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

Hydrogen-bonded liquid crystals derived from supramolecular complexes of pyridylated poly(propyleneimine) dendrimers and a cholesterol-based carboxylic acid

Theodoros Felekis[a]; Dimitris Tsiourvas[a]; Leto Tziveleka[a]; Constantinos M. Paleos[a]
[a] Institute of Physical Chemistry, NCSR "Demokritos", Aghia Paraskevi, Attiki, Greece

To cite this Article Felekis, Theodoros , Tsiourvas, Dimitris , Tziveleka, Leto and Paleos, Constantinos M.(2005) 'Hydrogen-bonded liquid crystals derived from supramolecular complexes of pyridylated poly(propyleneimine) dendrimers and a cholesterol-based carboxylic acid', Liquid Crystals, 32: 1, 39 — 43
To link to this Article: DOI: 10.1080/02678290412331320566
URL: http://dx.doi.org/10.1080/02678290412331320566

Liquid Crystals, Vol. 32, No. 1, January 2005, 39–43

Taylor & Francis
Taylor & Francis Group

Hydrogen-bonded liquid crystals derived from supramolecular complexes of pyridylated poly(propyleneimine) dendrimers and a cholesterol-based carboxylic acid

THEODOROS FELEKIS, DIMITRIS TSIOURVAS, LETO TZIVELEKA and CONSTANTINOS M. PALEOS*
Institute of Physical Chemistry, NCSR "Demokritos", 153 10, Aghia Paraskevi, Attiki, Greece

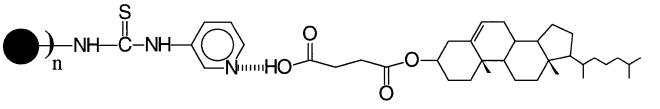
(*Received 26 April 2004; accepted 21 August 2004*)

Diaminobutane poly(propyleneimine) dendrimers of second to fifth generations were functionalized by the introduction of pyridyl moieties at their primary amino groups through their interaction with 3-pyridyl isothiocyanate. These pyridylated diaminobutane poly (propyleneimine) dendrimers were subsequently mixed with 3-cholesteryloxycarbonyl-propanoic acid to form the corresponding hydrogen-bonded supramolecular complexes. The materials obtained exhibit smectic A phases over a relatively broad temperature range from about 60°C to 140°C. Within the smectic layer the cholesteryl moieties are almost orthogonal above and below to the dendrimeric portion of the molecule. On cooling, the materials form liquid crystalline glasses which retain the structural characteristics of the smectic A phase.

1. Introduction

The functionalization of the external groups of dendrimers [1] is a facile and effective strategy [2] for the production of a diversity of novel materials including liquid crystals [3]. The functional groups have primarily been attached covalently at the surface groups of dendrimers, while, to our knowledge, non-covalent synthesis has received limited attention for the preparation of supramolecular complexes based on dendrimers and exhibiting liquid crystalline behaviour [4]. This is rather surprising if one considers the extensive work on hydrogen-bonded liquid crystals performed recently and extensively reviewed [5], which however employed non-dendritic building blocks. For preparing the dendrimeric-based complexes the established strategy of a two-level process was followed: first, the external groups of dendrimers are rendered recognizable by certain molecules, and second, these functional moieties interact with molecules bearing complementary moieties to form the supramolecular complexes.

In the present work pyridyl moieties were first introduced at the external primary amino groups of diaminobutane poly(propyleneimine) dendrimers of second to fifth generation, and subsequently interacted via hydrogen bonding with 3-cholesteryloxycarbonyl-propanoic acid. In this manner, cholesteryl moieties were non-covalently attached at the external surface of the dendrimers. The liquid crystalline behaviour of these supramolecular complexes will be compared with that exhibited by the dendrimeric materials in which the cholesteryl moieties were covalently [6] or ionically [7] attached to the same dendrimeric scaffold. The formation of hydrogen bonds was verified by FTIR spectroscopy while the liquid crystalline behaviour of the hydrogen-bonded systems (shown below) was identified using polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD).



