Macromolecules **2003,** *36,* 565−572

Liquid Crystalline Oligo(*p*-phenylene vinylene)-Terminated Poly(propylene imine) Dendrimers. Synthesis and Characterization

F. S. Precup-Blaga, A. P. H. J. Schenning,* and E. W. Meijer*

Laboratory for Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received August 15, 2002; Revised Manuscript Received October 28, 2002

ABSTRACT: Different generations of poly(propylene imine) dendrimers modified peripherically with urea oligo(*p*-phenylene vinylene)s (OPV) having a 3,4,5-tri(dodecyloxy)phenyl mesogenic unit (OPV−dendrimers) were successfully synthesized and fully characterized. Although intramolecular H-bonding exist between the urea linkages of the end groups, only weak interactions between the π-conjugated segments were observed in solution. The hydrogen-bonding interactions increased for higher generation dendrimers due to the closer proximity of the end groups, indicative of a more dense-shell packing. All generations of OPV−dendrimers showed liquid crystalline behavior in which the OPV−dendrimers have a homeotropic orientation. The temperature range of the liquid crystalline phase increased with higher generation.

Introduction

One of the most interesting features of dendrimers is the existence of a high number of functional groups at the periphery, which modulate the properties of these macromolecules.[1] Therefore, dendrimers can easily been used as polymeric materials in fields such as catalysis,[2] chiral recognition,[3] unimolecular micelles,[4] host−guest chemistry,[5] and light-harvesting antennas.[6] Modification of the dendritic macromolecules with mesogenic end groups has resulted in liquid crystalline (LC) materials.[7] One of the interesting properties of these materials is their supramolecular organization giving rise to long-range order. Moreover, as π-functional materials, they can be applied in electrooptical switches[8] and liquid crystal displays (LCDs).[9]

Dendrimers with π-conjugated oligomers at the periphery have also been synthesized.[10] Branching of π-conjugated systems by attaching them to dendrimers can be an attractive tool to avoid highly ordered (crystalline) domains resulting in low quantum efficiency of luminescence.[11] For example, high quality amorphous thin films can be prepared by conventional spin-coating from dendrimers.[12] Moreover, dendrimers modified with π-conjugated oligomers can be used as hosts for dye molecules[13] showing efficient energy transfer from the π-conjugated units to the encapsulated dye.

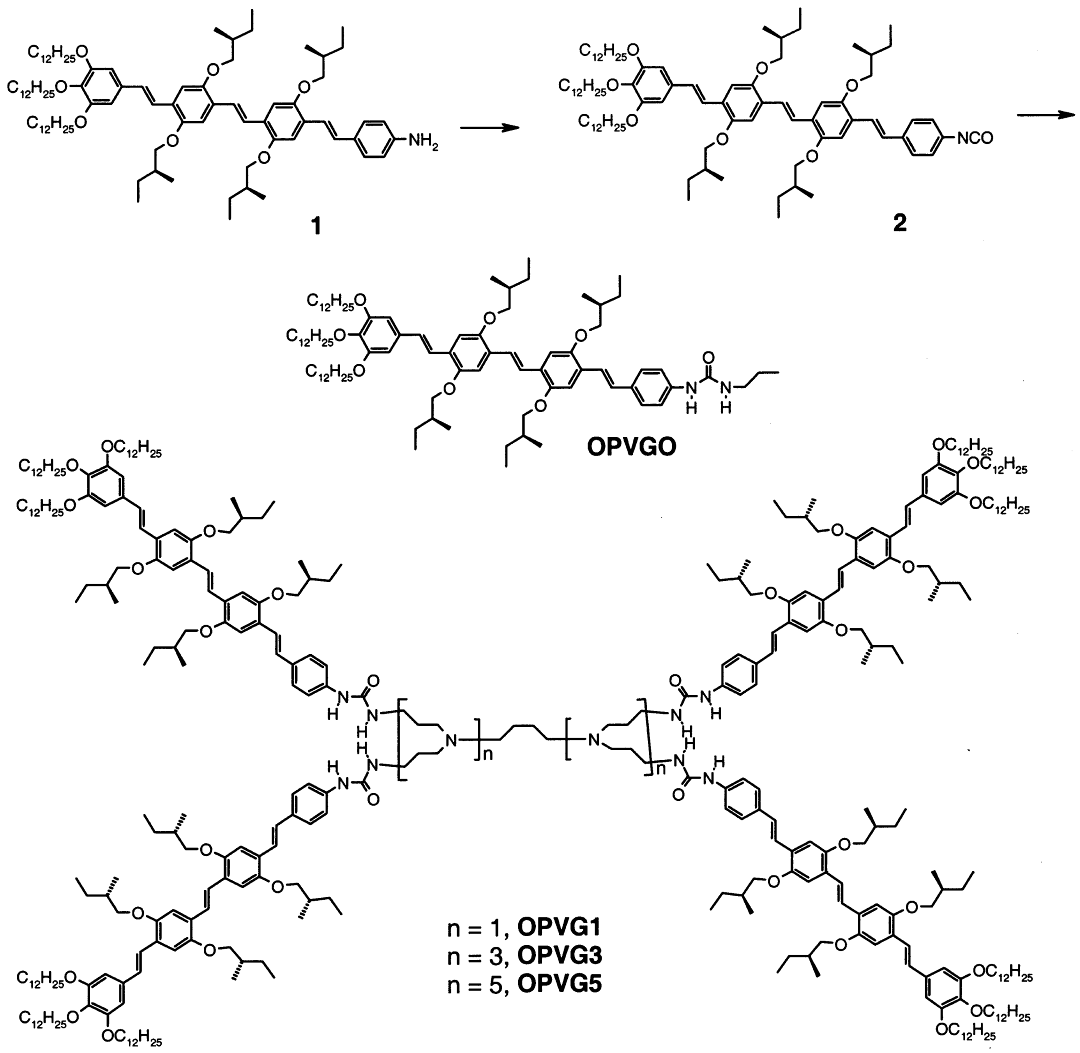
Dendrimers in which π-conjugated oligomers are combined with liquid crystalline behavior are quite rare.[14] Dendritic macromolecules modified peripherically with π-conjugated oligomers can bridge the gap between π-conjugated polymers (easy to process) and oligomers (well-defined). Substitution of the terminal π-conjugated end groups of the dendrimers with mesogenic units will lead to liquid crystalline behavior resulting in order on a supramolecular level. In this paper, we report the synthesis and characterization of liquid crystalline poly(propylene imine) dendrimers modified peripherically with π-conjugated oligo(*p*-phenylene vinylene)s. Physical properties of these functionalized dendrimers have been investigated in detail by IR and ^{1}H NMR spectroscopy, T_1 and T_2 relaxation measurements, UV−vis, fluorescence, and circular dichroism. Polarizing microscopy, thermogravimetric analysis, and differential scanning calorimetry have been used to study the thermotropic properties in the solid state.

Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on a Varian Gemini 300 or 400 MHz spectrometer in deuterated chloroform or 1,1,2,2-tetrachloroethane-d_2 (TCE-d_2) and tetramethylsilane (TMS) was used as internal reference. Abbreviations used are s = singlet, d = doublet, t = triplet, m = multiplet, and b = broad. For samples recorded in TCE-d_2, the solvent resonance was set to 5.9 ppm and all other signals were referred with respect to this peak. For the variable-temperature ^{1}H NMR measurements in TCE-d_2, a minimum of 64 scans were signal averaged for each measurement, and the samples were allowed to equilibrate at the experimental temperature for 15 min prior to each measurement. The NMR relaxation time experiments were carried out on a Varian Inova 500 spectrometer operating at 500.618 MHz and equipped with a 5 mm 500 SW/PFG probe. For preparative size exclusion chromatography, Bio-Beads S-X1 (mesh size 200−400, MW operational range 600−14000) was used. Infrared (FT-IR) spectra were recorded on a Perkin-Elmer 1605 FT-IR spectrometer. UV−vis spectra and fluorescence spectra were recorded on a Perkin-Elmer Lambda 40 spectrometer and a Perkin-Elmer luminescence spectrometer LS 50 B instrument, respectively. CD spectra were recorded on a Jasco J-600 spectrometer. Spectra at different temperatures were not corrected for volume changes of the solvents. Matrix assisted laser desorption ionization time-of-flight (MALDI−TOF) mass spectrometry were measured on a Perspective Biosystems Voyager-DE PRO instrument in reflector mode, using α-cyano-4-hydroxycinnamic acid as the matrix. Thermal optical properties of LC materials were studied using a Jenaval polarization microscope equipped with crossed polarizers and a Linkam THMS 600 hot stage. Differential scanning calorimetry was performed on a Perkin-Elmer DSC Pyris 1 at a heating rate of 10 °C/min. Thermal gravimetric analysis (TGA) data was collected under nitrogen on a Perkin-Elmer TGA 7 apparatus. Elemental analyses were performed on a Perkin-Elmer instrument, Series II, 2400. Spin-coated thin films were prepared by spin-casting 2 wt % toluene solutions using a Headway Research Spin-coat apparatus. Low-angle X-ray powder diffraction measurements were performed with a self-made instrument (Netherlands Institute for Sea Research, NIOZ, Texel) at room temperature. This high-accuracy $\phi-\phi$ diffractometer is equipped with a Cu tube, variable divergence and antiscatter slits, and an energy dispersive Si/Li Kevex detector, which enables a high peak-

10.1021/ma021338b CCC: $25.00

Scheme 1



to-background ratio. Special Si single-crystal wafers, cut along the (501) plane, were used for low-angle measurements. The compounds were spin-coated and subsequently annealed at 100 °C for 1 h.

Materials. Poly(propylene imine)dendrimers were kindly provided by DSM, The Netherlands. (*E*,*E*,*E*)-4-[4-{3,4,5-Tridodecyloxystyryl)-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2-methylbutoxy]styryl]aniline (**1**) was synthesized according a literature procedure.[15] *N*,*N*-Dimethylformamide was stored over BaO or 4.0 Å molsieves. THF (Biosolve, p.a.) was distilled over Na/benzophenone under an argon atmosphere. Dichloromethane was freshly distilled from P_2O_5. Diethyl ether was freshly distilled over potassium/sodium. All other reagents were purchased from Acros and Aldrich and used without further purification. For column chromatography Merck silica gel 60 (particle size 0.063−0.200 mm) was used.

(*E*,*E*,*E*)-4-[4-{3,4,5-Tridodecyloxystyryl)-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2-methylbutoxy]styryl]phenylisocyanate (2). Under an argon atmosphere, (*E*,*E*,*E*)-4-[4-{3,4,5-Tridodecyloxystyryl)-2,5-bis[(*S*)-2-methylbutoxy]styryl}-2,5-bis[(*S*)-2-methylbutoxy]styryl]aniline (**1**)[15] (0.5 g, 0.385 mmol) was suspended in 31 mL of a 20% phosgene solution in toluene. The reaction mixture was heated to reflux temperature. After 16 h the mixture was cooled to room temperature and the toluene was removed in vacuo to dryness and flushed with $CHCl_3$. Compound **2** was used without further purification. IR (KBr): ν (cm^{-1}) 2261 (isocyanate).

Typical Procedure for OPV Dendrimers (OPVG3). DAB-*dendr*-$(NH_2)_{16}$ (0.018 g, 0.0107 mmol; 1/16 equiv) dissolved in dichloromethane was added to the isocyanate **2**. The mixture was stirred for 48 h at room temperature. The reaction mixture was extracted with 1 N NaOH (2×). The organic layer was dried with Na_2SO_4, filtered, and dried in vacuo. The product was further purified with Bio-Beads column chromatography (CH_2Cl_2) yielding **OPVG3** (80%) as a yellow solid. ^{1}H NMR (TCE, 25 °C): δ 8.45 (s, 16H, ArN*H*CONH), 7.40 (s, 64H, Ar*H*), 7.20−7.47 (d, 96H, ArC*H*=C*H*), 7.30 (s, 16H, Ar*H*), 7.15 (s, 16H, Ar*H*), 7.10 (s, 16H, Ar*H*), 7.00 (s, 16H, Ar*H*), 6.90 (s, 16H, Ar*H*), 6.70 (s, 16H, Ar*H*), 6.40 (t, 16H, ArNHCON*H*$CH_2CH_2CH_2$), 3.80−4.00 (m, 224H, OCH_2), 3.40 (q, br, 32 H, $ArNHCONHCH_2CH_2CH_2N$), 2.80 (t, br, 84H, 32H, $NHCONHCH_2CH_2CH_2N$ + 4H $NHCH_2CH_2CH_2CH_2N$ + 48H $NCH_2CH_2CH_2N$), 1.70−2.00 (m, 64H, C*H*), 1.6−1.79 (m, 320H, $OCH_2CH(CH_3)CH_2CH_3$ + $OCH_2CH_2CH_2(CH_2)_8CH_3$), 1.50−1.60 (m, 60H, 4H $NHCH_2CH_2CH_2CH_2N$ + 56H $NHCONHCH_2CH_2$-CH_2N)), 1.30−1.46 (m, 768H, $O(CH_2)_3(CH_2)_8CH_3$), 0.95−1.30 (m, 528H, CCH_3). ^{13}C NMR (300 MHz, TCE, 25 °C): 154.90, 153.34, 153.30, 151.29, 151.26, 151.16, 151.10, 138.20, 138.04, 133.56, 133.50, 128.65, 128.17, 127.65, 127.54, 127.44, 127.31, 126.94, 126.87, 122.80, 122.76, 122.69, 122.56, 120.94, 120.73, 110.92, 110.65, 110.05, 109.81, 105.19, 75.75, 75.39, 75.37, 75.02, 36.74, 33.23, 31.82, 31.10, 31.02, 30.99, 30.95, 30.79, 30.61, 27.90, 27.56, 23.94, 18.18, 15.27, 12.71. IR (KBr): ν (cm^{-1}) 3326.7, 2959.5, 2875.1, 1645.2. UV/vis ($CHCl_3$): λ_{max} (ϵ) = 330 nm (321 850), 432 nm (621 175). Anal. Calcd. for: $C_{1480}H_{2368}O_{128}N_{46}$ (M_r = 22 854.8): C, 77.83; H, 10.38; N, 2.82. Found: C, 78.10; H, 10.02; N, 2.89.

