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Liquid crystalline properties of penta(*p*-phenylene)s modified with short lateral and long terminal alkoxy chains

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A series of penta(*p*-phenylene)s modified with short and long alkoxy groups was synthesized via palladium complex-catalysed cross-coupling reactions. Molecules substituted with butoxy groups in the central ring showed a nematic phase characterized by a schlieren optical texture, whereas those molecules lacking lateral groups, or substituted with shorter than butoxy groups, did not exhibit liquid crystallinity. Also, it was determined that both the mesophase stability and the clearing point were strongly dependent on the length of the terminal chains. Finally, optical studies of these compounds indicated that the observed light absorption/emission characteristics are independent of the chain lengths.

1. Introduction

Conjugated organic molecules showing both luminescent and liquid crystalline properties have attracted considerable interest in recent years because of the possibility of obtaining thin films with spontaneously aligned light emitters [1–5]. This is the case of the alkoxy-modified oligo- and poly-(*p*-phenylene) derivatives, whose π-conjugated core is composed exclusively of phenylene rings connected in the *para* position. Due to its rigid and rod-like molecular architecture, this moiety by itself is insoluble in common solvents leading to severe problems for its synthesis and processing. Fortunately, alkoxy-modified derivatives offer the possibility of obtaining soluble oligomeric and polymeric materials [6]. In addition, the combination of a rigid core with flexible chains promotes liquid crystalline behaviour [1, 7], which is of interest for the molecular alignment in many electronic devices. Oligomers are particularly interesting because, compared with polymers, they can be easily obtained as high purity monodisperse materials through well-controlled organic reactions, and they can develop a molecular arrangement of high order.

Many new soluble oligo(*p*-phenylene) derivatives have been synthesized in order to analyse their luminescent properties; however, few systematic studies have been performed on their thermal behaviour, particularly in relation to their mesomorphic properties. In a recent paper, we reported a series of oligo(*p*-phenylene)s substituted with lateral and terminal alkoxy chains that exhibit liquid crystalline properties [8]. In particular, pentamers showed a nematic phase, which is of interest for the preparation of thin films that may contain highly oriented molecules. In the present paper, we describe the synthesis and characterization of a series of penta(*p*-phenylene)s modified with short lateral alkoxy groups and long terminal alkoxy chains. The effect of the length of substituents on the thermotropic liquid crystalline behaviour is discussed.

2. Experimental

2.1. *Measurements*

^{1}H NMR spectra were recorded with a 300 MHz Jeol spectrometer and deuterated tetrahydrofuran (THF-d_8) or chloroform ($CDCl_3$). FTIR spectra (KBr pellets) were obtained using a Nicolet Magna 550 spectrometer. Elemental analysis (C and H) was performed in a Carlo-Erba (1106) instrument at the Charles Sadron Institute, Strasbourg, France. Differential scanning calorimetry (DSC) traces were obtained using an open Mettler FP94HT calorimeter at heating and cooling rates of $2^{\circ}C\,min^{-1}$. Optical textures of mesophases were registered during heating and cooling in a polarizing Olympus optical microscope coupled with a Mettler FP82HT hot stage. X-ray diffraction (XRD) patterns were recorded with an INEL CPS120 diffractometer

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($K_{\alpha 1}$, copper radiation and home-made electrical oven). The UV-visible spectra were recorded on a Shimadzu 2401PC spectrophotometer. Fluorescence was measured on a Perkin Elmer LS-50B spectrofluoremeter. Procedures were identical for all samples.

