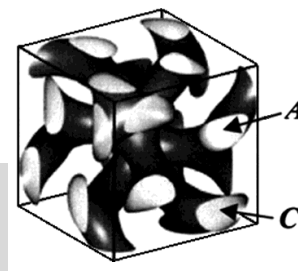


Polymer-Based Photonic Crystals**

By Alexander C. Edrington, Augustine M. Urbas,
Peter DeRege, Cinti X. Chen, Timothy M. Swager,
Nikos Hadjichristidis, Maria Xenidou,
Lewis J. Fetters, John D. Joannopoulos,
Yoel Fink, and Edwin L. Thomas*



In this report, we highlight the development of polymers as 1D photonic crystals and subsequently place special emphasis on the activities in self-assembled block copolymers as a promising platform material for new photonic crystals. We review recent progress, including the use of plasticizer and homopolymer blends of diblock copolymers to increase periodicity and the role of self-assembly in producing 2D and 3D photonic crystals. The employment of inorganic nanoparticles to increase the dielectric contrast and the application of a biasing field during self-assembly to control the long-range domain order and orientation are examined, as well as in-situ tunable materials via a mechanochromic materials system. Finally, the inherent optical anisotropy of extruded polymer films and side-chain liquid-crystalline polymers is shown to provide greater degrees of freedom for further novel optical designs.

1. Introduction

Polymers are already important materials for photonic applications; some examples are plastic optical components such as Fresnel lenses, light pipes, diffusers, and polarizers. Photonic crystals are a new class of periodic dielectric media that can provide novel ways to manipulate and control light. Much of the recent effort in construction of photonic crystals has focussed on lithographic approaches,^[1,2] colloidal self-assembly,^[3] and use of

opals and inverse opal structures as templates.^[4] Block copolymers (BCPs) are an interesting platform material for photonic crystal applications due to their ability to self-assemble into a variety of 1D, 2D, and 3D periodic structures^[5] (Fig. 1) and the ability to selectively incorporate additives.^[6] There are four main challenges that need to be overcome in order to achieve necessary photonic properties with BCPs. The primary challenge is to obtain the large domain sizes needed for the optical frequencies of interest (e.g., in telecommunications, 1.55 μm in the near-infrared (near-IR) requires domain thicknesses of about 250 nm).^[7] Additional significant concerns for creating useful BCP photonic crystals which should be addressed include long-range domain order, control over domain orientation, as well as production of sufficient dielectric contrast between domains.^[6,7]

2. One-Dimensional Polymeric Photonic Crystals

The simplest example of a photonic crystal is the multilayer stack. The wavelength of the reflected light from a multilayer material depends on the optical thickness ($n_i d_i$) of each layer. Each interface between layers reflects an amount of incident light dependent on the index contrast between the layers, with the first order reflected wavelength for layers of equivalent optical thickness given by:^[8]

$$\lambda_1 = 2(n_1 d_1 + n_2 d_2) \quad (1)$$

[*] Prof. E. L. Thomas, A. C. Edrington, A. M. Urbas, Prof. Y. Fink
Department of Materials Science and Engineering, MIT
Cambridge, MA 02139 (USA)
E-mail: elt@mit.edu

Dr. P. DeRege
Firmenich, Inc.
Port Newark, NJ 07114 (USA)

Dr. C. X. Chen, Prof. T. M. Swager
Department of Chemistry, MIT
Cambridge, MA 02139 (USA)

Dr. N. Hadjichristidis
Department of Chemistry, University of Athens
30 Panepistimiou St
GR-10679 Athens (Greece)

Dr. M. Xenidou, Dr. L. J. Fetters
ExxonMobil Research Corp.
Annandale, NJ 08801 (USA)

Prof. J. D. Joannopoulos
Department of Physics, MIT
Cambridge, MA 02139 (USA)

[**] The authors acknowledge NSF, AFOSR, the NSF-supported Center for Materials Science and Engineering at MIT, and Nanovation.

