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Thermochromism of a liquid crystalline dialkoxy substituted poly(1,4-phenylene-1,3,4-oxadiazol-2,5-diyl)

Andreas F. Thünemann,[*a] **Silvia Janietz,**[b] **Sonja Anlauf**[b] **and Armin Wedel**[b]

[a]*Max Planck Institute of Colloids and Interfaces, Am Mühlenberg, D-14476 Golm, Germany. E-mail: andreas.thuenemann@mpikg-golm.mpg.de*
[b]*Fraunhofer Institute of Applied Polymer Research, Geiselbergstr. 63, D-14476 Golm, Germany*

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The thermotropic liquid crystalline behavior of poly[2′,5′-bis(hexadecyloxy)-1,4-phenylene-1,3,4-oxadiazol-2,5-diyl] **C16pod** was investigated using differential scanning calorimetry, small- and wide-angle X-ray scattering techniques. An order–order transition was found at about 120 °C, which was attributed to the transition from a smectic H phase at a low temperature to a smectic A phase at a high temperature. The repeat unit of the smectic H phase is $d = 3.70$ nm which is composed of a polymer-rich layer ($d_1 = 1.70$ nm) and an alkyl chain rich layer ($d_2 = 2.00$ nm). For the smectic A phase we calculated $d = 3.85$ nm, $d_1 = 1.75$ nm and $d_2 = 2.10$ nm. The lamellae of the smectic A phase are assumed to show undulations with a periodicity of 6.3 nm. By contrast, the smectic H phase has no periodic undulations. The **C16pod** changes its color from yellow–green at 25 °C to blue at 130 °C. UV-vis and fluorescence spectroscopy were used for a quantitative determination of the thermochromicity of **C16pod**. It was found that the optical properties change continuously within a temperature range of 25 to 140 °C. Even at the order–order transition the UV-vis and fluorescence intensities change continuously. It was therefore concluded that the effective conjugation length of the **C16pod** reduces continuously with increasing temperature. The order–order transition is caused predominantly by the melting of the side-chains.

Introduction

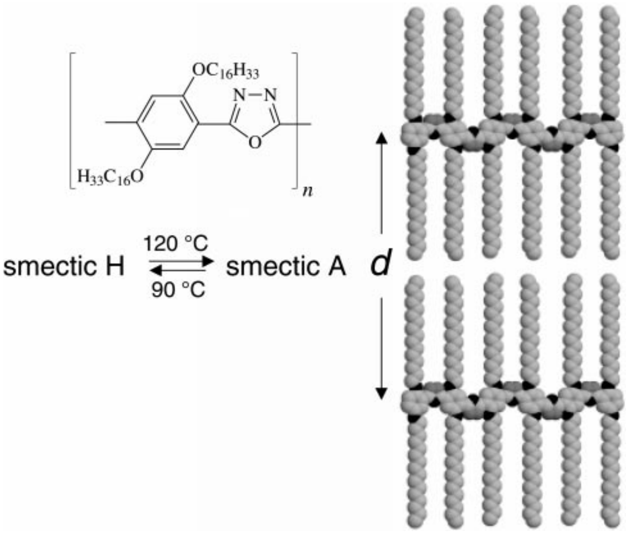
Poly(arylene-1,3,4-oxadiazol-2,5-diyl)s have interesting optical properties, excellent thermal stability and high mechanical strength. But they are difficult to process, for example as thin films. This results from their low solubility in normal organic solvents. For the application of these n-type semiconducting polymers it is essential to make them processable by common procedures. The typical way to overcome the poor solubility for several rigid-rod like polymers is to attach flexible side chains to the polymer backbone.[1] In an earlier study we showed that this strategy is also feasible for fully aromatized poly(1,3,4-oxadiazol-2,5-diyl)s.[2] The thermochromic behavior of processable conductive polymers has been described earlier, for example, that of poly(3-alkylthiophene),[3] poly(arylenevinylene)s[4] and poly[3,3′-dialkyl(ethyne-1,2-diyl)bis(thiophenyl)].[5] An interplay of thermochromicity and liquid crystalline behavior in poly(*p*-phenyleneethynylene)s has been investigated by Bunz *et al.*[6] They have been able to present a conjugated polymer which shows a pronounced thermochromism in the proximity of an order–disorder transition in the solid state.

