Self-organization in thin polycarbonate films and its optical and electro-optical applications

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The fabrication of micrometer and nanometer length-scaled ordered structures becomes progressively important for various electronic and optoelectronic applications [1, 2]. The future progress in the miniaturization of optical and electronic devices depends crucially on the ability to produce patterned, high density, strictly ordered micro- and nano-structures [3]. A great deal of attention has been devoted recently to the production of so-called photonic crystals—a new class of periodic dielectric media that can provide novel ways to manipulate and control light. Photonic crystals formed as a periodic lattice of tiny air holes are characterized by a bandgap that blocks the propagation of light at a certain frequency range, thus allowing realization of integrated optic devices [4, 5]. Polymers were used widely by different investigators for the production of micro- and nano-sized periodic dielectric structures [3–8]. It was shown that the phenomenon of self-organization, which takes place in colloidal suspensions, brings into existence strictly ordered patterns, which have a potential as photonic crystal-like structures [4–7]. However, the existing methods of fabrication of photonic crystals are complicated and limited by the possibilities of micromold production. We developed a very simple process allowing formation of self-organized structures that demonstrate periodicity on both micrometric and nanometric scales.

Formation of periodic photonic bandgap structures demands materials that differ significantly in their refractive index. That is why we chose polycarbonate (PC), optical-grade amorphous polymer, distinguished by its unusually high refractive index $n = 1.590$. We coated three kinds of substrates: quartz glass, polypropylene (PP) and poled polyvinylidene fluoride (PVDF) with polycarbonate PC Lexan 141 (supplied by GE Plastics) dissolved in pure dichloromethane CH_2Cl_2 (supplied by Karlo Erba Reagenti) for analysis by a fast dip-coating process. The temperature of the solution was kept constant: $t_s = 18\,^{\circ}C$, the concentration was 5 wt%.

When the substrate is dip-coated, the liquid film runs off the polymer solution, adheres to the substrate's surface and solidifies during the evaporation of the solvent (see Fig. 1). Dip-coating has been carried out with an unusually high pulling speed V up to 47 cm/min (the traditional speed of the dip-coating process is something near 0.1–1 cm/min). Films were immediately dried with an air current ($v = 3$ m/s), under isothermal conditions. The drying temperatures were varied in the range: $t_d = 18–46\,^{\circ}C$. The structure formation in our 'fast' dip-coating process relies on the balance between solvent evaporation and polymer consolidation occurring in the vertical flow of the solvent, analogously with the self-organization inherent for vertical deposition [1, 8]. However, our process is much simpler because it does not need preliminary preparation of particles or flow cells.

The drying temperature has a crucial influence on the process of self-assembling. Drying under the temperatures which were within 18–25 °C led to formation of the structures ordered both in micrometric (i.e., mesoscopic) and nanometric scales. Fig. 2 depicts optical microscopy and SEM images of polycarbonate films applied to quartz-glass substrates under conditions of fast dip-coating. Ordering on two-scales—mesoscopic and nanometric—is recognized. The orientation of the mesoscopic structure with a period of 50 μm is vertical and is obviously due to gravity.

The SEM image displayed in Fig. 2B presents PC domains separated by highly porous areas. Such mesoscopic structures have a potential as long-period gratings (LPGs). LPGs with a grating period of 50–1000 μm and have been effectively employed as spectral-selective filters in various optical and electro-optical devices [9]. However, the honeycomb structure of the porous area presented in Fig. 2C seems to be of much more interest in the light of photonic bandgap applications. The average size of pores is 2 μm, allowing near IR optics applications of obtained structures.

Use of PP substrates, which are highly transparent in the broad IR band (from 1 up to 25 μm wavelength, with the exception of the narrow absorption

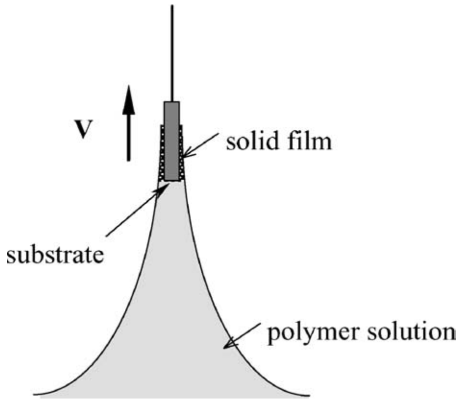

Figure 1 Scheme of the dip-coating process.