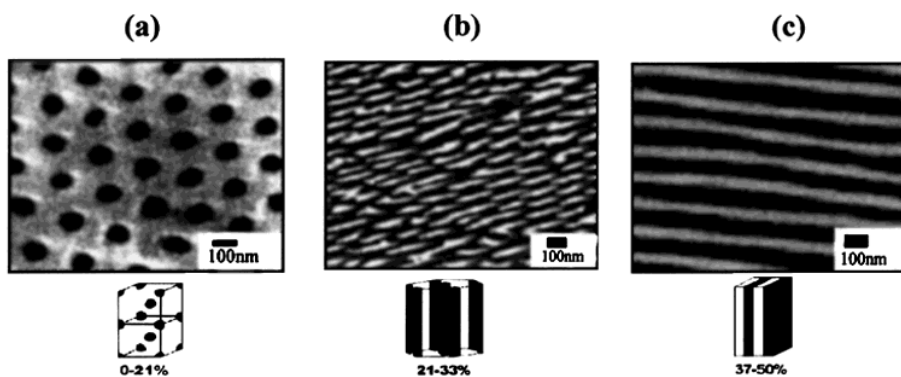


Fig. 1. a) Top: Scanning electron microscopy (SEM) image of spherical domains produced in a PS-PI (194/197 kg/mol) copolymer swollen with 50 % PS homopolymer. Bottom: Schematic of bcc packed spheres predicted for low minority block compositions. b) Top: Atomic force microscopy (AFM) image of cylindrical domains produced in a roll-cast PS-PI (320/680 kg/mol) copolymer. Bottom: Schematic of hexagonally packed cylinders predicted in BCPs for composition range indicated. c) Top: Transmission electron microscopy (TEM) image of lamellae produced in a PS-PI (194/197 kg/mol) copolymer swollen with PS and PI homopolymer. Bottom: Schematic of lamellar domains produced in BCPs with relatively balanced weight distribution. Note the length scales of these materials are such that they act as photonic crystals in the visible part of the spectrum.

where λ_1 is the 1st order reflected wavelength; n_i and d_i are the refractive index and width of the i th layer. The intensity of the reflected light from the multilayer film is proportional to the number of layers of equal thickness as well as to the index contrast between the layers. For incident light normal to a uniform layer thickness AB multilayer film, the ideal reflectivity for a material composed of N layers is given by:

$$R = \left[\frac{1 - \left(\frac{n_2}{n_1}\right)^{2N}}{1 + \left(\frac{n_2}{n_1}\right)^{2N}} \right]^2 \quad (2)$$

for $n_2 < n_1$. Higher order reflections are also produced in these multilayer materials and actually cannot be avoided in two-component systems.

A convenient way to display the optical characteristics of a periodic dielectric material is through the band diagram.^[9] For this 1D case the normalized frequency of the allowed modes is plotted over the Brillouin zone as a function of the normalized component of the incident wave vector parallel to the surface of the stack (k_{\parallel}). Figure 2 is the calculated band diagram for a quarter wave stack ($\lambda/4 = n_i d_i$ and $a = n_1 d_1 + n_2 d_2$). At normal incidence ($k_{\parallel} = 0$), there is a narrow reflectivity band with $\Delta\lambda/\lambda = 0.07$ for $n_1 = 1.59$ and $n_2 = 1.51$. As the incident beam is tilted with respect to the layer normal, the reflectivity band shifts to higher frequencies depending on the polarization of the beam. The polarization is defined by the orientation of the electric field or magnetic field with respect to the plane of incidence, defined by the plane containing the incident wave vector and the normal to the film. For transverse electric (TE) polarization the bandgap remains open up to grazing incidence (the light line, shown in bold) whereas for transverse magnetic (TM) polarization the band narrows and closes at the Brewster angle.

Polymeric multilayer films have been manufactured via three main methods: co-extrusion, spin coating, and self-

assembly. Co-extruded films containing large numbers of alternating layers of different refractive indices were produced over 30 years ago at Dow, with first order reflectivities approaching 100%.^[8,10] A fundamental problem encountered with co-extruded films is the occurrence of undesired thickness variations, which result in a broadening of the reflection spectrum and also unwanted higher order reflections. The addition of a third material of intermediate index has been shown to be successful in suppressing two or more consecutive higher order reflections. Schrenk et al. coextruded a multilayer material with a four layer repeat (A/B/C/B) and a thickness ratio of 2:1:2:1, successfully suppressing the second through fourth order reflectivity peaks.^[11] There are several applications for co-extruded multilayer films, including solar films for automobiles and buildings.^[10] Nearly half of all solar energy occurs in near infrared wavelengths (800–2000 nm) and can be substantially reflected while allowing for excellent transmission at visible wavelengths.

