Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Shear-induced lamellar phase of an ionic liquid crystal at room temperature

M. H. Godinho[a]; C. Cruz[b]; P. I. C. Teixeira[c]; A. J. Ferreira[a]; C. Costa[b]; P. S. Kulkarni[d]; C. A. M. Afonso[d]
[a] FCT/UNL, Dept. de Materiais, and I3N/CENIMAT, 2825-114 Caparica, Portugal [b] Instituto Superior Técnico, Depart. de Física, Av. Rovisco Pais, 1049-001 Lisboa, and Centro de Fisíca da Matéria Condensada, 1649-003 Lisboa, Portugal [c] Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emídio Navarro, 1950-062 Lisboa, and Centro de Física Teórica e Computacional, Universidade de Lisboa, 1649-003 Lisboa, Portugal [d] REQUIMTE, Depart. de Química, FCT-UNL, 2829-516 Caparica, and CQFM, Depart. de Engenharia Química e Biológica, IST, 1049-001 Lisboa, Portugal

To cite this Article Godinho, M. H. , Cruz, C. , Teixeira, P. I. C. , Ferreira, A. J. , Costa, C. , Kulkarni, P. S. and Afonso, C. A. M.(2008) 'Shear-induced lamellar phase of an ionic liquid crystal at room temperature', Liquid Crystals, 35: 2, 103 — 107

To link to this Article: DOI: 10.1080/02678290701824181

URL: http://dx.doi.org/10.1080/02678290701824181

Liquid Crystals,
Vol. 35, No. 2, February 2008, 103–107

Taylor & Francis
Taylor & Francis Group

Shear-induced lamellar phase of an ionic liquid crystal at room temperature

M. H. Godinho[a]*, C. Cruz[b], P. I. C. Teixeira[c], A. J. Ferreira[a], C. Costa[b], P. S. Kulkarni[d] and C. A. M. Afonso[d]

[a]FCT/UNL, Dept. de Materiais, and I3N/CENIMAT, Quinta da Torre, 2825-114 Caparica, Portugal; [b]Instituto Superior Técnico, Depart. de Física, Av. Rovisco Pais, 1049-001 Lisboa, and Centro de Fisíca da Matéria Condensada, Av. Prof. Gama Pinto 2, 1649-003 Lisboa, Portugal; [c]Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emídio Navarro, 1950-062 Lisboa, and Centro de Física Teórica e Computacional, Universidade de Lisboa, Avenida Professor Gama Pinto 2, 1649-003 Lisboa, Portugal; [d]REQUIMTE, Depart. de Química, FCT-UNL, 2829-516 Caparica, and CQFM, Depart. de Engenharia Química e Biológica, IST, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

(Received 31 May 2007; final form 23 November 2007)

The phase behaviour of a number of *N*-alkylimidazolium salts was studied using polarizing optical microscopy, differential scanning calorimetry and X-ray diffraction. Two of these compounds exhibit lamellar mesophases at temperatures above 50°C. In these systems, the liquid crystalline behaviour may be induced at room temperature by shear. Sheared films of these materials, observed between crossed polarisers, have a morphology that is typical of (wet) liquid foams: they partition into dark domains separated by brighter (birefringent) walls, which are approximately arcs of circle and meet at "Plateau borders" with three or more sides. Where walls meet three at a time, they do so at approximately 120° angles. These patterns coarsen with time and both T1 and T2 processes have been observed, as in foams. The time evolution of domains is also consistent with von Neumann's law. We conjecture that the bright walls are regions of high concentration of defects produced by shear, and that the system is dominated by the interfacial tension between these walls and the uniform domains. The control of self-organised monodomains, as observed in these systems, is expected to play an important role in potential applications.

