and a diameter of 12  $\mu$ m (b) The lens-profile obtained using atomic force microscopy (AFM). The average sag-height is 425 nm. (c) The image was recorded with a reflective transmission optical microscope by projecting a letter "L" through an array of microlenses. The object "L" was developed on the silicon substrate by electro beam lithography. (d) Enlarged picture of (c) with higher magnification.

be noted that the sag-height of the microlens is only in the region of hundreds of nanometres, which is smaller compared to the cell gap. The thickness of the remaining layer, depicted in Fig. 1(b), is around  $5\sim 6 \mu m$  because the non-reactive or redundant prepolymer would remain on the bottom layer of cell space due to gravitational forces. From these results it could be implied that the higher microlens could be improved by modifying the surface properties, increasing the UV intensity and reducing the cell gap, which are still under investigation.

#### 2.3 Calculation of the optical parameters

On the basis of geometry and optical theory,<sup>13</sup> the radius of curvature (*R*), focal length (*f*) and *f*-number ( $f_{\#}$ ) can be calculated using the following formulas:

$$R = \frac{h^2 + r^2}{2h}, f = \frac{R}{n-1}, f_{\#} = \frac{f}{2r}$$
(1)

where h is the sag height, r is the radius of the plano-convex lenses, R is the radius of the curvature of the lenses, n is the refractive index, and f is the focal length. In these calculations, the refractive index is 1.477 for methacrylate microlenses. Following the above equation, for example, the  $f_{\#}$  of the 12 µmlens is approximately 7.6. The optical parameters of the 12 µmlens are listed in Table 1. The smaller  $f_{\#}$ , which indicates the lightgathering power of the lens, is better. The obtained  $f_{\#}$  results in our work are comparable to those of the previous reports using other methods. <sup>14,15</sup> Fig. 5(c) demonstrates that the letter "L" was imaged through the microlens array by placing a silicon substrate behind the lens substrate. The "L" object was developed on the silicon substrate by electron beam lithography. An enlarged picture with higher magnification is shown in Fig. 5(d). These results indicate that the microlenses have good light gathering ability.

<i>h</i> [μm]	<i>d</i> [µm]	<i>R</i> [µm]	<i>f</i> [µm]	$f_{\#}{}^{I}$
0.42	12.42	45.5	95	7.6
<sup>1</sup> the <i>f-num</i>	ber $(f_{\#})$ , which inc	licates the light-ga	athering power of	the lens.

## 3. Conclusions

In summary, we have explored the simple fabrication of selfassembled microlens arrays by combining the LC/photopolymer phase separation, the subsequent photopolymerization, and polymer self-assembled process. The cured polymer arrays adhere to the top and bottom substrates, and produce a selfsustaining polymer column structure, giving it potential for use as a pioneer base for microlense structures. After the top glass layer is peeled off, the uncured polymer around the polymer pillars self-assembles to form a hemisphere shape covering each polymer pillar at room temperature. Such a sequential process leads to a dense plano-convex microlens array on the surface of the substrate. We believe microlens arrays with higher fill factors can be achieved by choosing appropriate photomasks with different dimensions and spacing. The method presented here is quite unique from several aspects. First, it provides a non-heating and non-pressure way to produce microlens arrays. Second, the process is not as complex as conventional photolithography. Furthermore, the methacrylate-based polymer is an indexmatching material which could reduce light scattering between the microlens arrays and the glass substrate. Finally, the microlens array developed in this study is a promising candidate for broad applications, for example, as key components in optical parallel-processing systems and large-scale flexible display technologies.

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## References

- K. Tvingstedt, S. Zilio, O. Inganäs and M. Tormen, *Opt. Express*, 2008, 16, 21608.
- 2 T. N. Oder, J. Shakya, J. Y. Lin and H. X. Jiang, *Appl. Phys. Lett.*, 2003, 82, 3692.
- 3 Q. Peng, Y. Guo, S. Liu and Z. Cui, Opt. Lett., 2002, 27, 1720.
- 4 R. Danzebrink and M. A. Aegerter, Thin Solid Films, 1999, 351, 115.
- 5 B. K. Lee, K. J. Cha and T. H. Kwona, *Microelectron. Eng.*, 2009, 86, 857.
- 6 C. Dorrer, O. Prucker and J. Rühe, Adv. Mater., 2007, 19, 456.
- 7 L. Dong, A. K. Agarwal, D. J. Beebe and H. Jiang, *Adv. Mater.*, 2007, 19, 401.
- 8 H. Sato, H. Fujikake, Y. Iino, M. Kawakita and H. Kikuchi, *Jpn. J. Appl. Phys.*, 2002, **41**, 5302.
- 9 R. Penterman, S. I. Klink, H. Koning, G. Nisato and D. J. Broer, *Nature*, 2002, **417**, 55.
- 10 J. I. Beadk, J. H. Shin, M. C. Oh, J. C. Kim and T.-H. Yoon, *Appl. Phys. Lett.*, 2006, 88, 161104.
- 11 T. Qian, J. H. Kim, S. Kumar and P. L. Taylor, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 2000, **61**, 4007.

- 12 A. J. Lovinger, K. R. Amundson and D. D. Davis, *Chem. Mater.*, 1994, 6, 1726.
- 13 S. Sinzinger and J. Jahns, in *Microoptics*, 2nd edition, Wiley-VCH, Weinheim, Germany 2003, p.86.
- 14 F. C. Chen, W. K. Huang and C. J. Ko, *IEEE Photonics Technol.* Lett., 2006, 18, 2454.
- 15 A. Tripathi, T. V. Chokshi and N. Chronis, *Opt. Express*, 2009, **17**, 19908.