

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry



journal homepage: www.elsevier.com/locate/fluor

Synthesis, characterization and surface wettability of polythiophene derivatives containing semi-fluorinated liquid-crystalline segment

Thierry Darmanin, Elisabeth Taffin de Givenchy, Sonia Amigoni, Frédéric Guittard *

Université de Nice – Sophia Antipolis, Laboratoire Chimie des Matériaux Organiques et Métalliques, Equipe chimie organique aux interfaces, Parc Valrose, 06108 Nice Cedex 2, France

ARTICLE INFO

Article history: Received 15 January 2011 Received in revised form 20 April 2011 Accepted 25 April 2011 Available online 6 May 2011

Keywords: Liquid crystal Superhydrophobic Wettability Electrodeposition Conductive polymers

ABSTRACT

In the scope of increasing our knowledge on the elaboration of smart surfaces, the aim of this work was to synthesize monomers as starting materials for the polymerization or copolymerization via electrochemical route. We report the synthesis and characterization of original structures containing a single phenyl unit bound, on one side, to a semi-fluorinated tail via a thioester connector and, on the other side, to a thiophene moiety. This design approach using cheap raw materials (a single phenyl ring as mesogenic core) associated to an electropolymerizable unit is of great interest in the development of liquid crystal low cost materials to build-up non-wetting surfaces based on the fluorophobic effect. The mesomorphic properties were characterized using differential scanning calorimetry and optical polarizing microscopy. The effect of the length of the fluorinated tail induced the formation of a smectic enantiotropic mesophase for *F*-hexyl and *F*-octyl tails. The polymerization of the films was performed in solution of sodium perchlorate in acetonitrile. Hydrophobic surfaces were obtained from the monomers containing a *F*-bexyl and *F*-octyl tail, while superhydrophobic surfaces (contact angle of water of 158°) were reached from the monomer containing a *F*-bexyl tail.

© 2011 Elsevier B.V. All rights reserved.

1. Research topics

Our main research prospects concern the conception and development of new active surfaces like superhydrophobic and superoleophobic, on one hand, or bioactive surfaces as for example biocides or biocidal surfaces, on the other hand. Our specific understanding on highly fluorinated compounds chemistry allows us to induce new molecular organisation and structuration by tuning their skeleton. Our results in the field of molecular design allow, for example, the creation of brain like giant vesicles with high specific surfaces by the assembly of hybrid fluorocarbon/ hydrocarbon surfactants, the particular liquid crystal orientation induced by the combination of a mesogenic group and a perfluorinated chain in solution as well as in polymer coatings, the increase of biocidal properties of highly fluorinated surfactants or polymers. Our most important hot success was induced by this knowledge that showed us the way to the extraordinary production of superhydrophobic as well as superoleophobic surfaces by the electropolymerization of perfluorinated monomers and/or hydrocarbon homologues. These monomers, depending on their structures, are able to create special building at the surface during the polymerization stage and the divergence of just, for exemple, one methylene unit can induce huge effects on the surface, changing it from super hydrophobic to superhydrophobic and superoleophobic properties. If our Group is developing strategies for fluorinated material, one of our strategy is also to find alternatives of fluorine by the development of biomimetic surfaces.

2. Introduction

Fluorinated compounds are used in a wide domain of applications such as the development of anti-wetting surfaces [1,2], surfactants [3,4], vesicles [5,6], liquid-crystals [7-8], coating of nanoparticles [9–10], dendrimers [11–12], membranes [13–14] or for their barrier [15] or antireflective properties [16]. In antiwetting surfaces for example, the introduction of highly fluorinated compounds is a general approach which confers to the resulting material a low surface energy [17,18]. The introduction of a physical parameter, such as surface structuration, in hydrophobic materials can be sufficient to switch from hydrophobic/oleophobic surfaces to superhydrophobic/superoleophobic surfaces (contact angles above 150°) [19,20]. Previously, our group showed that the electropolymerization of fluorinated monomers such as thiophene and pyrrole derivatives (some examples are given in Fig. monomers CX), often leads to micro/nanostructured surfaces displaying exceptional anti-water properties (superhydrophobic) and sometimes anti-oil properties (superoleophobic) [21,22].

