# Liquid crystalline comb-like polyimides with biphenyl-based side groups

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# Liquid crystalline comb-like polyimides with biphenyl-based side groups

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We have synthesized series of comb-like polyimides with mesogenic units in their side groups. Such comb-like polyimides were obtained by polycondensation of aromatic diamines bearing biphenyl-based mesogenic moieties with bicyclo[2,2,2]oct-7-ene 2,3,5,6-tetracarboxylic dianhydride (BCDA). The different diamines, with two lengths of spacer (with 6 and 11 methylene groups), were synthesized in three steps using as mesogenic groups: biphenyl, 4-cyanobiphenyl and 4-(2-methyl-1-butoxy)biphenyl. The synthesis of the polyimides was performed in two steps: polycondensation of a dianhydride with a diamine in $N$-methyl-2-pyrrolidone at room temperature giving the corresponding polyamic acid, followed by thermal cyclization into the corresponding polyimide. The comb-like polyimides were studied by X-ray diffraction between room temperature and 250°C. Two types of smectic structure were established: $SmA_1$ for the long spacer and $SmC_1$ for the short spacer.

## 1. Introduction

Computer and television screens widely utilize active-matrix twisted nematic liquid crystal displays (AM-TN-LCDs) because they provide good contrast images at high resolution. However, to obtain high contrast ratios with TN-LCDs it is necessary to prevent the formation of reverse tilt disclinations and that may be achieved by giving a high pretilt angle to the LC molecules [1]. Similarly, in surface stabilized ferro-electric liquid crystal (SSFLC) cells, the pretilt angle has to be high to realize a good bookshelf geometry [2].

One approach to generating a high pretilt angle is to use appropriately rubbed alkyl-branched polyimides [3, 4]. Nevertheless the tilt angle generated by using these films is largely determined by the rubbing conditions [5].

We believe that an interesting way to overcome such problems would be to synthesize comb-like polyimides bearing mesogenic units in their side groups. To prepare such comb-like polyimides which could induce orientation of the LC molecules, two different approaches can be considered: first by chemical modification of polyimides bearing functional groups, and second by polycondensation of diamines with dianhydrides, one or both monomers bearing a mesogenic group. In order to

obtain quantitatively substituted polyimides, we have chosen the second approach [6]. For reasons of synthesis, the mesogenic groups were linked to the aromatic diamine through an aliphatic spacer.

The polyimides reported here are based on an alicyclic dianhydride and various aromatic diamines containing the mesogenic group. Modification of the liquid crystalline behaviour of these polyimides using differing aromatic dianhydrides has also been investigated and reported elsewhere [6].

In this study we have chosen as mesogenic groups three biphenyl derivatives, namely biphenyl (BP), 4-cyanobiphenyl (BPCN) and 4-(2-methyl-1-butoxy)biphenyl (BPMeBu) which are known to give, with comb-like polyacrylamides, various types of smectic structures with high tilt angles over large ranges of temperature [7–9].

Very recently polyimides were prepared by polycondensation of 4,4′-oxydiphthalic anhydride (ODPA) with $m$-phenylenediamines bearing biphenyl groups at the end of an alkylene spacer [10]. No liquid crystalline structures were observed for such polymers. Nevertheless, after rubbing, these polymers were able to achieve high pretilts (8°–27°) of LC molecules in LC cells.

The present paper describes the synthesis and liquid crystalline properties of comb-like polyimides obtained by polycondensation of aromatic diamines bearing biphenyl-based mesogenic groups with bicyclo[2,2,2]-oct-7-ene 2,3,5,6-tetracarboxylic dianhydride (BCDA).

