

## THERMOTROPIC POLYAZOMETHINES CONTAINING KINKING GROUPS

LUMINIȚA MARIN and VASILE COZAN

In this paper, we present a new type of polyazomethines containing azomethinic mesogenic cores and diphenylsulfone or diphenylsulfone and bisphenol A units as kinking groups, which we have named poly(azomethine-ether-sulfone)s. The new polymers present liquid crystalline behavior, good thermal stability, good solubility and semiconducting properties. Special emphasis is put on the liquid crystalline behavior which improves processability and electrical properties of these materials. The study is completed by discussion of the effect of sulfonyl group on the mesomorphic behaviour and molecular properties. Additionally, the influence of thermotropic properties on the semi-conductivity was estimated.

*Key words:* polyazomethines, liquid crystalline, semiconducting properties.

### 1. INTRODUCTION

Conjugated polymers have gained widespread interest during the last two decades, due to their useful electronic, optoelectronic, electrochemical and non-linear optical properties. Among conjugated polymers, polyazomethines are an attractive class of high performance polymers, given their high thermal stability, excellent mechanical strength, chelate forming ability (and, generally, their ability to give supramolecular interactions with many electrophyles), semiconducting and good optoelectronic properties and thermotropic liquid crystalline behavior [9, 10, 21, 27]. All these properties are associated with the presence of the imine group, which generates an extended conjugation along the backbone. The extent of the conjugation is also responsible for their insolubility and infusibility, two drawbacks which reduce their application potential. In this context, the design of new polyazomethine structures with good property balance is rather difficult. There are many reported data about thermotropic liquid crystalline polyazomethines, such as poly(azomethine-ester)s [26], poly(azomethine-ether)s [18], poly(azomethine-carbonate)s [28], poly(amide-azomethine-ester)s [13], poly(acrylate-azomethine)s [29], thermosetting polyazomethines [22], in which various chemical structures were used, aiming to reduce the melting temperature, to improve the solubility and to promote specific properties, as mesomorphism [7]. As reported in the cited studies, transition temperatures decrease with the introduction of flexible spacers, but solubility is still unsatisfactory. Some investigations on poly(amide-ether-sulfone)s showed that the introduction of diphenylsulfone units into the backbone leads to a very good solubility,

while a high thermal stability is maintained [19, 20]. In fact, aromatic polysulfones and poly(ether sulfone)s are a family of aromatic amorphous thermoplastics with unique high-performance properties as engineering materials [23]. A key structural feature of these polymers that distinguishes them from other aromatic polymers is the presence of the para-linked diarylsulfone group (1) as part of the backbone repeat unit:



The introduction of the diarylsulfone group generates very effective kinks in the backbone, with an important influence on transition temperatures and solubility [8]. The same effect is provided by the isopropylidene-bisphenylene unit (coming from bisphenol A) (2), in which case two adjacent phenylene rings are joined through a single tetrahedrally coordinated carbon atom, thus forming very effective kinks with drastic influence on transition temperatures, although the effect on the melting point is not as pronounced as in the case of the flexible spacer [31]. On the other hand, the presence of  $>C(CH_3)_2$  units leads to good solubility [19].



In the light of literature data, we have designed a new kind of poly(azomethine)s containing diphenyl sulfone or diphenylsulfone and bisphenol A units as kinking groups, which we have named poly(azomethine-ether-sulfone)s (PAES), with the aim of combining valuable properties of both polyazomethines and polyethersulfones, due to the contribution of the anisotropic azomethine rigid cores and of the amorphous isotropic aryethersulfone and bisphenol A moieties.

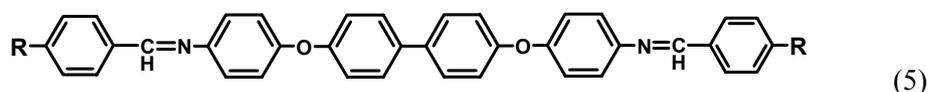
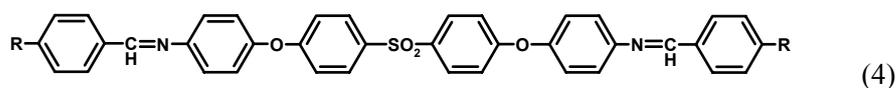
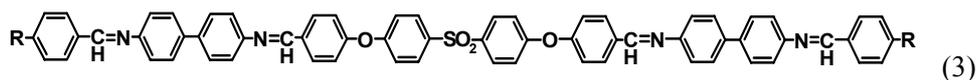
In this paper, we present this type of new polyazomethines presenting liquid crystalline behavior, good thermal stability and good solubility. Additionally, the semiconducting properties are preserved. Since we were the first to synthesize this class of polymers, a series of model compounds was obtained with the aim of accomplishing the structural characterization of the polymers by establishing a data set, and of better understanding their thermotropic behavior.

