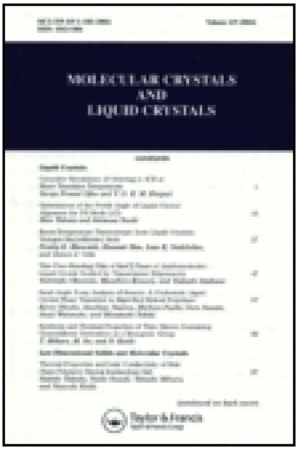


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Property of Dendrimers Having Peripherally Mesogenic Units

Osamu Haba [a] , Ken-Ichi Okuyama [a] & Koichiro Yonetake [a]

[a] Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 3-4-16, Jonan, Yonezawa, 992-8510, Japan

Version of record first published: 24 Sep 2006

To cite this article: Osamu Haba, Ken-Ichi Okuyama & Koichiro Yonetake (2001): Synthesis and Property of Dendrimers Having Peripherally Mesogenic Units, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 364:1, 929-936

To link to this article: http://dx.doi.org/10.1080/10587250108025066

Mol. Cryst. and Liq. Cryst., 2001, Vol. 364, pp. 929-936
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group,
Printed in the USA

Synthesis and Property of Dendrimers Having Peripherally Mesogenic Units

OSAMU HABA, KEN-ICHI OKUYAMA and KOICHIRO YONETAKE

Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 3–4–16, Jonan, Yonezawa 992–8510, Japan

Poly(propyleneimine)-based liquid crystalline dendrimers (**DCDs**) with a relatively flexible dendritic scaffold were successfully prepared by Michael addition reaction of polypropyleneimine)s to 6-(2,3-dicyano-4-butoxyphenyloxy) hexyl acrylate(**4**). The structure of **DCDs** were characterized by IR, NMR and MALDI-TOF mass spectroscopies. Liquid crystallinity were examined by DSC, polarized optical microscope, and X-ray diffraction methods. **DCDs** exhibited a smectic liquid-crystalline phase. The polar terminal 2,3-dicyanophenylene group gave a liquid crystalline properties to **DCDs**.

Keywords: Dendrimer; Poly(propylene imine); 2,3-Dicyanophenyl-1,4-diylene; Acrylate; Michael Addition; Smectic

INTRODUCTION

Dendrimers are well-defined, highly branched, and three-dimensional polymers.[1, 2, 3] Moreover, the large number of reactive end groups existing at the periphery of dendrimers easily react with many reagents to give dendrimers with various functionalities at the periphery. Therefore, they are receiving interest as new polymeric materials, such as catalysts, antennas for photo-induced energy, chiral recognition, and enantiomer separation, molecular electronics, and unimolecular micelles.[4-8] Dendrimers with terminal mesogens exhibited liquid crystalline behaviors. Poly(propylene imine) based liquid crystalline dendrimers (**PPILCDs**) exhibited smectic liquid crystalline behaviors. The homeotropic orientation was allowed to take place in **PPILCD** sandwiched between two glass plates on cooling.[9] The homeotropic structure is considered to come from the polar terminal group. Thus, structures and properties of liquid crystalline dendrimers are very interesting areas of research because dendrimers are already showing promise as exciting well-defined building blocks in the production of liquid crystals.

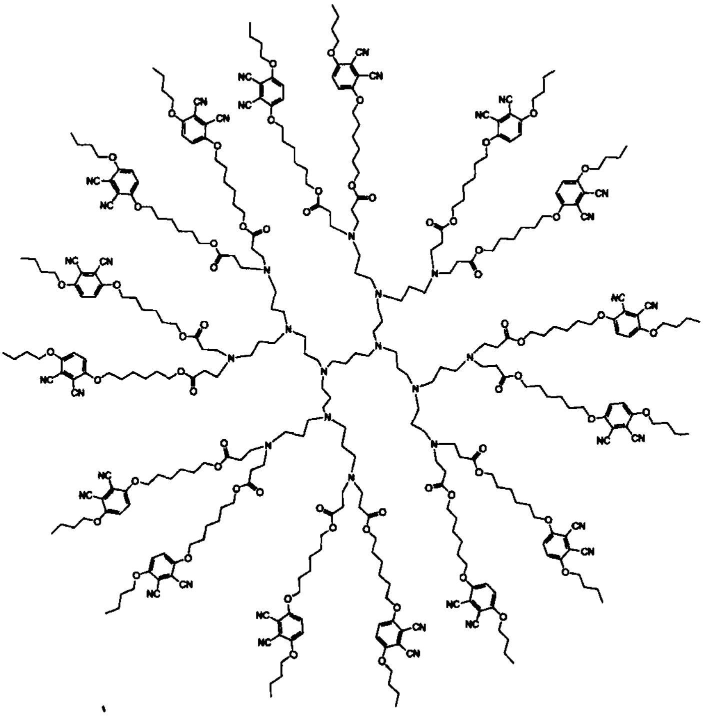
Our next stage was to verify the effects of terminal groups on the liquid crystalline properties and structures of dendrimers. The present paper describes the synthesis and properties of poly(propyleneimine) dendrimers with 2,3-

