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J. Barberá^a; L. Oriol^a; J. L. Serrano^a

^a Departamento de Química Orgánica, Facultad de Ciencias, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, Zaragoza, Spain

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Hydroxy-functionalized liquid-crystalline polyazomethines

I. Synthesis, characterization and structure-mesogenic behaviour relationship

by J. BARBERÁ, L. ORIOL and J. L. SERRANO*

Departamento de Química Orgánica,
Facultad de Ciencias-Instituto de Ciencia de Materiales de Aragón,
Universidad de Zaragoza-CSIC, 50009, Zaragoza, Spain

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A new series of polyazomethines based on hydroxy-functionalized mesogenic units has been synthesized and characterized. Different structural variations have been checked in order to obtain mesogenic polyazomethines with low melting temperatures and a broad nematic range. Completely conjugated mesogenic units with a lateral substituent or alteration of coaxiality are shown to be the most suitable structural variations. No mesogenic behaviour was observed for polyazomethines with a flexible mesogenic core due to unfavourable conformational equilibrium. Polyazomethines have complex thermal behaviour and show an increase in the degree of polymerization on annealing.

1. Introduction

Aromatic polyazomethines are widely reported to show mesogenic behaviour which can be used to obtain high-strength fibres [1,2]. However, the thermal characteristics of these polymers hinder the achievement of tractability and, consequently, the industrial development of derived fibres. The low thermal stability of azomethine groups can be increased by the introduction of ortho-hydroxyl groups which lead to the formation of strong chelation rings by means of hydrogen bonds. Moreover, these hydrogen bonds are reported to favour mesomorphism due to the increase in molecular planarity [3,4].

This paper deals with the synthesis and characterization of a series of potentially mesogenic homo and copolyazomethines. The repeating unit is shown in figure 1. All of the diamines used in the synthesis of the polyazomethines were from commercial sources and chosen in order to study the structure-mesogenic behaviour relationship of the potential mesogenic units containing hydroxyl groups.

The target polymers offer new possibilities derived from the hydroxyl groups which will be studied in future papers. First, thermally and chemically cross-linked fibres may be obtained with an improvement of the mechanical properties in the direction perpendicular to the molecular alignment. By choosing a suitable cross-linking agent it might be possible to preserve the liquid-crystalline order. Secondly, the mesogenic unit contains a salicylaldimine structure which can react as a ligand in complex formation with different metals [5,6]. Metals containing mesogenic polymers have received increasing attention in recent years as a consequence of the interesting properties which

* Author for correspondence.

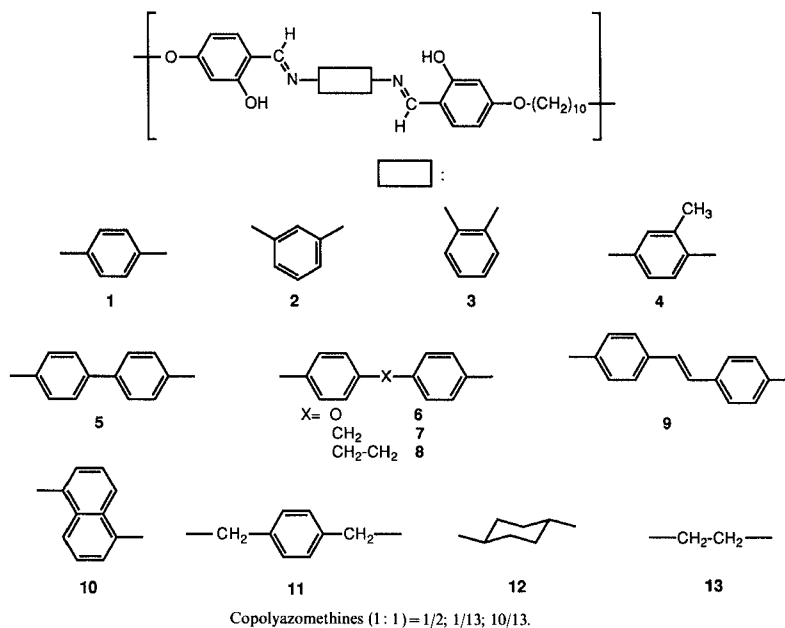


Figure 1. Schematic representation of the repeating unit of the homopolyazomethines. Copolyazomethines were synthesized with a 1 : 1 feed ratio.

may derive from the presence of metals in ordered fluid phases [7]. As can be inferred from the structure of the repeating unit, cross-linking may be obtained by the formation of metal chelates. In this case the two possibilities mentioned are interrelated.