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Table 1. Acronyms of monomers and polymers synthesized and studied.

| $n$ | $R$ | Diamine | Dianhydride | Polyimide |
|---|---|---|---|---|
| 6 | H | 6BP | BCDA | BCDA6BP |
| 6 | CN | 6BPCN | BCDA | BCDA6CN |
| 6 | $O-CH_2-CH(CH_3)-C_2H_5$ | 6BPMeBu | BCDA | BCDA6MeBu |
| 11 | H | 11BP | BCDA | BCDA11BP |

The general structural formula of the polymers prepared is shown in figure 1 and the acronym for each polymer is given in table 1.
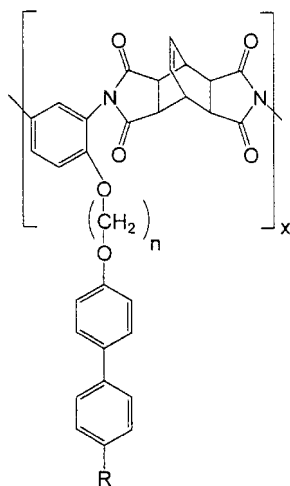


Figure 1. General structural formula of the polymers synthesized: $R$ = H or CN or $O-CH_2-CH(CH_3)-C_2H_5$; $n$ = 6 or 11.

We also compare the liquid crystalline properties of these comb-like polyimides with those of the polyacrylamides bearing the same mesogenic groups [7–9]. To our knowledge, it is the first time that smectic liquid crystalline structures have been described for comb-like polyimides.

## 2. Experimental
### 2.1. *Materials*

6-Bromo-1-hexanol, 11-bromo-1-undecanol, 4-hydroxybiphenyl, 4,4′-dihydroxybiphenyl, 4′-hydroxy-4-biphenylcarbonitrile from Aldrich, and 2,4-dinitrofluorobenzene from Lancaster synthesis were used as received; bicyclo[2,2,2]oct-7-ene 2,3,5,6-tetra-carboxylic dianhydride (BCDA) from Aldrich was recrystallized twice from acetonitrile before use. The chiral phenol 4-hydroxy-4′-(2-methyl-1-butoxy)biphenyl was prepared from $S(-)$-2-methylbutan-1-ol as described in the literature [11, 12]. Solvents were purified by classical methods.

### 2.2. *Synthesis of the diamines*

In the following, A, B, C refer to compound types, as indicated in the reaction scheme shown in figure 2.
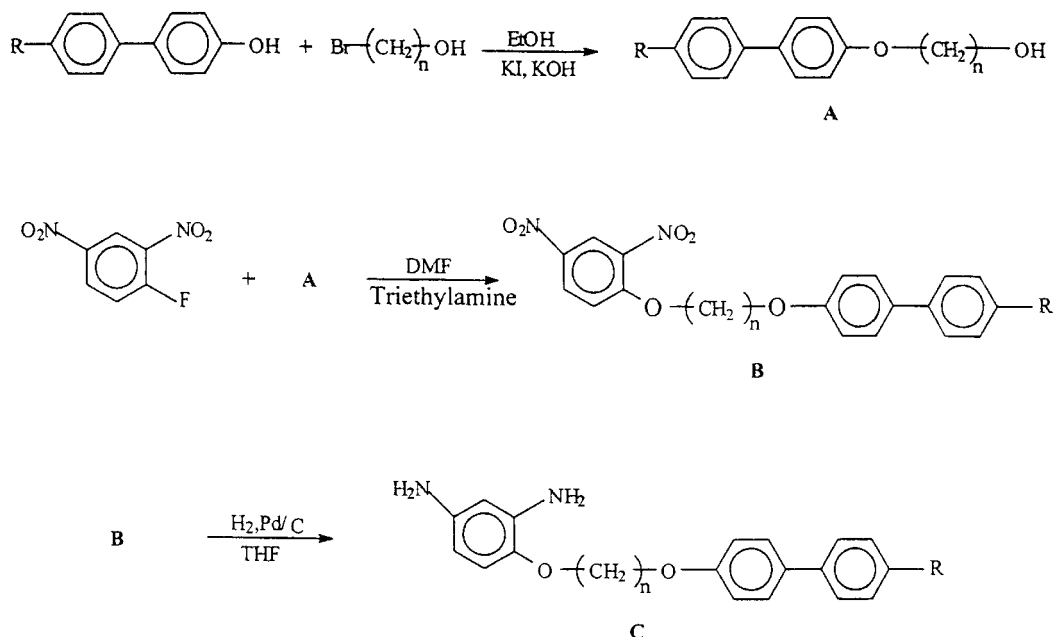


Figure 2. Scheme of synthesis of the diamines: $R$ = H or CN or $O-CH_2-CH(CH_3)-C_2H_5$; $n$ = 6 or 11.