OPVG0. ^{1}H NMR (TCE, 25 °C): δ 7.53 (s, 2H), 7.41 (d, 1H), 7.34 (d, 2H), 7.31 (d, 1H), 7.21 (s, 1H), 7.19 (s, 1H), 7.11 (s, 1H), 7.10 (s, 1H), 7.07 (d, 1H), 7.04 (d, 1H), 6.75 (s, 2H), 6.64 (d,2H), 6.29 (s,1H, ArN*H*CONH$CH_2CH_2CH_3$), 4.62 (t,1H, NHCON*H*$CH_2CH_2CH_3$), 4.08−3.78 (m, 14H), 3.20 (q, 2H,

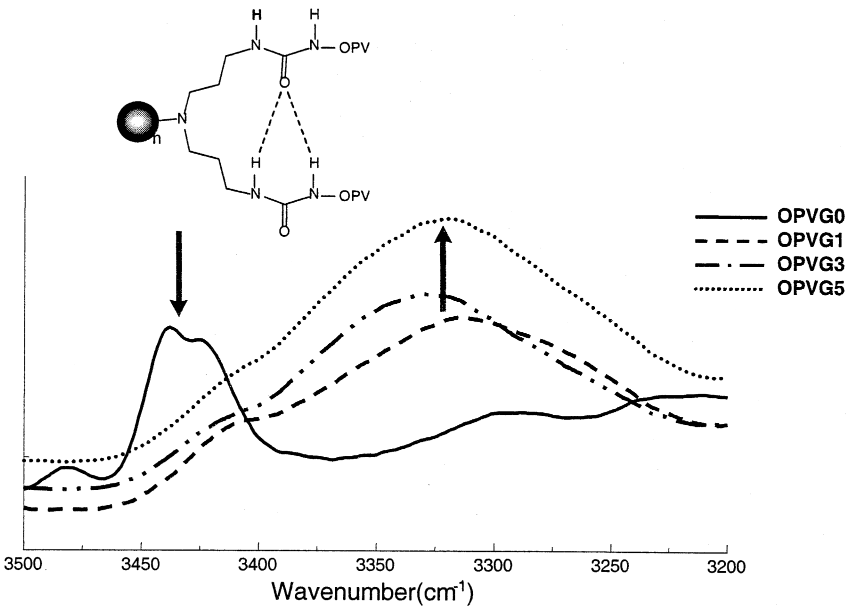


Figure 1. IR spectra of the OPV−dendrimers in dichloromethane at 298 K (end group concentration = 5 mM).

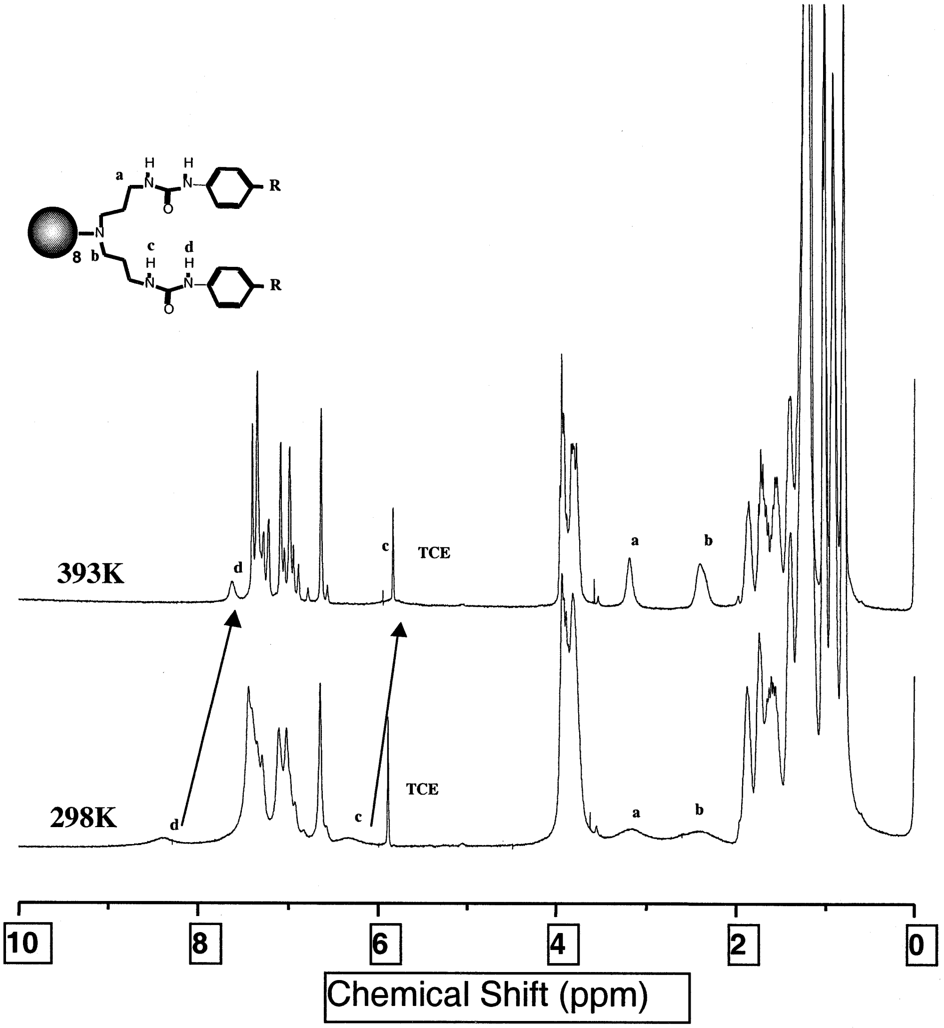


Figure 2. ^{1}H NMR spectra of **OPVG3** in TCE-d_2 at 293 and 393 K.

CH_2N), 2.05−1.92 (m, 4H), 1.92−1.18 (m, 73H), 1.18−0.80 (m, 33H). ^{13}C NMR (400 MHz, CDCl$_3$): δ 155.98, 153.34, 153.30, 151.29, 151.26, 151.16, 151.10, 138.20, 138.04, 133.56, 133.50, 128.65, 128.17, 127.65, 127.54, 127.44, 127.31, 126.94, 126.87, 122.80, 122.76, 122.69, 122.56, 120.94, 120.73, 110.92, 110.05, 109.81, 105.19, 74.96, 74.72, 74.46, 74.34, 73.93, 69.45, 69.36, 42.45, 35.53, 35.46, 35.35, 32.33, 32.31, 30.72, 30.14, 30.12, 30.10, 30.08, 30.05, 30.01, 29.83, 29.78, 29.76, 26.81, 26.79, 26.76, 26.53, 23.78, 23.09, 17.28, 17.26, 17.20, 14.53, 11.92, 11.83, 11.77. MALDI−TOF MS: 1381.14 [M]$^+$; calcd, 1381.09.

IR (KBr): ν ($\mathrm{cm^{-1}}$) 3335, 2957.8, 2877.1, 1641.2. UV/vis ($\mathrm{CHCl_3}$): $\lambda_{\max}$ (ϵ) = 330 nm (17 900), 434 nm (25 570). Anal. Calcd. for: $\mathrm{C_{90}H_{144}O_8N_2}$ ($M_r = 1382.1$): C, 78.26; H, 10.43; N, 2.03. Found: C, 78.38; H, 10.56; N, 2.05.