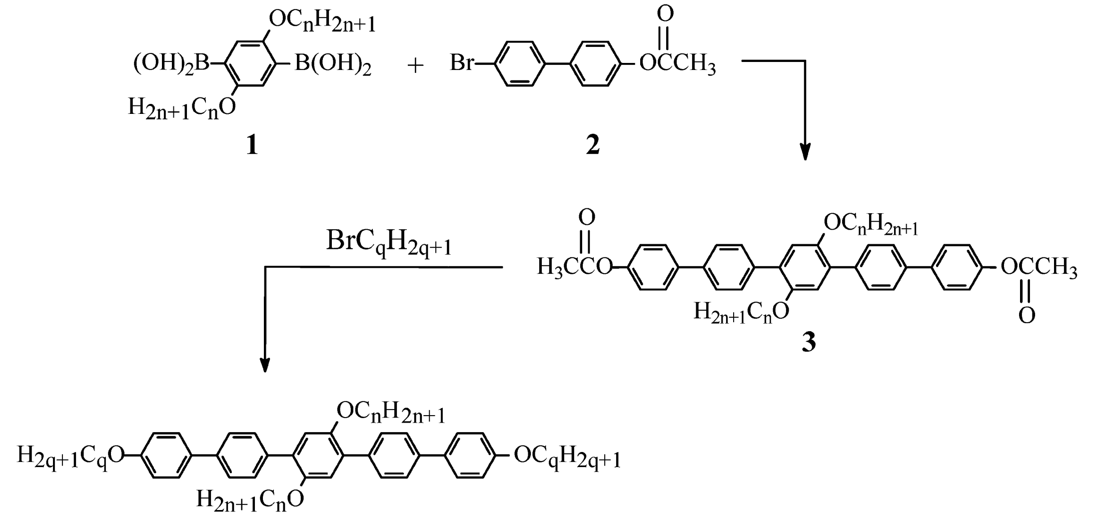
2.2. *Materials*

Chemicals used in this work were hydroquinone, 4′-bromo-4-hydroxybiphenyl, bromoalkanes of different lengths (C2, C3, C4, C6, C8, C10, C12, C14 and C16), butyllithium 1.6M in hexanes, trisopropylborate, bromine and some other reagents as described in the procedures. All chemicals were purchased from Aldrich and used as received, except for the tetrahydrofuran (THF), which was freshly distilled from a sodium/benzophenone complex.

All compounds were synthesized according to a method previously reported [9] with the exception of those marked with an asterisk in scheme 1, which were obtained by means of an alternative route described in a recent paper [8]. For the sake of brevity, synthesized molecules were labelled as P*q*-*n*, where P, *q*, and *n* represent penta(*p*-phenylene), the length of terminal chains and the length of lateral groups, respectively.

2.3. *Synthetic procedures*

2.3.1. 4′-Bromo-4-acetoxybiphenyl (2). To obtain this intermediate, we replaced the hydroxyl group of the 4′-bromo-4-hydroxybiphenyl by an acetoxy group according to the procedure described by Percec *et al.* [10]. A mixture of 17.3 mmol of 4′-bromo-4-hydroxybiphenyl, 11 cm^3 of acetic anhydride and a few drops of concentrated sulphuric acid was stirred and heated for one hour at 60°C. It was then cooled to room temperature and 50 cm^3 of cold water were added. The solution was stirred overnight and the resulting white precipitate was filtered and washed with methanol. Finally, the product was recrystallized from hexane. Yield 4.23 g, 77%, m.p. 130°C. ^1H NMR ($CDCl_3$): δ (ppm)=2.34 (s, 3H, $OCOCH_3$), 7.15–7.19 (d, 2H, Ar *ortho* to acetoxy),



Pq-n

q = 16	**n = 4**
P16-2*: n=2	P6-4 : q=6
P16-3 : n=3	P8-4 : q=8
P16-4*: n=4	P10-4 : q=10
	P12-4 : q=12
	P14-4*: q=14

Scheme 1. Synthesis route for the preparation of penta(*p*-phenylene)s modified with short (*n*) and long (*q*) alkoxy chains. (i) $[P(C_6H_5)_3]_4Pd(0)$/toluene/Na_2CO_3 2M; (ii) NaOH, DMF, RBr. For molecules marked with an asterisk (*) see text.

7.41–7.60 (m, 6H, Ar). FTIR (cm^{-1}): 1750, 1585, 1480, 1372, 1205, 1106, 1071, 1001, 911, 825, 803, 746.