n = 8, 16, 32, 64

2. Experimental

2.1. *Materials*

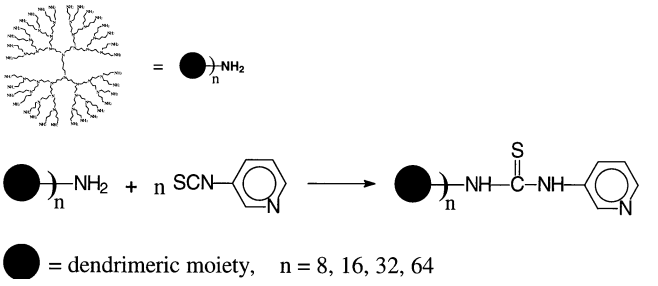
Amine-terminated diaminobutane poly(propyleneimine) dendrimers, DAB-8 to DAB-64, were purchased from DSM Fine Chemicals and used as received, while 3-pyridyl isothiocyanate was obtained from Aldrich. 3-Cholesteryloxycarbonylpropanoic acid was prepared as previously described [7].

*Corresponding author. Email: paleos@chem.demokritos.gr

Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2005 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290412331320566

2.2. *General synthesis of pyridylated poly(propyleneimine) dendrimers*

Diaminobutane poly(propyleneimine) dendrimer of the second to fifth generation (1 mmol dissolved in dichloromethane), was slowly added under argon to a stirred DMF/dichloromethane (6/1 v/v) solution kept at 0°C, containing 3-pyridyl isothiocyanate (15% molar excess relative to the primary amino groups of the dendrimers), as outlined in the scheme. The reaction mixture was allowed to reach room temperature and stirred under inert gas for about 3 days. The solvents were distilled off and the remaining oily residue dissolved in dry DMF and precipitated by acetonitrile. This procedure was repeated twice. The materials obtained, $DABP_n$ where n is the number of dendrimeric end groups, are highly hygroscopic. They were extensively dried under vacuum over phosphorous pentoxide, and their structure was established by elemental analysis and NMR. In addition, HSQC 2D-NMR experiments were employed for the unequivocal assignment of the peaks. The elemental analyses indicated the presence of a number of water molecules in each dendrimeric derivative, almost equal to the number of dendrimer end groups. The complete functionalization of the primary NH_2 groups with the introduction of pyridine moieties was also confirmed by reacting the resulting compounds with fluorescamine, a reagent suitable for the detection of primary amines in the picomole range [8]. It was found that for all the dendrimeric derivatives, at least 99% of the primary amino groups were reacted. ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ=1.33 (broad s, $NCH_2CH_2CH_2CH_2N$), 1.45 (broad s, NCH_2CH_2-CH_2N), 1.64 (m, $NCH_2CH_2CH_2NHCSNH$), 2.1–2.5 (broad s, $NCH_2CH_2CH_2N$), 3.47 (broad s, $NCH_2CH_2CH_2NHCSNH$), 7.3 (m, H_5), 7.9 (m, H_6), 8.0 (broad s, $CH_2NHCSNH$), 8.3 (m, H_4), 8.5 (m, H_2) 9.6 (broad s, $CH_2NHCSNH$). ^{13}C NMR (62.9 MHz, DMSO-d_6, ppm): δ=180.7 ($NHCSNH$), 144.6 (C_4), 144.4 (C_2), 136.2 (C_1), 130.2 (C_6), 123.1 (C_5), 53.3 ($NCH_2CH_2CH_2CH_2N$), 51.3 (NCH_2CH_2-CH_2N), 51.0 ($NCH_2CH_2CH_2NHCSNH$), 42.7 ($NCH_2CH_2CH_2NHCSNH$), 25.7 ($NCH_2CH_2CH_2N$, $NCH_2CH_2CH_2NHCSNH$), 23.4 ($NCH_2CH_2CH_2$-CH_2N). Elemental analysis: $DABP_8$ $6H_2O$: calc. C 53.63, H 7.16, N 21.32; found C 53.62, H 6.85, N 21.48%. $DABP_{16}$ $14H_2O$: calc. C 53.44, H 7.36, N 21.00; found C 53.22, H 7.33, N 21.18%. $DABP_{32}$ $32H_2O$: calc. C 53.46, H 7.45, N 20.89; found C 53.33, H 7.44, N 20.98%. $DABP_{64}$ $64H_2O$: calc. C 53.58, H 7.48, N 20.88; found C 52.92, H 7.44, N 20.61%.