OPVG1. ^{1}H NMR (TCE, 25 °C): δ 7.95 (s, 4H, $\mathrm{ArN}\mathit{H}\mathrm{CONH}$), 7.40 (s, 16H, $\mathrm{Ar}\mathit{H}$), 7.00−7.45 (m, 24H, $\mathrm{ArC}\mathit{H}{=}\mathrm{C}\mathit{H}$), 7.20 (s, 4H, $\mathrm{Ar}\mathit{H}$), 7.10 (s, 4H, $\mathrm{Ar}\mathit{H}$), 6.90 (s, 4H, $\mathrm{Ar}\mathit{H}$), 6.80 (s, 4H, $\mathrm{Ar}\mathit{H}$), 6.65 (s, 4H, $\mathrm{Ar}\mathit{H}$), 6.55 (s, 4H, $\mathrm{Ar}\mathit{H}$), 5.90 (t, 4H, $\mathrm{ArNHCON}\mathit{H}\mathrm{CH_2CH_2CH_2}$), 3.80−4.00 (m, 56H, $\mathrm{OC}\mathit{H}_2$), 3.25 (q, br, 8 H, $\mathrm{ArNHCONHC}\mathit{H}_2\mathrm{CH_2CH_2}$), 2.56 (t, br, 8H, $\mathrm{NHCONHCH_2CH_2C}\mathit{H}_2\mathrm{N}$), 2.40 (t, br, 4H, $\mathrm{NHC}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{N}$), 1.81−2.00 (m, 40H, $\mathrm{C}\mathit{H}$), 1.79 (m, 8H, $\mathrm{NHCONHCH_2C}\mathit{H}_2\mathrm{CH_2N}$), 1.60−1.70(m,80H,$\mathrm{OCH_2CH(CH_3)C}\mathit{H}_2\mathrm{CH_3}+\mathrm{OCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{(CH_2)_8CH_3}$), 1.46 (m, 4H, $\mathrm{NHCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$), 1.30−1.46 (m, 192H, $\mathrm{O(CH_2)_3(C}\mathit{H}_2\mathrm{)_8CH_3}$), 0.95−1.30 (m, 132H, $\mathrm{CC}\mathit{H}_3$). ^{13}C NMR (300 MHz, TCE, 120 °C): 154.90, 153.34, 153.30, 151.29, 151.26, 151.16, 151.10, 138.20, 138.04, 133.56, 133.50, 128.65, 128.17, 127.65, 127.54, 127.44, 127.31, 126.94, 126.87, 122.80, 122.76, 122.69, 122.56, 120.94, 120.73, 110.92, 110.65, 110.05, 109.81, 105.19, 75.76, 75.39, 75.03, 71.18, 36.75, 36.67, 33.26, 33.24, 31.82, 31.11, 31.03, 31.01, 30.99, 30.96, 30.79, 30.64, 30.61, 27.91, 27.57, 23.94, 18.18, 18.11, 15.28, 12.73, 12.64. MALDI−TOF MS: 5627.5 $[\mathrm{M+Na}]^+$; calcd, 5627.4. IR (KBr): ν ($\mathrm{cm^{-1}}$) 3317.8, 2958.6, 2876.4, 1645.4. UV/vis ($\mathrm{CHCl_3}$): $\lambda_{\max}$ (ϵ) = 329 nm (92 400), 433 nm (192 490). Anal. Calcd. for: $\mathrm{C_{364}H_{580}O_{32}N_{10}}$ ($M_r = 5608.7$): C, 77.95; H, 10.42; N, 2.50. Found: C, 77.92; H, 10.24; N, 2.54.

OPVG5. ^{1}H NMR (TCE, 25 °C): δ 8.45 (s, 64H, $\mathrm{ArN}\mathit{H}\mathrm{CONH}$), 7.40 (s, 256H, $\mathrm{Ar}\mathit{H}$), 7.20−7.47 (d, 384H, $\mathrm{ArC}\mathit{H}{=}\mathrm{C}\mathit{H}$), 7.30 (s, 64H, $\mathrm{Ar}\mathit{H}$), 7.15 (s, 64H, $\mathrm{Ar}\mathit{H}$), 7.10 (s, 64H, $\mathrm{Ar}\mathit{H}$), 7.00 (s, 64H, $\mathrm{Ar}\mathit{H}$), 6.90 (s, 64H, $\mathrm{Ar}\mathit{H}$), 6.70 (s, 64H, $\mathrm{Ar}\mathit{H}$), 6.40 (t, 64H, $\mathrm{ArNHCON}\mathit{H}\mathrm{CH_2CH_2CH_2}$), 3.80−4.00 (m, 896H, $\mathrm{OC}\mathit{H}_2$), 3.40 (q, br, 128 H, $\mathrm{ArNHCONHC}\mathit{H}_2\mathrm{CH_2CH_2N}$), 2.80 (t, br, 500H, 128H $\mathrm{NHCONHCH_2CH_2C}\mathit{H}_2\mathrm{N}$ + 4H $\mathrm{NHC}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{N}$ + 368H $\mathrm{NC}\mathit{H}_2\mathrm{CH_2C}\mathit{H}_2\mathrm{N}$), 1.81−2.00 (m, 256H, $\mathrm{C}\mathit{H}$), 1.60−1.79 (m, 1280H, $\mathrm{OCH_2CH(CH_3)C}\mathit{H}_2\mathrm{CH_3}+\mathrm{OCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{(CH_2)_8CH_3}$), 1.50−1.60 (m, 252H, 4H $\mathrm{NHCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2N}$ + 248H $\mathrm{NHCONHCH_2C}\mathit{H}_2\mathrm{CH_2N}$)), 1.30−1.46 (m, 3072H, $\mathrm{O(CH_2)_3(C}\mathit{H}_2\mathrm{)_8CH_3}$), 0.95−1.30 (m, 2112H, $\mathrm{CC}\mathit{H}_3$). ^{13}C NMR (300 MHz, TCE, 120 °C): 154.90, 153.34, 153.30, 151.29, 151.26, 151.16, 151.10, 138.20, 138.04, 133.56, 133.50, 128.65, 128.17, 127.65, 127.54, 127.44, 127.31, 126.94, 126.87, 122.80, 122.76, 122.69, 122.56, 120.94, 120.73, 110.92, 110.65, 110.05, 109.81, 105.19, 75.74, 75.37, 75.01, 33.25, 31.05, 30.97, 30.80, 30.64, 27.87, 27.56, 23.97, 18.21, 15.35, 12.78. IR (KBr): ν ($\mathrm{cm^{-1}}$) 3326.8, 2959.5, 2879.2, 1640.1. UV/vis ($\mathrm{CHCl_3}$): $\lambda_{\max}$ (ϵ) = 330 nm (1156 300), 432 nm (2204 305). Anal. Calcd. for: $\mathrm{C_{5944}H_{9520}O_{512}N_{190}}$ ($M_r = 91\,840$): C, 77.78; H, 10.38; N, 2.90. Found: C, 78.02; H, 9.67; N, 2.74.

Results and Discussion

Synthesis and Characterization. The oligo(p-phenylene vinylene) (OPV) containing dendrimers were synthesized from (E,E,E)-4-[4-{3,4,5-Tridodecyloxystyryl)-2,5-bis[(S)-2-methylbutoxy]styryl}-2,5-bis[(S)-2-methylbutoxy]styryl]aniline (**1**) (Scheme 1).[15] Reaction of **1** with phosgene in toluene yielded isocyanate derivative **2**. Reaction of **2** with n-propylamine and the first, third and fifth generation poly(propyleneimine) dendrimer[5] yielded **OPVG0**, **OPVG1**, **OPVG3**, and **OPVG5**, respectively. Efficient purification of the dendrimers was achieved by repeated preparative size exclusion chromatography, using dichloromethane as eluent. The dendrimers were fully characterized with infrared spectroscopy, elemental analysis and NMR spectroscopy. Mass spectrometry showed fully reacted dendrimer, in the case of **OPVG0** and **OPVG1**. It proved to be impossible to yield a considerable ionization for **OPVG3** and **OPVG5**, despite variations in the experimental conditions.[16]

Infrared spectroscopy was used to gain qualitative information on the hydrogen-bonding interactions in solution between the urea linkages in the dendrimers. Propylamine reference compound **OPVG0** showed a non-hydrogen-bonded vibration (3440 $\mathrm{cm^{-1}}$) in the NH stretching vibration region while the dendritic macromolecules **OPVG1**, **OPVG3**, and **OPVG5** revealed only the hydrogen-bonded urea absorption (3320 $\mathrm{cm^{-1}}$, Figure 1). Similar results were found earlier for urea-linked adamantyl- and palmitoyl-functionalized poly(propylene imine) dendrimers.[17,18] Remarkably, the carbonyl stretching vibration does not show the same trend (see Experimental Section).