In polymers the refractive index mismatch is normally small compared with other layered structures such as vacuum deposited inorganic dielectrics, but this limitation can be compensated for by employing a large number of layers.^[10–12] The refractive index of polymeric layers can also be adjusted through copolymerization^[11] or by the blending of miscible pairs of polymers. Copolymerization can improve structural integrity and resistance to ultraviolet (UV) light degradation, while the possibility for index adjustment also allows for the tuning of one or more of the high, intermediate, and low refractive index polymers present in three-component optical films.

assembly. Co-extruded films containing large numbers of alternating layers of different refractive indices were produced over 30 years ago at Dow, with first order reflectivities approaching 100%.^[8,10] A fundamental problem encountered with co-extruded films is the occurrence of undesired thickness variations, which result in a broadening of the reflection spectrum and also unwanted higher order reflections. The addition of a third material of intermediate index has been shown to be successful in suppressing two or more consecutive higher order reflections. Schrenk et al. coextruded a multilayer material with a four layer repeat (A/B/C/B) and a thickness ratio of 2:1:2:1, successfully suppressing the second through fourth order reflectivity peaks.^[11] There are several applications for co-extruded multilayer films, including solar films for automobiles and buildings.^[10] Nearly half of all solar energy occurs in near infrared wavelengths (800–2000 nm) and can be substantially reflected while allowing for excellent transmission at visible wavelengths.

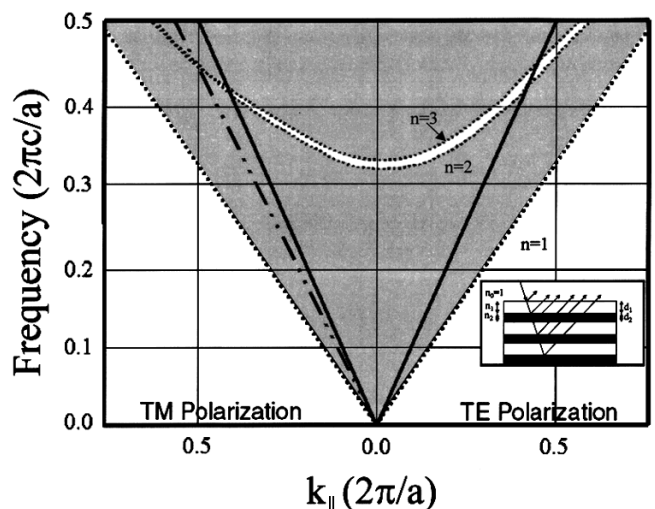


Fig. 2. 1D band diagram (TE and TM modes) of lamellar structure ($n_1 = 1.59$; $n_2 = 1.51$). The bandgap occurs in the white region between the $n = 2$ and $n = 3$ bands. Inset depicts incident light on a multilayer stack [12].

By changing the refractive index of the layers one can modify the band structure; increasing the dielectric contrast will in general lead to larger bandgaps. A careful choice of the refractive indices of the multilayer stack has recently led to the development of the 1D omnidirectional reflector that reflects a band of frequencies for both TE and TM polarized light regardless of angle of incidence.^[13]

3. One-Dimensional Self-Assembled Multilayers

BCPs with compositions of 35–65 % self-assemble into a periodic lamellar structure. The simplest BCPs are linear A/B diblock copolymers comprised of two distinct, non-crystalline polymer chains.^[14–16] A/B diblock copolymers form microphase-separated structures in which domains predominantly consisting of one block are separated from domains consisting primarily of the other block by a narrow interfacial region.^[14,15] BCPs with molecular weights in the 20–100 kg/mol range typically yield periodicities in the 20–50 nm range. The period scales with the two-thirds power of the molecular weight; however, ultrahigh molecular weight (>1 Mg/mol) materials are extremely viscous in the melt and do not easily self-assemble into well-ordered structures due to their strongly entangled nature.