2.3.2. 1,4-Bis (4′-acetoxybiphenyl)-2,5-alkoxy benzene (3). A mixture of 3.08 mmol of compound **1** [6], 15 cm^3 of toluene, 7.35 mmol of compound **2**, 0.2 mmol of $[P(C_6H_5)_3]_4Pd(0)$ and 6.5 cm^3 of 2M aqueous Na_2CO_3 was degassed twice, maintained under an argon atmosphere and then vigorously stirred at reflux for 24 h. After cooling to room temperature, the precipitate was filtered and washed with methanol and then with hexane. The product was recrystallized from a toluene/hexane boiling mixture. Compound **3** with butoxy groups: yield 45.5%, m.p. 219.5–220.5°C. ^{1}H NMR ($CDCl_3$): δ (ppm)=0.8–1.0 (t, 6H, 2 $OCH_2CH_2CH_2CH_3$), 1.3–1.5 (m, 4H, 2 $OCH_2CH_2CH_2$–), 1.6–1.8 (m, 4H, 2 OCH_2CH_2–), 2.34 (s, 6H, 2 $OCOCH_3$), 3.9–4.0 (t, 4H, 2 OCH_2–), 7.05 (s, 2H, Ar *ortho* to butoxy), 7.15–7.19 (d, 4H, 2 Ar *ortho* to acetoxy) and 7.41–7.60 (m, 12 H, Ar). Compound **3** with propoxy groups: yield 17.5%, m.p. 242–243°C. ^{1}H NMR ($CDCl_3$): δ (ppm)=0.8–1.0 (t, 6H, 2 $OCH_2CH_2CH_3$), 1.6–1.8 (m, 4H, 2 OCH_2CH_2–), 2.34 (s, 6H, 2 $OCOCH_3$), 3.9–4.0 (t, 4H, 2 OCH_2–), 7.05 (s, 2H, Ar *ortho* to butoxy), 7.15–7.19 (d, 4H, 2 Ar *ortho* to acetoxy) and 7.41–7.60 (m, 12 H, Ar); mp 242–243°C. Selected FTIR (cm^{-1}) data for compound **3** substituted with butoxy groups: 2958, 2931, 2869, 1756, 1489, 1372, 1197, 1006, 914, 836.

2.3.3. 1,4-Bis (4′-alkoxybiphenyl)-2,5-alkoxy benzene (P*q*-*n*). In a 250 cm^3 reaction flask equipped with magnetic stirring and a $CaCl_2$ humidity trap, 1 mmol of compound **3**, 3 mmol of ω-bromoalkane, 0.33 mmol of TBAH, 10 mmol of NaOH, and 50 cm^3 of dimethyl formamide were introduced. The mixture was vigorously stirred and heated for 48 h at 95°C. After cooling to room temperature, the precipitate was filtered, washed with distilled water, and dried under vacuum. The product was first isolated using a flash chromatography column (SiO_2, $CHCl_3$); it was then precipitated with methanol, filtered, and dried. Yield was dependent on the chain length and varied from 55% to 90% for the hexyloxy and dodecyloxy, respectively. Selected ^{1}H NMR ($CDCl_3$) data for P10–4: δ (ppm)=0.87–0.94 (m, 12H, 4 CH_3), 1.39–1.51 (m, 32H, 16 CH_2), 1.66–1.86 (m, 8H, 4 OCH_2CH_2–), 3.94–4.04 (m, 8H, 4 OCH_2–), 6.95–7.69 (2m, 18H, Ar). ^{1}H NMR spectroscopic data for compounds P6-4, P8-4, P12-4, P14-4, P16-2, P16-3 and P16-4 are similar to those of compound P10-4; the primary difference is the intensity of the methylene signals. Selected FTIR (cm^{-1}) data for P10-4: 2921, 2850, 1609, 1510, 1491, 1473, 1387, 1247, 1212, 1177, 1056, 1034, 820, 740. FTIR data for compounds P6-4, P8-4, P12-4, P14-4, P16-2, P16-3 and P16-4 are similar to those of compound P10-4. Elemental analysis: P10-4 $C_{58}H_{78}O_4$ (839.25) calcd C83.01, H9.37, found C83.08, H9.44%; P12-4 $C_{62}H_{86}O_4$ (895.36) calcd C83.17, H9.68, found C83.15, H9.82%; P14-4 $C_{66}H_{94}O_4$ (951.47) calcd C83.32, H9.96, found C83.25, H9.93%; P16-4 $C_{70}H_{102}O_4$ (1007.57) calcd C83.44, H10.20, found C83.35, H10.22%.