Keywords: ionic liquid crystals; shear; liquid foams; lamellar phases

1. Introduction

Ionic liquids exhibit a variety of interesting properties related to their applications as green solvents and ion conductive matrices for electrochemical devices (*1*). Anisotropic behaviour, leading to liquid crystalline phases, can be achieved through the induction of amphiphilic character by introducing long alkyl chains connected to one or both ionic counterparts. By adequate design of the molecular structure of such compounds, both lamellar and columnar mesophases may be induced (*1–3*). The ionic nature of these materials combined with their self-organizing properties allows for the optimization of functional characteristics including ionic conduction properties (*4, 5*). This is especially relevant as the ionic conductivity is clearly enhanced in the liquid crystalline phases (in particular in the lamellar phase) when compared to the isotropic phase. The mesomorphic behaviour of these materials is of particular interest when obtained at room temperature. This characteristic is generally achieved (and in particular in the case of imidazolium salts) by linking long alkyl chains to the imidazolium ion or by mixing ionic liquids with rod-like mesogenic compounds with polar groups connected to the ends of alkyl chains (*6, 7*). The mesomorphic behaviour of some materials (in particular polymers) may also be induced by shear. This effect is promoted by cooperative anisotropic behaviour resulting from the interactions of specific molecular segments (*4, 8, 9*). Despite the growing interest in the properties of thermotropic ionic liquid crystals based on imidazolium compounds (*10, 11*) very little is known about the effect of shear on these materials. In this work the phase behaviour of *N*-alkylmethylimidazolium salts (see Figure 1) was studied by polarising optical microscopy (POM) coupled to a shearing system, differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The materials under study exhibit lamellar phases for temperatures higher then 50°C. The molecular packing of these mesophases will be discussed on the basis of X-ray diffraction results. The effect of shear on the crystalline phase of these materials was studied at room temperature and it was verified that liquid crystalline behaviour may be induced in these conditions.

2. Experimental

General procedure for preparation of salts 1a and 1b

A mixture of 1-*n*-octyl-3-methylimidazolium chloride or 1-*n*-decyl-3-methyl-imidazolium chloride (3.0 g), and sodium *p*-toluenesulfonate (1.2 equiv.) in dichlor-

---

*Corresponding author. Email: mhg@fct.unl.pt

ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678290701824181
http://www.informaworld.com

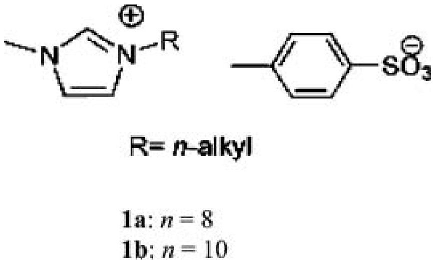

Figure 1. Chemical structure of *N*-alkylmethylimidazolium *p*-toluenesulfonate.

omethane (20 ml) was stirred at room temperature for 48 h. The resulting solid was collected by filtration and washed with dichloromethane (2 × 25 ml). The combined organic layers were collected, dried ($MgSO_4$) and filtered. The salt was then recovered after passing through a column containing silica and activated charcoal and the solvent removed under vacuum overnight. Yield: **1a** 78 %; **1b** 77 %.

Characterisation

DSC measurements were performed with a SETARAM DSC 131 at a scanning rate of 10°C min^{-1}. Polarising microscopy was performed with an Olympus BH microscope equipped with a Mettler FP52 hot stage, an Olympus Camedia C-5060 camera and a Linkam CSS 450 Cambridge shearing system. X-ray measurements were performed using a variable geometry device equipped with a Max-FluxTM Optic graded multilayer monochromator for Cu K_α radiation and a gas curved counter "INEL CPS 590" associated with a data acquisition computer controlled system. This device was also equipped with a computer controlled electric oven. The temperature of the sample was controlled to within ±0.1°C.

Preparation of ionic liquid crystal films

Solutions of compounds **1a** and **1b** in acetone (64% w/w) were prepared at room temperature followed by stirring to allow homogenisation. Films were cast and sheared simultaneously by moving a casting knife over a glass substrate at a controlled shear rate determined by $v=5\,\mathrm{mm\,s^{-1}}$. The thickness of the films after evaporation of the solvent was estimated using a Mitutoyo digital micrometer, with a range from 10 to 20 μm.

3. Results and discussion

The thermal properties of compounds **1a** and **1b**, as determined by DSC and POM, are presented in Table 1. XRD patterns were obtained for powder samples of compounds **1a** and **1b** as a function of temperature (Figures 2a and 2b, respectively).