dicyanophenylene groups on the surface (**DCDs**).

RESULTS AND DISCUSSION

Synthesis of DCDs

The mesogenic unit was prepared according to Scheme 1. 2,3-Dicyanohydroquinone (**1**) was converted to 4-butoxy-2,3-dicyanophenol (**2**) through Williamson ether synthesis using bromobutane with potassium carbonate and 18-crown-6 ether. This compound was reacted with 6-bromohexanol to produce 6-(4-butoxy-2,3-dicyanophenyl)-hexanol (**3**). Then this was reacted with acryloyl chloride in the presence of pyridine to give 6-(4-butoxy-2,3-dicyanophenyl)hexyl acrylate (**4**). Introduction of **4** to the commercial polypropylene imine dendrimer (PPID-1, PPD-2 and PPID-3, Generation = 1, 2 and 3, respectively) was achieved by Michael type addition of the peripheral amino



DCD-2

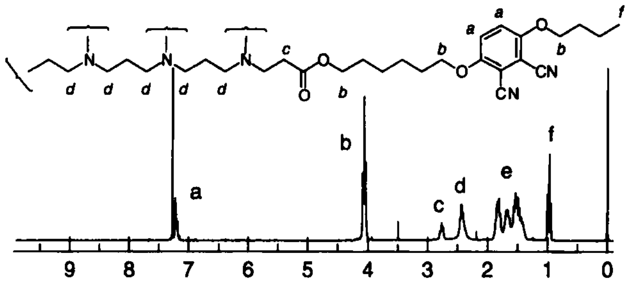
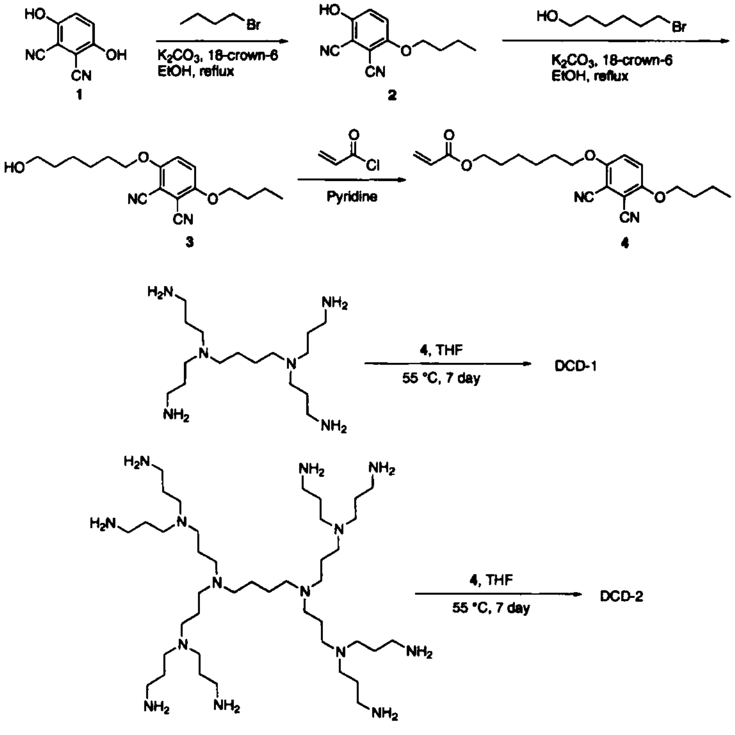


Figure 1. 270 MHz ^{1}H NMR spectrum of **DCD-3** measured in $CDCl_3$ at RT.