In this work we report on the temperature dependency of the liquid crystalline structure of the conjugated polymer poly[2′,5′-bis(hexadecyloxy)-1,4-phenylene-1,3,4-oxadiazol-2,5-diyl] **C16pod** (Scheme 1) as well as its thermochromic behavior in the solid state.

Experimental

Materials

Monomer synthesis. *Diethyl 2,5-bis(hexadecyloxy)terephthalate*[7]*.* A total of 0.02 mol (5 g) of diethyl 2,5-dihydroxyterephthalate and 0.4 mol (122.1 g) of the corresponding bromohexadecane were dissolved in 100 ml dry cyclohexanone. After the addition of 0.29 mol (40 g) powdered K_2CO_3 and 0.004 mol (0.65 g) of KI , the mixture was refluxed under nitrogen until no more starting material could be detected by TLC (about 5 h). The hot reaction mixture was filtered and the residue thoroughly washed twice with 100 ml of cyclohexanone. The solvent and the excessive amount of the bromohexadecane were distilled in a vacuum. The solid residue was obtained after cooling, they were then recrystallized in ethanol to obtain the pure diethyl 2,5-bis(hexadecyloxy)terephthalate. The yield was 89% and the melting point 62 °C. The purity was checked by elemental analysis. Calculated ($C_{44}H_{78}O_6$): C, 75.23; H, 11.10. Found: C, 74.98; H 10.82%.



Scheme 1 Molecular structure of poly[2′,5′-bis(hexadecyloxy)-1,4-phenylene-1,3,4-oxadiazol-2,5-diyl] **C16pod** and a molecular model of segments of two polymer chains from **C16pod**.

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2,5-Bis(hexadecyloxy)terephthalic acid. The saponification of the synthesised diethyl 2,5-bis(hexadecyloxy)terephthalates was carried out according to the literature.[7] The crude product was recrystallized in ethanol. The yield was 92% and the melting point 187 °C, where decomposition takes place. The purity was checked by elemental analysis. Calculated ($C_{40}H_{70}O_6$): C, 74.30; H, 10.83; O 14.86. Found: C, 73.88; H, 10.70; O, 15.34. The 2,5-bis(hexadecyloxy)terephthalic acid was converted to the corresponding acid chloride in the presence of thionyl chloride corresponding to the description in the literature.[7] The recrystallisation was carried out in hexane. The yield was 85% and the melting point 74 °C. The purity was checked by elemental analysis. Calculated ($C_{40}H_{68}O_4Cl_2$): C, 70.25; H, 10.02; O, 9.36; Cl, 10.37. Found: C, 69. 84; H, 10.27; O, 10.23; Cl 9.86%.

Polymer synthesis. *Poly[hydrazo-2,5-bis(hexadecyloxy)terephthaloyl].* 2,5-Bis(hexadecyloxy)terephthaloyl chloride (0.0036 mol) was dissolved in 140 mL methylene chloride and cooled to 15 °C. Hydrazine sulfate (0.0036 mol), dissolved in 140 ml of an ice-cold 0.1 M KOH solution, was added slowly. The temperature rose up to 20 °C and the reaction mixture was stirred at this temperature for about 2 h. The polymer precipitated during the reaction. The crude product was separated by filtration and washed alternately with methanol, water, acetone, benzene and dried in vacuum. The yield was 94%. The purity was checked by elemental analysis. Calculated ($[C_{40}H_{70}N_2O_4)$: C, 74.77; H, 10.90; N, 4.36; O, 9.97. Found: C, 73.53; H, 11.09; N, 3.83; O, 10.59%. IR-spectroscopy/cm^{-1}): 3350 (N–H, s), 2925 (C–H, s), 1624 (C=O, s), 1434 (s), 1217, 1029; ^{13}C-NMR (CP-MAS, 100 MHz), δ(ppm): 155.2 (C=O), 149.7 (C_3, C_6), 121.2 (C_1, C_4), 113.6 (C_2, C_5), 68.6 (OCH_2), 33.4 (broad, CH_2-chain), 14.4, (CH_3).

