

Soft lithography fabricating micropatterns of an azo-containing side-chain liquid crystalline polymer prepared by RAFT polymerization

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Abstract: A side-chain liquid crystalline polymer PCN2 was prepared by RAFT polymerization and characterized by UV-Vis, FTIR, ¹H-NMR spectroscopies and GPC, DSC analyses, and three kinds of micropatterns of PCN2 were successfully fabricated by employing solvent-assisted micromolding (SAMIM) of the soft lithography techniques and were studied with optical microscopic and SEM investigations. The results show that the achieved PCN2 has a narrow molecular weight distribution of ca. 1.22, and that the micromolding method can produce fine micropatterns with a comparatively high fidelity, which are expected to be applied in the development of polymer materials with specific structures and functions.

Key words: side-chain liquid crystalline polymer; RAFT polymerization; solvent-assisted micromolding, soft lithography; micro-pattern

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一种侧链型偶氮液晶聚合物的 RAFT 合成及其微图形的软刻蚀制备

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摘要: 通过 RAFT 聚合方法制备了一种侧链型偶氮液晶聚合物 PCN2, 并通过紫外-可见吸收光谱、红外光

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谱、核磁共振氢谱、凝胶色谱、差示扫描量热等方法对其结构和性质进行了表征。利用软刻蚀中的溶剂辅助微模塑技术制备了 3 类不同形貌的聚合物微图形,并通过光学显微镜、扫描电镜进行了观察。结果表明,RAFT 聚合得到的 PCN2 分子量分布为 1.22,溶剂辅助微模塑法制备的聚合物微图形结构完整、精细度和保真度较高,有望在具有特殊结构和功能的高分子材料开发中得到应用。

关键词:侧链型液晶聚合物; RAFT 聚合; 溶剂辅助微模塑; 软刻蚀; 微图形

0 Introduction

During the last decades, the progress in manufacturing micro- and nanostructures with fascinating practical and potential applications has attracted worldwide attentions. Meeting the increasing demands for the so-called lab-on-a-chip (LOC) systems with smaller, faster, better, cheaper and multifunctional characteristics, “bottom-up” and “top-down” strategies or a more promising combination of them both provides a variety of solutions in chemistry, biology, optics, mechanics and electronics^[1-2]. The bottom-up strategy depends on predesigned and well-defined molecular structures and self-organization based on the intrinsic properties of novel materials, while the top-down approach focuses on the advances in micro- and nanofabrication processes and techniques^[1].

Especially for the top-down strategy, lithography and the associated processes are the backbone of the micro- and nano-revolution and central to the evolution of electronics and information technologies. Regardless of conventional or unconventional methods, lithographic techniques, which are highly developed and widely used or relatively new and still being improved, can make ever-smaller ordered functional micro- or nano- patterns and structures^[3-5].

As a new rapidly developing unconventional lithographic method, soft lithography is a suite of techniques fabricating organic materials on multiple length scales (from μm to nm) and becoming a simple and cost-effective technique^[4,6]. Soft lithography has been successfully used in forming micro-structures of a variety of materials

(metals, inorganic and organic compounds, colloids, proteins and polymers), and its procedures are easy to operate because it applies elastomeric stamps to directly generate or transfer the patterns^[7-8]. Particularly for polymers, with the advantages of structures and properties, soft lithography is also used to produce or realize polymer-based photonic crystals, optoelectronic polymer devices, micro-patterns or structures with different interesting morphologies^[9].

As a class of functional polymers with unique photoresponsive properties, azobenzene-containing liquid crystalline polymers (LCP) are a well-investigated kind of attractive material widely applied in optical devices involving photophysics and photochemistry, such as information storage, optical switches, optical gratings and waveguides, etc^[10-11]. In the above contexts, surface relief gratings (SRGs), which can be realized via an interference of coherent lights with regular relief structures based on microscopic photoisomerization of the azobenzene groups and macroscopic mass migration, is one of the most interesting targets especially recently^[12]. Although the processing of SRGs is repeatable without needing pre- or post-treatments, it depends on lasers or coherent light sources with a higher capital expenditure and its further developments and wide applications rely on increasing the depth of modulation, the diffraction efficiency and the stability. Even so, the precise mechanism of mass migration in this process is still not very clear and a hot issue of concern^[12-13].