Scheme 1.



groups to the acrylate. The reaction was conducted by heating PPID and **4** at 55 °C in THF for 1 week. The reaction mixture was poured into methanol and the precipitate was filtered and washed with methanol by several times.

Characterization of DCDs

The IR spectra of all dendrimers showed characteristic ester carbonyl and nitrile bands at 1730 and 2230 cm^{-1}, respectively; no peaks at 3290-3300 cm^{-1} due to the primary amino groups were observed. Figure 1 shows the ^1H NMR spectrum for **DCD-2**, which has 16 dicyanophenyl units at the chain ends. Some distinct features are apparent. The terminal 2,3-dicyanophenylene unit, which is para-substituted with two ethers, gives rise to a singlets at 7.22 ppm for the phenyl protons. The other protons in the structure were identified. All assignments are insetted in Figure 1. Other **DCDs** also showed similar ^1H NMR spectra. The molecular weights of dendrimers were determined by MALDI-TOF mass spectrometry. The MALDI-TOF mass spectrum of **DCD-1** and **-2** shows one signal that is clearly due to the formation of the desired dendrimers with 8 and 16 mesogens, respectively (Figure 2). The m/z value of the signal (3278.1 and 6695.8 for **DCD-1** and **-2**, respectively) corresponds to the calculated value of m/z (3278.5 and 6695.8, respectively). The molecular ion peaks containing Na^+ ions or protons for the dendrimers were consistent with those expected for the **DCDs**. These results clearly indicate the formation of the desired **DCDs**.

Phase transitions and structures of DCDs

DSC traces of **DCD-1**, **DCD-2** and **DCD-3** for the 2nd-heating/cooling processes are illustrated in Figure 3. There were endothermic peaks on heating trace and large exothermic peaks on cooling. It reveals that the **DCDs** are not amorphous and they have high-ordered coagulate structure like liquid crystal or crystal structures. It is due to the terminal groups, i.e., the terminal phenyl ring formed by substituting the two hydrogen atoms with cyano groups might be highly co-

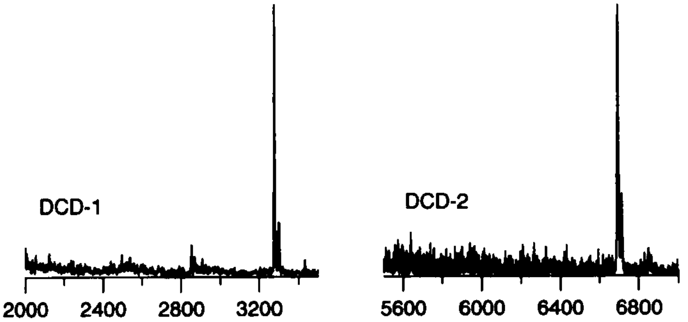


Figure 2. MALDI-TOF mass spectra of **DCD-1** and **-2**, measured using DHBA as a matrix.

hesive. In addition, the comparatively long spacer decoupled the motion of the terminal groups from the dentritic core. The DSC traces show double or triple peaks on cooling. They suggest that polymorphism or mesophase transition took place in the **DCDs**.

Polarizing optical micrographs of **DCD-1** in Figure 4 show liquid crystalline

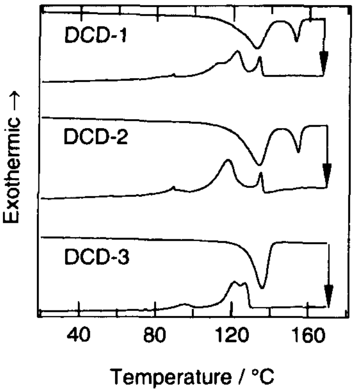


Figure 3. DSC traces of **DCDs**. ΔT=10 °C•min^{-1}.

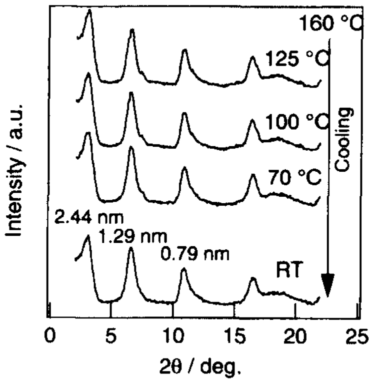


Figure 5. Change in the WAXS traces of **DCD-2** on cooling from melt.