Ring closure reaction. *Poly[2′,5′-bis(hexadecyloxy)-1,4-phenylene-1,3,4-oxadiazol-2,5-diyl].* Poly[hydrazo-2,5-bis(hexadecyloxy)terephthaloyl] (0.00325 mol) was suspended in 65 ml 1,2-dichlorobenzene, and 7.3 ml of $POCl_3$ was added at room temperature while stirring. The reaction mixture was slowly heated to 135 °C and the polyhydrazide was dissolved and kept at that temperature for 2 h. The reaction mixture was cooled down to about 80 °C and the polymer was precipitated in 700 ml methanol–water 4 : 1 mixture. After separation the polymer was washed several times with water, methanol and acetone. The crude product was extracted in a Soxhlet apparatus with methanol for 48 hours. After this the polymer was dissolved in hot toluene and precipitated in acetone and dried in a vacuum at 80 °C. The yield was 94%. The purity was checked by elemental analysis. Calculated ($[C_{40}H_{68}N_2O_3]_n$): C, 76.87; H, 10.97; N, 4.48; O, 7.68. Found: C, 76.39; H, 11.37; N, 3.49; O, 9.37%. The polymer was further characterized by IR- and NMR-spectroscopy. Bands were found at (KBr, cm^{-1}) = 3410, 2923 (–CH), 1545 (ar–C=C, m), 1434 (s), 1235 (s), 1028(s); ^{13}C-NMR (CP-MAS, 100 MHz) : δ(ppm): 161.3 (C-oxadiazole ring), 149.1 (C_3, C_6), 113.2 (C_1, C_4, C_2, C_5), 68.3 (CH_2-O), 33.3 and 23.5(broad, CH_2-chain), 14.2 (CH_3).

Measurements

Differential scanning calorimetry (DSC) measurements were performed on a Netsch DSC 200 (Germany). The samples were examined at a scanning rate of 10 K min^{-1} by applying one cooling and two heating scans. Thermogravimetric analysis (TG) was performed in a nitrogen atmosphere and with a heating rate of 10 K min^{-1} using a Netsch TG 209 instrument. Wide-angle X-ray scattering (WAXS) measurements were carried out with a Nonius PDS120 powder diffractometer in transmission geometry. A FR590 generator was used as the source of CuK_α radiation. Monochromatization of the primary beam was achieved by means of a curved Ge crystal, and the scattered radiation was measured with a Nonius CPS120 position sensitive detector with a resolution in 2θ of 0.018°. The small-angle X-ray scattering measurements were recorded with an X-ray vacuum camera with pinhole collimation (Anton Paar, Austria; model A-8054) equipped with image plates (type BAS III, Fuji, Japan). The image plates were read by a MACScience Dip-Scanner IPR-420 and IP reader DIPR-420 (Japan). The scattering vector s is defined as $s = 2/\lambda \sin\theta$, where 2θ is the angle between the primary beam and the scattered beam. For thin film preparation a 1% (w/w) solution of **C16pod** in xylene was spin cast onto ITO glass slides at a speed of 1000 rpm. The film thicknesses were about 100 to 400 nm. In order to measure the optical properties of the **C16pod** films, the sample temperatures were adjusted by resistance heating, and a thermocouple monitored the temperature on the top of the polymer layers. The film samples and the heating equipment are mounted inside both an UV-VIS-NIR spectrophotometer (Lambda 19 from Perkin Elmer) and a fluorescence spectrophotometer (LS50 B from Perkin Elmer) so that the absorption and fluorescence spectra could be measured at constant temperatures.