## 2. SYNTHESIS

### 2.1. MODEL COMPOUND SYNTHESIS

Model compounds containing a diphenylsulfone unit (MCS) (**3**, **4**) were synthesized via the Williamson etherification reaction of the diphenylsulfone

dichloride and appropriate mesogenic bisphenols [15]. For better understanding the influence of the sulfonyl group on the properties of the compounds containing it, some model compounds with a diphenyl unit against a diphenylsulfone unit were synthesized by an acid catalyzed condensation reaction of a diamine and the appropriate aldehydes (MCD) (5) [16].

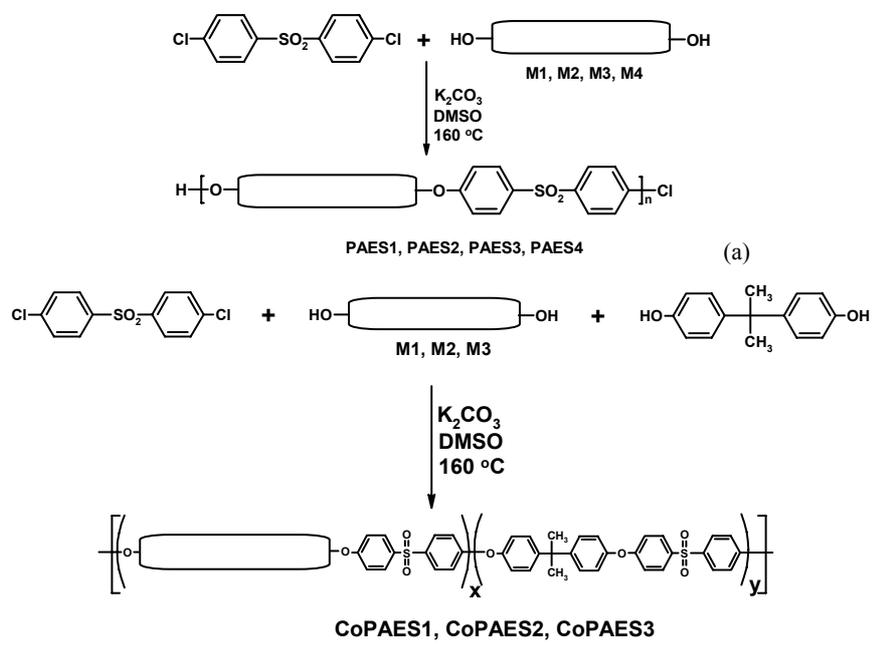


Code	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>
R	-NO <sub>2</sub>	-N(CH <sub>3</sub> ) <sub>2</sub>	-O-C <sub>6</sub> H <sub>4</sub> -pNO <sub>2</sub>

## 2.2. POLYMER SYNTHESIS

There are two ways of introducing the imine linkage into a polymer chain: (a) the reaction of monomers containing amine and aldehyde or ketone functional groups leading to the formation of an imine group, in which case the reacting groups are aldehyde or ketone and amine; (b) the reaction of monomers containing preformed imine linkages and functional groups capable of polyreactions. The first method (a) is fast at room temperature, but the products contain functional groups, which can polymerize in melted state (post-polymerization), increasing the polymer mass and therefore changing their thermotropic properties. In order to avoid the post-polymerization process we preferred to use the second method (b) to obtain the target polymers.

The synthetic pathway to poly(azomethine-ether-sulfone)s was the classical Williamson etherification method, in which the diphenyl sulfone dichloride reacted with a bisphenol as nucleophile. Alternated or random polymers were thus obtained (Scheme 1a, b). In both cases, mesogenic bisphenols containing preformed azomethine linkages (Table 1) were used [5]. The polymers generally precipitated out of the polycondensation media, after 6 h reaction time. The polymers were repeatedly washed with water and methanol in a Soxhlet apparatus, in order to remove the solvent and oligomeric fractions [17, 24].



Scheme 1. Schematic reactions to (a) alternated and (b) random poly(azomethine-ether-sulfone)s.

Table 1

The structures of the mesogenic bisphenols

Code	Structure	Thermotropic behavior <sup>a</sup>
M1	<p>4,4'-bis(<i>p</i>-hydroxybenzylidene-iminophenoxy)-biphenyl</p>	Cr 299 LC 303 I
M2	<p>4,4'-bis(<i>p</i>-hydroxybenzylidene-imino)-diphenylether</p>	Cr 244 I
M3	<p>4,4'-Terephthalylidene-bis(<i>p</i>-hydroxyaniline)</p>	Cr 284 I
M4	<p>4-(<i>p</i>-hydroxybenzylideneimino)-phenol</p>	Cr 218 I