### 2.2.1. 6-[4′( 2-Methyl-1-butox y)biphenyl-4-ylox y) ]-hexanol (A)

7.7 g (0.03 mol) of 4-hydroxy-4′-(2-methyl-1-butoxy)-biphenyl, 5.0 g of KOH and a small amount of KI were dissolved in 100 ml of ethanol. Then 5.5 g (0.03 mol) of 6-bromo1-1-hexanol were added dropwise. The solution was heated at reflux for 24 h and the reaction progress was followed by TLC (eluant *n*-hexane/ethanol, 70/30). The biphenylyloxyhexanol was precipitated by dilution in 600 ml of water, filtered off and recrystallized from ethanol, yield 73.4%.

### 2.2.2. 6-( 4′-Cyanobiphenyl-4-ylox y)hexanol (A)

This was prepared in a similar way from 4-hydroxy-4′-cyanobiphenyl in a yield of 67.6%.

### 2.2.3. 6-(Biphenyl-4-ylox y)hexanol (A)

This was prepared in a similar way from 4-hydroxybiphenyl in a yield of 50.4%.

### 2.2.4. 11-(Biphenyl-4-ylox y)undecanol (A)

This was prepared in a similar way from 4-hydroxybiphenyl and 11-bromo-1-undecanol in a yield of 73.8%.

### 2.2.5. 1,3-Dinitro-4-{6-[4′-( 2-methyl-1-butox y)biphenyl-4-yloxy]hexyloxy} benzene (B)

7.5 g (0.021 mol) of 6[4′-(2-methyl-1-butoxy)biphenyl-4-yloxy]hexanol were dissolved in 140 ml of DMF and an excess of triethylamine (3 mols for 1 mol of biphenyl-hexanol) was added. Then 3.94 g (0.021 mol) of 2,4-dinitrofluorobenzene was added dropwise. The system was maintained at 90°C with stirring for 6 h. The reaction progress was followed by TLC (eluant *n*-hexane/ethanol, 70/30). The 4-substituted 1,3-dinitrobenzene was precipitated in water, filtered off and recrystallized from the solvent mixture cyclohexane/toluene, 4/1. The yellow product was obtained in a yield of 62.5%.

The three other dinitro compounds were prepared in a similar way from the appropriate alcohols [6].

### 2.2.6. 1,3-Diamino-4-{6-[4′-( 2-methyl-1-butoxy)biphenyl-4-yloxy]hexyloxy}benzene (6BPMeBu) (C)

To a reactor for hydrogenation equipped with a mechanical stirrer, 8.0 g (0.0156 mol) of 1,3-dinitro-4-{6-[4′-(2-methyl-1-butoxy)biphenyl-4-yloxy]hexyloxy}-benzene (B), 120 ml of THF and 4 wt % of palladium on charcoal were added before applying an initial cold pressure of hydrogen of 40 bar. The reaction was exo-thermic. When the hydrogen pressure became constant, the temperature was maintained at 40°C for 3 h. Then the mixture was filtered through celite and the diamine precipitated from the filtrate in water. The reduction was quantitative. The diamine was recrystallized from a mixture of cyclohexane/toluene, 4/1. The three other dinitro compounds were reduced to the corresponding diamines following the same experimental conditions [6].

### 2.3. *General procedure for the synthesis of the polyamic acids*

To a three-necked flask equipped with a mechanical stirrer and operating under nitrogen, were successively added at room temperature the two monomers (diamine and dianhydride) in stoichiometric amounts and mixed. They were then solubilized in *N*-methyl-2-pyrrolidone (NMP) solvent to obtain a solution of 35 wt % concentration. After total solubilization of the monomers, the polymerization was carried out for 24 h.