Results and discussion

Liquid crystalline structures

The thermal properties of the **C16pod** were investigated by differential scanning calorimetry (DSC) and by thermogravimetry (TG). Typical DSC traces of the heating and cooling scans, measured with a heating rate of 10 K min^{-1}, are given in Fig. 1. An endothermic transition with a maximum at 120 °C was found upon heating. After cooling the transition was found to be at 90 °C. Tentatively, the transition was assigned to an order–order transition. The large hysteresis of the transition at a width of 30 °C indicates the slow kinetics of the transition. TG investigations showed that no weight loss was observed in a nitrogen atmosphere up to a temperature of 300 °C (not shown). This observation is within our expectation; namely that **C16pod** has a good thermal stability. Because of the molecular geometry of the polymer with a rigid rod-like backbone and long flexible side-chains, we expected that the ordering of the polymer in the solid state would be liquid crystalline. Therefore, temperature-dependent wide- and small-angle scattering measurements were carried out to investigate its molecular and supramolecular ordering. In the small-angle X-ray patterns of the **C16pod** which where recorded at 30 and 130 °C (Figs. 2a and b) five equidistant reflections were found. This can be interpreted as highly ordered smectic structures for the lower and the higher temperature phases. It can be seen that the sharpness of the reflections at higher temperatures is greater than it is at lower temperatures and that a weak additional reflection is present at very small values of the scattering vector.

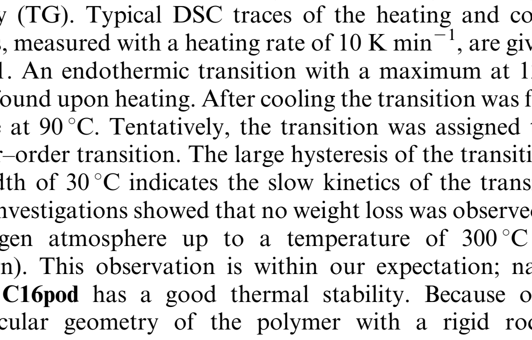

Fig. 1 DSC traces of **C16pod** while heating and cooling. The endothermic transition at 120 °C in the heating scan and the exothermic transition at 90 °C in the cooling scan indicate a reversible order–order transition.

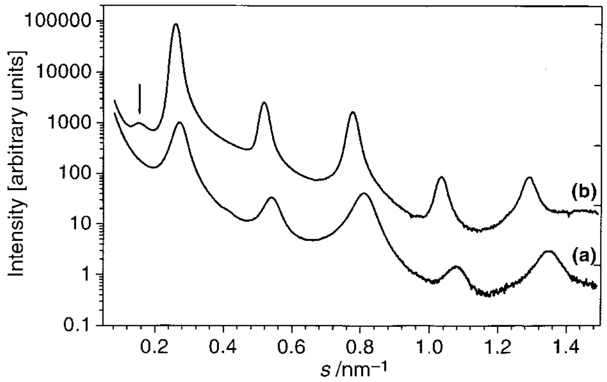

Fig. 2 The small-angle X-ray scattering of the **C16pod** polymer in the lower temperature phase at 30 °C (a) and in the higher temperature phase at 130 °C (b).

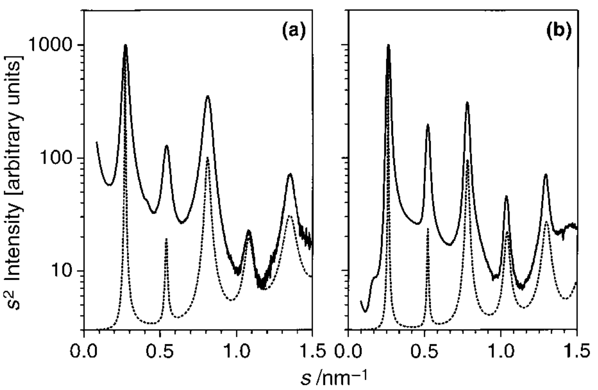

Fig. 3 The small-angle X-ray scattering intensities (solid lines, multiplied with s^2) and analytical profiles according to eqn. (1) are given for the lower temperature phase at 30 °C (a) and for the higher temperature phase at 130 °C (b).

From the width of the first intense small-angle reflection the correlation lengths in the direction of the lamellae normals were determined to be 37 nm (10 repeat units) for the lower temperature phase and 77 nm (20 repeat units) for the higher temperature phase. This was unexpected and could only be explained by the change of the molecular order at the transition. We assume that a partial crystallinity of the side chains at the lower temperature phase causes packing constraints which reduce the correlation length of the structure. By contrast the additional reflection in the higher temperature phase indicates periodic undulations of the lamellae which increase the correlation lengths of the higher temperature phase.