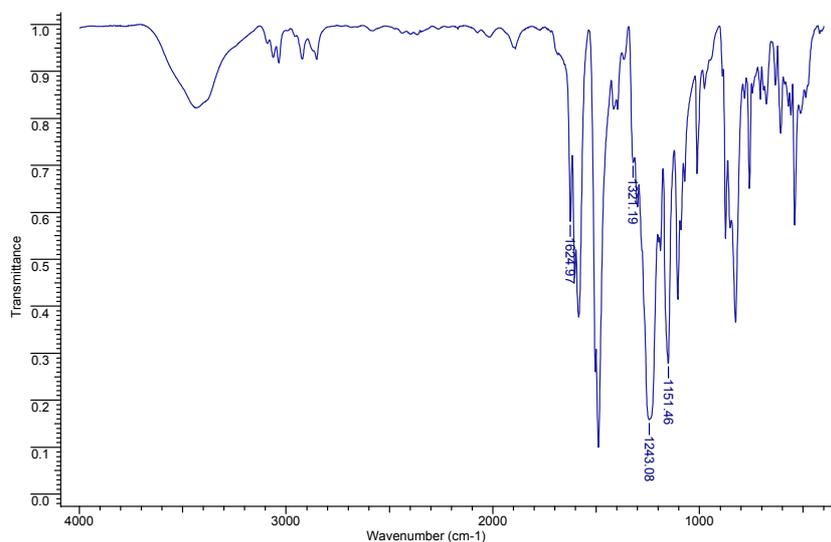
<sup>a</sup> Thermotropic behavior determined through optical polarized microscopy (POM); Cr = crystalline; LC = liquid crystalline; I = isotropic.

The polymer codes were assigned, taking into account the mesogenic bisphenol code *e.g.*: the polymer containing the monomer M1: PAES1; M2: PAES2; M3: PAES3; M4: PAES4, respectively. The copolymers will be referred to by the name of the respective polymers, preceded by the letters 'Co', and followed by the mesogenic bisphenol/bisphenol A ratio *e.g.*: the copolymer containing the mesogenic bisphenol M1 and the mesogenic bisphenol/bisphenol A ratio of 30/70 was named CoPAES1 30/70, and so on.

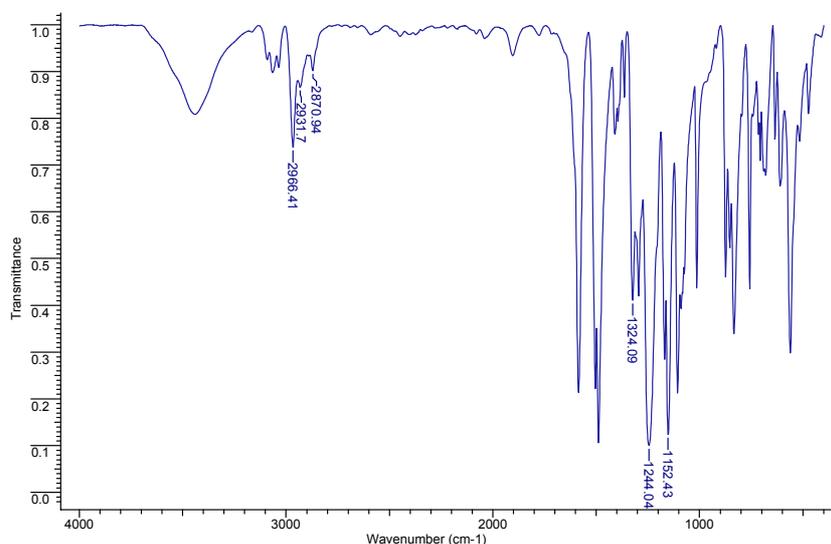
### 3. CHARACTERIZATION OF MOLECULAR STRUCTURE

The structure of the synthesized model compounds (MCS) and polymers (PAES) was confirmed by IR and  $^1\text{H-NMR}$  spectra and by elemental analysis [14, 16, 17, 24]. The agreement of the MCS and PAES data confirmed that the reaction proceeded successfully.

The assignment of the characteristic vibration bands in the IR spectra is summarized as follows: 3500 ( $\nu$  -O-H), 3100–3030 ( $\nu$  =C-H aromatic), 2990–2950 and 2895–2860 ( $\nu$  CH<sub>3</sub>), 1640–1625 ( $\nu$  CH=N), 1600–1590, 1510 and 1500 ( $\nu$  C=C aromatic), 1335–1300 ( $\nu$  SO<sub>2</sub> asym.), 1255–1250 ( $\nu$  C-O-C), 1160–1155 ( $\nu$  SO<sub>2</sub> sym.), 1098–1096 (C-Cl para), 875, 860 and 840 (1,4-phenylene ring). The absorption band of the azomethine linkage appears as a peak or as a shoulder, depending on the percentage of mesogenic units in the backbone. The absorption band of the -O-H linkage appears as a broad peak because of water, which forms hydrogen bonds with azomethine groups. Two typical IR spectra are presented in Figure 1.



a)



b)

Fig. 1. IR spectra of a) PAES1 and b) PAES1 30/70.