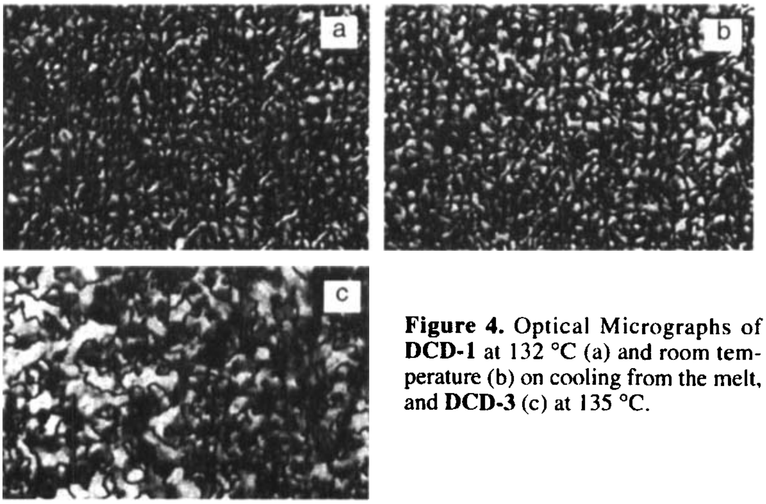


Figure 4. Optical Micrographs of **DCD-1** at 132 °C (a) and room temperature (b) on cooling from the melt, and **DCD-3** (c) at 135 °C.

optical textures, which were taken at 132°C (a) and room temperature (b) after cooling from the melt. Thus, smectic phase seemed to occur in the higher temperature range between two endothermic peaks. The optical texture almost remained unchanged on further cooling, as shown in Figure 4(b). Figure 4(c) represents the optical texture of **DCD-3** taken at 135°C on cooling. The optical texture also remained unchanged on the cooling process. The textures of **DCD-2** were the same as those of **DCD-1**, though they were not shown. Thus, the terminal group might act as a mesogen in **DCDs**, because of the strong polarity.

Change in X-ray diffraction curves of **DCD-2** on cooling were illustrated in Figure 5. The patterns exhibited sharp reflection in the low angle area, indicating d-spacing of 2.44 nm. It results from the smectic layer structures. The other reflections at 2θ= ac.7° and 11° were 1.29 nm, and 0.79 nm. They are considered to be 2nd and 3rd reflections, respectively, as shown in Figure 5. The layer structure formed in the sample seemed to be regular. The findings of other samples were similar to those of **DCD-2**.

Thus, the **DCDs** introduced by terminal 2,3-dicyanophenylene group exhibited liquid crystalline behaviors. In conclusion, such a polar terminal group also gives a liquid crystalline nature to dendrimers.

EXPERIMENTAL SECTION

Measurements

The infrared spectra were recorded on a HORIBA FT-210 spectrometer, and the NMR spectra on JEOL EX-270 (^{1}H: 270 MHz, ^{13}C: 68.5 MHz) spectrometer. The differential scanning calorimetory (DSC) was recorded on a Seiko SSC/5200 (DSC 220) instrument at a heating/cooling rate 10 °C/min in nitrogen. A gel permeation chromatography (GPC) was carried out using polystyrene as the standard on a JASCO TRIROTAR-III HPLC equipped with Shodex KF-80M column at 40 °C in tetrahydrofuran (THF). Matrix assisted laser desorption ionization time-of-flight ultraviolet mass spectroscopy (MALTI-TOF) was performed on a PE Biosystems Voyeger-DE Pro spectrometer using 2,4-dihydroxybenzoic acid as a matrix. Optical textures of the samples were examined using the polarizing optical microscope (POM) equipped with a hot stage (Linkam Co., TH-600RMS) under nitrogen. X-ray diffraction experiments were carried out on a RAD-rA diffractometer (Rigaku Denki Co. Ltd.) equipped with a heating device. Nickel-filtered CuKa radiation was employed. Wide angle X-ray scattering (WAXS) traces were recorded by a scintillation counter system with a 1.0 mm diameter pinhole collimator and 1×1° receiving slit. The diffractometry was performed in transmission. The WAXS traces were obtained by a step-scanning method: step width and fixed time were programmed for steps of 0.05° every 10 s. The X-ray diffraction photographs were taken by a flat Laue camera with a 0.5 mm diameter pinhole collimator.