In the recent 10 years, another noteworthy trend is incorporating the “top-down” soft lithography with the above liquid crystalline polymers or copolymers, which spawns different “smart materials” with micro- or nano-sized

responsive structures. In 2005, Trajkovska-Petkoska et al.^[14] manufactured shaped flakes of polymer cholesteric liquid crystal in different colors and shapes with soft lithography, providing a new way for particle displays. In 2006, Buguin et al.^[15] developed a pillar micro-actuator made of a nematic liquid crystal elastomer and fabricated with PDMS-based soft lithography, which was thermostimulable and could contract and extend in heating and cooling cycles.

Analogous to the above practices, Yan et al. and Yu et al. successively reported the fabrication of a crosslinked azobenzene-containing LCP into a microarrayed film^[16] and a photoresponsive 2D microarray^[17], respectively, which could respond to alternate irradiation with ultraviolet and visible lights and the reversible on-off switching of intrinsic properties might provide potential applications in optical actuators. In addition to the above advances, it is worth noting that three-dimensional ordered arrays can also be derived from SmA liquid crystal defects^[18].

With a similar approach, Liu et al. achieved photoinduced surface-relief-gratings (SRGs)^[19], photoprocessible microwires^[20] and microspherical cap arrays^[21] by taking an epoxy-based azo polymer as soft lithographic masters or fabricating objects, through which it was proved that azo polymers can be applied in fabrications of optical functional surfaces, sensors and photonic devices.

So if combining soft lithography with azo-containing LCPs, ordered structures can be constructed with comparative ease and these microstructures can not only serve as a suite of new functional materials but also be promising for improving the light absorbing ability by a light trapping effect^[22], which has so far remained scarcely studied yet. Meanwhile, if taking into account the mass migration of azo-containing LCPs in the process of photo-induced alignment, the fabricated periodic microstructures may be more helpful for understanding the mass transport mechanism^[23] than usual bulk materials based on

establishing an appropriate model in advance.

Thus in this work, a conventional azo-containing side-chain LCP, PCN2, which can be more easily cast into films and then light-induced to both in-plane and out-of-plane photoorientation to form a banded texture^[24], was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization and then several micropatterns were successfully achieved by soft lithography, which laid a foundation for researching the conceptions described in the foregoing.

1 Experimental

1.1 Materials

4-aminobenzonitrile, 2-chloroethanol, methacryloyl chloride and other auxiliary reagents of analytical grade were all obtained from the Sinopharm Chemical Reagent Co., Ltd (China) and used without further purification.

The monomer CN2, namely 2-(4-((4-cyanophenyl)diazenyl)phenoxy)ethyl methacrylate was prepared via a four-step reaction process beginning with 4-aminobenzonitrile according to Refs. [25-26] with a total yield of ca. 22% after purification by affinity column chromatography.

Azobisisobutyronitrile (AIBN) was recrystallized with methanol before usage and all solvents such as tetrahydrofuran (THF) and chloroform, were used after usual drying and distillation. The RAFT agent, 2-phenyl-2-propyl benzodithioate or cumyl dithiobenzoate (CDB), was purchased from Sigma-Aldrich with a purity of 99%.

Polydimethylsiloxane (PDMS, $(C_2H_6OSi)_n$) was bought as a two-part elastomer kit from Dow Corning (Sylgard® 184), single-side polished n-type 4-inch silicon wafers (100) and quartz slides were purchased from Haerbin Tebo Technology Co., Ltd. and the latter were carefully washed clean with acetone, water and then dried at 180 °C for 2 h.