In both cases, diffraction patterns characteristic of lamellar structures are obtained for temperature ranges corresponding to the mesophases detected by DSC and POM. In the small-angle region, a sharp peak corresponding to a strong (001) reflection, followed by a weak (002) peak, is present for both compounds. The characteristic distances corresponding to the smectic layer thicknesses are 23 and 26 Å for compounds **1a** and **1b**, respectively. In the wide-angle region, the XRD patterns of both compounds present a very broad peak indicating the fluid-like alkyl chain region with a characteristic average lateral distance of about 4.5 Å. In the case of compound **1a**, which has the shorter aliphatic chain (C8), the smectic temperature range is narrow and a small sharper peak appears superimposed on the broad peak characteristic of liquid-like order. This peak is characteristic of some in-plane order in the smectic phase, possibly remaining from the lower temperature crystalline phase. The layer thicknesses as determined by XRD may be understood considering the approximate molecular dimensions of the ions and the aliphatic chains as obtained by simulation (*12*). In the simulations, the lengths of the alkyl chains are estimated considering the planar zigzag conformations. The approximate excluded volume of the ions is estimated by considering an average ellipsoid with a shorter axis of length about 5 Å, corresponding to the rings (phenyl and imidazole), and longer axis of length about 6 or 7 Å for the cation and the anion, respectively. It is important to notice that these dimensions are average values considering the liquid crystalline structure of the material. In particular the alkyl chains are partially melted assuming statistically a large number of possible conformations. The layer thicknesses as obtained by XRD may be explained, as is usual in other ionic lamellar liquid crystals, by the alternation of microsegregated ionic and aliphatic sublayers (*2, 3, 9, 10*). In the present case, a single layer stacking with alternating cations and anions may be assumed, as shown in Figure 3. This structure is similar to other *N*-alkylimidazolium salts liquid crystals discussed in the literature (*9*).

A general feature of ionic liquid crystals is the strong tendency to show spontaneous homeotropic

Table 1. The thermal properties of compounds **1a** and **1b**.

Compound	Phase transitions [a]/°C				
1a	Cr	79.8	SmX	89.5 (66.1)	I
1b	Cr	49.4 (6.2)	SmA	79.0 (38.3)	I

Note: [a], Transition temperatures (°C) and enthalpies of transition (J/g). Cr: crystalline; SmX: ionic LC ordered smectic; SmA: smectic A; I: isotropic.