2.3. *Formation of complexes by the interaction of pyridylated poly(propyleneimine) dendrimers with 3-cholesteryloxycarbonylpropanoic acid*

To 1 mmol of pyridylated poly(propyleneimine) dendrimer, $DABP_n$, dissolved in dry DMF, an equimolar quantity (relative to the pyridyl moieties) of 3-cholesteryloxycarbonylpropanoic acid was added. The solvent was distilled off under reduced pressure and the remaining material extensively dried under vacuum affording the DABP-C_n complexes. The structure of the complexes obtained was established by NMR. ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ=0.6–2.5 (m, cholesterol skeleton and dendritic α and β-CH_2), 3.5 (t, $NCH_2CH_2CH_2NHCSNH$), 4.5 (m, $H_{3'a}$), 5.4, (d, $H_{6'a}$), 7.3 (m, H_5), 7.9 (dd, H_6), 8.1 (broad s, $CH_2NHCSNH$), 8.2 (m, H_4), 8.5 (m, H_2) 9.7 (broad s, $CH_2NHCSNH$). ^{13}C NMR (62.9 MHz, DMSO-d_6, ppm): δ=180.7 ($NHCSNH$), 173.4 ($COOH$), 171.4 (COO), 144.6 (C_1), 144.4 (C_4), 139.4 ($C_{5'}$), 136.2 (C_2), 130.1 (C_6), 123.0 (C_5), 122.0 ($C_{6'}$), 73.2 ($C_{3'}$), 56.0 ($C_{14'}$), 55.5 ($C_{17'}$), 51.3 ($NCH_2CH_2CH_2CH_2N$, NCH_2-CH_2CH_2N), 51.0 ($NCH_2CH_2CH_2NHCSNH$), 49.3 ($C_{9'}$), 42.6 ($NCH_2CH_2CH_2NHCSNH$), 41.8 ($C_{13'}$), 37.6 ($C_{4'}$), 36.4 ($C_{1'}$), 36.0 ($C_{10'}$), 35.6 ($C_{22'}$), 35.1 ($C_{20'}$), 31.3 ($C_{7',8'}$), 28.9 (CH_2COOH), 28.7 (CH_2-CH_2COOH), 27.7 ($C_{12'}$), 27.3 ($C_{25'}$), 27.2 ($C_{2'}$), 25.6 ($NCH_2CH_2CH_2N$, $NCH_2CH_2CH_2NHCSNH$), 23.8 ($C_{15'}$), 23.4 ($NCH_2CH_2CH_2CH_2N$), 23.1 ($C_{23'}$), 22.6 ($C_{27'}$), 22.3 ($C_{26'}$), 20.5 ($C_{11'}$), 18.9 ($C_{19'}$), 18.5 ($C_{21'}$), 11.6 ($C_{18'}$).

2.4. *Characterization*

Liquid crystal textures were observed using a Leitz–Wetzlar polarizing microscope equipped with a Linkam hot stage. Thermotropic polymorphism was investigated by DSC employing a DSC-10 calorimeter (TA Instruments) operating under nitrogen at heating and cooling rates of 10°C min^{-1}. Glass transition temperatures were determined during the second heating run, after heating the samples to 120°C. The thermal stability of the functionalized dendrimers was assessed by thermogravimetry employing a TGA-2050 instrument

(TA Instruments) with heating rates of 5°C min^{-1}. Liquid crystalline phases were investigated by XRD using CuK_α radiation from a Rigaku rotating anode X-ray generator (operating at 50 kV, 100 mA) and an R-AXIS IV image plate. Powder samples were sealed in Lindemann capillaries and heated with an INSTEC hot stage. FTIR studies were performed using a Nicolet Magna spectrometer at a resolution of 4 cm^{-1}.