The PDMS elastomer stamps with three

different micropatterns for fabrication were prepared as reported by replicating the silicon masters starting from photomasks (seen in Scheme. 1)^[27]. Firstly, the designed micropatterns were produced on photomasks and transferred onto silicon wafers by photolithographic etching with UV light. Secondly, PDMS prepolymer and the hardener were mixed in a ratio of 10 : 1 (mass ratio), degassed and poured into a cardboard mold (1.5 cm × 1.5 cm × 1.0 cm) fixed on silicon masters, and then dried in an oven at 60 °C for 1 h. After curing and cross-linking, the PDMS stamps were carefully peeled off at thicknesses of ca. 1.0 cm^[28-29].

1.2 Synthesis of PCN2 by RAFT polymerization

Analogous to our previous work^[30], poly(2-(4-((4-cyanophenyl) diazenyl) phenoxy) ethyl methacrylate) (PCN2) was synthesized by solution polymerization with AIBN as the initiator and CDB as the RAFT agent. Specifically, CN2 monomer (1.68 g, 5.0 mmol) and AIBN (16.5 mg, 0.10 mmol) were put into a homemade 25 mL polymerization ampule with a magnetic stirrer, then 10 mL freshly distilled THF was added with CDB (60 μL, 0.25 μmol) subsequently so that the initial concentrations of CN2, CDB and AIBN were 0.5, 0.025 and 0.01 mol · L⁻¹, respectively, and the ratio was 1 000 : 2.5 : 1^[31].

The above mixture was then degassed by a freeze-pump-thaw procedure for three times under nitrogen and sealed under vacuum. The sealed ampule was heated in an oil bath held at 70 °C for 24 h with stirring. After polymerization, the ampule was broken open and the resulting mixture was poured into methanol to precipitate, and then the precipitated PCN2 was purified by dissolution/precipitation (THF/CH₃OH) three times and dried overnight under vacuum.

1.3 Soft lithographic fabricating micropatterns of PCN2

Based on the preparation of PDMS stamps, fabricating micropatterns of PCN2 was subsequently attempted. However, on the one

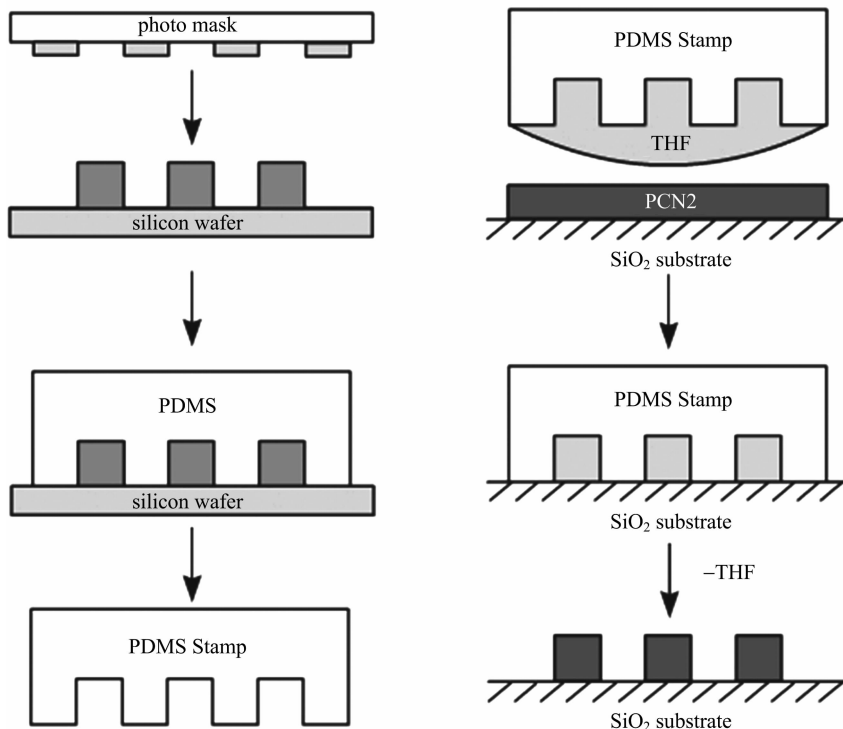
hand, because PCN2 is a polymer in solid state with a comparatively high glass transition temperature (T_g), and the corresponding monomer can not serve as a prepolymer or precursor, or any form of self-assembly can not take place, several common soft lithographic methods such as replica molding (REM), microtransfer molding (μ TM), microcontact printing (μ CP), are not applicable in this system. Therefore, another two soft lithographic methods of micromolding in capillaries (MIMIC) and solvent-assisted micromolding (SAMIM) involving some solvents are the key considerations. On the other hand, the micropatterning involves PDMS stamps, whose swelling caused by solvents may cast a shadow on the fabricating process for it may change the surface properties of PDMS stamps and seal the crucial microchannels in the MIMIC method, therefore the SAMIM method is preferred in this system^[3].