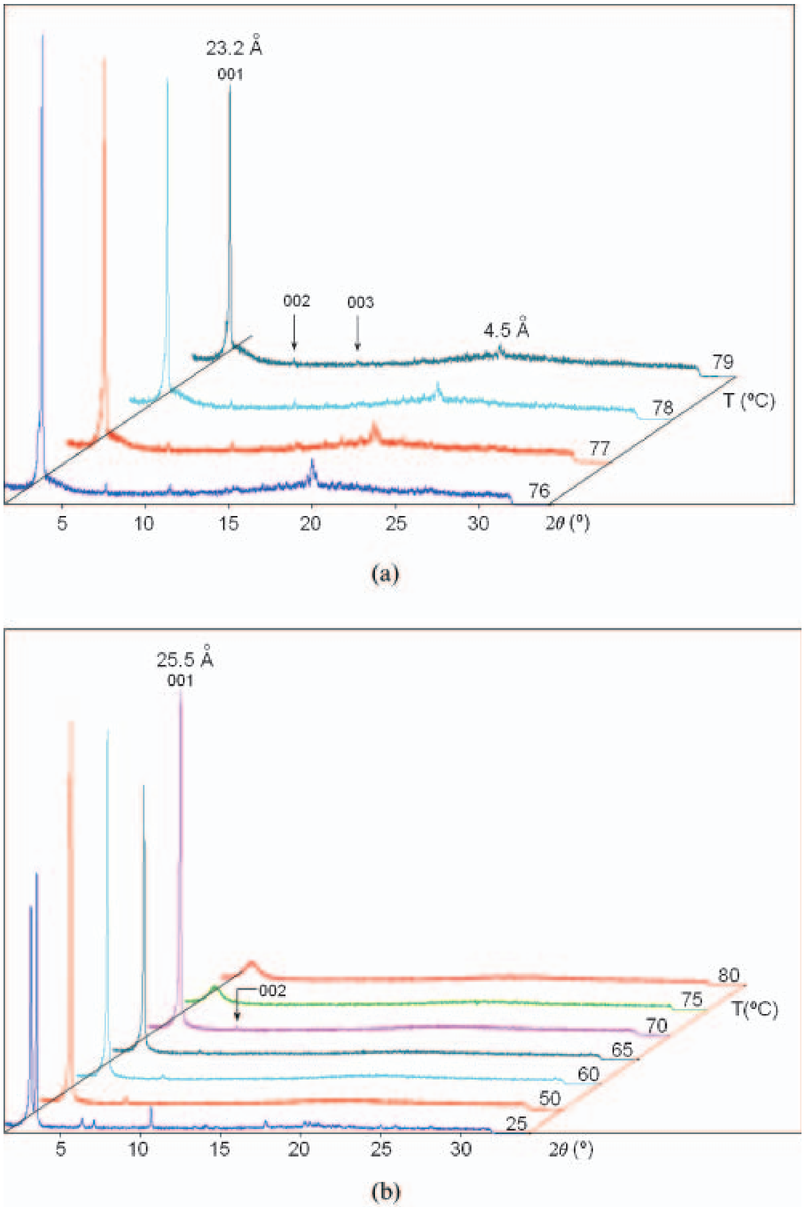

Figure 2. X-ray diffraction patterns obtained from powder samples as a function of temperature for compounds **1a** (a) and **1b** (b).

alignment promoted by the ionic species that act as a surface treatment reagent (*3*). Accordingly, the observed optically uniaxial smectic phases appear as a dark field between crossed polarizers. In this case, the smectic planes are parallel to the microscope glass side and the optical axis is perpendicular to it. Usually this alignment can be destroyed by pressing with a needle on the cover glass, and optical birefringence can be noticed.

The ionic liquid crystals studied are crystalline at room temperature, as indicated in Table 1. However, it was found that shearing the crystalline sample between microscope slides induces liquid crystalline behaviour at room temperature. Using this procedure, mosaic textures could be observed in the case of compound 1a (Figure 4a) and banded focal conics were found for compound 1b (Figure 4b). Both these textures are characteristic of lamellar phases ordered within the layers. The fluid character of the observed phases is immediately confirmed by shifting the cover glass over the microscope slide and observing the displacement of the defects thus induced. The resulting mesophases are stable at least at the time-scale corresponding to experimental procedure: at rest, the microscope preparation shows the same appearance for several days.

Motivated by this observation, controlled experimental conditions were established in order to

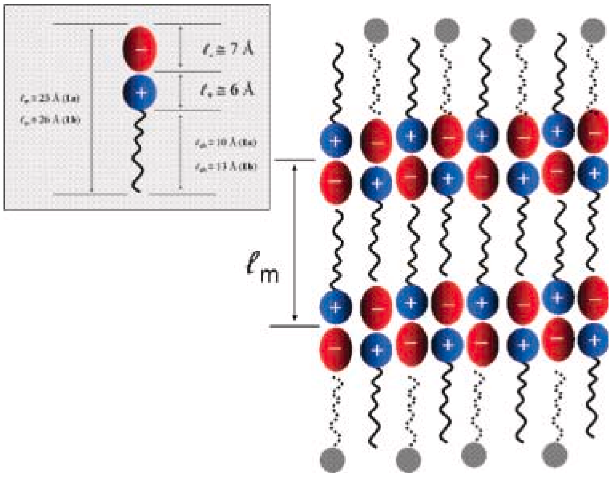

Figure 3. The molecular arrangement within lamellar phases of compounds **1a** and **1b**. Inset: Dimensions of molecular segments estimated from simulation.