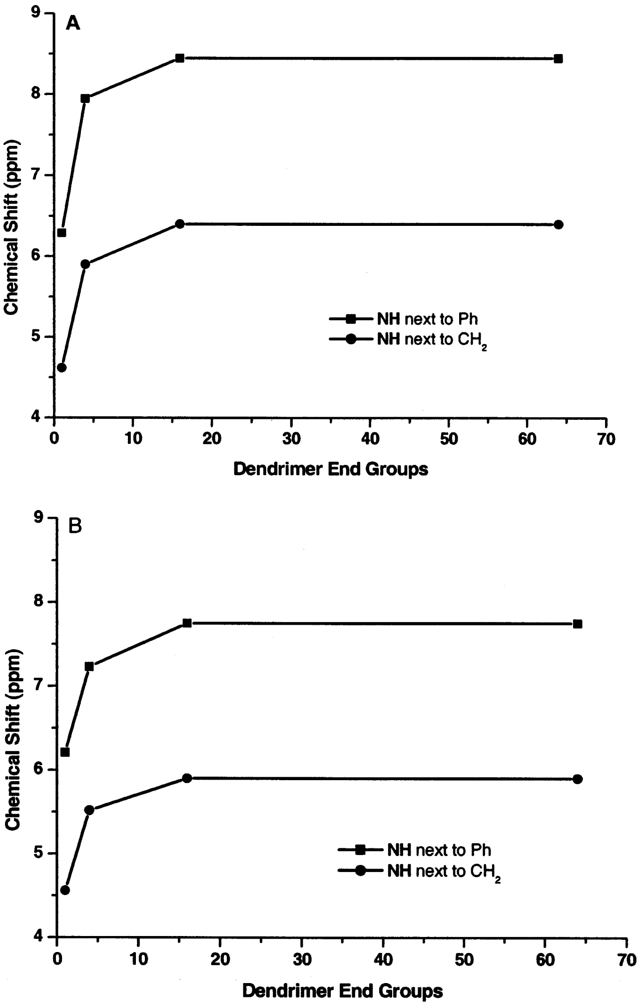


Figure 3. Chemical shift as a function of the number of end groups of the OPV−dendrimers at 293 and 393 K.

The hydrogen-bonding interactions between the urea moieties were further investigated by ^{1}H NMR spectroscopy at room temperature[19] (Figures 2 and 3) by monitoring the chemical shift of the two N−H resonances of OPV-dendrimers. Deuterium exchange measurements in $\mathrm{CD_3OD}$ showed that the NH resonances are positioned at 4.62 and 6.29 ppm for **OPVG0**, 5.9 and 7.95 ppm for **OPVG1**, and 6.4 and 8.45 ppm for **OPVG3** and **OPVG5** (Figure 2). These results indicate an increase of the hydrogen-bonding interactions in the higher generation dendrimer. Moreover, a constant value of the chemical shift for both N−H protons is already reached at the third generation (n = 16), suggesting that all end groups are hydrogen-bonded at the third generation stage.[17,20]

^{1}H NMR spin−lattice (T_1) and spin−spin relaxation (T_2) measurements were performed for all generations

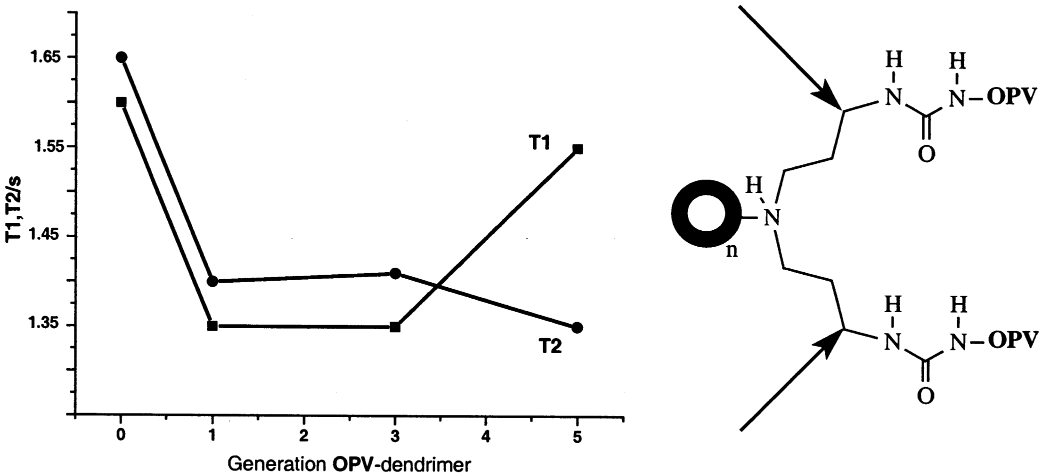


Figure 4. Relaxation time as a function of the number of end groups of the OPV–dendrimers.

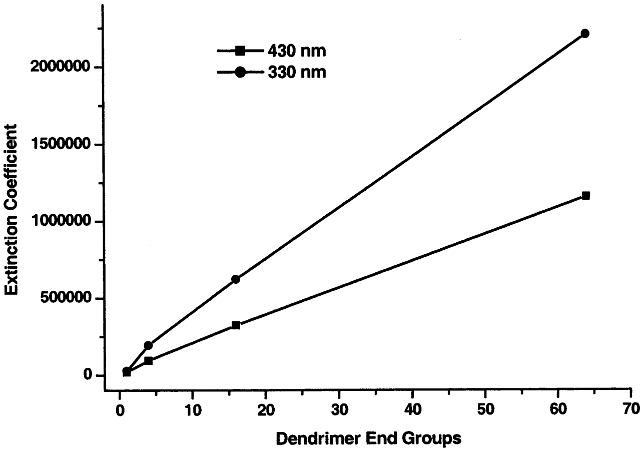


Figure 5. Extinction coefficient vs the number of end groups of each generation dendrimer.

OPV–dendrimers in order to investigate restricted motions in the dendrimer.[21] The changes in T_1 relaxations upon going from **OPVG0** to **OPVG1** is due to the hindered mobility (Figure 4).[22] The dipoles become closer in space and start to interact with each other. Moreover, an increase in relaxation times is observed passing from **OPVG1** to **OPVG5** due to segmental mobilities and steric hindrance. The motion in the dendrimers decreases upon increasing the number of end groups. T_2 is decreasing by increasing the number of end groups, which can be observed by line broadening of the signals. These results suggest a denser shell packing of the dendrimer by increasing generation.[23]

Absorption spectra of the OPV–dendrimers in chloroform show the typical π–π^* transition of the OPV tetramer units.[24] The absorption of the main band is located at $\lambda_{max} = 434 \pm 2$ nm for all generations. The extinction coefficient shows a linear dependence with the number of dendrimer end groups (Figure 5). This behavior indicate that only weak interchromophoric interactions exist between the π-conjugated segments.[25] The fluorescence spectrum of all OPV–dendrimers ($\lambda_{em,max} = 434$ nm) has a maximum at 500 nm and shows the vibronic fine structure typical of molecular dissolved chromophores. The lack of a CD (circular dichroism) signal (optical density of 1), despite the stereocenters present in the side chains of the OPV units, also supports the absence of strong interchromophoric interactions.