Based on previous results [8,9] which we have obtained in the synthesis of polyazines and after a bibliographical study, we chose the polymerization method described by D'Alelio *et al.* [10]. This method works in solution, using absolute ethanol as a solvent, and is acid-catalysed. The polymers were characterized by infrared spectroscopy, elemental analysis and ^1H NMR spectroscopy (compounds **10**, **13**, **1/13** and **10/13**). Their solubility and viscosity were determined. Their thermal properties were studied by thermogravimetric and derivative thermogravimetric analysis, and their mesogenic properties were characterized by optical microscopy and differential scanning calorimetry. A viscosimetric study was carried out in order to establish the influence of the annealing on the degree of polymerization. A strong increase in the molecular weight is observed with reactions in the solid state.

2. Experimental

2.1. Polymer synthesis

1.4 mmol of the appropriate diamine (or 0.7 mmol of two different diamines for the 1 : 1 copolymers) dissolved in the minimum volume of absolute ethanol (10–30 ml) were added to a three necked 250 ml flask provided with an inlet and outlet of nitrogen containing a stirred solution of 1.4 mmol of 1,10-bis-(4-formyl-2-hydroxyphenyl-oxy)decane in 110 ml of absolute ethanol under reflux. 0.14 ml of glacial acetic acid were added at once as a catalyst and the reaction mixture was maintained under reflux with stirring for 4 h. After cooling, the polymer precipitate was filtered and washed with a large amount of water and methanol. The product obtained was extracted in a soxhlet with acetone for 24 h and dried under vacuum at 80°C with P_2O_5 for 24 h.

Table 1. Yield, elemental analysis and C=N (st) IR frequency of the polymers.

| Polymer | Yield% | Elemental analysis (found) | | | C=N (st), ν/cm^{-1} |
|--------------|--------|----------------------------|-------------|-------------|--------------------------------|
| | | %C | %H | %N | |
| 1 | 87 | 74.05 (74.42) | 7.04 (7.49) | 5.76 (5.44) | 1616 |
| 2 | 88 | 74.05 (74.94) | 7.04 (7.61) | 5.76 (5.63) | 1626 |
| 3 | 50 | 74.05 (75.28) | 7.04 (7.49) | 5.76 (5.51) | 1609 |
| 4 | 86 | 74.37 (73.73) | 7.25 (7.59) | 5.60 (5.42) | 1607 |
| 5 | 81 | 76.84 (76.76) | 6.81 (7.49) | 4.98 (4.79) | 1619 |
| 6 | 84 | 74.72 (75.01) | 6.62 (7.20) | 4.84 (4.51) | 1622 |
| 7 | 85 | 77.05 (76.78) | 6.99 (7.49) | 4.86 (4.24) | 1620 |
| 8 | 85 | 77.26 (76.34) | 7.17 (7.51) | 4.74 (4.04) | 1619 |
| 9 | 92 | 77.52 (77.04) | 6.85 (7.10) | 4.76 (4.76) | 1621 |
| 10 | 78 | 76.09 (75.43) | 6.76 (6.76) | 5.22 (4.53) | 1628 |
| 11 | 75 | 74.68 (74.89) | 7.44 (8.06) | 5.44 (5.28) | 1627 |
| 12 | 80 | 73.14 (72.91) | 8.18 (8.88) | 5.69 (5.13) | 1628 |
| 13 | 84 | 71.21 (70.80) | 7.81 (8.27) | 6.39 (6.06) | 1625 |
| 1/2 | 86 | 74.05 (73.42) | 7.04 (7.61) | 5.76 (5.21) | 1624 |
| 1/13 | 91 | 72.70 (73.26) | 7.41 (8.20) | 6.06 (5.80) | 1625 |
| 10/13 | 76 | 73.89 (73.64) | 7.23 (7.46) | 5.75 (5.44) | 1628 |

The diamines were either purchased commercially or obtained from the commercial quaternary ammonium salts (2-methyl-1,4-phenylenediammonium sulphate and 4,4'-stylobenediammonium dihydrochloride). All of the diamines were purified before use. 1,10-bis-(4-formyl-2-hydroxyphenoxy)decane was prepared as described elsewhere [8]. Yields, elemental analysis and the C=N (st) IR frequency of the polyazomethines are summarized in table 1.