For a quantitative interpretation of the small-angle data we considered an idealized lamellar two-phase system with sharp boundaries. A model which can describe a stack of lamellae is the stacking model in which the statistics of the lamellar stack are determined by the distributions $h_1(d_1)$ and $h_2(d_2)$ for the thicknesses of the two lamellae d_1 and d_2. These distributions are considered to be statistically independent; *i.e.*, there is no correlation between the two variances $\sigma_1{}^2$ and $\sigma_2{}^2$. The period d is given by $d = d_1 + d_2$. Only by assuming the distributions $h_1(d_1)$ and $h_2(d_2)$ to be normalized, one finds for the scattering intensity[8] (infinite stack size) [eqn. (1)]

$$4\pi s^2 I(s) = \frac{k}{\pi^2 s^2}\mathrm{Re}\left[\frac{(1-H_1(s))(1-H_2(s))}{1-H_1(s)H_2(s)}\right] \qquad (1)$$

where H_n is the one-dimensional Fourier transform of h_i: $H_i(s) = \exp(2\pi i d_i s - 2\pi^2\sigma_i^2 s^2)$. Re stands for the "real part". Eqn. (1) is used widely for the determination of the lamellar thicknesses of two-phase systems, for example, those of block copolymers[9] and polyelectrolyte surfactant complexes.[10] A comparison of the curves according to eqn. (1) with the small-angle scattering curves (intensities were multiplied by s^2) is shown in Fig. 3. The intensity ratios of the reflections are very sensitive to a variation of the relative thicknesses of d_1 and d_2 and therefore these values can be determined with an accuracy of about 0.05 nm. For the lower temperature phase the calculated values are $d = 3.70$ nm, $d_1 = 1.70$ nm and $d_2 = 2.00$ nm at 30 °C. The corresponding values for the high temperature phase (130 °C) are 3.85, 1.75 and 2.10 nm, respectively. From the particular amount of alkyl side chains in relation to the polymer backbone we assign d_1 to the thickness of the polymer layer and d_2 to the thickness of the alkyl chain rich layer. In addition to this we assume that the lamellae are regularly undulated with a period of 6. 3 nm. Undulations could explain the weak reflection at small angles (see arrow in Fig. 2, curve b). Such layer undulations of liquid crystalline polymers were described earlier by Davidson.[11] Antonietti *et al.* have shown that layer undulations are a typical characteristic of many polyelectrolyte surfactant complexes.[12]

In contrast to the higher temperature phase there are no indications of undulations of the lamellae in the lower temperature phase. An idealized computer model of two **C16pod** chain segments is shown in Scheme 1. A distance of about 3.7 nm between two polymer chains was calculated. This is in agreement with the lamellar repeat units that were determined by small-angle X-ray scattering measurements.

It can be seen in Fig. 4 that the wide-angle scattering pattern measured below the order–order transition (Fig. 4a, 30 °C) differs significantly from that above the transition (Fig. 4b, 130 °C). A group of three reflections was found at 30 °C with their respective maxima at 2.24 nm^{-1}, 2.42 nm^{-1} and 2.69 nm-$^{-1}$. A further sharp reflection was present at 2.96 nm^{-1}. The positions and widths of the reflections were determined by fits of Lorentzian profiles onto the scattering curve (dashed lines of Fig. 4a and b). We regard the first group of reflections as resulting from a tight packing of the alkyl chains. Tentatively we propose a two-dimensional oblique unit cell with lattice parameters of $a = 0.483$ nm, $b = 0.447$ nm and $\gamma = 68°$ from the reflex positions. These cell dimensions give an area of 0.20 nm^2 per alkyl chain and are consistent with the typical area requirement for elongated alkyl-chains in the crystalline state.[14] Here the side-chains are crystalline and the phase was regarded as a smectic H phase. The position of the sharp reflection at higher angles corresponds to a Bragg spacing of 0.338 nm, which is close to polymeric systems with strong π–π interactions, as is the case for graphite or carbon fibers (0.335 nm).[13] We explain the distance of 0.338 nm as resulting from the scattering of a regular order of the conjugated polymer chains. A correlation length of 5 nm was