3. Results and discussion

3.1. *Synthesis*

There are several routes for the preparation of π-conjugated oligophenylenes through metal complex-catalysed coupling reactions of aryl derivatives. In the present work, the method proposed by Kostandankopoulou *et al.* [9] was selected because it provides an easy method for preparing significant amounts of the acetoxy-bifunctionalized penta(*p*-phenylene) (**3**), which can be further modified in just one final step with alkoxy terminal chains of different length. This bifunctionalized rigid core is obtained through the Pd(0)-catalysed cross-coupling reaction (i) between an alkoxy-disubstituted arylbisboronic acid (**1**) and a bromoacetoxyaryl derivative (**2**) (Suzuki reaction [11]), which can be synthesized according to known procedures [6, 11–13]. The use of arylboronic acids as intermediates is convenient because they are highly stable during storage and handling and they readily react with arylbromides under relatively mild conditions [6, 12]. Finally, a Williamson reaction [14] (ii) was used to introduce the two terminal alkyl chains into compounds **3**. Because of the strong solubility problems shown by the ethoxy- and propoxy-modified diacetoxyaryl intermediates (**3**), an alternative procedure was followed for the synthesis of the alkoxy-modified pentaphenylenes [8].

3.2. *Thermotropic behaviour*

Molecules with conjugated phenylene rings in the *para* position provide interesting organic materials because they exhibit luminescent properties in the blue region. Oligomers such as *p*-pentaphenyls are insoluble and may be chemically modified to give soluble derivatives that can be cast or spin-coated on a substrate to obtain films with desirable characteristics. Interestingly, when these molecules are modified with flexible chains like alkyl or alkoxy groups, which are normally introduced to solve solubility problems, a second interesting property can be developed. This second property is related to the capacity of the molecules for a spontaneous molecular self-organization typical of liquid crystals (LCs).

In previous work on alkoxy-substituted oligophenylenes of three, five, and seven conjugated units, we observed that a terphenyl modified only at both ends with one long alkoxy chain develops a rich mesomorphism (tilted smectic type phases), whereas a *p*-pentaphenyl and *p*–heptaphenyl with similar modifications do not develop mesomorphism. By contrast, terphenyls modified with two short lateral alkoxy groups and two long terminal alkoxy chains do not show mesomorphism, whereas a *p*-pentaphenyl and *p*-heptaphenyl with similar modification exhibit a nematic phase. From these observations, it was deduced that, for π-conjugated cores such as trimers, the substitution of short alkoxy groups into the central ring hinders the molecular arrangement in the liquid state, probably because such the core is quite short. In contrast, for longer rigid cores like pentaphenyls and heptaphenyls, these short lateral groups in the central ring become necessary to decouple the strong π–π interactions occurring in such long rigid cores, promoting the liquid crystalline behaviour. From these results, it appeared to be of interest to study the LC properties of alkoxy-substituted penta(*p*-phenylene)s whose optical and liquid crystalline properties are of great interest in the preparation of thin films for electronic devices.