2.2. Techniques

DSC measurements were performed with a Perkin-Elmer DSC-7. The apparatus was calibrated with indium (mp 156.6°C, heat of fusion 28.4 J g⁻¹) and tin (mp 321.9°C, heat of fusion 60.4 J g⁻¹). Transition temperatures were read at the maximum of the peak. Thermogravimetric analysis was carried out with a Perkin-Elmer TGS-2 equipped with a System 4 microprocessor controller. The mesogenic behaviour of the polymers was confirmed by optical microscopy using a Nikon polarizing microscope fitted with a Mettler FP-82 heating stage and a FP-80 control unit. The inherent viscosity (η_{inh}) was determined using a Cannon-Fenske viscosimeter at a concentration of 0.5 g dL⁻¹ in methanesulphonic acid at 40°C. Samples were used immediately after preparation because methanesulphonic acid degrades the polymers. Elemental analyses were carried out with a Perkin-Elmer 240 C microanalyser and IR spectra with a Perkin-Elmer FTIR 1600. ¹H NMR measurements of polymer solutions were obtained with a Varian Unity-300 operating at 300 MHz using trifluoroacetic acid as a solvent. Fresh samples were used in order to avoid degradation.

3. Results and discussion

3.1. Solubility and viscosimetry

One characteristic common to the different series of polyazomethines described in the literature is their low solubility and high melting points, as this kind of polymer has

Table 2. Viscosimetric data for the polymers.

| Polymer | η_{inh} | Observations |
|--------------|--------------|-------------------|
| 1 | 0.41 | |
| 2 | 0.58 | |
| 3 | 0.39 | |
| 4 | 0.45 | |
| 5 | — | Insoluble |
| 6 | 0.32 | |
| 7 | 0.5–0.6 | Partially soluble |
| 8 | — | Insoluble |
| 9 | — | Insoluble |
| 10 | 0.32 | |
| 11 | > 0.46 | Fast degradation |
| 12 | > 0.74 | Fast degradation |
| 13 | > 0.84 | Fast degradation |
| 1/2 | 0.51 | |
| 1/13 | 0.80 | |
| 10/13 | 0.59 | |

a very rigid mesogenic core. In the light of some previous tests, we chose methanesulphonic acid as the solvent for the viscosimetry measurements. The inherent viscosities obtained are listed in table 2. It can be observed that some polymers are not completely soluble. These are linear polymers without structural irregularities where conjugation extends through all of the mesogenic entity (**5** and **9**). Stirred suspensions of these polymers in methanesulphonic acid are stable for a long time (> 48 h). Neither dissolution nor degradation was observed. The solutions of polyazomethines derived from aliphatic or cycloaliphatic diamines degrade quickly; therefore the η_{inh} data are only approximate.

The values obtained are of the same order as those reported for similar polymers without ortho-hydroxy groups in the same solvent at the same temperature. In view of the structural differences between these polyazomethines a comparison of η_{inh} should be treated cautiously. Nevertheless, the data for **13** and its copolymers suggest the formation of longer chains from ethylenediamine as a consequence of its higher nucleophilic power.

Additional viscosimetry measurements were carried out in order to study the influence of the thermal history on the molecular weight. Two samples of **10** were heated at 180°C for 30 min and 1 h. An increase in the η_{inh} of a solution in methanesulphonic acid (concentration 0.3 g dL⁻¹) at 40°C was observed. The sample which was not thermally treated showed a η_{inh} of 0.42 which increased to 0.69 after (residuum < 3 per cent) annealing for 30 min at 180°C. Moreover, the annealed sample was not completely soluble. Annealing for 1 h yielded a material which was partially soluble after 48 h of stirring and showed a η_{inh} of 0.71 (residuum < 5 per cent). These results may originate from reactions in the solid state which lead to an increase in the degree of polymerization. Similar conclusions were reached for the rest of the polyazomethines. Samples annealed close to T_m showed lower solubility and higher η_{inh} than virgin samples.