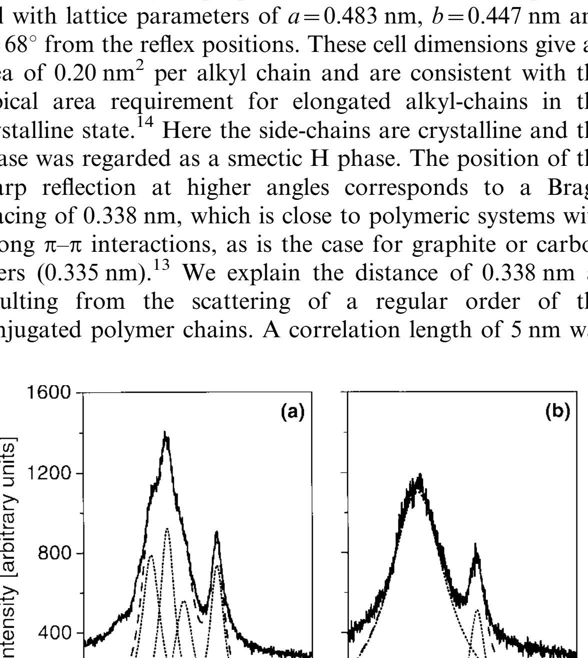

Fig. 4 The wide-angle X-ray scattering of the **C16pod** polymer in the lower temperature phase at 30 °C (a) and in the higher temperature phase at 130 °C (b). The solid lines represent experimental curves, the dashed lines are fits of sums of Lorentzian profiles and the dotted lines represent the single peak profiles.

determined for the interchain direction from the width of the reflection. Therefore we conclude that considerable π–π interactions between adjacent chains are present. In the wide-angle diagram of the higher temperature phase at 130 °C only a broad reflection at 2.26 nm^{-1} and a sharper reflection at 2.91 nm^{-1} were found. The first can be explained as a result of the scattering of alkyl chains of a liquid-like order. In combination with the results of the small-angle scattering measurements we can assign the higher temperature phase to a smectic A structure, namely a lamellar structure with molten alkyl chains. This is typical for liquid crystals.[14] The second reflection, as shown in the diagram of the lower temperature phase, results from the interchain order of the polymeric chains with a distance of 0.343 nm. The interchain correlation length is the same as at lower temperatures (5 nm). The larger interchain distance compared to the lower temperature phase can be explained by the higher thermal energy, which increases the interchain distance.

Optical properties

The optical properties of **C16pod** were found to be thermochromic. Thin films of **C16pod** prepared on glass slides appear yellow-to-green at 25 °C and became blue at 130 °C. The color changes were found to be fully reversible. UV-vis and fluorescence spectroscopic measurements were carried out for a quantitative evaluation of the thermochromic behavior of **C16pod**. It can be seen in the UV-vis spectra (Fig. 5) that two absorption peaks are present at about 415 nm and 445 nm when the temperature is low (25 °C). The intensity of these peaks decreased gradually when the temperature was raised and a new peak appeared at 370 nm (see Fig. 5). The UV-vis spectra are in agreement with the observed color changes from yellow–green to blue. It can be seen further in Fig. 5 that an isosbestic point is present at 380 nm. Such an isosbestic point indicates that different structure intermediates coexist[15] in **C16pod**. The question arose as to whether the optical properties change in a step-like manner, or continuously at the order–order transition. We found that the UV-vis spectrum changes continuously. This can be seen from the temperature dependency of the absorbance at 370 nm, 415 nm and 442 nm shown in Fig. 6. The first intensity increases monotonically while the second and third decrease monotonically. The continuity of the changes indicates that the conformation of the polymeric backbone is not significantly involved in the order–order transition. As found for the UV-vis spectra, the fluorescence spectra are also dependent on the temperature. This can be seen in Fig. 7. An intense emission maximum occurs at 484 nm and a weaker emission at 515 nm (25 °C). The first maximum shows a hypsochromic shift to 475 nm and the intensity of the second emission band almost disappears when the temperature is raised to 135 °C. As for the UV-vis spectra we found no step-like changes of the spectra in the region of the order–order transition. The shift of the position of the peak maximum, for example, is regular within the temperature range of 25 to 135 °C (Fig. 7, insert). We explain the observed blue shift in the absorption and in the fluorescence spectra of **C16pod** as a result of a successive decrease of its effective conjugation length. The order–order transition of the **C16pod** affects the ordering of the side chains of the polymer but it has no significant effect on the conjugation length of the polymer main chains. In a recent work, Bunz *et al.* demonstrated that the optical properties of poly(*p*-phenyleneethynylene)s show a pronounced thermochromicity at a liquid crystalline transition.[6] But in their work the transition was of an order–disorder type, while here it is on the order–order type. In contrast to **C16pod**, the poly(*p*-phenyleneethynylene)s show conformational changes at the transition. We assume that a torsional motion around the ring–ring linkages of the polymeric backbone takes place when the temperature is increased. This leads to a reduction of the intervening conjugation and consequently to a reduction of the effective conjugation length.