Fabricating PCN2 micropatterns by SAMIM method is shown schematically in Scheme 1 and the experimental details are as follows^[9].

Firstly, a 5% (mass fraction) PCN2 solution by dissolving the solute in THF was spin-coated onto carefully cleaned quartz slides (2.0 cm × 2.0 cm) at a speed of 2 500 r/min for 1 min, then the slides were placed on a super-clean bench to evaporate the solvent and then dried in an oven at 40 °C for 48 h under vacuum to obtain PCN2 films with thickness of ca. 4 μm.

Secondly, 0.5 mL THF was applied to the patterned surface of each PDMS stamps, which were subsequently brought to contact with the PCN2 films with a pressure of 0.5 N (using a 50 g weight).

Finally, the PCN2/THF/PDMS/weight combinations were put into an oven and heated to complete dryness at 60 °C for 1 h, then the PDMS stamps were carefully peeled away and the targeting of micropatterns of PCN2 were achieved. Actually, we have experimentally tried to directly lithograph micropatterns through a THF solution



Scheme 1 A schematic diagram of fabricating PCN2 micropatterns by the solvent-assisted micromolding (SAMIM) method

of PCN2 with PDMS stamps, yet a long contacting and solvent evaporating time results in a high swelling ratio of PDMS and difficult formation of micropatterns in a large size range.

1.4 Characterization

The ultraviolet-visible (UV-Vis) absorption spectrum of a cast PCN2 film (ca. 4 μm) was measured on a Shimadzu UV-2550 spectrophotometer and the Fourier transform infrared (FTIR) spectrum was acquired using a Nicolet 870 spectrometer. The $^1\text{H-NMR}$ spectrum was recorded on a 400 MHz Bruker AV-400 spectrometer in CDCl_3 solution.

The molecular weight with polydispersity of PCN2 was characterized by gel permeation chromatography (GPC, Toyo Soda HLC-802) based on standard polystyrenes and the eluent solvent was THF. The differential scanning calorimetry (DSC) curve was carried out over a temperature range from room temperature to 200 $^\circ\text{C}$ using a Shimadzu DSC60 calorimeter purged with nitrogen ($10 \text{ mL} \cdot \text{min}^{-1}$) with a heating and cooling rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$.

The optical micrographs of fabricated micropatterns of PCN2 and the scanning electron microscopy (SEM) images of the corresponding silicon masters were recorded on a Rathenow optical microscope and a Hitachi X-650 scanning electronmicroscope, respectively.

2 Results and discussion

2.1 FTIR, UV-Vis spectra and DSC determinations of PCN2

FTIR spectrum of PCN2 was recorded using the KBr pellet technique and the main FTIR absorption peaks with the corresponding assignments were as follows. FT-IR (KBr, cm^{-1}): 2 910 (vs, $\nu_{\text{C-H}}$), 2 854 (s, $\nu_{\text{C-H}}$); 2 222 (s, $\nu_{\text{C=N}}$); 1 716 (vs, $\nu_{\text{C=O}}$), 1 602 (w, ν_{ph}), 1 587 (w, ν_{ph}), 1 462 (w, ν_{ph}), 1 250 (s, $\nu_{\text{C-O-C}}$), 1 010 (w, $\nu_{\text{C-O}}$), 849 (s, $\delta_{\text{C-H}}$).