3.2. IR and ^1H NMR measurements

The IR data show the band corresponding to the $-\text{CH}=\text{N}$ -group obtained in the polymerization. In spite of the different structures of the polymers no conclusions can be obtained from the analysis of the position of this band. In the analysis of end groups, only small bands corresponding to carbonyl groups ($-\text{CH}=\text{O}$) were detected in some cases. No $-\text{NH}_2$ end groups were observed.

^1H NMR spectra of polymers **10**, **13**, **1/13** and **10/13** using CF_3COOD as a solvent, agreed with IR data (see table 3). In all cases significant signals of $-\text{CH}=\text{O}$ were observed. On the other hand, only for polymer **13** was the amine end group detected ($-\text{CH}_2-\text{NH}_2$). Even then this signal confirms a small proportion (< 10 per cent) of this end group. For this reason we can assume that the aldehyde group is the main end group. Based on this we calculated \bar{M}_n (which is collected in table 3). The results are in good agreement with the viscosity data. For the copolymers the ^1H NMR data confirm that the proportion of the two comonomers is the feed composition.

3.3. Thermogravimetric analysis

All of the polyazomethines synthesized showed good thermal stability (see table 4). The presence of aromatic rings increases the stability of the polymeric chain. Structural modifications which introduce kinks in the chain ($-\text{CH}_2-$ or $-\text{O}-$) slightly decrease the thermal stability due to the loss of coplanarity and to less efficient conjugation between the aromatic rings.

Table 3. ^1H NMR data corresponding to the signals involved in the calculation of \bar{M}_n †.

| Polymer | $-\text{CH}=\text{N}-\text{Ar}$ | $-\text{CH}=\text{N}-\text{R}$ | $-\text{CH}=\text{O}$ | \bar{M}_n |
|--------------|---------------------------------|--------------------------------|-----------------------|-------------|
| 10 | 8.53 (96.8) | | 9.73 (3.2) | 2700 |
| 13 | | 9.02 (80.8) | 9.73 (19.2) | 13800 |
| 1/13 | 8.55 (46.8) | 9.00 (46.6) | 9.73 (6.6) | 6900 |
| 10/13 | 8.53 (43.6) | 9.03 (49.8) | 9.74 (6.6) | 7200 |

† Chemical shift in ppm and relative integration of signals in brackets.

Table 4. Thermogravimetric data of polymers.

| Polymer | $T_{\text{TGA}}/^\circ\text{C}$ | $T_{\text{DTGA}}/^\circ\text{C}$ |
|--------------|---------------------------------|----------------------------------|
| 1 | 388 | 397 |
| 2 | 364 | 378 |
| 3 | 382 | 422 |
| 4 | 387 | 399 |
| 5 | 406 | 415 |
| 6 | 381 | 393 |
| 7 | 378 | 389 |
| 8 | 380 | 400 |
| 9 | 406 | 412 |
| 10 | 374 | 388 |
| 11 | 385 | 425 |
| 12 | 362 | 405 |
| 1/2 | 377 | 398 |
| 1/13 | 355 | 379, 441 |
| 10/13 | 335 | 366, 448 |

3.4. Mesogenic properties

For both the microscopic and the DSC studies the samples underwent the following thermal treatment: (i) Two initial scans at $40^{\circ}\text{C min}^{-1}$ starting from 50°C to a final temperature $10\text{--}20^{\circ}\text{C}$ higher than the clearing point (in the samples where decomposition does not take place at these temperatures). For the rest of the samples a final temperature was chosen in such a way that decomposition was minimized. After the first scan the samples were cooled very quickly ($>200^{\circ}\text{C min}^{-1}$). (ii) Two heating and two cooling scans of a fresh sample at $10^{\circ}\text{C min}^{-1}$ from 50°C to the final temperature determined as described previously. (iii) In view of the complexity of the first scans, some samples were submitted to previous thermal treatment below the melting temperature (for 1 h generally).