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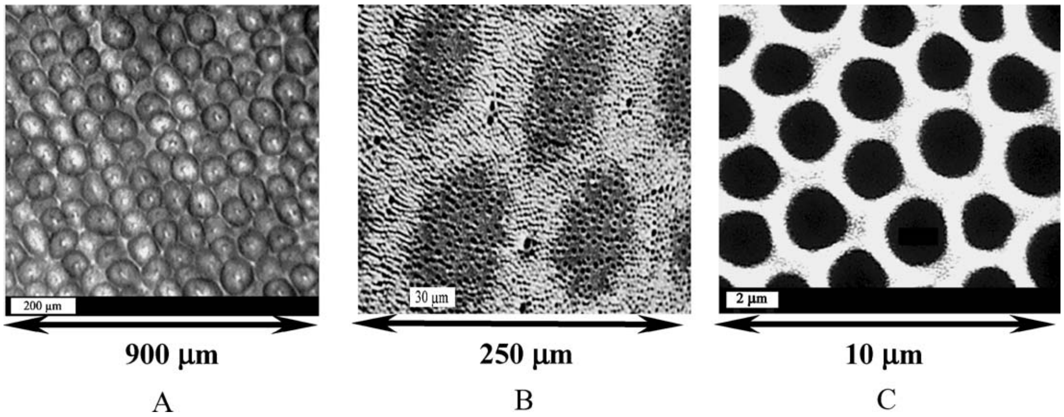

Figure 2 Optical microscopy and SEM images of self-organized mesoscopic and nanoscaled structures obtained under fast dip-coating deposition of PC films on quartz glass substrates. The drying temperature—25 °C. (A) Optical microscopy reveals ordered mesoscopic structure. (B) SEM image of the same sample shows domains of PC separated by porous areas. (C) Magnified SEM image of the porous area demonstrates honeycomb nanoscaled structure.

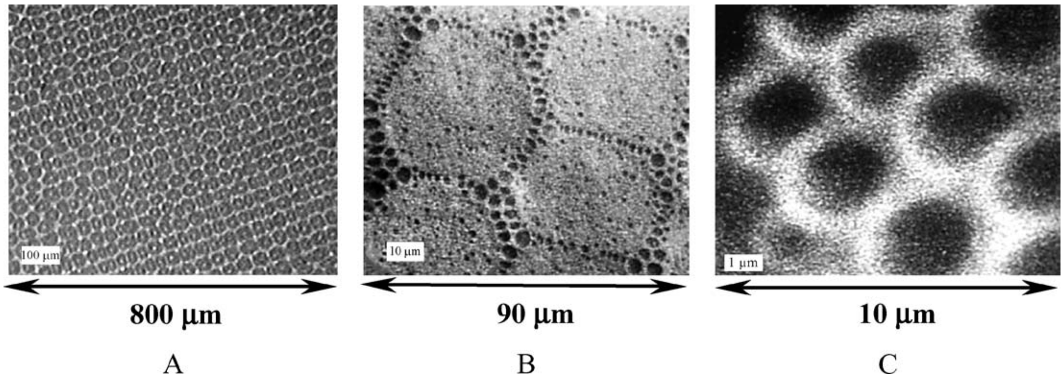

Figure 3 Optical microscopy and SEM images of self-organized mesoscopic and nanoscaled structures obtained on PP substrates. The drying temperature—25 °C. (A) and (B) Optical microscopy images of the ordered mesoscopic structure. (C) SEM image of the porous boundary.

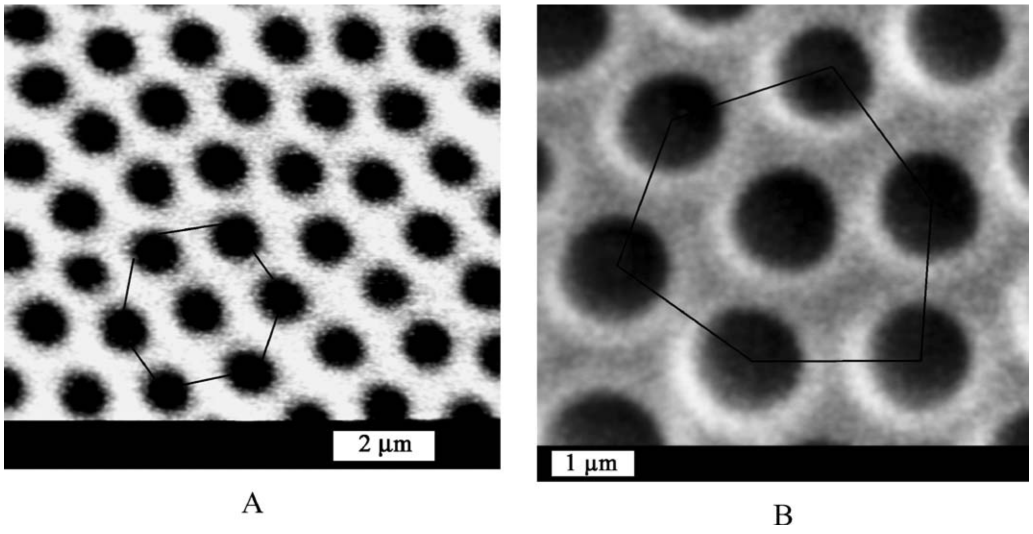

Figure 4 SEM images of self-assembled nanoscaled structures obtained under fast dip-coating deposition of PC films on the poled PVDF substrates. The drying temperature—36 °C.