As an azobenzene-containing photoresponsive polymer, the position of the maximum absorption is very important for the photoisomerization between trans- and cis- states. The UV-Vis spectrum of PCN2 is shown in Fig. 1 and it can be

seen that the absorption maximum at 363.0 nm corresponds to the $\pi\text{-}\pi^*$ transition of the trans-azobenzene moieties. Compared with a maximum absorption at 320 nm of azobenzene^[32], it obviously shows a ca. 43.0 nm bathochromic shift (red-shift) due to the electron withdrawing effect caused by cyano groups. Besides, the absorption maxima at 467.0 nm corresponds to the $n\text{-}\pi^*$ transition of the trans-azobenzene moieties, while the absorption band at 253.5 nm belongs to the $n\text{-}\pi^*$ transition of the cis-azobenzene.

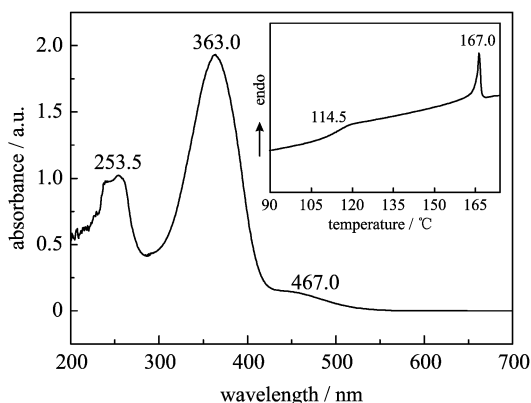


Fig. 1 UV-Vis absorption spectrum of a PCN2 film (ca. 4 μm thick) and the DSC curve (inset, G 114.5 N 167.0 °C)

In addition, as PCN2 is a typical side-chain liquid crystalline azo-containing polymer, its thermodynamic behavior plays an important role in photoresponsive materials, so the thermodynamic properties need to be investigated by DSC. For DSC testing, the PCN2 sample was heated to 200 °C to a uniform isotropic state and quenched to room temperature to eliminate any thermal history, and then a DSC heating curve (second cycle) was obtained and plotted in inset in Fig. 1. In this curve, two endothermic processes can be observed and correspond to a glass transition and a nematic-to-isotropic phase transformation (N \rightarrow I), respectively. The detailed glass transition and clear transition are G 114.5 N 167.0 °C^[24,33].

2.2 $^1\text{H-NMR}$ and GPC characterizations of PCN2

The $^1\text{H-NMR}$ spectrum of PCN2 is shown in Fig. 2, and all proton resonance peaks

corresponding to the polymer structure are labeled and also described in detail as follows. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , ppm): 7.90~7.57 (d, m overlapped, $-\text{C}_6\text{H}_4-$, $-\text{C}_6\text{H}_5$), 7.02~6.77 (d, m overlapped, $-\text{C}_6\text{H}_4-$, $-\text{C}_6\text{H}_5$), 4.40~3.86 (brm, $-\text{CH}_2\text{CH}_2-$), 2.20 ~ 1.70 (brs, $-\text{CH}_2-$ of the repeating units), 1.70~1.51 (brs, $-\text{CH}_2-$ of CDB), 1.33~0.80 (brs overlapped, $-\text{CH}_3$ of the repeating units).