Table 5 lists the most significant thermal data. When no treatment is specified the data correspond to the second heating scan at $10^{\circ}\text{C min}^{-1}$. Glass transition temperatures were taken as the middle point of the baseline jump observed.

The identification of the mesophases by optical microscopy is hindered by the appearance of granular textures, not easy to ascribe, as well as by the wide melting ranges. Furthermore, the high melting temperatures cause decomposition before the clearing temperature is reached, which hinders the display of characteristic textures by cooling the isotropic liquid into the mesophase. Only polyazomethine **10** exhibits an easily recognizable nematic texture of schlieren type showing many disclination lines (threaded texture). On mechanical stress the schlieren texture changes into a marbled one (see figure 2). Copolyazomethine **10/13** and polyazomethines **4**, **6**, **8** and **12** display less defined textures of schlieren, threaded or granular type. In all of these cases the existence of a mesophase was confirmed by DSC.

Table 5. Thermal and optical data of polymers.

| Polymer | $T_m/^{\circ}\text{C}$ | $T_i/^{\circ}\text{C}$ | $\Delta T/^{\circ}\text{C}$ | Mesophase | Observations |
|--------------|------------------------|------------------------|-----------------------------|-----------|----------------------------|
| 1 | dec. | | | | |
| 2 | 197 | | | | |
| 3 | 147 (a) | | | | $T_g = 69^{\circ}\text{C}$ |
| 4 | 181 (b) | 331 | 150 | Nematic | |
| 5 | 383 | | | | |
| 6 | 240 | 258 | 18 | Nematic | $T_g = 72^{\circ}\text{C}$ |
| 7 | 237 | | | | |
| 8 | 289 (c) | Dec. | | Nematic | |
| 9 | 376 | | | | |
| 10 | 216 | 308 | 92 | Nematic | $T_g = 88^{\circ}\text{C}$ |
| 11 | 176 | | | | |
| 12 | 310 (d) | 334 | 24 | Nematic | $T_g = 61^{\circ}\text{C}$ |
| 13 | 195 | | | | |
| 1/2 | 299 (e) | | | | |
| 1/13 | Dec. | | | | |
| 10/13 | 184 (f) | 260 (g) | 82 | Nematic | |

(a) Annealed sample at 125°C for 1 h (heating rate (h.r.) = $20^{\circ}\text{C min}^{-1}$).

(b) Annealed sample at 150°C for 1 h (h.r. = $10^{\circ}\text{C min}^{-1}$).

(c) Annealed sample at 230°C for 1 h (h.r. = $10^{\circ}\text{C min}^{-1}$).

(d) Annealed sample at 240°C for 1 h (h.r. = $20^{\circ}\text{C min}^{-1}$).

(e) Annealed sample at 250°C for 1 h (h.r. = $20^{\circ}\text{C min}^{-1}$).

(f) Annealed sample at 150°C for 1 h (h.r. = $20^{\circ}\text{C min}^{-1}$).

(g) Optical data. No endotherm was observed in DSC measurements.

The polyazomethines studied are semicrystalline materials and give complicated DSC curves with many transitions prior to melting, which vary depending on their thermal history. Generally these transitions disappear in the second scan or after annealing at temperatures higher than those of the transitions. In these cases, they correspond to reorganization processes or melting of metastable or imperfect crystals. Other transitions correspond to crystal polymorphism and remain in successive scans.

All of the polymers crystallize from the melt, except polyazomethine **3**, where an amorphous solid is obtained.

In general, the transitions observed in these polymers and more particularly that to the isotropic phase, appear as wide peaks typical of polydisperse samples.

3.5. Structure–mesomorphism relationship

In view of the high melting points of the polyazomethines reported in the literature, the different structures of the central core were chosen in order to test their mesogenic behaviour as well as their ability to lower the transition temperatures below the decomposition thermal range.

The structures studied fulfil the following criteria.