To complete the identification of the molecular structure,  $^1\text{H-NMR}$  spectra (DMSO- $d_6$ ,  $\delta$  in ppm, at 400 MHz) of the polymers were recorded.  $^1\text{H-NMR}$  spectra of the polymers showed three or four types of signals (depending on the presence of the bisphenol A unit), which were assigned correspondingly: the singlet around 9.2 ppm (O-H), the singlet around 8.6 ppm ( $-\text{CH}=\text{N}-$ ); the multiplets at 6.6–8.2 ppm (aromatic protons); the peaks centered at 1.50–1.75 ppm for aliphatic protons from bisphenol A segment  $(\text{CH}_3)_2\text{C}<$  in different conformations. No other remarkable signal due to a possible bisaminal formation (doublet, triplet respectively) was observed in the  $^1\text{H-NMR}$  spectrum of the model compounds or polymers. Thus, the  $^1\text{H-NMR}$  spectra, correlated with the FTIR spectra of the polymers, suggested that they had the proposed structure.

Additional characterization of the molecular structure of the polymers was done through elemental analysis. When compared to the calculated content of nitrogen and sulfur in the proposed structures, the elemental analyses showed a very good concordance, which indicated a narrow polydispersity index.

Poly(azomethine)s belong to a group of conjugated polymers that are in most cases hardly soluble in organic solvents, while polysulfones and poly(ether-sulfone)s are quite soluble. The introduction of the diphenyl sulfone or diphenyl sulfone and bisphenol A units into the polyazomethine backbone improved solubility, especially in the case of random poly(azomethine-ether-sulfone)s. All the polymers were completely soluble in tetrahydrofuran, 1,4-dioxane, N-methylpyrrolidine-2-one (NMP), N,N-dimethylformamide (DMF), dimethyl-sulfoxide (DMSO) and partially

soluble in chloroform. The improved solubility of the synthesized polymers can be explained by the presence of diphenylsulfone and bisphenol A units in the backbone, which kink the macromolecular chains, as can be seen in the molecular modeling (see Geometrical features section). This kinked shape of the backbone facilitates the diffusion of small molecules of solvent, which leads to a better solubility. Furthermore, the study of model compound solubility clearly reveals the positive influence of introducing the sulfone group on improving solubility. While the MCD model compounds are partially soluble in aprotic dipolar solvents (such as dimethylsulfoxid, N,N-dimethylformamide) and insoluble in protic solvents (acetone, methanol), the MCS model compounds are completely soluble in aprotic dipolar solvents and partially soluble in protic solvents.

Table 2

Physical characteristics of the polymers

Code	$M_n^a$	$M_w/M_n^b$	$\lambda_{max}(nm)$	$E_g(eV)$
PAES1	11 695	2.66	342	3.62
PAES2	8362	1.19	337	3.67
PAES3	8812	1.21	342	3.62
PAES4	5313	1.15	332	3.73
CoPAES1 70/30	8300	1.20	332	3.73
CoPAES1 50/50	7100	1.30	332	3.67
CoPAES1 30/70	6700	1.30	332	3.67
CoPAES2 90/10	4500	1.30	337	3.67
CoPAES2 80/20	7700	1.20	337	3.67
CoPAES2 70/30	8200	1.20	337	3.67
CoPAES2 60/40	7100	1.30	337	3.67
CoPAES2 50/50	6500	1.30	337	3.67
CoPAES2 40/60	6800	1.20	337	3.67
CoPAES2 30/70	6900	1.20	337	3.67
CoPAES3 50/50	8126	1.12	332	3.73

<sup>a</sup> From GPC measurements on DMF solutions; <sup>b</sup> Polydispersity index;

<sup>c</sup> Inherent viscosity measured for polymer solutions in DMF, at a concentration of 0.2 wt.% at 20°C

Gel permeation chromatography (GPC) measurements on DMF solutions of polymeric samples provided numerical average molecular weight ( $M_n$ ) values ranging between 4500–11695 g/mol, which are good molecular weights for the polymers with rigid backbone (Table 1). The molecular weight of the polymers is clearly subject to the limitation of the reaction scheme employed, since the polymers generally precipitated out of the polycondensation media. The low molecular weights are reflected in the absence of the ability to form flexible films from solution. The polydispersity index has values ranging between 1.12–1.30 (except for the PAES1 polymer). These polymers have a narrow molar mass distribution (Table 2), which favors self-assembling into ordered state.