Recently, we have demonstrated in fluorinated polyacrylate films that the introduction of a mesogenic core between the fluorinated

^{*} Corresponding author. *E-mail address:* guittard@unice.fr (F. Guittard).

^{0022-1139/\$ -} see front matter © 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.jfluchem.2011.04.014



Fig. 1. Previously reported (A, B, CX, DX for X = NH) and investigated (DX for X = S) monomers.

chains and the polyacrylate backbone (Fig. 1 monomers B) can also modulate the surface mobility and the dynamic anti-wetting properties [23].

For the construction of electropolymerized materials, a mesogenic core can also be introduced between the semi-fluorinated chains and the polymer backbone to modulate the surface properties. Very recently, by comparing the surface properties of polypyrroles bearing fluorinated segments (Fig. 1 monomers CX for X = NH) and polypyrroles bearing fluorinated liquid crystalline segments (Fig. 1 monomers DX for X = NH), we showed that a mesogenic part can modulate the surface properties but also modify the surface morphology [24].

Using this process, the surface morphology and wettability of the electrodeposited films are highly depending on the polymerizable core (pyrrole, thiophene, fluorene, etc.). Hence, to study the influence of the polymerizable core, here, we reported the synthesis, characterization and polymerizability of analogues containing the same liquid crystalline segment than previously (Fig. 1 monomers DX for X = NH) linked to a thiophene heterocycle as polymerizable unit (Fig. 1 monomers DX for X = S).

3. Experimental

3.1. Techniques and materials

All chemical products were purchased from Sigma-Aldrich. The retention time (r.t.) of the compounds were determined with a 5890 series II gas chromatography from Hewlett Packard equipped with a capillary column HP5 (30 m, 0.32 mm) and with this following programming: heating from 60 °C to 250 °C at 10 °C min⁻¹ and 30 min at 250 °C. The onset temperatures and the enthalpies of transition of the monomers were investigated with a Jade DSC of PerkinElmer at a rate of 10 °C min⁻¹. The polarizing optical microscopy (POM) images were obtained with an Olympus BX60 microscope. Electrochemical experiments were performed with an Autolab PGSTAT 30 potentiostat from Eco Chemie B.V. equipped with General Purpose Electrochemical System (GPES) software. A three-electrode cell was used with a platinum disk working electrode, a glassy carbon rod counterelectrode and a saturated calomel reference electrode (SCE). The electrochemical polymerization of these monomers was performed in anhydrous acetonitrile solutions containing 0.01 M of the monomer and 0.1 M of tetrabutylammonium hexafluorophosphate or sodium perchlorate (electrochemical grade). The solutions were degassed with argon before each experiment.

3.2. Synthesis of 4-(2-F-alkylethylthio)carbonyl)phenyl 2-(thiophen-3-yl)acetate (DS_n)

2-*F*-alkylethyl 4-hydroxythiobenzoate was synthesized in three steps following a synthesis procedure previously reported [20–22]. Dicyclohexylcarbodiimide (DCC) (1.07 g, 5.2 mmol) was added to a solution of 3-thiopheneacetic acid (0.74 g, 5.2 mmol) in dichlor-omethane. After stirring during 30 min at 50 °C, 2-*F*-alkylethyl 4-hydroxythiobenzoate (5.2 mmol) was added. After a day, the solvent was removed and the crude was purified by column chromatography (silica gel; eluent: dichloromethane) to yield the products as white solids.