Alternatively, homopolymer–BCP blends can be utilized to obtain increased length scales via swelling of the block domains by the respective homopolymers.^[17,18] By using high molecular weight diblocks (e.g., 400 kg/mol) and swelling with homopolymer, domains have been produced which are sufficiently thick ($d \approx \lambda/4n$) to act as photonic materials in the visible regime.^[17] An example of the cross sectional structure of a lamellar polystyrene–polyisoprene (PS–PI) BCP swollen with PS and PI homopolymer ($n_{PS}=1.59$; $n_{PI}=1.51$) is shown in Figure 1c. Self-assembled PS–PI BCPs can produce narrow reflectivity peaks at visible wavelengths ($\Delta\lambda/\lambda < 0.1$) indicative of excellent layer order, constant thickness and low defect content (Fig. 3). The wavelength of peak reflectance of a particular AB diblock can be conveniently tuned across a wide range of visible wavelengths in an approximately linear manner by simply adjusting the amount of homopolymer.^[17]

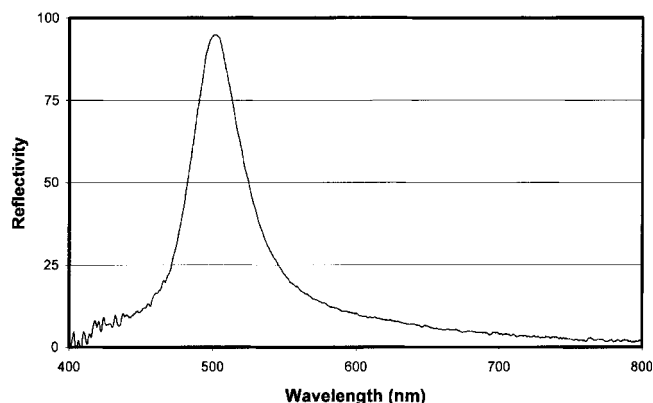


Fig. 3. Relatively narrow, high reflectivity peak ($\Delta\lambda/\lambda = 0.08$) for a styrene–ethylene(propylene) copolymer (800 kg/mol) plasticized with dioctylphthalate.

4. Two- and Three-Dimensional Self-Assembled Structures

The co-extrusion and spin coating processes which can produce multilayered 1D optical films have proven unsuccessful in producing 2D and 3D photonic crystals. However, self-assembly from a pair of immiscible homopolymers and relatively high molecular weight BCPs has produced 2D cylindrical domains and 3D body-centered cubic (bcc) packed spherical domains which reflect in the visible spectrum. The hexagonally packed cylinders produced with 21–33 % minority block composition are a type of 2D photonic crystal.^[9] With sufficient refractive index contrast, hexagonally packed cylindrical systems are able to produce a complete photonic bandgap for both TE and TM modes. This means that for light propagating in the plane perpendicular to the cylinder axis, there is reflection for a band of frequencies for both polarizations at any azimuthal angle. Cylindrical domains with relatively large periodicity ($d_{\text{cylinders}} \approx 120$ nm) and controlled orientation have been produced through roll casting of a PS–PI (320/680 kg/mol) BCP with molecular weight of 1.0 Mg/mol (see Fig. 1b). In this case the self-assembly process takes place in an evaporating solution undergoing orientation due to the action of the rollers.^[19]

Thus far, there are three known types of microdomain structures with cubic symmetry: spheres ($Im\bar{3}m$), double gyroid ($Ia\bar{3}d$), and double diamond ($Pn\bar{3}m$). The double gyroid microdomain structure is comprised of two interpenetrating, 3-coordinated labyrinthine networks of the minority component and occurs in the composition regime between the lamellar and cylindrical phases for BCPs. Theoretical calculations demonstrate that a complete bandgap can be produced in the gyroid structure provided that sufficient index contrast exists.^[20] Spherical domains of intermediate range order and a unit cell size of about 140 nm have been produced via self-assembly using a highly asymmetric blend comprised of 50 % PS homopolymer in a high molecular weight PS–PI diblock copolymer (Fig. 1a).