## 4. CHARACTERISTIC PROPERTIES OF POLY(AZOMETHIN-ETHER-SULFONE)S

### 4.1. OPTICAL PROPERTIES

The extended conjugated  $\pi$ -system is mirrored by the electronic absorption spectrum. Ultraviolet spectra of polymer solutions in DMSO showed similar absorption patterns between 300 and 410 nm with an absorption maximum peaking between 332 and 342 nm, which is attributed to spin-allowed  $\pi$ - $\pi^*$  transitions involving the azomethine-phenyl framework (Table 1). Similar values are usually reported for polyazomethines [1]. A marked broadening of the absorption peak of all the samples can be related to different conformations adopted in solution. The observed changes of optical absorption spectra, when the mesogenic unit structure varies, can be attributed to the modification of the mesogenic unit length and planarity. This is indeed observed in the MCS model compound series. The compounds containing a low length mesogenic core (**3**) have lower values of absorption maxima than model compounds (**4**) whose mesogenic core length is higher. The same effect is also observed for the PAESs; the presence of a more coplanar diphenyl related to the phenylene ring leads to a decrease of energy gap in PAES1 versus PAES2 and PAES4, whereas the more nonplanar bisphenol A results in an increased energy gap in the corresponding copolymers. The  $\lambda_{\max}$  and optical gap are the same for all copolymers containing the same mesogenic unit (CoPAES1, CoPAES2), which indicates that these parameters are not affected by the percentage that the mesogenic units hold in the polymer chains. The emission spectra recorded at their own excitation wavelength did not present the emission peaks.

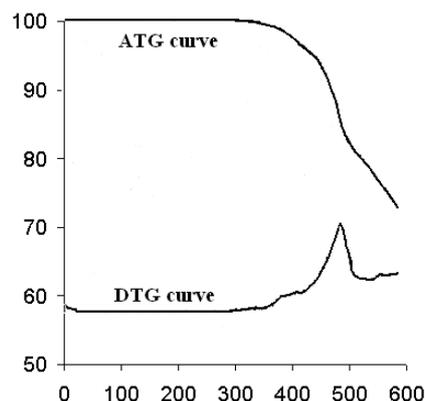
### 4.2. THERMAL STABILITY

As small amounts of the thermally decomposed material drastically affect the thermotropic behavior of liquid crystals, we evaluated the thermal stability by TGA considering the onset of thermal decomposition, *i.e.* the temperature corresponding to initial 1% of weight loss ( $T_{1\%}$ ). TGA thermograms were measured at a heating rate of  $12^\circ\text{C min}^{-1}$ , in air. Figure 2 shows representative plots of weight residue (wt.%) versus temperature, up to  $600^\circ\text{C}$ .

The polymers exhibit high thermal stability, with similar behavior during the degradation process: a slight decomposition started above  $200^\circ\text{C}$ , but with insignificant weight loss up to  $330^\circ\text{C}$ ; the 10% weight loss appeared at temperatures above  $400^\circ\text{C}$ . The derivative thermogravimetric DTG curves evidence that the degradation process takes place in two steps, the polymers undergoing a main weight loss within the  $360$ – $450^\circ\text{C}$  domain; as an example, the TGA and DTG curves of CoPAES1 30/70 are presented in Figure 2. Based on similar structures, one may assume that the first step corresponds to the breaking of the -O- linkage in the polymers and the second

step corresponds to the breaking of the  $-N=CH-$  linkage [4, 30]. Comparing to the thermal stability of the fully aromatic polyazomethines and polysulfones, we can assert that the thermal stability of both polymer classes is preserved in the polymers under study.

Fig. 2. TGA curve of CoPAES1 30/70 in air, heating rate of  $12^{\circ}\text{C}/\text{min}$ .



#### 4.3. THERMOTROPIC PROPERTIES

The thermotropic behavior of the poly(azomethine-ether-sulfone)s was monitored through differential scanning calorimetry (DSC) and polarized light microscopy (PLM) method.

The DSC thermograms recorded during a heating-cooling-heating cycle at a heating rate of  $10^{\circ}\text{C}/\text{min}^{-1}$  and under flowing nitrogen show different shapes. Some of them present only a melting transition in the first heating scan and a glass transition in the second heating scan (PAES2, PAES4, CoPAES2 40/60, CoPAES2 30/70); some of them exhibit neither endothermic nor exothermic peaks (PAES3, CoPAES3 50/50) and others present two small endothermic peaks in the first heating scan, no exothermic peaks during the cooling scan and a glass transition in the second heating scan (PAES1, CoPAES1 70/30, CoPAES1 50/50, CoPAES1 30/70, CoPAES2 90/10, CoPAES2 80/20, CoPAES2 70/30, CoPAES2 60/40, CoPAES2 50/50) (Figure 3, Table 2).