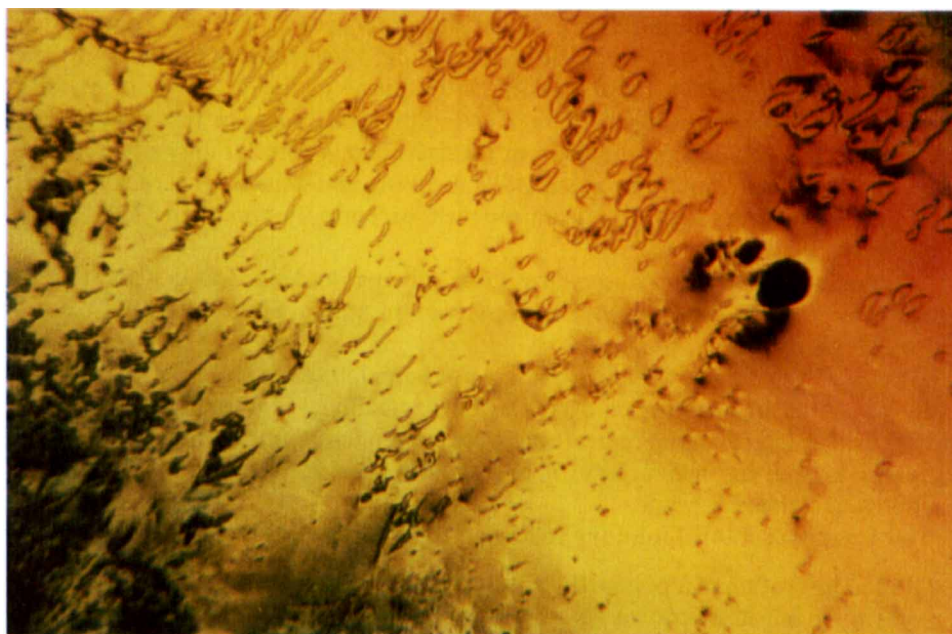
- (1) Incorporation of a polymethylene flexible spacer. The decamethylene unit was chosen as it is known to give polymers with melting temperatures in a reasonable range. The decamethylene group is bonded to the rigid unit by ether linkages.
- (2) Introduction of structural modifications in the diamine which are known to lower the transition temperatures by affecting the polymer symmetry in several ways:
 - (i) Substitution in the aromatic rings.
 - (ii) Introduction of kinks on the polymeric chain.
 - (iii) Disturbance of chain coaxiality.
 - (iv) Incorporation of aliphatic or cycloaliphatic central groups.
 - (v) Copolymerization of the dicarbonyl monomer with two diamines.

The introduction of the methyl group in the *p*-phenylenediamine ring (polymer **4**) markedly decreases, as expected, the melting temperature compared to **1**, which allows a wide mesophase range to be observed.

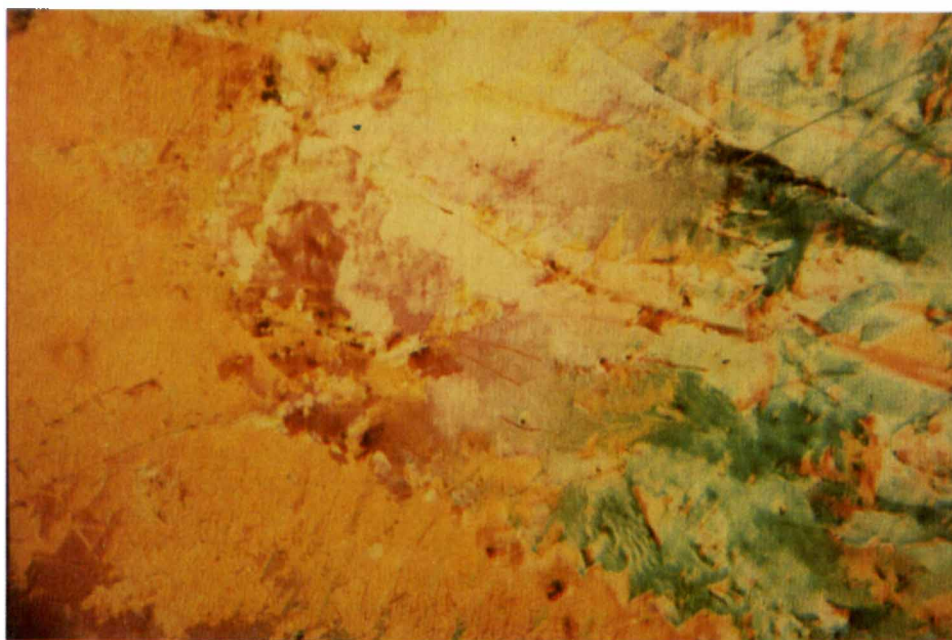
In polymers **2** and **3** derived from *m* and *o*-phenylenediamine the melting temperature decreases if compared with polymer **1**, but the liquid-crystallinity is destroyed by disruption of the molecular linearity. In polymer **3** the disturbance of the geometry causes frustration of the crystal packing, an amorphous material being obtained from the isotropic melt.