3. Results and discussion

Pyridylated dendrimeric compounds were easily prepared in an one-step reaction under mild experimental conditions. The complete functionalization of the dendrimeric end groups was achieved employing an appropriate mixture of solvents, in which the product remains soluble throughout the reaction. In this manner, the precipitation of partially functionalized derivatives is prevented. The resulting pyridylated dendrimers were obtained in the form of pastes which did not show mesomorphism. Thiourea bond formation was confirmed by the appearance in the ^{1}H NMR spectra of the characteristic peak at 3.5 ppm corresponding to the α-methylene protons adjacent to the thiourea groups, and of two broad peaks at 8.0 and 9.6 ppm attributed to the two NH protons of the thiourea group. This was further established by the disappearance in the ^{13}C NMR spectra of the signals due to the α- and β-methylene carbons relative to the terminal NH_2 groups at 40.05 and 30.83 ppm, respectively, and the concomitant appearance of the signals at 42.7 and 25.64 ppm of the α- and β-methylene carbons relative to the thiourea groups. In addition, the thiourea carbon appeared at 180.7 ppm.

Hydrogen-bonded complexes were obtained by the interaction of cholesteryloxycarbonylpropanoic acid and the pyridylated dendrimers, through slow evaporation of DMF solutions. The formation of hydrogen-bonded complexes was established by infrared spectroscopy. The bands of the acid at 2555 and 2655 cm^{-1} attributed to OH Fermi resonances, due to the presence of the parent acid in the dimeric form, are replaced in the spectra of DABP-C_n by two new bands at 2500 and 2100 cm^{-1} attributed to intermolecular hydrogen bonding between the nitrogen of the pyridine ring and the hydroxyl group of the carboxylic acid [9]. In addition, the carbonyl stretching band of the dimeric acid at 1710 cm^{-1} is replaced in the spectra of the complexes by a new band at 1720 cm^{-1}, partially overlapping the band of the ester carbonyl group at 1732 cm^{-1} (figure 1), due to complexation between the unionized carboxylic acid and the pyridine ring [10].

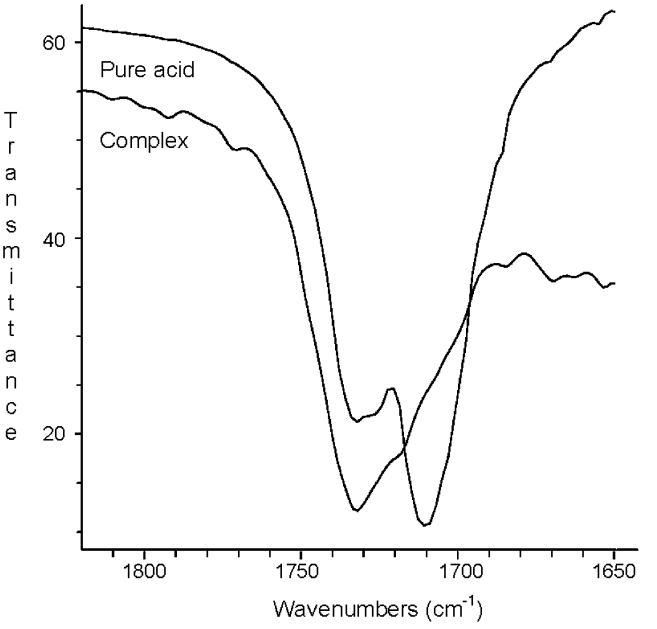


Figure 1. Infrared spectra of the hydrogen-bonded complex DABP-C_{32} and of 3-cholesteryloxycarbonylpropanoic acid at room temperature.

As well as hydrogen bond formation between the pyridylated dendrimer and the cholesteric acid derivative, ionic bonds can, in principle, also be formed due to the protonation of the dendrimer's tertiary amino groups. To investigate this possibility, titration of triethylamine with 3-cholesteryloxycarbonylpropanoic acid was initially performed in DMSO-d_6 and studied by NMR. During the titration, a downfield shift of the α-methylene protons, relative to the tertiary amino groups, was observed at 2.53 ppm, compared with 2.41 ppm for the non-protonated groups. No significant changes were observed for the methylene protons relative to the carboxyl group of the acid. Thus, if protonation was occurring, a downfield shift of the α-methylene protons relative to the tertiary amino groups of the dendrimers would be seen, along with an upfield shift of the respective methylene carbons of the dendrimers and a downfield shift of the respective carbons of the interacting acid in the ^{13}C NMR spectrum, as found in our previous work [7]. However, upon complexation of the pyridylated dendrimers with 3-cholesteryloxycarbonylpropanoic acid, the only difference observed in their ^{1}H NMR spectra compared with the pyridylated dendrimers, was a downfield shift of *c.* 0.1 ppm for the thiourea N–H protons. Nevertheless, it was found that by diluting the pyridylated sample, a similar shift was observed, suggesting that this difference results from a concentration effect, possibly due to interaction of DMSO with