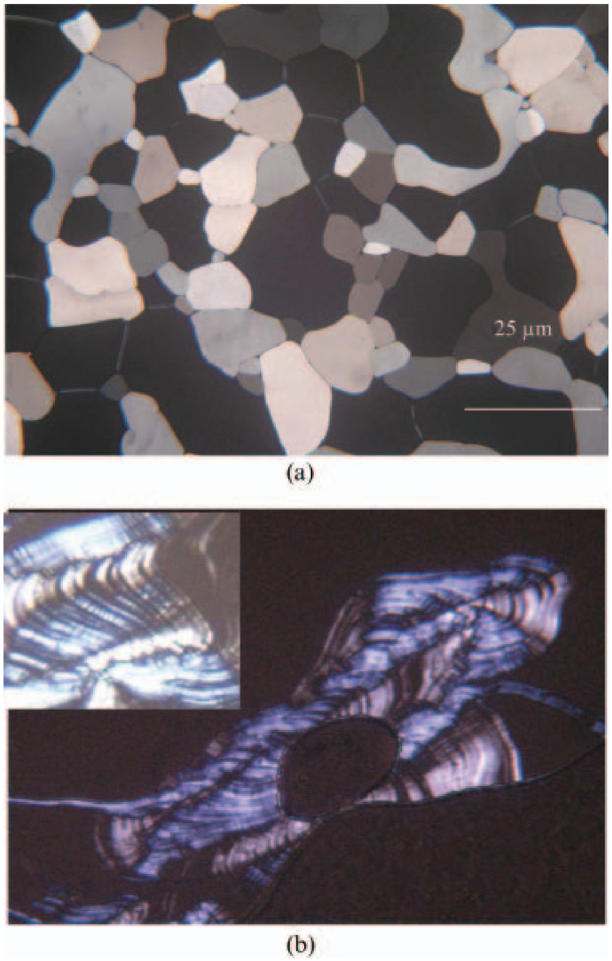

Figure 4. Polarised light micrograph textures (between cross polarisers) of shear induced mesophases obtained at room temperature. Mosaic texture observed for compound **1a** (a) and banded focal conics texture observed for compound **1b** (b).

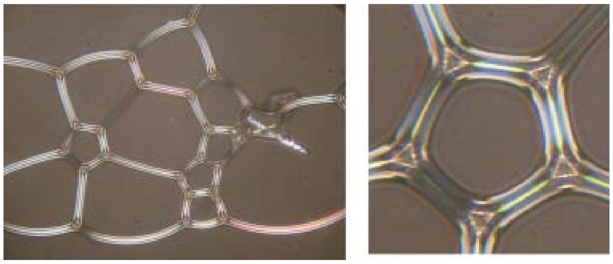

Figure 5. Detail of wet foam patterns observed after shearing, shear rate ~5×10^2 s^{-1} of a previously prepared homeotropic aligned LC sample of compound **1a**.

highlight the liquid-crystalline character induced by shear at room temperature. For this purpose films were prepared from isotropic solutions of compounds **1a** and **1b** in acetone.

The films resulting after acetone evaporation were observed by POM. A dark field, characteristic of a homeotropic texture, is obtained between cross polarizers, which is a general feature of ionic liquid crystals as described above. By shearing these films at room temperature, a network of moving defects can be observed, as shown in Figure 5.

The dynamics of these structures is dependent upon shear rate and the compound under observation. After shearing the films (shear rate$=5 \times 10^2$ s^{-1}), the evolution of these patterns was recorded and images were taken every two minutes (Figure 6). These images correspond to a morphology that is typical of (wet) liquid foams: they partition into dark domains separated by brighter (birefringent) walls that are approximately arcs of circle and meet at "Plateau borders" with three or more sides. Where walls meet three at a time, they do so at approximately 120° angles. These patterns coarsen with time, both T1 and T2 processes having been observed, as in foams. The time evolution of domains is also consistent with von Neumann's law (*13*): domains with fewer than six sides shrink and disappear, whereas those with six or more sides either remain roughly unchanged, or increase in area, as shown in Figure 6. We conjecture that the bright walls are regions of high concentration of defects produced by shear, and that the system is dominated by the interfacial tension between these walls and the uniform domains.

4. Conclusions

The main conclusion of these preliminary results on *N*-alkylimidazolium salt ionic liquid crystals is the ability of the system to generate a lamellar mesophase at room temperature induced by shearing. The mechanism responsible for this result may be associated with the particular structure of crystalline

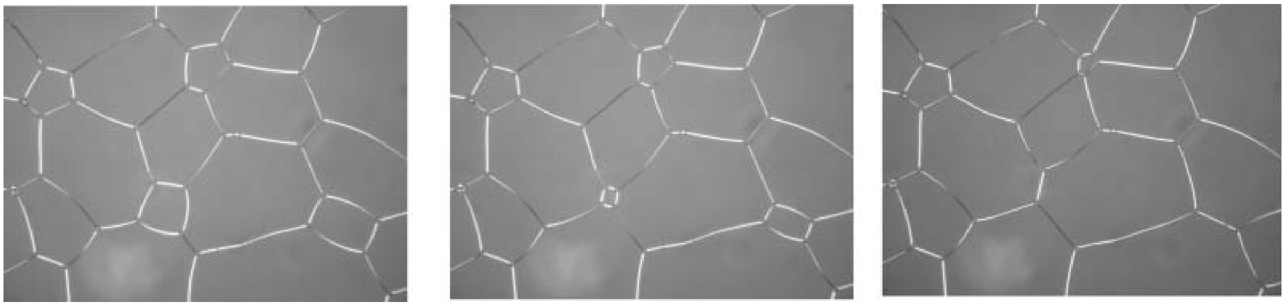

Figure 6. Time evolution of the morphology of a sheared film of lamellar ionic mesogen. Images were taken every two minutes.