Materials

Polypropyleneimine dendrimers (generation 1-3) (Aldrich) and 2,3-dicyanohydroquinone (Tokyo Kasei Kogyo) were purchased and used without further purification. Tetrahydrofuran was distilled from sodium-benzophenone ketyl. The other chemicals were commercially available and used as received. 4-Butoxy-2,3-dicyanohydroquinone (**2**) was prepared according to the literature[10].

6-(4-Butoxy-2,3-dicyanophenoxy)hexanol (3).

A suspension of **2**[10] (5.41 g, 25 mmol), bromohexanol (3.24 ml, 30 mmol) and potassium carbonate (6.91 g, 50 mmol) in ethanol was heated to reflux for 14 h under nitrogen atmosphere. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in ethyl acetate (300 ml), which was washed with water (500 ml) several times. The organic layer was dried over sodium sulfate and concentrated. The residue was recrystalized from methanol to give white powder. Yield 6.80 g (21.5 mol, 86%). ^{1}H NMR (CDCl$_3$, 270 MHz): δ (ppm) =0.98 (t, *J*=7.29 Hz, 3H, CH$_3$), 1.42-1.88 (m, 12H, CH$_2$), 3.67 (dt, *J*=6.01,5.40 Hz, 2H, *CH$_2$*-OH), 4.06 (t, *J*=6.62 Hz, 4H, PhO*CH$_2$*), 7.16 (s, 2H, ArH). IR (KBr): ν (cm^{-1}) =1270 (Ph-O-),2230 (CN),3330 (OH),2930 (CH$_2$). Anal. Calcd for CHNO: C, 68.33 H, 7.65 N, 8.85. Found: C, 68.25 H, 7.66 N, 8.77

6-(4-Butoxy-2,3-dicyanophenoxy)hexyl acrylate (4).

To a solution of **3** (6.32 g, 20 mmol) and triethylamine (3.3 ml, 24 mmol) in tetrahydrofuran was added dropwise acryloyl chloride (2.4 ml, 30 mmol) at 0 °C. The reaction mixture was stirred for 1 h at room temperature and then concentrated under reduced pressure. The residue was dissolved in ethyl acetate (100 ml) and washed with water (50 ml) several times. The organic layer was dried over sodium sulfate and evaporated. The residue was recrystalized from methanol to give white powder. Yield 9.20 g (18.8 mol, 94%). ^{1}H NMR (CDCl$_3$, 270 MHz): δ (ppm) = 0.98 (t, *J*=7.29 Hz, 3H, CH$_3$), 1.49-1.86 (m, 12H, CH$_2$), 4.05 (t, *J*=6.48 Hz, 2H, PhO*CH$_2$*), 4.06 (t, *J*=6.75 Hz, 2H, PhO*CH$_2$*), 4.17 (t, *J*=6.48 Hz, 2H, COOCH$_2$), 5.83 (dd, *J*=1.76, 10.13 Hz, 1H, CH$_2$), 6.13 (dd, *J*=10.26, 17.01 Hz, 1H, CH$_2$=*CH*-), 6.41 (dd, *J*=1.49, 17.42 Hz, 1H, CH$_2$), 7.15 (s, 2H, ArH). IR (KBr): ν (cm^{-1}) = 1720 (C=O),2230 (CN),1640 (C=C). Anal. Calcd for CHNO: C, 68.09 H, 7.07 N, 7.56. Found: C, 68.00, H, 7.08, N, 7.47

Introduction of the mesogenic unit into polypropireneimine dendrimers.

A typical procedure was as follows: A solution of **4** in tetrahydrofuran (5 ml) was added to a solution of polypropyleneimine dendrimer in tetrahydrofuran (3 ml). The solution was stirred at 50 °C for 7 days under nitrogen atomosphere. The mixture was poured into diethyl ether (300 ml) and the precipitate was filtered. The obtained white or gray solid was continuously washed with ether using a Shoxlet's extractor to give white solid.

Mesogen incorporated dendrimer, generation 1 (DCD-1).

Reaction was carried out using 1.78 g (4.8 mmol) of **4** and 0.063 (0.2 mmol) g of polypropyleneimine dendrimer (Generation 1). Yield 0.63 g (96%, 0.19 mmol).