the thiourea groups. Therefore, due to the preferential hydrogen bond formation between the acid and the easily accessible pyridyl moieties, no ionic bonds were formed between the interacting molecules.

The thermogravimetric analyses of the DABP-C_n complexes show a gradual weight loss starting at temperatures above 140°C, thus confirming the thermal stability of the complexes. No significant changes were observed between the various generation derivatives. However, at temperatures exceeding 160°C, the materials degrade rapidly as also observed by optical microscopy.

The complexes are birefringent glasses at room temperature when viewed under the polarizing microscope. At temperatures exceeding about 60°C the compounds become birefringent viscous fluids with ill developed oily-streak textures, and remain anisotropic even after their thermal decomposition. It was not possible therefore to obtain well developed textures. On cooling the samples from temperatures below the onset of decomposition, glassy birefringent phases were observed.

DSC studies show that the dendrimeric complexes exhibit glass transitions at about 55°C with the exception of the lowest generation derivative DAB PC_2, which, as expected, shows this transition at a lower temperature (see table 1). No other phase transitions were observed up to the onset of decomposition.

The XRD patterns of the dendrimeric complexes in the glassy phase contain four equidistant peaks in the low angle region, indicating a lamellar ordering; also two diffuse partially overlapping peaks in the wide angle region centred at 5.45 and 4.45 Å arising from the lateral distance of the cholesteryl moieties and the dendrimeric alkyl repeating units, respectively, in a disordered conformation. In the glassy state, the lamellar periodicity increases slightly with temperature as a result of the thermal expansion of the compounds. At temperatures above T_g, the XRD patterns are essentially unchanged, consisting of three equidistant peaks in the low angle region and two diffuse peaks at 5.5 and 4.6 Å (figure 2). The lamellar spacings decrease slightly but unequivocally with temperature due to the lateral expansion of the cholesteryl and alkyl repeating units, suggesting the presence of a SmA phase. The lamellar spacings obtained (figure 3) are greater than those reported for the dendrimeric derivatives in which the cholesteryl moieties are attached either through ionic forces [7] or covalently [6] by about 8 Å. This is attributed to the presence of the pyridyl moiety. It may

Table 1. Glass transition temperatures of hydrogen-bonded poly(propyleneimine) dendrimeric complexes of second to fifth generations.

Dendrimeric complex	T_g/°C
DABP-C_8	48.9
DABP-C_{16}	56.4
DABP-C_{32}	55.8
DABP-C_{64}	55.3

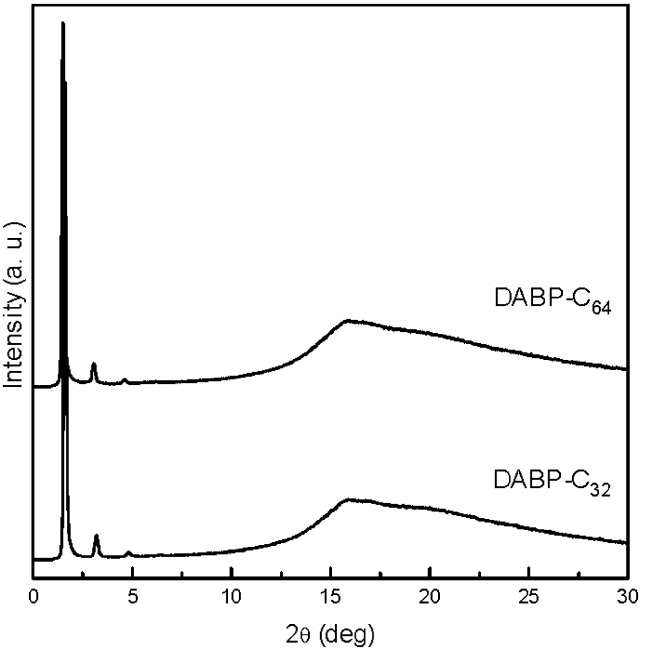


Figure 2. X-ray diffraction patterns of the fourth and fifth generation hydrogen-bonded dendrimeric derivatives in the SmA phase.