DS4. Yield 61%. r.t. 21.9 mn. 250 MHz ¹H NMR (CDCl₃): δ 2.49 (tt, 2H, ${}^{3}J_{HH} = 7.8$ Hz, ${}^{3}J_{HF} = 18.2$ Hz), 3.28 (t, 2H, ${}^{3}J_{HH} = 7.8$ Hz), 3.93 (s, 2H), 7.13 (dd, 2H, ${}^{3}J_{HH} = 4.9$ Hz, ${}^{4}J_{HH} = 1.3$ Hz), 7.20 (d, 2H, ${}^{3}J_{HH} = 8.7$ Hz), 7.27 (m, 1H), 7.35 (dd, 2H, ${}^{3}J_{HH} = 4.9$ Hz, ${}^{4}J_{HH} = 2.9$ Hz), 7.98 (d, 2H, ${}^{3}J_{HH} = 8.7$ Hz). 50 MHz 13 C NMR (CDCl₃): δ 20.14 (t, ${}^{3}J_{CF} = 4.8$ Hz), 31.62 (t, ${}^{2}J_{CF} = 21.8$ Hz), 35.87, 121.87, 123.41, 126.19, 128.27, 128.83, 132.35, 134.02, 154.86, 168.84 (OC = 0), 189.61 (SC = 0). ¹⁹F NMR (CDCl₃): δ -126.45 (m, 2F), -124.77 (m, 2F), -115.17 (m, 2F), -81.42 (m, 3F). IR ν_{max} (cm⁻¹): 3105, 2942, 1759 (OC = 0), 1664 (SC = 0), 1596, 1500, 1238, 1215, 1130 cm⁻¹. MS (70 eV, *m/z*): 524 (M⁺, 1%), 245 (C₁₃H₉O₃S⁺, 100%), 121 (C₇H₅O₂⁺, 97%), 97 (C₅H₅S⁺, 95%).

DS₆. Yield 35%. r.t. 23.1 mn. 250 MHz ¹H NMR (CDCl₃): δ 2.49 (tt, 2H, ³*J*_{HH} = 7.8 Hz, ³*J*_{HF} = 18.2 Hz), 3.28 (t, 2H, ³*J*_{HH} = 7.8 Hz), 3.93 (s, 2H), 7.13 (dd, 2H, ³*J*_{HH} = 4.9 Hz, ⁴*J*_{HH} = 1.3 Hz), 7.20 (d, 2H, ³*J*_{HH} = 8.7 Hz), 7.27 (m, 1H), 7.35 (dd, 2H, ³*J*_{HH} = 4.9 Hz, ⁴*J*_{HH} = 2.9 Hz), 7.98 (d, 2H, ³*J*_{HH} = 8.7 Hz). 50 MHz ¹³C NMR (CDCl₃): δ 20.17 (t, ³*J*_{CF} = 4.8 Hz), 31.71 (t, ²*J*_{CF} = 21.8 Hz), 35.87, 121.88, 123.41, 126.19, 128.28, 128.83, 132.35, 134.03, 154.86, 168.85 (OC = 0), 189.61 (SC = 0). ¹⁹F NMR (CDCl₃): δ –126.57 (m, 2F), –123.82 (m, 2F), –123.29 (m, 2F), –122.32 (m, 2F), –114.94 (m, 2F), –81.19 (m, 3F). IR ν_{max} (cm⁻¹): 3092, 2948, 1755 (OC = 0), 1657 (SC = 0), 1599, 1500, 1238, 1212, 1144 cm⁻¹. MS (70 eV, *m/z*): 624 (M⁺, 1%), 245 (C₁₃H₉O₃S⁺, 68%), 121 (C₇H₅O₂⁺, 100%), 97 (C₅H₅S⁺, 87%).

DS₈. Yield 38%. r.t. 25.1 mn. 250 MHz ¹H NMR (CDCl₃): δ 2.49 (tt, 2H, ${}^{3}J_{HH}$ = 7.8 Hz, ${}^{3}J_{HF}$ = 18.2 Hz), 3.28 (t, 2H, ${}^{3}J_{HH}$ = 7.8 Hz), 3.93 (s, 2H), 7.13 (dd, 2H, ${}^{3}J_{HH}$ = 4.9 Hz, ${}^{4}J_{HH}$ = 1.3 Hz), 7.20 (d, 2H, ${}^{3}J_{HH}$ = 8.7 Hz), 7.27 (m, 1H), 7.35 (dd, 2H, ${}^{3}J_{HH}$ = 4.9 Hz, ${}^{4}J_{HH}$ = 2.9 Hz), 7.98 (d, 2H, ${}^{3}J_{HH}$ = 8.7 Hz). 50 MHz 13 C NMR (CDCl₃): δ 20.17 (t, ${}^{3}J_{CF}$ = 4.8 Hz), 31.72 (t, ${}^{2}J_{CF}$ = 21.8 Hz), 35.87, 121.87, 123.41, 126.19, 128.28, 128.83, 132.35, 134.03, 154.86, 168.85 (OC = O), 189.61 (SC = O). ¹⁹F NMR (CDCl₃): δ -126.53 (m, 2F), -123.76 (m, 2F), -123.13 (m, 2F), -122.29 (m, 6F), -114.91 (m, 2F), -81.16 (m, 3F). IR ν_{max} (cm⁻¹): 3092, 2948, 1755 (OC = O),