### 2.4. *General procedure for the preparation of polyimide films*

The NMP solution of the polyamic acid was cast on a clean glass sheet using a Filmograph with a mister blade able to give a maximum film thickness of 500 μm. The film was submitted to the following thermal treat-ment: 80°C for 1 h, 130°C for 4 h, 200°C for 1.5 h and 250°C for 1 h. After cooling, the film was separated from the glass sheet by soaking in methanol. The film thick-ness obtained in our case from the polyamic solutions was about 150 μm.

### 2.5. *X-ray diffraction*

X-ray diffraction experiments were performed on unoriented samples using a home made pinhole camera, operating under vacuum, with a Ni filtered Cu beam ($\lambda = 1.54 \text{ Å}$) and equipped with a device which allows the diffraction patterns of samples to be recorded as a function of temperature ranging from 20 to 300°C with an accuracy of 1°C.

Several exposures were made to measure the strongest and the weakest reflections. Intensities of the reflections were measured with a home made microdensitometer specially designed to analyse X-ray diagrams provided by linear focusing and pinhole cameras. Experimental amplitudes of diffraction of the various orders of reflection from the smectic layers were corrected for the Lorentz-polarization factor [13] and normalized in order to obtain a value of one for the strongest amplitude.

## 3. Results

### 3.1. *Chemical synthesis*

The liquid crystalline polyimides were prepared by polycondensation of an aromatic diamine bearing the mesogenic group and bicyclo[2,2,2]oct-7-ene 2,3,5,6-tetracarboxylic dianhydride (BCDA).

### 3.1.1. *Synthesis of the aromatic diamine monomers*

The various diamines, which are not commercially available, were synthesized in three steps as illustrated in figure 2. First the mesogenic group is linked to one end of the spacer, then the aromatic dinitro entity is attached to the other end of the spacer, and finally the nitro groups are reduced to give the corresponding amines.

The first step is a Williamson reaction between the hydroxybiphenyl derivative and the bromo alkanol in the presence of KOH, and catalysed by KI to improve the reactivity and increase the yield of compound (A).

The second step is a nucleophilic aromatic substitution involving the alkanoate of (A) and dinitrofluorobenzene. The presence of the nitro substituents in the *para-* and *ortho*-positions allows the reaction to take place under mild conditions and gives the dinitro compound (B) in good yield.

The third step is a classical hydrogenation reaction in the presence of palladium giving the diamine (C) quantitatively. An example of the proton NMR spectrum of a diamine is given in figure 3.

### 3.1.2. *Synthesis of the polymers*

The synthesis of the liquid crystalline polyimides was performed in two steps: preparation of the polyamic acid by condensation of the aromatic diamine with the BCDA dianhydride in NMP solution at room temperature, followed by thermal cyclization of the polyamic acid into the corresponding polyimide as illustrated in figure 4.

NMP was chosen as polymerization solvent for the following reasons: first it is a good solvent at room temperature for both monomers (diamines and dianhydride) and the intermediate polyamic acid; second it is also a solvent for the polyimides at temperatures higher than 120°C; third NMP evaporates rather easily under atmospheric pressure and after the thermal treatment allows polyimide films to be obtained by casting from solutions of polyamic acid.

While the classical method of preparation of polyimides involves thermal cyclization of the polyamic acid in solution at 200° and leads to amorphous polyimides, our method of preparation, which consists of casting the polyamic acid solution followed by heat treatment, gives liquid crystalline polyimides.