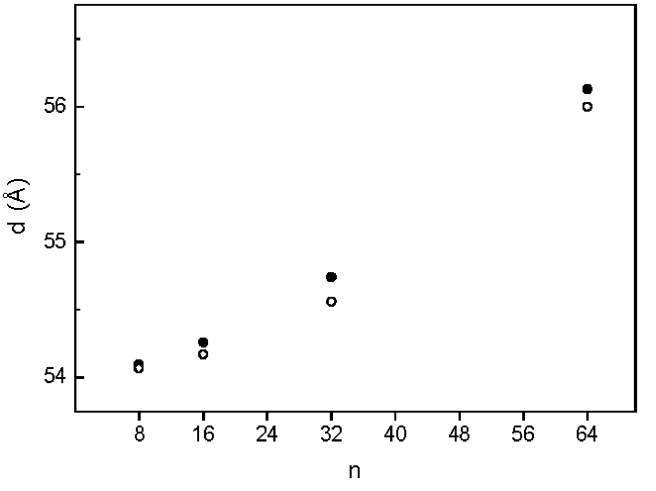


Figure 3. Smectic periodicities of the DABP-C_n compounds in the smectic A phase (100°C, closed circles) and in the glassy smectic A phase obtained on cooling (20°C, open circles) as a function of the number of cholesteryl groups.

be suggested, therefore, by analogy with the *SmA* structure proposed for the poly(propyleneimine) dendrimers covalently functionalized with cholesteryl groups [6], that within each layer the pyridyl–cholesteryl hydrogen-bonded moieties are orthogonal with respect to the dendrimeric scaffold, and occupy the space between them. For space-filling reasons the flexible poly(propyleneimine) moieties [11] are flattened to satisfy the preferentially lamellar ordering of the mesogenic moieties.

Finally, from the X-ray data it may also be concluded that the glassy phase obtained at room temperature has a similar structure to the high temperature SmA phase. The lamellar *d*-spacings at room temperature differ by less than 0.3 Å, while the diffraction patterns are essentially identical to those at 100°C, implying the formation of liquid crystalline glasses.

In summary, the functionalization of the surface end groups of poly(propyleneimine) dendrimers with pyridyl moieties leads to dendrimeric derivatives capable of forming supramolecular hydrogen-bonded complexes by their interaction with 3-cholesteryloxycarbonylpropanoic acid. As a result, liquid crystalline glasses at low temperatures and smectic A phases at temperatures above T_g were obtained. Within each layer the cholesteryl–pyridyl moieties are located above and below the dendrimeric scaffold.

Acknowledgements

This work was partially supported by the 'Excellence in the Research Institutes' Program, Action 3.3.1, co-funded by the Greek Ministry of Development and EU.

References

[1] (*a*) P.R. Dvornic, A. Tomalia. *Macromol. Symp.*, **88**, 123 (1994); (*b*) G.R. Newkome, C.N. Moorefield, F. Vögtle. *Dendritic Molecules. Concepts, Syntheses, Perspectives* (Weinheim: Wiley-VCH) (1996); (*c*) N. Ardoin, D. Astruc. *Bull. Soc. Chim. Fr.*, **132**, 875 (1995); (*d*) F. Zeng, S.C. Zimmerman. *Chem. Rev.*, **97**, 1681 (1997); (*e*) A.W. Bosman, H.M. Janssen, E.W. Meijer. *Chem. Rev.*, **99**, 1665 (1999);(*f*) A.D. Schlüter, J.P. Rabe. *Angew. Chem. int. Ed. Engl.*, **39**, 864 (2000); (*g*) D.C. Tully, J.M.J. Fréchet. *Chem. Commun.*, 1229 (2001).