Temperature-Dependent Behavior in Solution. A temperature-dependent proton NMR measurement was carried out for **OPVG0**, **OPVG1**, **OPVG3**, and **OPVG5** in order to study in more detail the hydrogen bonding interactions (Figure 2). An increase in temperature from 293 to 393 K produces an upfield shift of the δ value of N–H protons of all generations of OPV–dendrimers. Upfield shifts from 4.62 to 4.56 ppm and from 6.29 to 6.21 ppm ($\Delta\delta = 0.08$) for **OPVG0**, from 5.9 to 5.52 ppm and from 7.95 to 7.23 ppm ($\Delta\delta = 0.38$ and 0.72) for **OPVG1,** and from 6.4 to 5.9 ppm and from 8.45 to 7.75 ppm ($\Delta\delta = 0.50$ and 1.20) for both **OPVG3** and **OPVG5** were observed. For the propylamine model compond, the N–H shift is smaller compared with those of the dendrimers. This is in a good agreement with the IR measurements, where propylamine reference compound **OPVG0** shows an almost completely non-hydrogen-bonded species at room temperature while the dendritic macromolecules revealed only the hydrogen-bonded urea absorption. These changes in chemical shifts indicate that upon increasing the temperature the hydrogen bonding interactions decrease.[17] This behavior is further supported by the sharpening of the signals at higher temperatures.

The variable-temperature UV–vis measurements in orthodichlorobenzene (ODCB) for all generations of OPV–dendrimers were also carried out (Figure 6). Upon decreasing the temperature from 353 to 283 K, a gradual red shift of λ_{max} was observed for all generations ($\lambda_{max} = 434 \pm 2$ to 442 ± 2 nm). Remarkably, when the absorption maxima of the OPV–dendrimers in ODCB with chloroform solutions at room temperature are compared, a hypsochromic shift of 4–7 nm is observed. If the wavelength of the absorption maximum is plotted against the temperature a linear dependence is observed for all generations (Figure 7). This relation demonstrates that this behavior is not due to hydrogen bond interactions (which are generation dependent). Isosbestic points (420 nm) were observed in the temperature-dependent absorption spectra, indicating the existence of two phases. These phases can be the result of backbone conformational changes, i.e., a planar and twisted conformation.[26] To have a better understanding of this behavior the fluorescence spectra of all generations of OPV–dendrimers were recorded in ODCB at different temperatures (from 263 to 353 K). At low temperature (263 K), photoexcitation ($\lambda_{ex} = 434 \pm 2$ nm) of **OPVG0**, **OPVG1**, **OPVG3,** and **OPVG5** result in an

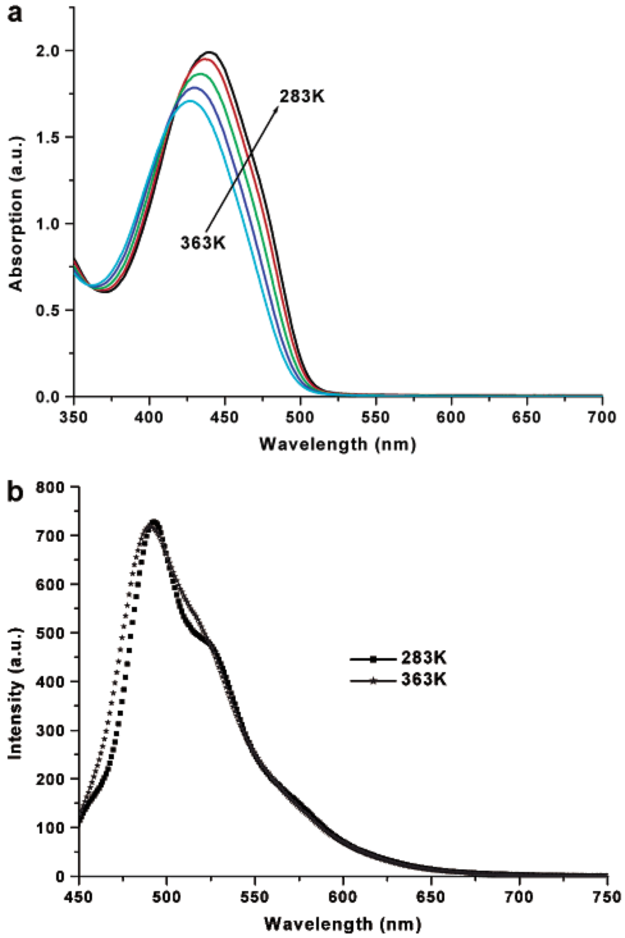


Figure 6. (a) Temperature dependence UV–vis spectra of **OPVG3** and (b) temperature dependence fluorescence spectra of **OPVG3** in ODCB.

Table 1. Temperature Ranges at Which the OPV Dendrimers Are Liquid Crystalline

	LC temp ranges, °C
OPVG0	90–120
OPVG1	70–170
OPVG3	55–180
OPVG5	50–160

emission maximum at $\lambda_{\mathrm{em,max}} = 500$ nm attributed to the emission of the molecularly dissolved chromophores. At higher temperatures the fluorescence emission spectra matched well with the one at low temperature. When the excitation wavelength was changed similar fluorescence spectra were obtained. The fluorescence data show that the observed red shift in the absorption spectra is not due to aggregation of the chromophores but to conformational changes in the oligomer backbone.[24,26]

Thermotropic Properties. The thermal stabilities of **OPVG0**, **OPVG1**, **OPVG3**, and **OPVG5** have been studied with thermal gravimetric analysis (TGA). For **OPVG0** the degradation starts at about 170 °C, while **OPVG1**, **OPVG3**, and **OPVG5** were thermally stable to about 200 °C.

Polarizing microscopy revealed birefringence for all compounds (temperature ranges summarized in Table 1). Dropletlike textures (Maltese crosses) were observed during slow cooling typical for homeotropic orientated molecules while the surface of the glass substrate was not treated to bring about a homeotropic orientation for the mesogens (Figure 8). Homeotropic orientation of poly(propylene imine) dendrimers peripherically modified with cyanobiphenylene mesogens has recently been observed by the Yonetake and co-workers.[27]

DSC measurements, however, did not give phase transition temperatures, probably due to the high viscosity of the polymeric phases and hence to the subsequent slow transition from one phase to the other. Similar behavior has been reported in the literature for polypropylene dendrimers containing trialkoxybenzene wedges as mesogenic units.[28]

The liquid crystalline behavior was further investigated by X-ray powder diffraction. No reflections were observed in the case of **OPVG0**. However **OPVG1**, **OPVG3**, and **OPVG5** gave in all cases one reflection corresponding to a distance of 55.9, 59.0, and 53.9 Å, respectively (Figure 9). According to CPK models, such a distance could correspond to an interdigitated bilayer in which the mesogenic units and the dendritic interior are separated. The arrangement of the mesogenic end groups is perpendicular with respect to the dendritic backbone. The behavior is similar to poly(propylene-imine) dendrimers with cyanobiphenyl or mesogenic ester units.[27,29,30]