All the penta(*p*-phenylene)s modified with butoxy groups (P*q*-4) exhibited multiple thermal transitions on heating (except P4-16) and cooling, as shown in the DSC traces depicted in figures 1 and 2, respectively. The high temperature transition showed a marked inverse dependence on the length of the terminal alkoxy chains. It varied from 114°C for pentamers with hexadecyloxy substitutions to 173°C for those modified with hexyloxy chains. All pentamers substituted with butoxy groups developed a schlieren texture typical of a nematic phase (figure 2). The nematic nature was corroborated by the absence of diffraction peaks on the X-ray patterns (figure 3). On cooling from the nematic phase, a strong and sharp thermal transition indicates a liquid–solid transition or crystallization, also corroborated by XRD analysis (figure 3). On further cooling, some oligomers showed an exotherm, which was associated with an arrangement of alkyl chains in the solid state, as it has been observed in some semi-flexible polymers modified with long lateral alkyl chains [15]. Here it is supposed that alkyl chains crystallize from the amorphous state [16].

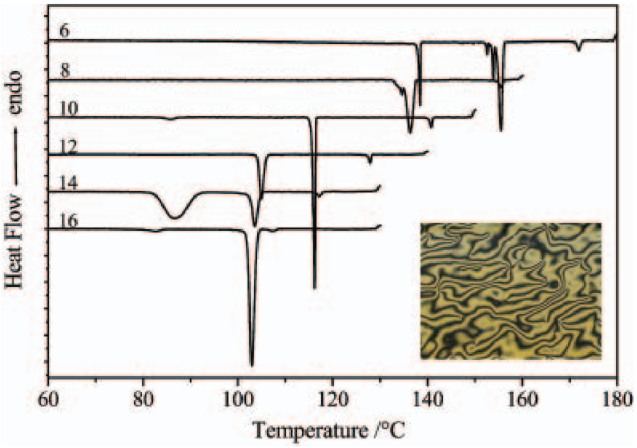


Figure 2. DSC cooling traces of butoxy-substituted penta(*p*-phenylenes) modified with alkoxy terminal chains of different length. The insert shows the schlieren texture of the nematic phase.

In order to determine the ‘mesomorphic region’ of pentamers modified with butoxy groups, the melting

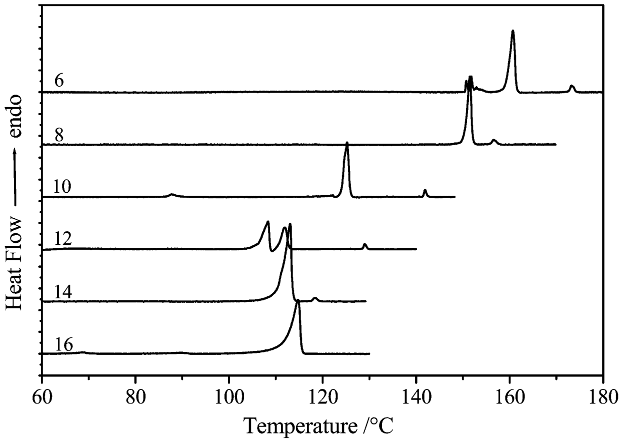


Figure 1. DSC heating traces of butoxy-substituted penta(*p*-phenylene)s modified with alkoxy terminal chains of different length.

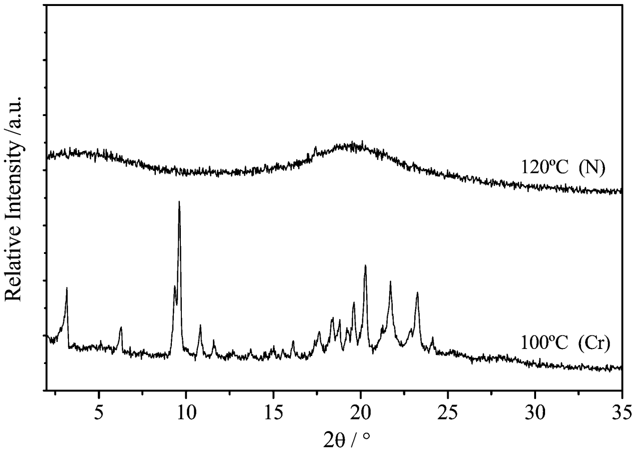


Figure 3. X-ray patterns of compound P12-4 at two different temperatures.