The effect of the bending angle between two phenyl rings (polymers **6** and **7**) depends on the group causing the bending. The ether group (–O–, polymer **6**) possesses a dipole moment and increases the anisotropy of the electronic polarizability compared to the methylene group. Both factors favour mesomorphism, although the mesophase range observed is narrow. Polymer **7**, derived from 4,4'-diaminodiphenylmethane, is not mesogenic, in contrast to the results obtained by Al-Dujaili *et al.* [11] with similar polyazomethines without ortho-hydroxyl groups, although in that case the flexible spacer was bonded to the mesogenic core by means of an ester link which increases the anisotropy of the molecular polarizability.

We have tested four different structures that disturb coaxiality of the chain (crankshaft monomers). In polymer **9** the alteration of the coaxiality is balanced by the

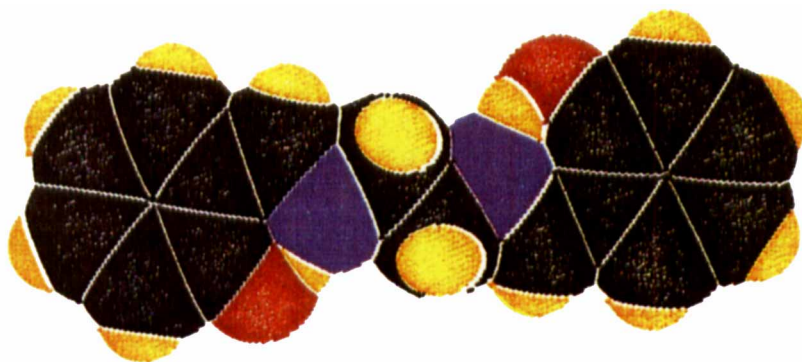


(a)

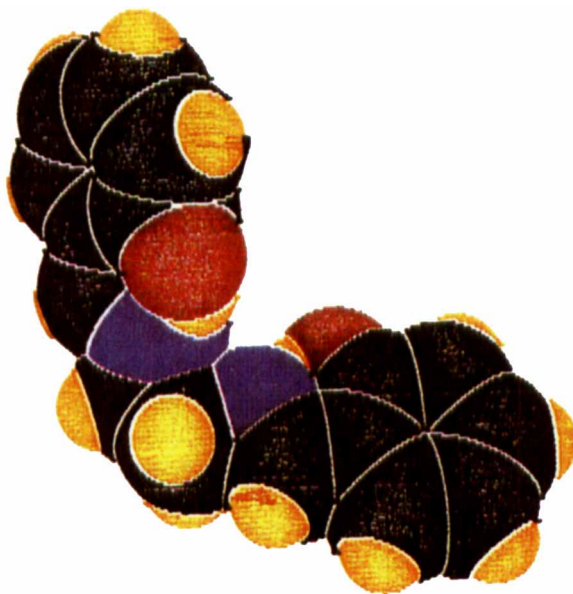


(b)

Figure 2. Polarized light micrographs of polymer **10** at 275°C ($\times 85$): (a) threaded texture with closed loops; (b) marbled texture obtained by mechanical stress.