Fig. 2. Reaction pathway for the synthesis of DS_{4-8} (n = 4, 6 and 8).

1657 (SC = O), 1599, 1497, 1242, 1208, 1147 cm⁻¹. MS (70 eV, m/z): 724 (M⁺, 1%), 245 (C₁₃H₉O₃S⁺, 82%), 121 (C₇H₅O₂⁺, 100%), 97 (C₅H₅S⁺, 75%).

4. Synthesis and discussion

The studied monomers DS_n incorporating a liquid-crystal segment, which consists in a rigid single phenyl group bound to a pro-mesogenic fluorinated tail (which can induce liquid crystal behaviour by phase microsegregation) by a thioester connector, were prepared following the chemical pathway represented in Fig. 2. The ability to have LC behaviour with a single phenyl unit is based on microphasic separation from fluorophobic effect [25,26]. This is remarkable because such behaviour would not be expected for hydrocarbon series without additional hydrogen bonding. The choice of a thioester connector (structure C) is related to previous work showing its ability to form LC properties over a wide range [27]. So, to synthesize structure **DS**_n, the first step is the protection of the acid function of 4-hydroxybenzoic acid with methyl chloroformate. The reaction proceeds in an aqueous solution of sodium hydroxide and during 18 h at -7 °C. The obtained product was coupled with 2-F-alkylethanethiol using dicyclohexylcarbodiimide (DCC) in dichloromethane. After purification on a silica-gel column, the hydroxyl function was released with a mixture of ammonium hydroxide, dichloromethane and ethanol (1:1:1). Afterwards, the incorporation of the LC segment on the thiophene backbone was performed from commercially available 3-thiopheneacetic acid and via an esterification reaction with DCC as coupling agent in dichloromethane. After purification by column chromatography, the monomers DS₄₋₈ were obtained as white powders and in 35-61% isolated yields.

5. Mesomorphic behaviour

The phase behaviour of these original fluorinated monomers was studied by combining differential scanning calorimetry (DSC) and optical polarizing microscopy. The phase transition temperatures and enthalpies of the monomers are gathered in Table 1. These observations revealed an enantiotropic behaviour dependent on the fluorinated tail length. The presence of a mesomorphic behaviour was detected for the monomers DS_6 and DS_8 but no evidence of mesomorphism was detected for DS_4 . Indeed, the higher mobility of the *F*-butyl tail [28] can, in this case, destabilize the arrangement of the molecules, which has a high influence on the liquid crystal behaviour. An example of a DSC curve obtained

 Table 1

 Phase transition temperatures and enthalpies obtained for the monomers on heating.

Compound	п	Yield, %	Transition temperatures (onset), °C				
			Cr		Sm		Ι
DS ₄	4	61	•	41.6 [48.98] ^a			
DS ₆	6	35	•	59.3 [32.58]	•	63.2 [2.20]	•
DS ₈	8	38	•	90.5 [26.21]	•	98.9 [2.60]	٠

^a Figures in square brackets denote enthalpies of transition (J/g).



Length of the *F*-alkyl tail

Fig. 4. Phase diagram for the monomers as a function of the fluorinated chain length.



Fig. 5. Optical polarizing micrograph of DS_8 (×66): T = 96 °C on cooling.