(T_m) and isotropization (T_i) temperatures were plotted against the length of the terminal alkoxy chains (figure 4). The temperature interval between T_m and T_i corresponds to the mesophase stability [17]. It may be noted that oligomers with short terminal chains (C6 and C8) show the highest T_m (159°C) and T_i (173°C), while those whose terminal chains are longer than ten carbon atoms, P12-4, P14-4 and P16-4, show a similar T_m (around 112°C) and a decreasing T_i of 130, 129 and 112°C, respectively. Also, from figure 4 it is expected that pentamers longer than P16-4 may not exhibit mesomorphism. By contrast, pentamers shorter than P6-4 may develop LC properties, but with very high thermal transitions and serious solubility problems, as encountered during the synthesis of shorter oligomers.

For penta(*p*-phenylenes), it was thought that by decreasing the hindering effect produced by butoxy groups, the enhanced lateral interactions between molecules would lead to the formation of some other mesophases. Unfortunately, pentamers with ethoxy and propoxy lateral groups do not show mesomorphic behaviour, see figures 5 and 6. On heating and cooling, both ethoxy and propoxy derivatives show only solid–liquid and liquid–solid transitions, respectively. It is worth noting that the pentamer with no lateral chains is completely insoluble and decomposes before melting, indicating the strong π–π interactions occurring in this linear polyaromatic core. On the other hand, the thermal properties of penta(*p*-phenylenes)s modified with longer lateral chains (hexyloxy groups), have been studied and according to reported DSC traces, no mesophases were seen [9]. This indicates that butoxy groups are of ideal length for the development of liquid crystalline properties in pentaphenylenes.

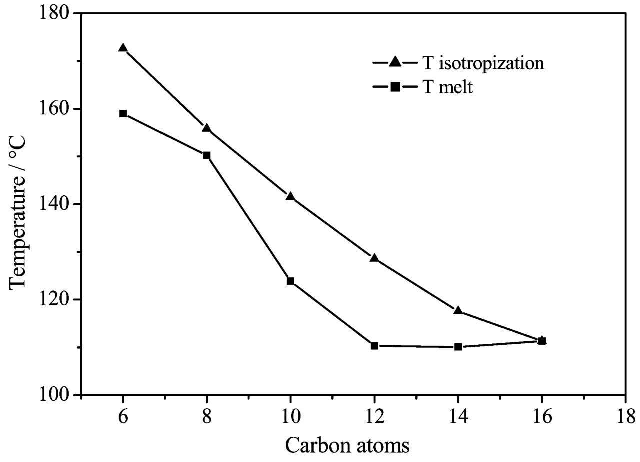


Figure 4. Melting and isotropization temperatures of butoxy-substituted penta(*p*-phenylene)s modified with different length alkoxy terminal chains.

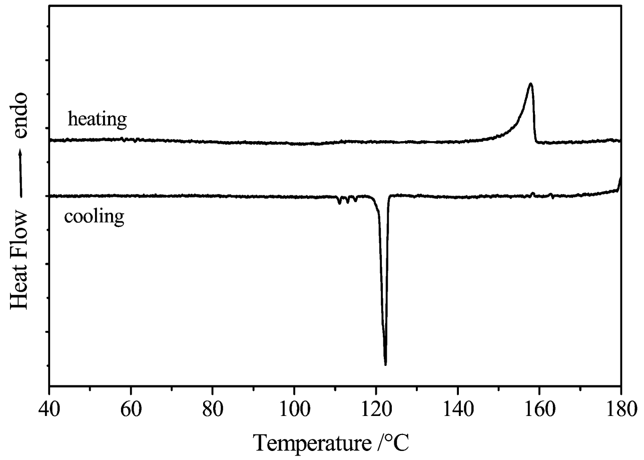


Figure 5. Cooling and second heating DSC traces of compound P16-2.