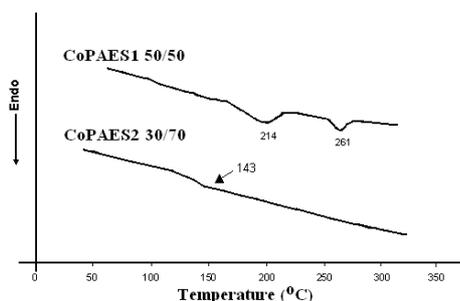
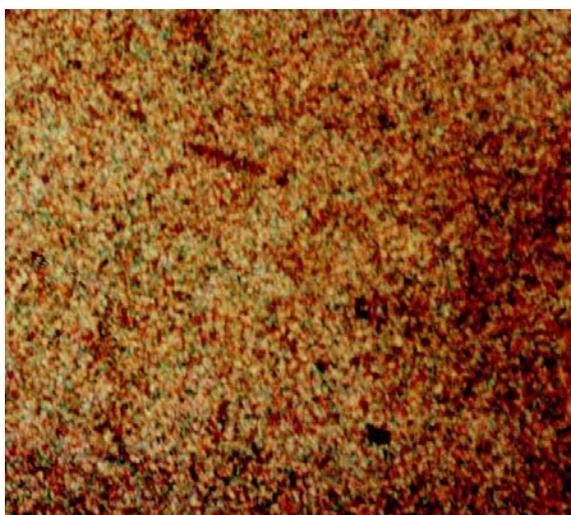
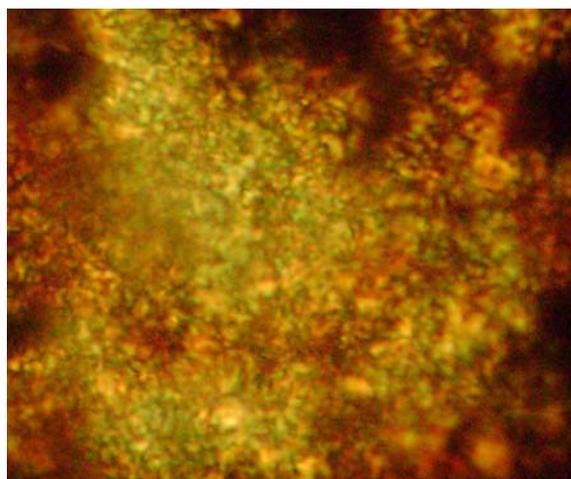


Fig. 3. Differential scanning calorimeter traces of CoPAES1 50/50,  $10^{\circ}\text{C}/\text{min}$ , first heating (1H) scan and CoPAES2 30/70,  $10^{\circ}\text{C}/\text{min}$ , first heating scan.

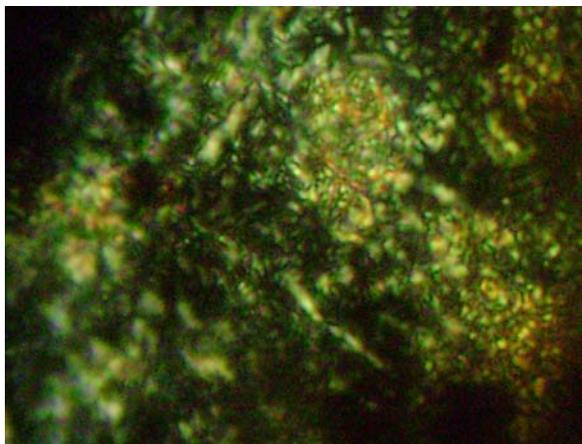
To clarify this behavior, polarized optical microscopy investigations were performed. Thus, a viscous fluid with strong birefringence was observed through PLM in the temperature range between the first and second peaks, for almost all polymers. The textures had a granular aspect, difficult to ascribe – a behavior also observed for liquid crystalline polyazomethines by other authors (Figure 4b, d) [2, 6, 31]. Some samples (CoPAES1, CoPAES2 60/40, CoPAES2 50/50) exhibited both birefringence and isotropic domains, which became birefringent under shear (Figure 4c). A similar behavior was reported by Lenz for statistic copolyesters containing both mesogenic and non-mesogenic moieties [11, 12].



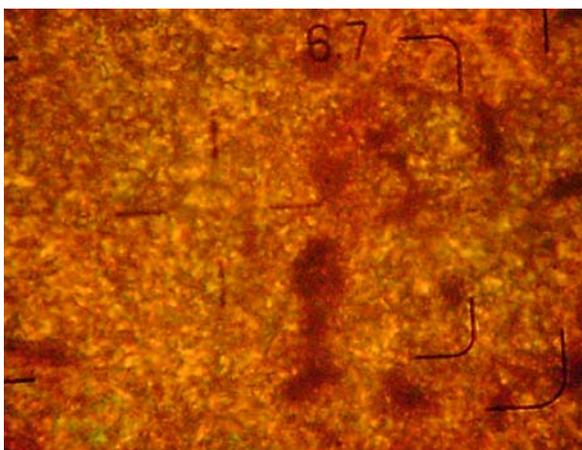
a) MCS II3, 1H, 278.12 °C, 400×.



b) CoPAES2 70/30, 1H, 162.12 °C, 200×.



c) CoPAES2 50/50, 1H, 156.12 °C, 200×.



d) PAES1, 1H, 270.12 °C, 200×.