### 3.2. *Liquid crystalline behaviour of the polymers*
#### 3.2.1. *Description of the structures*

For the four types of polymer, all X-ray patterns recorded between room temperature and 250°C exhibit in the low angle domain two sharp reflections and in
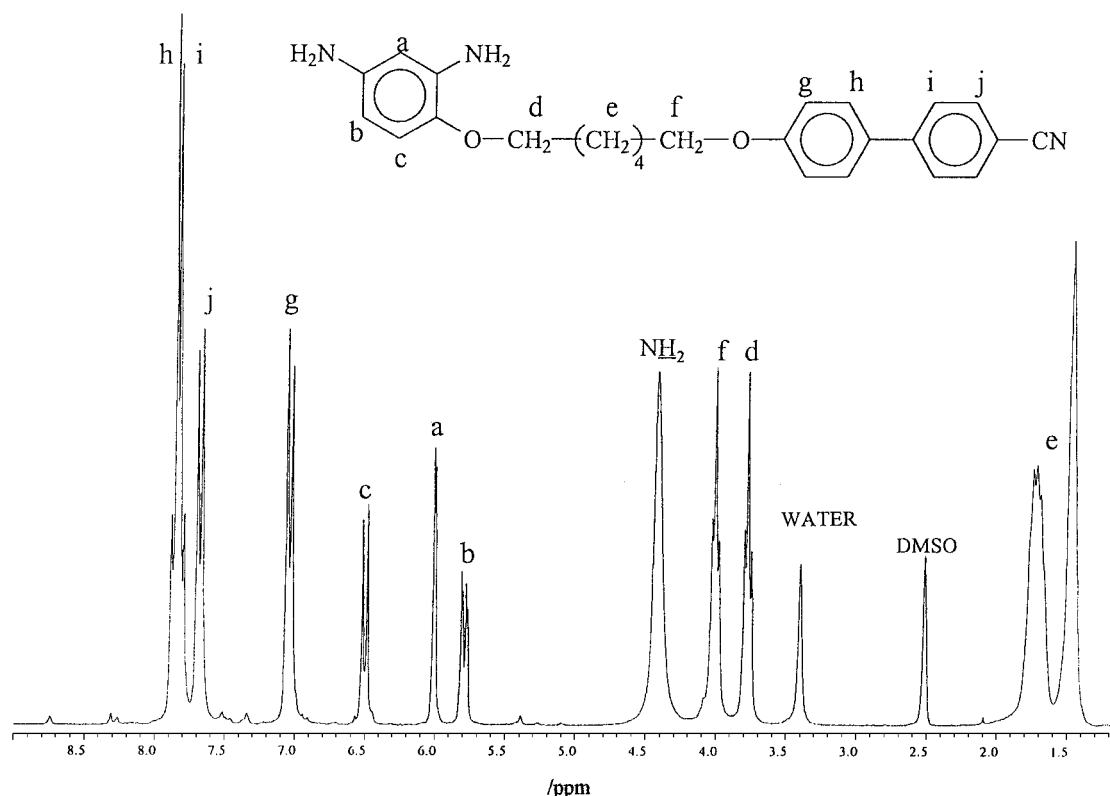