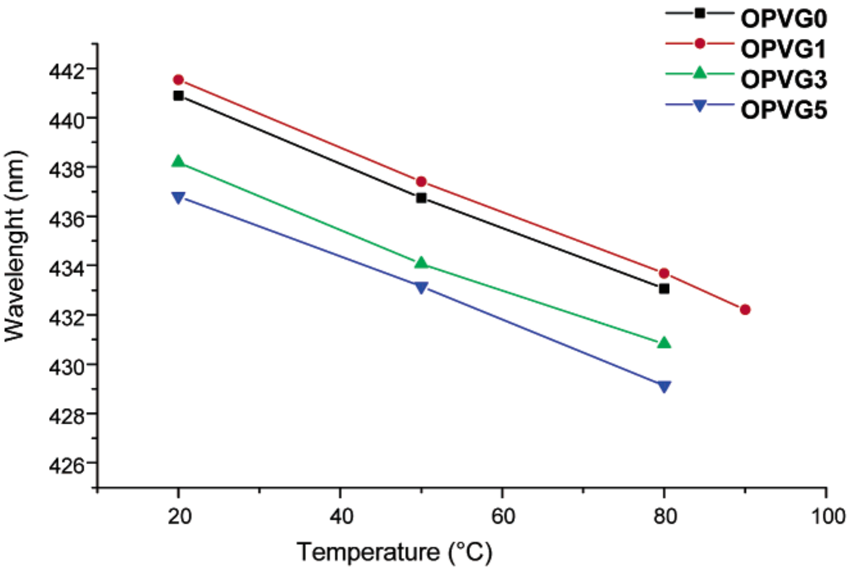


Figure 7. Absorption maximum of **OPVG0**, **OPVG1**, **OPVG3**, and **OPVG5** in ODCB as a function of the temperature.

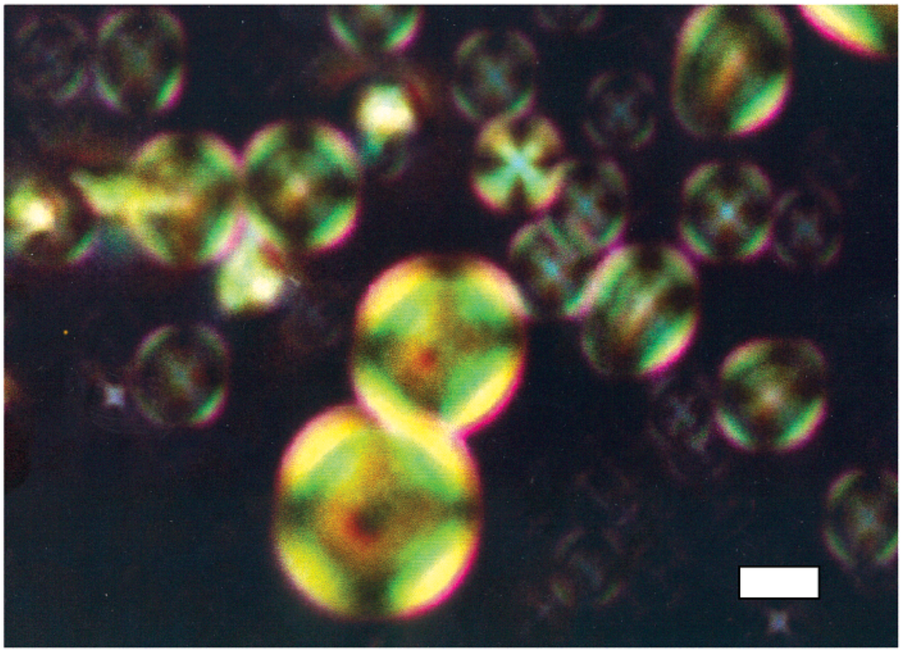


Figure 8. Polarizing optical textures of **OPVG3** during cooling at 1 °C $\min^{-1}$ at 170 °C (bar represents 400 μm).

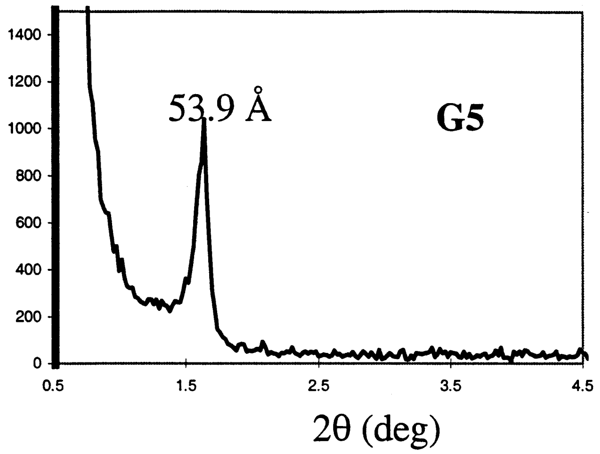


Figure 9. X-ray powder diffraction pattern observed for **OPVG5**.

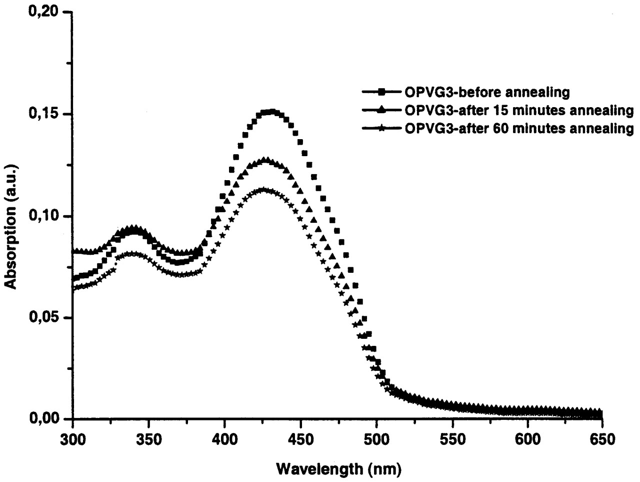


Figure 10. UV–vis spectra of **OPVG3** in spin-coated film before and after annealing.

Optical Studies in Solid State. The thermotropic behavior in the solid state was investigated by UV–vis (Figure 10) and fluorescence spectroscopy. **OPVG1**, **OPVG3**, and **OPVG5** could be spin-coated from a toluene solution giving good quality thin films.[13] A nonhomogeneous very thin film was obtained in the case of **OPVG0**. The absorption spectra of the reference compound **OPVG0** is hypsochromically shifted compared with the behavior in $CHCl_3$ solution ($\lambda_{solution}$ = 434 nm in $CHCl_3$; λ_{film} = 419 nm). In the dendrimer films (**OPVG1**, **OPVG3**, and **OPVG5**) small blue-shifts ($\Delta\lambda$ = 4 nm, λ_{film} = 430 ± 2 nm) of the absorption maxima were observed in comparison with the dendrimer solution. After annealing at 120 °C, the absorption decreases for all generations, which is presumably due to the homeotropic oriention of the OPV moieties. The chromophores are oriented parallel to the incoming light beam resulting in a lower absorption. The remaining absorption is probably due to nonoriented chromophores, e.g., defects in the film or slightly tilted orientation.

Conclusions

Different generations of dendrimers with peripheral liquid crystalline OPV units can be synthesized. In these systems, intramolecular H-bonds exist between the urea linkages, and a gradual increase in hydrogen bond interactions with increasing dendrimer generation is observed. Remarkably, only weak interactions between the attached OPV chromophores exist. All generations of OPV–dendrimers show liquid crystalline behavior. A homeotropic orientation was observed for all OPV–dendrimers on a glass plate. Currently we are investigating if these materials can be applied in electrooptical switches and light-emitting diodes.

Acknowledgment. We would like to thank S. van der Gaast, Dr. Annika J. Karlsson, and Dr. Stefan Meskers for stimulating discussions and assistance with the relaxation data measurements and X-ray powder diffraction measurements. We would like to acknowledge Joost van Dongen for performing the MALDI TOF measurements. The research of A.P.H.J.S. has been made possible by a fellowship of the Royal Netherlands

Academy of Arts and Sciences. The Dutch Science Foundation (NWO) is acknowledged for financial support (F.S.P.-B.).