Fig. 4. Polarized optical microphotographs.

As known, a birefringent fluid is the confirmation of liquid crystallinity [3] and, based on the PLM and DSC data, we can assume that some of the synthesized poly(azomethine-ether-sulfone)s exhibited thermotropic LC behavior.

Other evidence supporting the presence of the liquid crystalline state is the similarity between the polymer textures and the textures obtained for the model compounds containing the diphenylsulfone unit (Figure 4a). The recovering of the mesophases in the cooling scan for some model compounds reflects their faster self-assembling in liquid crystalline state *versus* rigid macromolecular chains with definitely higher length, which hinder the self-assembling in the isotropic state.

Table 3

Thermal data of poly(azomethine-ether-sulfone)s

Code	$T_m^a$	$T_i^b$	$T_g^c$	$\Delta T^d$	$T_1^e$	$T_{10}^e$
PAES1	284	302	127	18	330	470
PAES2	180	–	162	–	290	455
PAES3	>350	–	–	–	310	378
PAES4	188	–	110	–	290	420
CoPAES1 70/30	205	259	134	54	330	475
CoPAES1 50/50	210	261	125	51	300	450
CoPAES1 30/70	184	237	114	53	360	250
CoPAES2 90/10	165	187	133	22	310	435
CoPAES2 80/20	167	187	115	20	340	430
CoPAES2 70/30	168	183	108	15	300	415
CoPAES2 60/40	162	187	145	25	300	425
CoPAES2 50/50	153	188	143	35	320	445
CoPAES2 40/60	151	–	123	–	330	435
CoPAES2 30/70	143	–	–	–	310	430
CoPAES3 50/50	>350	–	–	–	300	394

<sup>a</sup>  $T_m$  = melting temperature; <sup>b</sup>  $T_i$  = isotropization temperature; <sup>c</sup> Glass transition temperature measured in the second heating scan, at a heating rate of 10°C/min; <sup>d</sup>  $\Delta T$  = mesophase range stability; <sup>e</sup> From TGA measurements in air:  $T_1$  = initial decomposition temperature at which 1% weight loss occurred;  $T_{10}$  = temperature at which 10% weight loss occurred

The formation of a mesophase in the first polymer heating scan could be explained by the preformed arrangement of the macromolecules in a semicrystalline state. After the semicrystalline state – mesophase transition, the macromolecules gain enough thermal energy to move, but the ordered structure is maintained due to the strong attractive  $\pi$ -interactions between the aromatic cores. In isotropic state, during the cooling scan, the rigid macromolecules have enough energy to move, but in the absence of a flexible spacer, self-assembling does not occur and the macromolecules freeze in disordered state. However, the presence of a liquid crystalline mesophase in the first heating is certainly demonstrated and this behavior opens up new opportunities for processing from the ordered melted state.

The presence or the absence of the liquid crystalline mesophase is correlated with the rigidity and aspect ratio of the mesogenic units and the percentage of the mesogenic units in the backbones. Therefore, for the PAES3 and CoPAES3 50/50, the melting point is high and above the temperature at which the polymers begin to decompose, due to the fact that the mesogenic unit is too rigid. In contrast, the PAES4 and CoPAES2 30/70 present a low melting temperature without mesophase formation, because the aspect ratio of the mesogenic units is too low, and because the mesogenic content in the macromolecular chains is also too low.

While classical aromatic polyazomethines are infusible polymers and polysulfones and polyether sulfones are amorphous polymers, the obtained hybrid

polymers, which we have named poly(azomethine-ether-sulfone)s, generally have intermediate transition temperatures ranging between those of parent polymers and, additionally, some of them have thermotropic liquid crystalline behavior. Their glass transitions ( $T_g$ ) are lower than the  $T_g$  of the classical polysulfones for which  $T_g$  is around 180°C.

#### 4.4. GEOMETRICAL FEATURES

The geometrical features were studied through molecular modeling methods (MM+) [\*\*\*] for the polymers and the copolymers (Figure 5), in order to simulate the possible conformation of a poly(azomethine-ether-sulfone).