5. Intricate Block Polymer Structures

Other self-assembled structures can be produced with block polymers through various synthesis techniques, for instance through the production of linear multi-block polymers as well as star and other molecular architectures (Fig. 4). In general, the morphologies of ABC terblock polymers are much richer than those displayed by AB diblocks. A linear polystyrene–block–polybutadiene–block–poly(methyl methacrylate) polymer formed a morphology in which both the A (PS) and C (PMMA) blocks formed small and large diameter cylindrical microdomains respectively with a unique hexagonal $p6mm$ symmetry.^[21] The novel “knitting pattern” structure of another ABC polymer results in $c2mm$ symmetry.^[22] A three arm ABC star polymer forms yet another type of two-dimensionally periodic, three-phase microdomain structure with

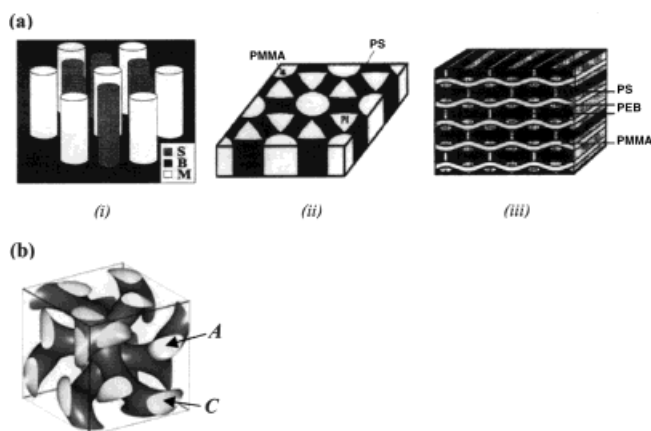


Fig. 4. Schematics of novel 2D periodic ABC block terpolymer structures. a) i) Linear ABC polymer with hexagonal $p6mm$ symmetry. ii) ABC miktoarm star three-phase microdomain structure with $p6mm$ symmetry. iii) Linear ABC "knitting" pattern, which displays a $c2mm$ symmetry. b) A double gyroid with 3D cubic ($Ia3d$) symmetry. A and C represent interpenetrating networks in a B matrix.

$p6mm$ symmetry.^[23] A linear three component triblock can also produce a double gyroid structure, with the two different networks (A and C blocks) separated by a matrix (B).^[24] Based on the large array of structures and compositions available and the ability to tailor the relative domain sizes through control of molecular weight and through blending, the potential for self-assembled materials with photonic crystal geometries not readily attainable by other synthetic/processing approaches is apparent.

6. Polymers as Birefringent Multilayer Films and Elastomeric Films

The systems described above are all materials with isotropic indices of refraction. The refractive index of a polymer can also be made strongly directional by orienting the chains. Optically anisotropic multilayer A/B co-extruded polymer films have recently been developed by 3M which have an index mismatch in one direction ($n_{A1} \neq n_{B1}$) while minimizing the mismatch in the orthogonal direction ($n_{A2} \approx n_{B2}$). Such films can retain or increase their reflectivity with increasing incidence angle.^[25] The broad band character of the reflectivity arises from both the birefringence and by purposeful production of a stack of different optical thicknesses chosen such that the individual reflectivity bands overlap to give a composite film which acts as a good mirror over essentially all of the visible spectrum.

Self-assembled polymeric photonic crystals can also be fabricated to have novel optical properties. One example is a mechanochromic film: a material which responds to deformation by changing color. In these materials, the wavelength reflected changes reversibly with the applied strain due to the change in optical thickness. Co-extruded AB multilayers composed of elastomers can reflect in the visible through near-

infrared regimes.^[10] Kimura et al.^[26] performed biaxial compression on a hydrophobic/hydrophilic multilayers fabricated by successive spin casting alternating layers of polystyrene and polyvinyl alcohol and found a shift of 65 nm in the peak reflectivity for an applied pressure of 18 MPa.

7. Future Outlook

Increasing the dielectric contrast between domains in a BCP offers the ability to further tailor the optical properties. One approach is to employ high index nanoparticle additives which are coated with a surfactant layer and selectively incorporated into one of the domains. For example, we have sequestered 4 nm diameter CdSe particles of high refractive index into a poly(styrene/isoprene/2-vinyl pyridine) triblock terpolymer using amine terminated polystyrene oligomers attached to the CdSe surface.^[6] Another self-assembly approach employs micelle formation in a solution of rod-coil diblock copolymers that aggregate into micrometer-sized hollow spheres and cylinders.^[27] These materials show potential for use as photonic bandgap structures due to good dielectric contrast ($n_{\text{air}} = 1.0$; $n_{\text{eff,diblock}} \approx 1.7$), which has been further enhanced with the incorporation of fullerenes ($n_{C_{60}} = 2.1$).^[27]