References and Notes

(1) (a) Tomalia, D. A.; Naylor, A.; Goddard, W. A. *Angew. Chem., Int. Ed.* **1990**, *29*, 138. (b) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules: Concepts, Synthesis and Perspectives*; VCH: Weinheim, Germany, 1996. (c) Fréchet, J. M. J. *Science* **1994**, *263*, 1710. (d) Dvornic, P. R.; Tomalia, D. A. *Macromol. Symp.* **1994**, *88*, 123. (e) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665.

(2) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681.

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

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

(5) Baars, M. W. P. L.; Meijer, E. W. *Top. Curr. Chem.* **2000**, *210*, 131.

(6) (a) Matthews, O. A.; Shipwa, A. N.; Stoddart, J. F. *Prog. Polym. Sci.* **1998**, *23*, 1. (b) Stewart, G. M.; Fox, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 4354. (c) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635. (d) Bar-Haim, A.; Klafter, J.; Kopelman, R. *J. Am. Chem. Soc.* **1997**, *119*, 6197. (e) Jiang, D. L.; Aida, T. *Nature (London)* **1997**, *388*, 454. (f) Tretiak, S.; Chernyak, V.; Mukamel, S. *J. Phys. Chem. B* **1998**, *102*, 3310. (g) Kawa, M.; Fréchet, J. M. J. *Chem. Mater.* **1998**, *10*, 286. (h) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26. (i) Sylvain, L.; Gilat, A. A.; Fréchet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1422. (j) Sato, T.; Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1999**, *121*, 10658. (k) Adronov, A.; Gilat, S. L.; Fréchet, J. M. J.; Ohta, K.; Neuwahl, F. V. R.; Fleming, G. R. *J. Am. Chem. Soc.* **2000**, *122*, 1175.

(7) For example: (a) Percec, V.; Chu, P.; Kawasumi, M. *Macromolecules* **1994**, *27*, 4441. (b) Bauer, S.; Fischer, H.; Ringsdorf, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1589. (c) Ponomarenko, S. A.; Rebrov, E. A.; Bobrovsky, A. Y.; Boiko, N. I.; Muzafarov, A. M.; Shibaev, V. P. *Liq. Cryst.* **1996**, *21*, 1. (d) Chen, F. L.; Jamieson, A. M.; Kawasumi, M.; Percec, V. *J. Polym. Sci. B* **1995**, *33*, 1213. (e) Tsiourvas, D.; Felekis, T.; Sideratou, Z.; Paleos, C. M. *Macromolecules* **2002**, *35*, 6466.

(8) Baars, M. W. P. L.; van Boxtel, M. C. W.; Bastiaansen, C. W. M.; Broer, D. J.; Söntjens, S. H. M.; Meijer, E. W. *Adv. Mater.* **2000**, *12*, 715.

(9) Scheffer, T.; Nehring, J. *Liquid Crystals, Applications and Uses*; Bahadur, B., Ed.; World Scientific: Singapore, 1990; Vol. 1.

(10) (a) Wang, F.; Rauh, R. D.; Rose, T. L. *J. Am. Chem. Soc.* **1997**, *119*, 11106. (b) Miller, L. L.; Kunugi, Y.; Canavesi, A.; Rigaut, S.; Moorefield, C. N.; Newkome, G. R. *Chem. Mater.* **1998**, *10*, 1751. (c) Sebastian, R. M.; Caminade, A. M.; Majoral, J. P.; Levillain, E.; Huchet, L.; Roncali, J. *Chem. Commun.* **2000**, 507.

(11) Schenning, A. P. H. J.; Weener, J. W.; Meijer, E. W. In *Conjugated Polymers and Molecular Interfaces*; Salaneck, W. R., Seki, K., Kahn, A., Pireaux, J.-J., Eds.; Marcel Dekker: New York and Basel, Switzerland, 2002; pp 1−21.

(12) Wang, P.-W.; Liu, Y.-J.; Devadoss, C.; Barathi, P.; Moore, J. S. *Adv. Mater.* **1996**, *8*, 237.

(13) Schenning, A. P. H. J.; Peeters, E.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 4489.

(14) (a) Meier, H.; Lehman, M. *Adv. Mater.* **1998**, *37*, 643. (b) Meier, H.; Lehmann, M.; Kolb, U. *Chem.−Eur. J.* **2000**, *6*, 2462.

(15) (a) Peeters, E.; van Hal, P. A.; Meskers, S. C. J.; Janssen, R. A. J.; Meijer, E. W. *Chem.−Eur. J.* **2002**, *8*, 4470. (b) Syamakumari, A.; Schenning, A. P. H. J.; Meijer, E. W. *Chem.−Eur. J.* **2002**, *8*, 3353.

(16) Schenning, A. P. H. J.; Elissen-Román, C.; Weener, J.-W.; Baars, M. W. P. L.; van der Gaast, S. J.; Meijer, E. W. *J. Am. Chem. Soc.* **1996**, *118*, 8199.

(17) IR and ^{1}H NMR data on adamantyl and palmitoyl urea-functionalized dendrimers: Baars, M. W. P. L. Ph.D. Thesis, Eindhoven University of Technology, 2000.

(18) Boas, U.; Karlsson, A. J.; de Waal, B. F. M.; Meijer, E. W. *J. Org. Chem.* **2001**, *66*, 2136.

(19) ,1,2,2-Tetrachloroethane-d_2 (TCE) was used as solvent for the variable-temperature measurement based on the fact that the solubility of all OPV−dendrimers described here was comparable to that in $CDCl_3$ and one could go up to much higher temperatures.

(20) Bosman, A. W.; Bruining, M. J.; Kooijman, H.; Spek, A. L.; Janssen, R. A. J.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 8547.

(21) Friebolin, H. *Basic One-and Two-Dimensional NMR Spectroscopy*, 2nd ed.; VCH: Weinheim, Germany, 1993.

(22) Baars, M. W. P. L.; Karlsson, A. J.; Sorokin, V.; de Waal, B.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 4262.

(23) van Genderen, M. H. P.; de Brabander-van den Berg, E. M. M.; Meijer, E. W. *Adv. Dendritic Macromol.* **1971**, *4*, 61.

(24) Peeters, E.; Janssen, R. A. J.; Meskers, S. C. J.; Meijer, E. W. *Polym. Prepr.* **1999**, *40*, 519.

(25) Meskers, S. C. J.; Bender, M.; Hübner, J.; Romanovskii, Y. V.; Oestreich, M.; Schenning, A. P. H. J.; Meijer, E. W.; Bässler, H. *J. Phys. Chem. A* **2001**, *105*, 10220.

(26) ten Hoeve, W.; Wynberg, H.; Havinga, E. E.; Meijer, E. W. *J. Am. Chem. Soc.* **1991**, *113*, 5887.

(27) Yonetake, K.; Masuko, T.; Suzuki, K.; Ueda, M.; Nagahata, R. *Macromolecules* **1999**, *32*, 6578.

(28) Cameron, J. H.; Facher, A.; Lattermann, G.; Diele, S. *Adv. Mater.* **1997**, *9*, 398.

(29) Baars, M. W. P. L.; Sontjens, S. H. M.; Fisher, H. M.; Peerlings, H. W. I.; Meijer, E. W. *Chem.−Eur. J.* **1998**, *4*, 2456.

(30) Lorenz, K.; Holter, D.; Stuhn, B.; Mulhaupt, R.; Frey, H. *Adv. Mater.* **1996**, *8*, 414.

MA021338B