Table 2



Fig. 6. Cyclic voltammogram of DS₄ in Bu₄NPF₆/MeCN: 1 scan.

for **DS**₈ on heating and on cooling is given in Fig. 3. It follows from Fig. 4 that the mesophase range and the transition temperatures (both melting and clearing temperatures) increase with the *F*-alkyl tail length. The mesophase range of **DS**₈ was about 10 °C during the heating or the cooling and a decrease of about 5 °C was observed for a diminution of the *F*-alkyl tail length of two fluoromethylene units. The transition temperatures and mesophase ranges of the thiophene derivatives were much lower than the previously reported pyrrole analogues [24], which was probably due to the presence of hydrogen bonding with the hydrogen bound by the nitrogen of pyrrole and the oxygen of the carbon groups.

By optical microscopic observation and on cooling from isotropic melt, the mesophases of DS_8 and DS_6 appeared as rods and after coalescence gave rise to fan-shaped textures with focal-conic domains (Fig. 5), which are characteristic of smectic mesophases.

Compound	Static contact angles, $^{\circ}$				
	Water	Diiodomethane	Hexadecane		
PolyDS ₄	158.0	131.4	84.2		
PolyDS ₆	115.0	101.1	72.4		
PolyDS ₈	113.9	94.1	72.2		

6. Polymerizability study

The study of the polymerizability of the monomers was performed in anhydrous acetonitrile and tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) (0.1 M). After determination of the oxidation potential of the monomers (Fig. 6) by single voltammetric scan ($E_{peak,m}^{ox} = 2.23 \text{ V}$ vs SCE for **DS**₄ and 2.24 V for **DS**₆ and **DS**₈), the polymerizability of the monomers were studied by consecutive voltammetric scan from -1 V and until a potential slightly lower than $E_{peak,m}^{ox}$. The polymer electrodeposits if oxidation and reductions peaks of the electroactive polymer appear before $E_{peak,m}^{ox}$ and with intensities increasing at each scan. However, no redox system was observed for the three monomers contrary to the previously reported pyrrole analogues [24]. Other experiments were also performed by imposed potential on gold substrates but no films were also obtained with this condition. These molecules did not give electrodeposited films probably because of the high spatial volume of the substituents and the high oxidation potential of thiophene in comparison to that of pyrrole.

To form electrodeposited films with that series, Bu_4NPF_6 was replaced by sodium perchlorate, a more powerful salt for the electrodeposition. With that salt, polymer films were obtained by imposed potential with the three monomers but a high decrease of



Fig. 7. SEM images of $polyDS_4$ with a magnification of (A) ×2500 and (B) ×10,000, $polyDS_6$ with a magnification of (C) ×10,000 and $polyDS_8$ with a magnification of (D) ×10,000.

the conductivity of the film with the deposition time was observed for DS_8 and DS_6 . Hence, the deposition speed was higher with DS_4 .

7. Surface characterization

The polymer films were characterized by contact angle measurements. Surprisingly, superhydrophobic films with static contact angle of water (CA_{water}) of 158° were obtained with the monomer containing the shortest fluorinated chains (**DS**₄), as shown in Table 2. Using the tilted-drop method, water droplets did not roll off the surfaces after inclination, which means that the surfaces were sticky. Hence, these surfaces were more hydrophobic than that previously obtained from pyrrole analogues [24]. In contrast, polyDS₆ and polyDS₈ were only hydrophobic with quite the same value for the two polymers ($CA_{water} \approx 114-115^{\circ}$). The static contact angles of diiodomethane and hexadecane were also higher for polyDS₄. The very high contact of polyDS₄ being probably due to surface morphology, the polymer was analyzed by scanning electron microscopy (SEM).

SEM images of the polymer are given in Fig. 7. On one hand, polyDS₄ was extremely structured and the surface morphology consisted in an assembly of sub-micronic needles (Fig. 7A and B), which confirms their exceptional surface anti-wetting properties. On the other hand, polyDS₆ surfaces were composed of wellordered (in two dimensions) nanoparticles (Fig. 7C) and polyDS₈ was relatively smooth (Fig. 7D). The low roughness of these two films explains their low anti-wetting properties.