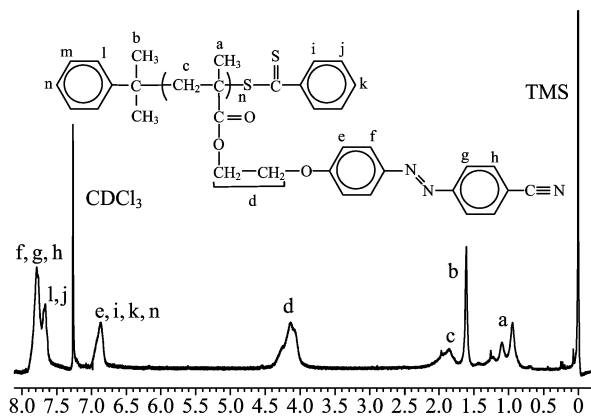


Fig. 2 $^1\text{H-NMR}$ (400 MHz) of PCN2 in CDCl_3 at 298 K

In general, the resonance signals of unsaturated double bonds in monomers (5.5~6.5 ppm) disappears and all peaks broaden, which reveals the successful synthesis of PCN2 by RAFT polymerization. By calculating the integrated areas of two independent peaks, namely H-b protons of CDB agent (6H per molecule) and H-d of methylene protons (4H per unit), the number-average degree of polymerization is 11.8 and the corresponding M_n is 4 225 $\text{g} \cdot \text{mol}^{-1}$.

The GPC analysis of PCN2 shows that the weight-average molecular weight is ca. 5,500 $\text{g} \cdot \text{mol}^{-1}$ with a polydispersity index of 1.22, which is basically consistent with the calculated results of NMR, and the relatively narrow molecular weight distribution would be beneficial for improving the film uniformity PCN2 in the following work of fabrication.

2.3 Micropatterns of PCN2

Before fabrication of PCN2, three kinds of fractal micropatterns, with honeycomb, snowflake and linear morphologies, were computer-aided

designed and processed on silicon wafers to prepare rigid masters. Because patterns on PDMS stamps were embossed complementary to those on the surfaces of the silicon masters and complementarily transferred back onto PCN2 films spin-coated on quartz slides, the fabricated patterns of PCN2 were replicas of the original masters.

In the fabrication process with SAMIM, as mentioned in Section 1.3, the most important thing is to choose the most appropriate solvent because the swelling of PDMS stamps will affect the delicateness of the micropatterns, so avoiding long-time contact of the stamps with high-solubility solvents should also be taken into account.

Due to the intrinsic soluble property of PCN2, there is not much choices of good solvents, which are listed as chloroform (b. p. 61 °C), tetrahydrofuran (THF, b. p. 66 °C), dichloromethane (DCM, b. p. 40 °C), dimethylsulfoxide (DMSO, b. p. 189 °C) and dimethylformamide (DMF, b. p. 153 °C) in the order of decreasing the swelling ability for PDMS^[34]. Among the above solvents, swelling ability, the boiling point and environmental friendliness determine the final reasonable choice of an appropriate solvent. Chloroform has the highest swelling ability, DMSO and DMF have higher boiling points and DCM is harmful with a lower

boiling point, so that SAMIM method was performed with THF as the assisting solvent to produce micropatterns of PCN2 based on the above analysis.

After fabrication, the imprinting effect needs to be evaluated through comparing the original patterns on the masters with micropatterns of the prepared PDMS stamps and PCN2 on quartz slides. Fig. 3 gives SEM graphs of the original micropatterns with good periodicity on silicon wafers, in which one can see that the feature dimensions of the honeycomb, snowflake and linear microstructures are side length of 15 μm with 5 μm intervals, an equivalent diameter of 12 μm with 3 μm intervals and line spacing of ca. 12 μm , respectively.

Optical micrographs of PDMS stamps and three fabricated PCN2 micropatterns are shown in Fig. 4 and Fig. 5, respectively, with parts of the corresponding SEM photographs placed on the lower-left corners. In order to facilitate the comparison, the scale bars were adjusted to be uniform in length.

As can be seen from Fig. 4 and Fig. 5, in addition to the defects caused by the quartz piece itself, the results show that the surface morphologies and structures of both the stamps