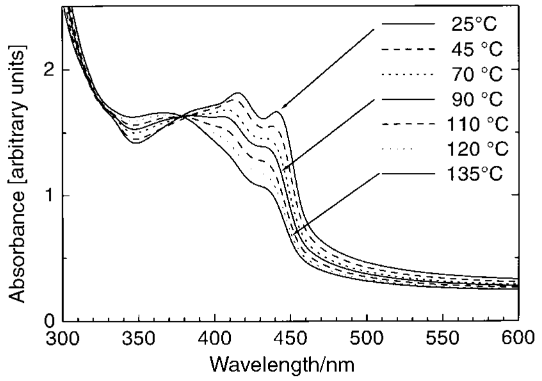

Fig. 5 UV-vis spectra of a **C16pod** film at different temperatures.

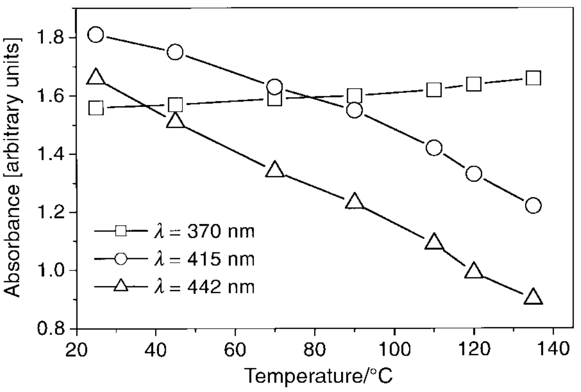

Fig. 6 Temperature dependency of the UV-vis intensities at wavelengths of 370 nm (squares), 415 nm (circles) and 442 nm (triangles).

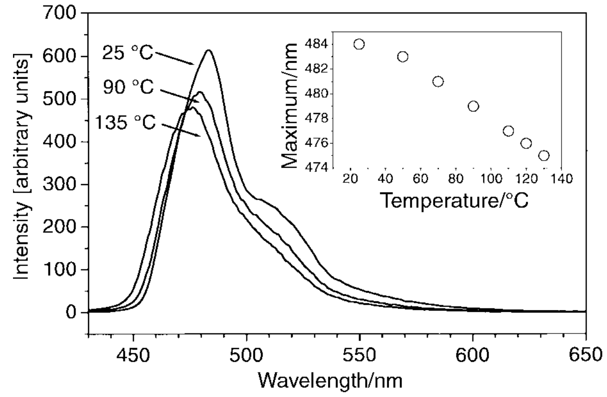

Fig. 7 Fluorescence emission spectra of **C16pod** at different temperatures. The excitation wavelength is 370 nm. The insert shows the temperature dependency of the positions of the fluorescence maxima.

Conclusions

The structural and optical properties of a rigid rod *n*-type dialkoxy substituted poly(1,4-phenylene-1,3,4-oxadiazol-2,5-diyl) was investigated by DSC, temperature dependent wide- and small-angle scattering, UV-VIS- and fluorescence-spectroscopy. We conclude that this polymer forms two smectic structures: at temperatures below 120 °C the side-chains are crystalline and probably the phase can be assigned to the smectic H. Above 120 °C the side-chains are molten and the structure is smectic A, probably with periodic undulations of the lamellar surfaces. Further the aromatic cores form regular structures with a regular distance of 0.34 nm in both phases.

This feature is common to both structures and was interpreted as resulting from strong π–π-interactions. The polymer shows thermochromic behavior. The color changes from yellow–green at room temperature to blue at 130 °C. It is interesting that the thermochromicity is not affected at the order–order transition.

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