8. Conclusion

We have reported the synthesis of a series of monomers bearing a single phenyl unit as mesogenic group between the heterocyclic core (thiophene) and the highly fluorinated tail with four, six or eight fluoromethylene units (DS_4 , DS_6 , DS_8). These compounds exhibited a liquid crystal behaviour of smectic A type which can be used to avoid or limit the surface reconstructions of the corresponding polymers in the presence of polar media. Polymer films were obtained using sodium perchlorate as salt for the electrodeposition. Superhydrophobic films with static contact angle of 158° were obtained from the monomer containing a *F*-butyl chain. The surface morphology of these films consisted in an assembly of sub-micronic needles.

References

- (a) T. Hayakawa, J. Wang, M. Xiang, X. Li, M. Ueda, C.K. Ober, J. Genzer, E. Sivaniah, E.J. Kramer, D.A. Fisher, Macromolecules 33 (2000) 8012–8019;
 (b) M. Xiang, X. Li, C.K. Ober, K. Char, J. Genzer, E. Sivaniah, E.J. Kramer, D.A. Fisher,
- Macromolecules 33 (2000) 6106–6119. [2] K. Grundke, D. Pospiech, W. Kolling, F. Simon, A. Janke, Colloid Polym. Sci. 279
- (2001) 727–735. [3] (a) M. Oumar, E. Taffin de Givenchy, S.Y. Dieng, S. Amigoni, F. Guittard, Langmuir
- 27 (2011) 1668–1674; (b) P. Thebault, E. Taffin de Givenchy, R. Levy, Y. Vandenberghe, S. Géribaldi, F.
- Guittard, J. Fluorine Chem. 131 (2010) 592–596.

- [4] (a) L. Li, Z.S. Xu, G.W. Song, J. Fluorine Chem. 130 (2009) 225–230;
 (b) P. Raychaudhuri, Q. Li, A. Mason, E. Mikhailova, A.J. Heron, H. Bayley, Bio-
- chemistry 50 (2011) 1599–1606. [5] G. Martini, M. Balzi, A. Becciolini, S. Ristori, S. Rossi, J. Fluorine Chem. 125 (2004)
- 253–259. [6] (a) Z. Hu, W. Verheijen, J. Hofkens, A.M. Jonas, J.-F. Gohy, Langmuir 23 (2007)
- 116–122; (b) A. González-Pérez, M. Schmutz, G. Waton, M.J. Romero, M.P. Krafft, J. Am.
- Chem. Soc. 129 (2007) 756–757.
 [7] M. Ragnoli, E. Pucci, M. Bertolucci, B. Gallot, G. Galli, J. Fluorine Chem. 125 (2004) 283–292.
- [8] (a) M. Al-Hussein, Y. Séréro, O. Konovalov, A. Mourran, M. Möller, W.H. de Jeu, Macromolecules 38 (2005) 9610–9616;
- (b) K. Zimny, J.L. Blin, M.J. Stébé, J. Phys. Chem. C 113 (2009) 11285-11293.
- [9] (a) H. Sawada, T. Narumi, M. Kiyohara, M. Baba, J. Fluorine Chem. 128 (2007) 1416–1420;
- (b) H. Skaat, G. Belfort, S. Margel, Nanotechnology 20 (2009) 225106.
- [10] (a) C. Gentilini, F. Evangelista, P. Rudolf, P. Franchi, M. Lucarini, L. Pasquato, J. Am. Chem. Soc. 130 (2008) 15678–15682;
- (b) M. Mugisawa, H. Sawada, Langmuir 24 (2008) 9215-9218.
- [11] (a) Z.-X. Jiang, Y.B. Yu, J. Org. Chem. 75 (2010) 2044–2049;
 (b) H. Yoshioka, M. Suzuki, M. Mugisawa, N. Naitoh, H. Sawada, J. Colloid Interface Sci. 308 (2007) 4–10.
- [12] (a) A.-M. Caminade, C.-O. Turrin, P. Sutra, J.-P. Majoral, Curr. Opin. Colloid Interface Sci. 8 (2003) 282–295;
- (b) W.R. Glomm, M.-H. Glomm Ese, S. Volden, C. Pitois, A. Hult, J. Sjöblom, Colloids Surf. A 299 (2007) 186–197.
- (a) R. Tayouo, G. David, B. Améduri, J. Rozière, S. Roualdès, Macromolecules 43 (2010) 5269–5276;
 (b) A. Gurdinger, M. Aseta, G. Simona, E. Currie, P. Madanga, G. Di Parfa, F. Prieli,