(a)

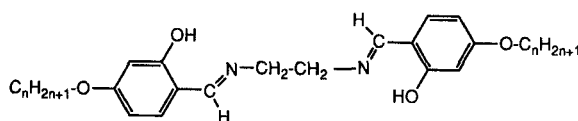


(b)

Figure 3. Molecular models of the flexible mesogenic core of the repeating unit of polymer 13: (a) *anti* conformation; (b) *gauche* conformation.

enhanced conjugation all along the 4,4'-*trans*-stilbenylene group. As a consequence of this high rigidity the polymer melts at too high a temperature for mesomorphism to be observed. On the other hand, in polymer **8**, derived from 4,4'-diaminodiphenyl-1,2-ethane, the disrupted conjugation and the flexibility due to the ethylene group decreases the melting point and allows mesomorphism to occur. 1,5-Disubstituted naphthalene (polymer **10**) abruptly disturbs the coaxiality, which leads to a lowering of the melting temperature and a wide mesophase range. In this case, the mesogenic core is planar and possesses a high anisotropy of the electronic polarizability due to the presence of four aromatic rings and two chelating hydrogen bonds. The 4,4'-xylylene group (polymer **11**) disturbs coaxiality and at the same time the methylene groups make the core more flexible and prevent conjugation from extending throughout. This accounts for the absence of mesomorphism in this polymer.

In our laboratory a number of mesogenic low molecular weight Schiff's bases were synthesized with a flexible central group [12]:



The incorporation of this mesogenic unit into the main chain of a polymer was expected to provide the high molecular weight analogues with mesomorphic properties. However, polyazomethine **13**, derived from ethylenediamine, melts directly into the isotropic liquid. This suggests that the structural characteristics and geometry of the mesogenic core have been disturbed with respect to the low molecular weight analogues. The molecular geometry is determined by the possibility of turning round the bonds in the flexible central group. The geometrical features were studied by semiempirical (MNDO) methods for simple model molecules [13]. This study led us to the conclusion that the *gauche* and *anti* conformers have similar energies and are consequently almost equally probable. Only the *anti* conformer leads to a rod-like structure (see figure 3); so in the case of **13** the *anti-gauche* ratio in the melt must be lower than in the corresponding low molecular weight analogues due to the higher transition temperatures. This means that there is a direct relationship between mesogeneity and conformational isomerism, as has been shown by Percec *et al.* in some series of polyethers [14].

In polymer **12** the *trans*-1,4-cyclohexylene group decreases the transition temperatures in comparison to the more rigid *p*-phenylene group (polymer **1**), and it is possible therefore, to observe anisotropic melts below its decomposition temperature. Nevertheless, the transition temperatures are still relatively high.

Copolymerization has not been shown to be a suitable way of decreasing the transition temperatures. Copolymer composition may not correspond to the feed composition due to the different reactivity of the comonomers. Copolymer **10/13** is a suitable example, in view of the differences of η_{inh} and degree of polymerization of the corresponding homopolymers. However, $^1\text{H NMR}$ spectroscopy showed a 10:13 monomer ratio of 1:1.1, near to the feed ratio. No information about the blockiness of the copolymers can be obtained by this technique. Obviously, during the copolymerization of the two comonomers, which are different in reactivity, block formation may take place instead of or as well as random copolymerization. A blend of homopolymers might even be obtained. However, thermal analysis, especially the absence of a melting

transition corresponding to the homopolymer of lower T_m in the case of 1/2 or 1/13, does not point to the presence of blends of homopolymers. In the same way, these results preferably point to random copolymers.

4. Conclusions

A series of sixteen polyazomethines derived from bis(4-formyl-2-hydroxy-phenyloxy)decane and different diamines were prepared in order to obtain more information about the relationship between molecular structure and mesomorphic behaviour in high molecular weight compounds. The melting temperature decreases noticeably when the rigid rod geometry is disturbed by the introduction of lateral substituents, angular units, non-coaxial units, flexible groups or copolymerization. The presence of a substituent in the aromatic ring (polyazomethine **4**) or units that alter the coaxiality (polyazomethines **8** and **10**) allowed us to obtain nematic melts with a wide temperature range. The angular units prevent mesomorphism, except for polyazomethine **6** as a consequence of the dipole moment of the ether bond. The ethylene group decreases the melting point but does not lead to liquid crystal properties, in contrast with the low molecular weight analogues. This can be attributed to an unfavourable conformational balance. An increase in molecular weight was observed on heating samples of these polyazomethines close to T_m for short periods of time.

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