band located close to 3 μm), allows an extended area of application of self-assembled structures to middle and far IR bands. That is why we paid special attention to the deposition of ordered structures on PP substrates. The impact of substrates on the structure of thin polymer films deposited under conditions of dip-coating has been recently discussed [10, 11]. We also demonstrated that the structure of the obtained films depends strongly on the kind of substrate. PP substrates bring into existence ordered self-organized structures as presented in Fig. 3. Strictly ordered mesoscopic structure is formed on the PP substrates, characterized by large domains of PP separated by the rows of nanoscaled pores. The average size of the PC domains is larger compared to those formed on the quartz glass substrates.

When the drying temperature was increased up to 30 °C the mesoscopic order was destroyed at all substrates. At the same time 2D regular nanoscaled structures were formed on the poled PVDF films under the higher drying temperatures: $t_\mathrm{d} = 30$–$46\,^\circ\mathrm{C}$. The average size of the pores was 400–1000 nm, depending on the drying temperature. The higher drying temperature led to the formation of smaller holes. The holes size distribution for a fixed drying temperature is narrow. Fig. 4 presents nanoscaled self-assembled structure based on the hexagonal elementary cell, formed on the poled PVDF substrates with a thickness of 25 μm (supplied by Precision Acoustics Ltd.) under the drying temperature $t = 36\,^\circ\mathrm{C}$. Poled PVDF is distinguished by its strong piezoelectric properties [12]. Thus electronically controlled distortion of the structure presented in Fig. 4 is possible, opening the way to a fabrication of the tunable photonic crystals [13, 14]. Great interest has been recently expressed on the strain tunable photonic crystals, allowing electronically controlled bandgaps. Such a possibility plays an important role in the miniaturization of opto-electronic equipment. Thus we conclude, that self-assembled PC films deposited on the organic and non-organic substrates offer the promise of photonic bandgap structures, including tunable photonic crystals. The process, presented in the letter, is simple, highly reproducible, and permits fabrication of large areas (up to 1 cm^2) of structured films.

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References

1. YU. A. VLASOV, X.-Z. BO, J. S. STURM and D. J. NORRIS, *Nature* **414** (2001) 289.
2. B.-SH. SONG, S. NODA and T. ASANO, *Science* **300** (2003) 1537.
3. I. NODA and M. YAMADA, *Adv. Mater.* **14**(17) (2002) 1236.
4. S. G. ROMANOV, T. MAKA, C. M. SOTOMAYOR TORRES, M. MÜLLER and R. ZENTEL, *Synth. Met.* **116** (2001) 479.
5. L. M. GOLDENBERG, J. WAGNER, J. STUMBE, B.-R. PAULKE and E. GÖRNITZ, *Mater. Sci. Eng.* **C22** (2002) 233.
6. N. MARUYAMA, T. KOITO, J. NISHIDA, T. SAWADAISHI, X. CIEREN, K. IJIRO, O. KARTHAUS and M. SHIMOMURA, *Thin Solid Films* **327–329** (1998) 854.
7. M. WANG and L. ZHANG, *ibid.* **359** (2000) 82.
8. L. M. GOLDENBERG, J. WAGNER, J. STUMBE, B.-R. PAULKE and E. GÖRNITZ, *Langmuir* **18** (2002) 3319.
9. Y. ZHU, B. M. LACQUET, P. L. SWART, ST. J. SPAMMER, P. SHUM and CH. LAO, *Opt. Engng.* **42**(5) (2003) 1445.
10. L. ZNAIDI, I. SOLER, S. BENYAHIA, C. SANCHEZ and A. V. KANAEV, *Thin Solid Films* **428** (2003) 257.
11. Y. S. PARK, Y. ITO and Y. IMANISHI, *Langmuir* **14**(4) (1998) 910.
12. M. NAGAI, K. NAKAMURA, H. UEHARA, T. KANAMOTO, Y. TAKASHI and T. FURUKAWA, *J. Polym. Sci.: B: Polym. Phys.* **37** (1999) 2549.
13. S. XIONG and H. FUKSHIMA, *J. Appl. Phys.* **94**(2) (2003) 1286.
14. CH.-S. KEE, K. KIM and H. LIM, *Physica B: Cond. Matt.* **338**(1–4) (2003) 153.

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