Figure 3.   1H NMR spectrum in DMSO of the diamine with $n = 6$ and $R = O-CH_2-CH(CH_3)-C_2H_5$.
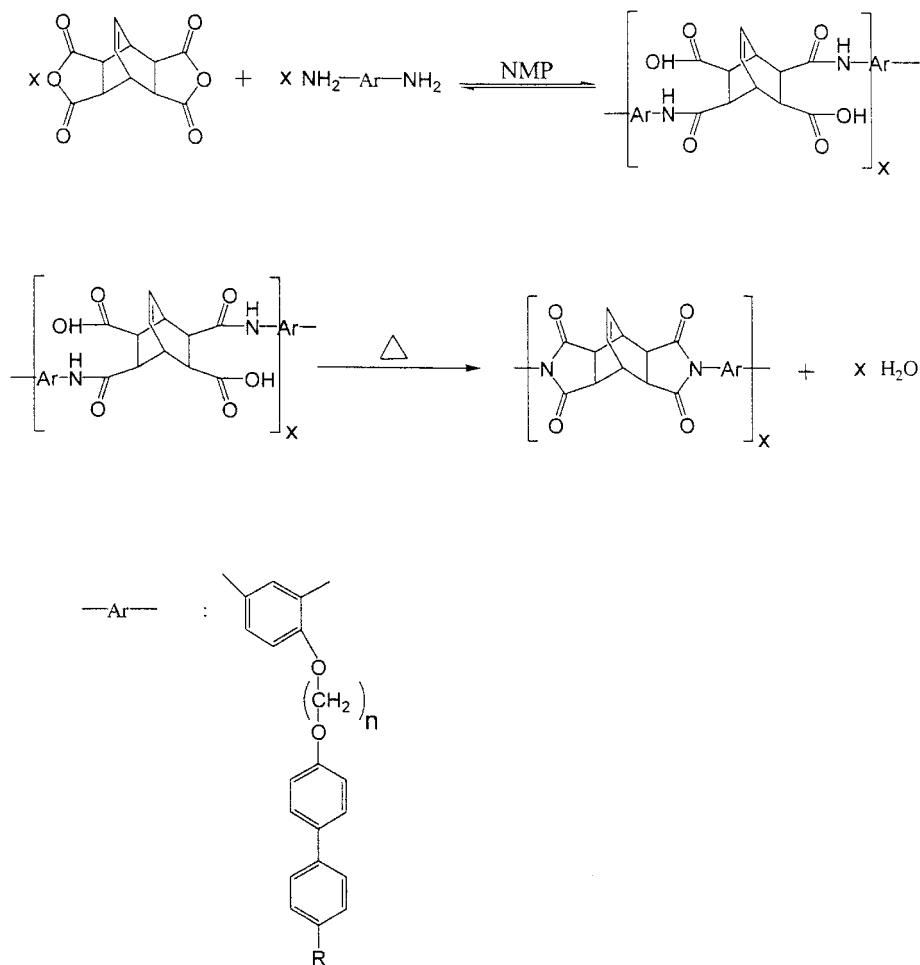
Figure 4. Scheme of synthesis of the liquid crystalline polyimides: $R = H$ or CN or $O-CH_2-CH(CH_3)-C_2H_5$; $n = 6$ or 11.

the wide angle domain a diffuse band (figure 5). The low angle reflections can be indexed as the 0 0 1 reflections of a lamellar structure of thickness $d$. The wide angle



Figure 5. Pinhole camera powder X-ray diagram of the $SmC_1$ mesophase of polymer BCDA6BP, showing the two small angle sharp reflections and the wide angle diffuse band.

band (either 5.5 or 4.9 Å depending on the length of the spacer) is characteristic of a disordered smectic structure (smectic A or C) [14].

In order to make a choice between the two possible disordered smectic structures, we have compared the thickness $d$ of the smectic layers with the length $L$ of the repeating unit of the polymers (corresponding to a monolayer structure), measured using CPK models with the spacer in an all *trans*-conformation (table 2). For the polymer BCDA11BP with a spacer of 11 methylenes $d$ is slightly higher than $L$ and the smectic structure is of the

Table 2. Acronyms and structural parameters of the comb-like polyimides.

| Polymer | $L$/Å | $d$/Å | $d/L$ | $\theta$/° | $a$/Å | Structure |
|---------|-------|-------|-------|-----------|-------|-----------|
| BCDA6BP | 25 | 23.4 | 0.936 | 22 | 5.2 | $SmC_1$ |
| BCDA6CN | 26 | 23.2 | 0.892 | 27 | 5.2 | $SmC_1$ |
| BCDA6MeBu | 31 | 29.3 | 0.945 | 19 | 5.5 | $SmC_1$ |
| BCDA11BP | 31 | 37.7 | 1.119 | 0 | 4.9 | $SmA_1$ |

monolayer, orthogonal $SmA_1$ type. For the three polymers BCDA6BP, BCDA6CN and BCDA6MeBu with spacers of 6 methylene groups, $d$ is smaller than $L$ (table 2) and the structure is of the disordered tilted $SmC_1$ type with an angle of tilt $\theta$ given by $\cos \theta = d/L$.