(b) A. Gugliuzza, M. Aceto, S. Simone, E. Curcio, R. Madonna, G. Di Profio, E. Drioli, Desalination 199 (2006) 200–203.

[14] (a) N. Idupulapati, R. Devanathan, M. Dupuis, J. Phys. Chem. B 115 (2011) 2959–2969;

(b) M. Ramanathan, H.-J. Müller, H. Möhwald, R. Krastev, Appl. Mater. Interfaces 3 (2011) 633–637.

- [15] (a) R.D. Weinstein, J. Moriarty, E. Cushnie, R. Colorado Jr., T.R. Lee, M. Patel, W.R. Alesi, G.K. Jennings, J. Phys. Chem. B 107 (2003) 11626–11632.
- [16] (a) G. Schottner, Chem. Mater. 13 (2001) 3422-3435;
- (b) J.-W. Ha, I.J. Park, S.-B. Lee, Macromolecules 41 (2008) 8800–8806.
 [17] R.R. Thomas, in: G. Hougham, P.E. Cassidy, K. Johns, T. Davidson (Eds.), Fluor-opolymers 2, Kluwer Academic/Plenum Publishers, New York, 1999.
- [18] R.E. Banks, J.C. Tatlow, in: R.E. Banks, B.E. Smart, J.G. Tatlow (Eds.), Organofluorine Chemistry, Plenum Press, New York, 1994.
- [19] (a) A.B.D. Cassie, S. Baxter, Trans. Faraday Soc. 40 (1944) 546–551;
 (b) S. Baxter, A.B.D. Cassie, J. Text. Ind. 36 (1945) T67–90.
- [20] R.N. Wenzel, Ind. Eng. Chem. 28 (1936) 988–994.
- [21] (a) T. Darmanin, F. Guittard, J. Am. Chem. Soc. 131 (2009) 7928-7933;
 - (b) T. Darmanin, F. Guittard, J. Mater. Chem. 19 (2009) 7130–7136;
 (c) A. Zenerino, T. Darmanin, E. Taffin de Givenchy, S. Amigoni, F. Guittard,
- Langmuir 26 (2010) 13545–13549. [22] (a) T. Darmanin, E. Taffin de Givenchy, S. Amigoni, F. Guittard, Langmuir 26
- (2010) 17596-17602;
 (b) T. Darmanin, F. Guittard, S. Amigoni, E. Taffin de Givenchy, X. Noblin, R. Kofman, F. Celestini, Soft Matter 7 (2011) 1053-1057;
 - (c) T. Darmanin, F. Guittard, Langmuir 25 (2009) 5463-5466.
- [23] L. Caillier, E. Taffin de Givenchy, S. Géribaldi, F. Guittard, J. Mater. Chem. 18 (2008) 5382–5389.
- [24] T. Darmanin, E. Taffin de Givenchy, F. Guittard, Macromolecules 43 (2010) 9365–9370.
- [25] L. Caillier, F. Guittard, E. Taffin de Givenchy, S. Géribaldi, Mol. Cryst. Liq. Cryst. 437 (2005) 1315–1324.
- [26] G. Fornasieri, F. Guittard, S. Géribaldi, Liq. Cryst. 30 (2003) 251-257.
- [27] E. Taffin de Givenchy, F. Guittard, F. Bracon, A. Cambon, Liq. Cryst. 26 (1999) 1163–1170.
- [28] K. Honda, M. Morita, H. Otsuka, A. Takahara, Macromolecules 38 (2005) 5699– 5705.