^{1}H NMR ($CDCl_3$, 270 MHz): δ (ppm) = 0.98 (t, *J*=7.56 Hz, 24H, CH_3), 1.42-1.86 (m, 120H, CH_2), 2.44 (t, *J*=7.56 Hz, 24H, N-CH_2), 2.77 (t, *J*=7.29 Hz, 16H, $CH_2CH_2C{=}O$), 4.07 (t, *J*=6.21 Hz, 48H, -O-CH_2), 7.19 (s, 16H, ArH). IR (KBr): ν (cm^{-1}) =1734 (C=O),2229 (CN).

Mesogen incorporated dendrimer, generation 2 (DCD-2)

Reaction was carried out using 1.78 g (4.8 mmol) of **4** and 0.077 g (0.1 mmol) of polypropyleneimine dendrimer (Generation 2). Yield 0.65 g (94%, 0.094 mmol). ^{1}H NMR ($CDCl_3$, 270 MHz): δ (ppm) = 0.98 (t, *J*=7.02 Hz, 48H, CH_3), 1.42-1.86 (m, 256H, CH_2), 2.44 (t, *J*=7.02 Hz, 48H, N-CH_2), 2.77 (t, *J*=6.21 Hz, 32H, $CH_2CH_2C{=}O$), 4.07 (t, *J*=6.21 Hz, 96H, -O-CH_2), 7.19 (s, 32H, ArH). IR (KBr): ν (cm^{-1}) =1734 (C=O), 2230 (CN)

Mesogen incorporated dendrimer, generation 3 (DCD-3).

Reaction was carried out using 2.37 g (6.4 mmol) of **4** and 0.068 g (0.04 mmol) of polypropyleneimine dendrimer (Generation 3). Yield 0.49 g (89%, 0.034 mmol). ^{1}H NMR ($CDCl_3$, 270 MHz): δ (ppm) = 0.98 (t, *J*=7.02 Hz, 96H, CH_3), 1.42-1.86 (m, 528H, CH_2), 2.44 (t, *J*=6.75 Hz, 96H, N-CH_2), 2.77 (t, *J*=6.48 Hz, 64H, $CH_2CH_2C{=}O$), 4.07 (t, *J*=6.21 Hz, 192H, -O-CH_2), 7.22 (s, 64H, ArH). IR (KBr): ν (cm^{-1}) = 1734 (C=O), 2229 (CN).

Acknowledgements

This work was financially supported by the New Energy and Industrial Technology (NEDO) for the project on "Technology for Novel High-Functional Materials" and the Agency of Industrial Science and Technology (AIST).

References

[1] D.A. Tomalia, A.M. Naylor, W.A. Goddard, *Angew. Chem., Int. Ed. Engl.* **29**, 138 (1990).

[2] J.M. Frechet, *Science* **263**, 1710 (1994).

[3] E.M.M. de Brabander-van den Berg, E.W. Meijer, *Angew. Chem., Int. Ed. Engl.* **32**, 1308 (1993).

[4] F. Zeng, S.C. Zimmerman, *Chem. Rev.* **97**, 1681 (1997).

[5] O.A. Matthews, A.N. Shipwa, J.F. Stoddart, *Prog. Polym. Sci.* **23**, 1 (1998).

[6] S. Stevelmans, J.C.M. Van Hest, J.F.G.A. Jansen, D.A.F.J. Van Boxtel, E.M.M. de Brabander-van den Berg, E.W. Meijer, *J. Am. Chem. Soc.* **118**, 7398 (1996).

[7] C.J. Hawker, K.L. Wooley, J.M.J. Frechet, *J. Chem. Soc. Perkin Trans. I* **21**, 1287 (1993).

[8] Y. Sayed-Sweet, D.M. Hedstrand, R. Spinder, D.A. Tomalia, *J. Mater. Chem.* **7**, 1199 (1997).

[9] K. Yonetake, T. Masuko, T. Morishita, K. Suzuki, M. Ueda, R. Nagahata, *Macromolecules*, **32**, 6578 (1999).

[10] T. Inukai, K. Furukawa, H. Inoue, K. Terashima, *Mol. Cryst. Liq. Cryst.* **94**, 109–118 (1983).