In order to obtain further information on the smectic structures, we have derived the electron density profiles $\rho(z)$ along the direction $z$ perpendicular to the smectic layers from the intensities of the low angle reflections of the X-ray diagrams [13]. Taking into account the fact that equal numbers of mesogenic cores are pointing in the $+z$ and $-z$ directions and that we measure only the fluctuations around $\rho(0)$, the electron density $\rho(z)$ is given [15] by:

$$\rho(z) = \Sigma \, a_n \cos(n 2 \pi z / d).$$

Experimentally the intensity of the diffraction orders is measured, and therefore we lose the phase. Due to the symmetry of the electron density distribution, the phase factor and the structure factor must be 0 or $\pi$, so the $a_n$ are real, but may be positive or negative. The phase problem then reduces to choosing the right combinations of sign for $a_n$ ($n = 1, 2$). For instance $\rho + - (z)$ will correspond to the combination where $a_1$ is chosen positive and $a_2$ is chosen negative. As we observe two orders of diffraction, we obtain four combinations of sign for $a_n$, i.e. four electron density profiles $\rho(z)$, as illustrated in figure 6 for the polymer BCDA6BP where $R = $ H.

In order to choose between the profiles and obtain the physically acceptable one, we have calculated the electron density for the different parts of the repeating unit of the polymer by dividing their numbers of electrons by their lengths measured using CPK models. We found: $7.6 \, e^- \, Å^{-1}$ for the skeleton, $6.4 \, e^- \, Å^{-1}$ for the alkylene spacer and between 8.5 and $9.6 \, e^- \, Å^{-1}$ for the mesogenic groups, depending upon the nature of $R$.

For the monolayer smectic structures, the electron density profiles will exhibit a central maximum for the mesogenic cores, surrounded by minimuma for the alkyl spacers and secondary maximuma for the main chains.

For the $SmC_1$ phase of polymer BCDA6BP (figure 6), the two electron density profiles (c) and (d) must be rejected as they exhibit a minimum for the mesogenic cores and the main chains and maximuma for the spacers. The electron density profiles (a) and (b) both exhibit a central maximum for the mesogenic cores, surrounded by minimuma for the alkyl spacers and maximuma for the main chains, but differ in the respective amplitudes of the maximuma due to the mesogenic cores and the main chains. As the electron density of the mesogens is higher than that of the main chain, the electron density profile (b) must be preferred.
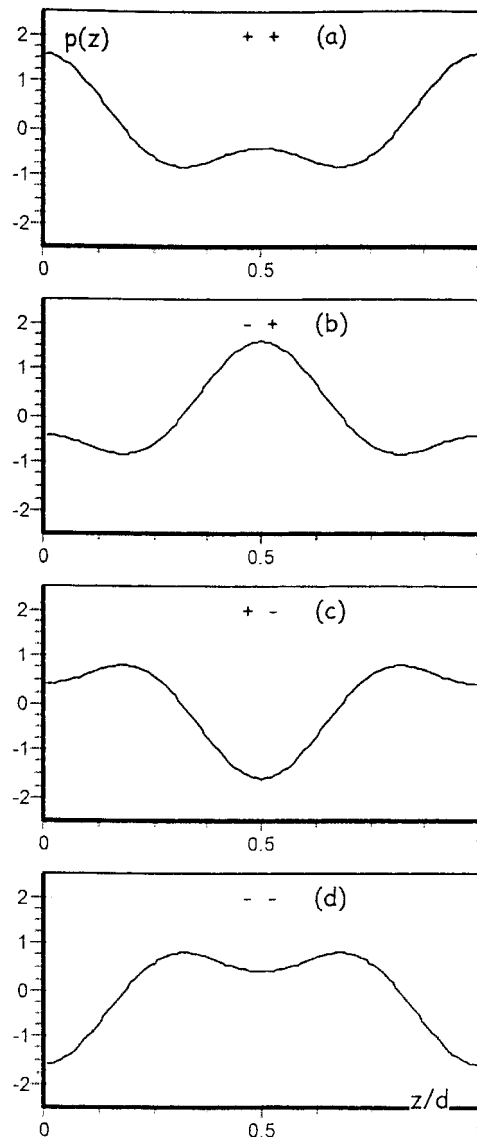


Figure 6. Projections of the electron density profiles corresponding to the four different sign combinations of $a_n$ for the polymer BCDA6BP in the $SmC_1$ phase ($a_1 = 1$ and $a_2 = 0.6$).