phase exhibited by the ionic compound at room temperature. The remarkably high relative intensity of the peak corresponding to a 001 reflection in the XRD pattern of the crystalline phase is typical of a lamellar crystal. The fact that the periodicity associated with the 001 reflection in the crystal match the layer thickness of the liquid crystalline lamellar phase indicates that the crystal phase structure is to some extent similar to that observed for the mesophase. This means that a microsegregated structure consisting of ionic and aliphatic sublayers is most certainly also present in the crystal phase. In this phase structure, the stability of the ionic sublayer is assured by strong electrostatic interactions whilst the aliphatic sublayer arrangement is maintained by quite weaker van der Waals and hydrogen bonding interactions. It is thus reasonable to assume that the weaker interactions associated with the aliphatic sublayer are (at least partially) disrupted by the shearing process while the ionic sublayer is not significantly affected. The shearing, which may occur at room temperature, will thus give rise to a lamellar liquid crystalline phase. This process is favoured by the tendency of the ionic sublayer to be kept parallel to the glass substrate. The present results do not exclude the influence to some extent of the presence of water molecules due to the hygroscopic character of the material. This fact, combined with the large surface/volume ratio involved in the preparation of the films, may also explain the formation of the observed wet foam structure. All these observations indicate the possibility of the amphitropic (*14*) character of these systems, which is the object of further investigation.

Acknowledgments

We would like to thank Fundação para a Ciência e Tecnologia (POCI 2010) and FEDER for the financial support (Ref. POCI/QUI/57735/2004, Ref. POCI/CTM/56382/2004, PTDC/FIS/65037/2006 and Ref. SFRH/BPD/14848/2003).

References

(1) Mukai T.; Yoshio M.; Kato T.; Yoshizawa M.; Ohno H. *Chem. Commun.* **2005**, 1333–1335, Martín-Rapún, R.; Marcos, M.; Omenat, A.; Barberá, J.; Romero, P.; Serrano, J.L. *J. Am. chem. Soc.* **2005,** *127,* 7397–7403; Branco, L.C.; Rosa, J.N.; Moura Ramos, J.J.; Afonso, C.A.M. *Chem. Eur. J.* **2002,** *8,* 3671–3677.

(2) Cruz C.; Heinrich B.; Ribeiro A.C.; Bruce D.W.; Guillon D. *Liq. Cryst.* **2000**, *27*, 1625–1631.

(3) Binnemans K. *Chem. Rev.* **2005**, *105*, 4148–4204 and references therein.

(4) Yoshio M.; Kagata T.; Hoshino K.; Mukai T.; Ohono H.; Kato T. *J. Am. chem. Soc.* **2006**, *128*, 5570–5577.

(5) Yoshio M.; Mukai T.; Ohono H.; Kato T. *J. Am. chem. Soc.* **2004**, *126*, 994–995.

(6) Chiou J.Y.Z.; Chen J.N.; Lei J.S.; Lin I.J.B. *J. Mater. Chem.* **2006**, *16*, 2972–2977.

(7) Yoshio M.; Mukai T.; Kanie K.; Yoshizawa M.; Ohono H.; Kato T. *Adv. Mater.* **2002**, *14*, 351–354.

(8) Lee C.K.; Huang H.W.; Lin J.B. *Chem. Commun.* **2000**, 1911–1912.

(9) Lee K.-M.; Lee Y.-T.; Lin I.J.B. *J. Mater. Chem.* **2003**, *13*, 1079–1084.

(10) Dobbs W.; Douce L.; Allouche L.; Louati A.; Malbosc F.; Welter R. *New J. Chem.* **2006**, *30*, 528–532.

(11) Pal S.K.; Kumar S. *Tetrahedron Lett.* **2006**, *47*, 8993.

(12) *Chem3D*, version 3.1.1. CambridgeSoft Corp: 2000.

(13) Weaire D.; Hutzler S. *The Physics of Foams*; Oxford University Press: Oxford, 1999.

(14) Gowda G.A.N.; Chen H.; Khetrapal C.L.; Weiss R.G. *Chem. Mater.* **2004**, *16*, 2101–2106.