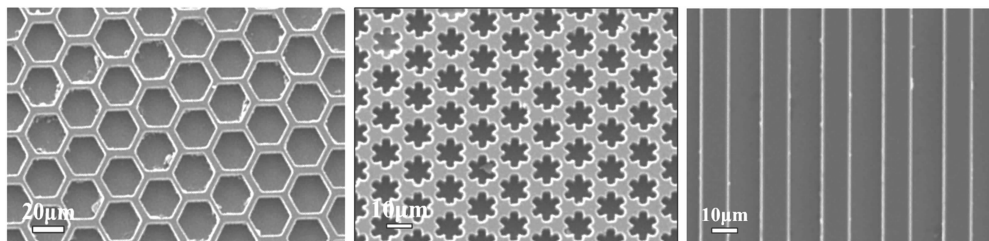


Fig. 3 SEM topographies of the molding templates on silicon wafers

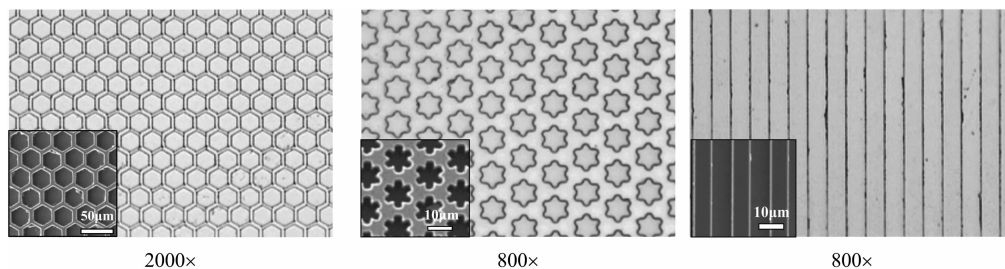


Fig. 4 Optical micrographs of micropatterns on PDMS stamps

(the lower-left corner showing the SEM topographies of the molding templates)

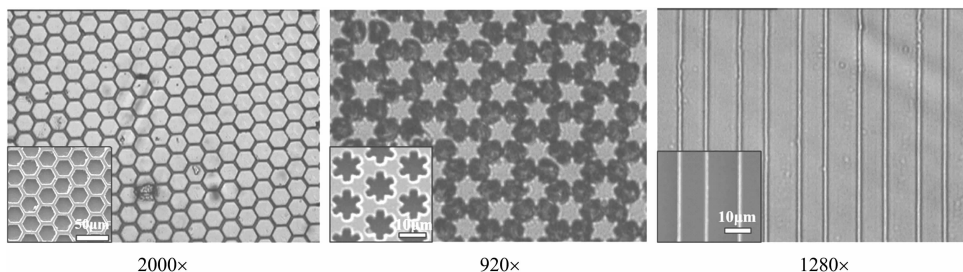


Fig. 5 Optical micrographs of three fabricated micropatterns of PCN2
(the lower-left corner showing the SEM topographies of the molding templates)

and PCN2 have been fabricated with good pattern-transfer fidelity and no cracking or apparent scale changes although the solvent THF is involved in the replicating process.

As a result, the soft lithography provides a top-down strategy for the applications in liquid crystals^[35] and demonstrates that these practically feasible methods can be used to fabricate complex periodic microstructures of a functional polymer PCN2 with a good pattern-transfer fidelity. The results similar to this can deepen the theoretical and practical studies of liquid crystalline polymers and expand their applications in optical storage^[36], photoinduced surface-relief gratings^[19], photomechanics, photodeformation^[17], light-driven actuators^[37] and other micro- and nanopatterning related areas. Based on the resulting fabricated micropatterns in this work, efforts are being made to study light-driven mass transport in light-induced orientation and alignment and to improve the efficiency of light collection in this process with light trapping effects.

3 Conclusion

In conclusion, from an azo-containing side-chain liquid crystalline polymer PCN2, we have successfully fabricated different kinds of micropatterns through a SAMIM method of soft lithography techniques. By controlling the molecular weight distribution with a RAFT polymerization, and selecting a suitable soft lithographic method with an appropriate solvent, the micro-patterns can be achieved with comparatively high fidelities. Due to the intrinsic

properties of light-induced photoorientation, polymer materials analogous to PCN2 with pre-fabricated periodic microstructures may be promising not only for improving the light absorbing ability but also for studying the mass transport mechanism of photo-induced alignments, which may be helpful to the development of polymer materials with specific structures and functions.

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