3.3. *Optical properties in solution*

The UV-vis absorption spectra of P*q*-4 derivatives diluted in chloroform showed two absorption maxima at around 295 and 330 nm (figure 7) independent of the length of the alkoxy substituents. These values agree well with those observed by Kallitsis *et al.* [18] for aromatic polyethers containing pentaphenyl units. It may be noted that the intensity of the first absorption band is higher than that of the second band; however, when the central ring is modified with two ethoxy groups, the spectra exhibit two bands of similar intensity. Based on previous studies on unsubstituted poly(*p*-phenylenes)s, the low wavelength band can be attributed to transitions between localized orbitals,

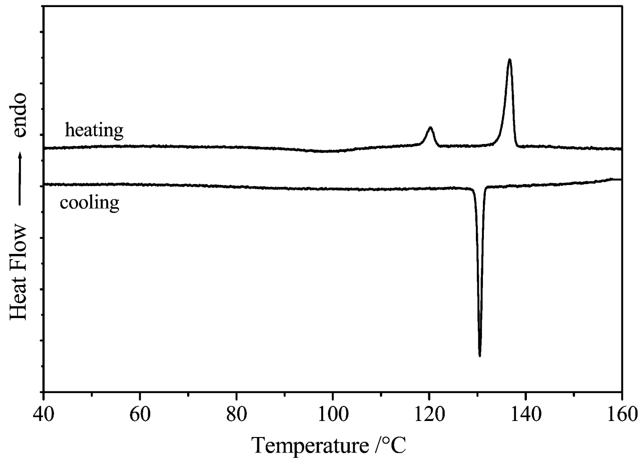


Figure 6. Cooling and second heating DSC traces of compound P16-3.

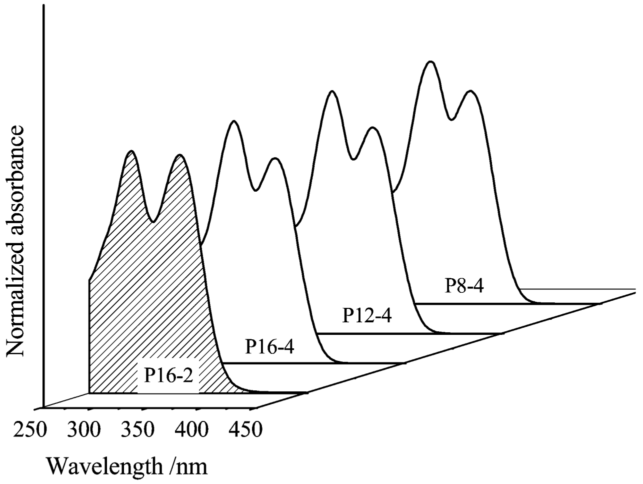


Figure 7. UV-vis absorption spectra of penta(*p*-phenylene)s P16-2, P16-4, P12-4, P8-4 obtained in diluted chloroform solution.

while the high wavelength band is associated with the conjugation of the phenylene rings [19]. On the other hand, molecules without substituents in the central ring show only one absorption peak [20].

Finally, pentamers exhibit only one emission peak centred at about 400 nm as we previously reported for compounds P14-4 and P16-4 [8]. This value is in agreement with those observed for similarly substituted compounds [6].

4. Conclusions

Symmetrical penta(*p*-phenylene)s substituted with short lateral and long terminal alkoxy chains were synthesized and their thermal properties studied by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction. The results indicate that penta(*p*-phenylene)s substituted with butoxy groups exhibit a nematic mesophase at temperatures which depend inversely on the length of the alkoxy terminal groups. Penta(*p*-phenylene)s substituted with ethoxy and propoxy lateral groups do not show mesomorphism, probably because these groups do not sufficiently hinder the strong π–π lateral interactions between aromatic cores. The compounds synthesized here show two absorption peaks (295 and 330 nm) and one emission band (around 400 nm), independent of the length of substituents. Compounds showing both liquid crystalline and luminescent properties, such as the alkoxy-modified oligo(*p*-pentaphenylene)s studied here, are potential materials for electronic devices.

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