### 3.2.2. *Influence of temperature*

For the four polymers, over the whole temperature range studied, the thickness $d$ of the smectic layers is independent of temperature and remains constant. The values of the structural parameters found on heating were obtained reversibly on cooling.

### 3.2.3. *Influence of the length of the spacer*

For the polymers with the shorter spacer ($n = 6$) the structure is of the tilted smectic $SmC_1$ type, while for the polymer with the longer spacer ($n = 11$) the structure is of the orthogonal smectic $SmA_1$ type.
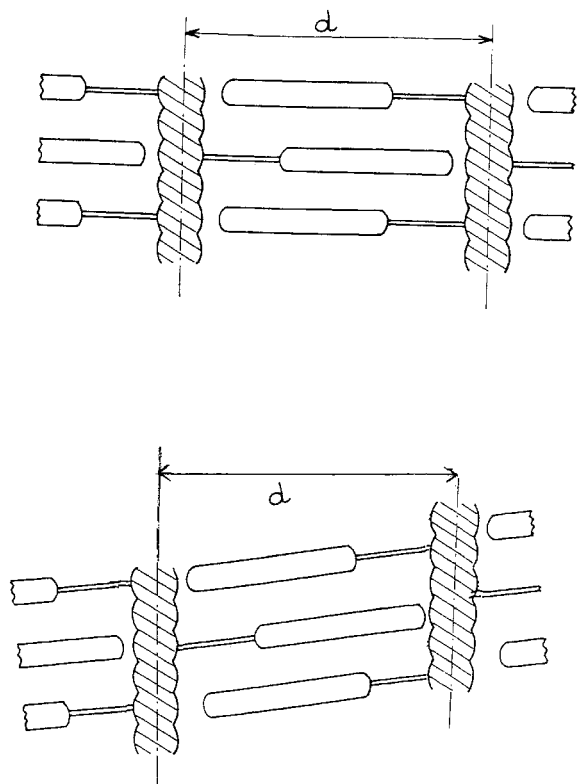
Figure 7. Schematic representation of the smectic structures. Region with cross hatching = main chain; rod with curved ends = mesogenic group; two close-spaced parallel lines = spacer. Upper figure: orthogonal smectic structure, $SmA_1$. Lower figure: tilted smectic structure, $SmC_1$.

### 3.2.4. *Influence of the substituent R*

In the case of the polymers with the short spacer ($n = 6$), a monolayer disordered smectic $SmC_1$ phase is obtained for the three types of substituent $R$ of the mesogen, but the tilt angle depends upon the nature of $R$ and decreases from $R = CN$ to $R = H$ to $R = O-CH_2-CH(CH_3)-C_2H_5$.

### 4. Concluding remarks

If we compare the thermotropic behaviour of the polyimides with polyacrylamides having the same mesogenic groups, we observe many differences. First, the nature of the mesophase depends upon the length of the spacer for the polyimides (they exhibit orthogonal smectic A phases for long spacers and tilted smectic C phases for short spacers); this is independent of spacer length (at least in the range of spacer lengths used) for polyacrylamides [9]. Second, the polyimides exhibit one monolayer mesophase, whereas the polyacrylamides exhibit two mesophases as a function of temperature. Third, the nature of the mesophases is independent of the nature of the substituent $R$ on the biphenyl group for polyimides. On the contrary the nature of $R$ governs the type of mesophase for the polyacrylamides [7, 8]; for $R = H$ polyacrylamides exhibit $SmI_2$ and $SmC_2$ mesophases, for $R = CN$ they exhibit $SmC_2$ and $SmA_2$ mesophases, and for $R = O-CH_2-CH(CH_3)-C_2H_5$ they exhibit $SmF_2$ and $SmC_2$ mesophases [7, 8]. The influence of the chemical structure of the polyimide chain on the nature of the mesophases, as well as on the pretilt angle induced in LC cells, will be described in forthcoming publications.

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