[2] (*a*) D.K. Smith, F. Diederich. *Chem. Eur. J.*, **4**, 1353 (1998); (*b*) F. Vögtle, S. Gestermann, R. Hesse, H. Schwierz, B. Windisch. *Prog. polym. Sci.*, **25**, 987 (2000).

[3] (*a*) J.H. Cameron, A. Facher, G. Lattermann, S. Diele. *Adv. Mater.*, **9**, 398 (1997); (*b*) R.M. Richardson, S.A. Ponomarenko, N.I. Boiko, V.P. Shibaev. *Liq. Cryst.*, **26**, 101 (1999); (*c*) M.W.P.L. Baars, S.H.M. Söntjens, H.M. Fischer, H.W.I. Peerlings, E.W. Meijer. *Chem. Eur. J.*, **4**, 2456 (1998); (*d*) K. Yonetake, T. Masuko, T. Morishita, K. Suzuki, M. Ueda, R. Nagahata. *Macromolecules*, **32**, 6578 (1999); (*e*) S. Bauer, H. Fischer, H. Ringsdorf. *Angew. Chem. int. Ed. Engl.*, **32**, 1589 (1993); (*f*) V. Percec, G. Johansson, G. Ungar, J. Zhou. *J. Am. chem. Soc.*, **118**, 9855 (1996); (*g*) D.J.P. Yeardley, G. Ungar, V. Percec, M.N. Holerca, G. Johansson. *J. Am. chem. Soc.*, **122**, 1684 (2000); (*h*) D. Tsiourvas, K. Stathopoulou, Z. Sideratou, C.M. Paleos. *Macromolecules*, **35**, 1746 (2002); (*i*) D. Guillon, R. Deschenaux. *Curr. Opin. solid state mater. Sci.*, **6**, 515 (2002).

[4] S.C. Zimmerman, L.J. Lawless. *Topics Curr. Chem.*, **217**, 95 (2001); (*b*) V. Percec, C.-H. Ahn, T.K. Bera, G. Ungar, D.J.P. Yeardley. *Chem. Eur. J.*, **5**, 1070 (1999); (*c*) F.S. Precup-Blage, A.P.H.J. Schenning, E.W. Meijer. *Macromolecules*, **36**, 565 (2003).

[5] (*a*) C.M. Paleos, D. Tsiourvas. *Liq. Cryst.*, **28**, 1127 (2001); (*b*) T. Kato. 1998 in *Handbook of Liquid Crystals*, edited by D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, V. Vill (Weiheim: Wiley-VCH), pp. 969–979; (*c*) C. Tschierske. *Prog. polym. Sci.*, **21**, 775 (1996); C.M. Paleos, D. Tsiourvas. *Curr. Opin. colloid interface Sci.*, **6**, 257 (2001).

[6] D. Tsiourvas, T. Felekis, Z. Sideratou, C.M. Paleos. *Macromolecules*, **35**, 6466 (2002).

[7] D. Tsiourvas, T. Felekis, Z. Sideratou, C.M. Paleos. *Liq Cryst.*, **31**, 739 (2004).

[8] S. Udenfriend, S. Stein, P. Böhlen, W. Dairman, W. Leimgruber, M. Weigele. *Science*, **178**, 871 (1972).

[9] (*a*) S.E. Odinokov, A.A. Mashkovsky, V.P. Glazunov, A.V. Iogansen, B.V. Rassadin. *Spectrochim. Acta*, **32A**, 1355 (1976); (*b*) S.L. Johnson, K.A. Rumon. *J. phys. Chem.*, **69**, 74 (1965).

[10] Y. Tian, F. Su, Y. Zhao, X. Luo, X. Tang, X. Zhao, E. Zhou. *Liq. Cryst.*, **19**, 743 (1995); Z. Sideratou, D. Tsiourvas, C.M. Paleos, A. Skoulios. *Liq Cryst.*, **22**, 51 (1997); T. Kato, A. Fujishima, J.M.J. Fréchet. *Chem. Lett.*, 919 (1990).

[11] R. Scherrenberg, B. Coussens, P. van Vliet, G. Edouard, J. Brackman, E. de Brabander, K. Mortensen. *Macromolecules*, **31**, 456 (1998).