Finally, the capability for polymeric materials to not only display anisotropic dielectric properties but to be able to vary the anisotropy by applied fields, for example in electric field switchable side-chain liquid-crystalline block-coil BCPs, points the way towards the use of self-assembled block polymeric materials in optical switches, couplers, and isolators.^[28]

- [1] J. G. Fleming, S.-Y. Lin, *Opt. Lett.* **1999**, *24*, 49.
- [2] S.-Y. Lin, J. G. Fleming, *J. Lightwave Technol.* **1999**, *17*, 1944.
- [3] S. A. Asher, J. Holtz, L. Liu, Z. Wu, *J. Am. Chem. Soc.* **1994**, *116*, 4997.
- [4] A. Zakhidov, R. Baughman, Z. Iqbul, C. Cui, I. Khayrullin, S. Dantas, J. Marti, V. Ralchenko, *Science* **1998**, *282*, 897.
- [5] E. L. Thomas, R. L. Lescanec, *Philos. Trans. R. Soc. London A* **1994**, *348*, 149.
- [6] Y. Fink, A. M. Urbas, M. G. Bawendi, J. D. Joannopoulos, E. L. Thomas, *J. Lightwave Technol.* **1999**, *17*, 1963.
- [7] A. M. Urbas, Y. Fink, E. L. Thomas, *Macromolecules* **1999**, *32*, 4748.
- [8] T. Alfrey Jr., E. F. Gurnee, W. J. Schrenk, *Polym. Eng. Sci.* **1969**, *9*, 400.
- [9] J. D. Joannopoulos, R. Meade, J. N. Winn, *Photonic Crystals: Molding the Flow of Light*, Princeton University Press, Princeton, NJ **1995**.
- [10] J. A. Radford, T. Alfrey Jr., W. J. Schrenk, *Polym. Eng. Sci.* **1973**, *13*, 216.
- [11] W. J. Schrenk, J. A. Wheatley, R. A. Lewis, C. B. Arends, *Tappi J.* **1992**, 169.
- [12] W. J. Schrenk, R. A. Lewis, J. A. Wheatley, C. B. Arends, in *Proc. Infrared Thin Films Conference 1991*, p. 35.
- [13] Y. Fink, J. N. Winn, S. Fan, C. Chen, J. Michel, J. D. Joannopoulos, E. L. Thomas, *Science* **1998**, *282*, 1679.
- [14] F. S. Bates, *Science* **1991**, *251*, 898.
- [15] I. W. Hamley, *The Physics of Block Copolymers*, Oxford University Press, New York **1998**.
- [16] E. L. Thomas, *Science* **1999**, *286*, 1307.
- [17] A. M. Urbas, R. Sharp, Y. Fink, E. L. Thomas, M. Xenidou, L. J. Fetters, *Adv. Mater.* **2000**, *12*, 812.
- [18] K. Winey, E. L. Thomas, L. J. Fetters, *Macromolecules* **1991**, *24*, 6182.
- [19] R. J. Albalak, E. L. Thomas, *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 341.
- [20] L. Martin-Moreno, F. J. Garcia-Vidal, A. M. Somoza, *Phys. Rev. Lett.* **1999**, *83*, 73.

- [21] S. Brinkmann, R. Stadler, E. L. Thomas, *Macromolecules* **1998**, *31*, 6566.
- [22] U. Breiner, U. Krappe, E. L. Thomas, R. Stadler, *Macromolecules* **1998**, *31*, 135.
- [23] S. Sioula, N. Hadjichristidis, E. L. Thomas, *Macromolecules* **1998**, *31*, 8429.
- [24] Y. Matsushita, J. Suzuki, M. Seki, *Phys. Rev. B: Condens. Matter* **1998**, *248*, 238.
- [25] M. F. Weber, C. A. Stover, L. R. Gilbert, T. J. Nevitt, A. J. Ouderirk, *Science* **2000**, *287*, 2451.
- [26] M. Kimura, K. Okahara, T. Miyamoto, *J. Appl. Phys.* **1979**, *50*, 1222.
- [27] S. A. Jenekhe, X. L. Chen, *Science* **1999**, *283*, 372.
- [28] G. Mao, J. Wang, C. Ober, M. Brehmer, M. O'Rourke, E. L. Thomas, *Chem. Mater.* **1998**, *10*, 1538
-