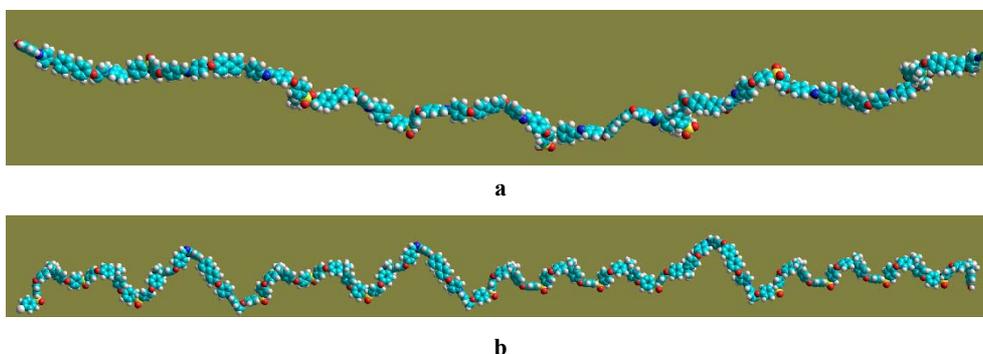


Fig. 5. Simulation of PAES1 and CoPAES1 50/50 structures.

We observed that rotations around the ether bonds minimize the disruptive influence of the kinked units (bis(*p*-chlorophenyl)sulfone, bisphenol A) on the straightness of the chain. The repeat units are kinked, but the macromolecular chains keep a quite straight geometry in the long run, especially in the case of polymers, which is fully in agreement with solubility and transition temperature results. This straight geometry also explains the presence of a mesophase very well.

#### 4.5. X-RAY MEASUREMENTS

In order to investigate the morphology of the synthesized polymers, the wide-angle X-ray diffractograms (WAXD) on powder samples were recorded at room temperature. All the curves exhibited some diffraction maxima mainly around  $2\theta$ : 20–35. The shape of the curves is different, with one up to four diffraction peaks, sharper or broader, suggesting various degrees of crystallinity. Looking at all diffractograms, three types can be distinguished: (1) diffractograms with sharper peaks in the region  $2\theta$ : 15–40; (2) diffractograms with two peaks, one sharper in the  $2\theta$ : 15–30 domain and one broader at  $2\theta$ : 30–40; (3) diffractograms with only one peak in the  $2\theta$ : 15–30 region. Representative diffractograms are illustrated in Figure 6.

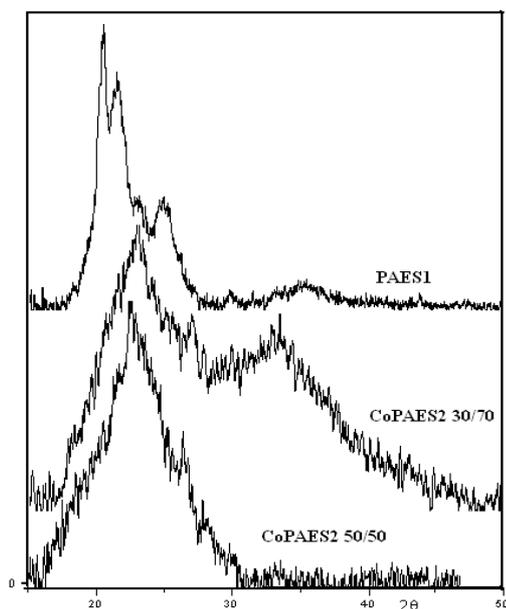


Fig. 6. WAXD curves of PAES1, CoPAES2 30/70, CoPAES 50/50, at room temperature

The shapes of the diffractograms are directly connected with the mesomorphic behavior of the corresponding polymers. Thus, the polymers with higher degrees of crystallinity (1) have mesomorphic behavior, while the less crystalline polymers (2) do not show any mesomorphic state. The polymers with medium crystallinity (3) present mesomorphic and isotropic domains. This correlation supports the supposition that the mesomorphic state particularly appears in the case of these rigid polymers due to the close packing of the rigid macromolecules in solid state.

#### 4.6. THE EFFECT OF SULFONYL GROUPS ON LIQUID CRYSTALLINE PROPERTIES

To evaluate the influence of sulfonyl groups on the thermotropic behavior, two series of low molecular weight Schiff bases, containing biphenyl units MCD (5) and nonmesogenic diphenyl sulfone moieties MCS (4), were synthesized. The expected structures of the synthesized model compounds were confirmed by IR,  $^1\text{H}$  NMR spectroscopy and elemental analysis measurements [15, 16]. Polarized optical microscopy and differential scanning calorimetry measurements clearly demonstrate the presence of a thermotropic liquid crystalline mesophase for all compounds. A comparison of the liquid crystalline parameters shows a decrease of melting temperatures and an increase in the mesophase stability range for MCS model compounds, *versus* MCD model compounds [16]. Figure 7 shows the dependence of the solid-to-mesophase transition temperature on the structure type, for the MCS and MCD series.

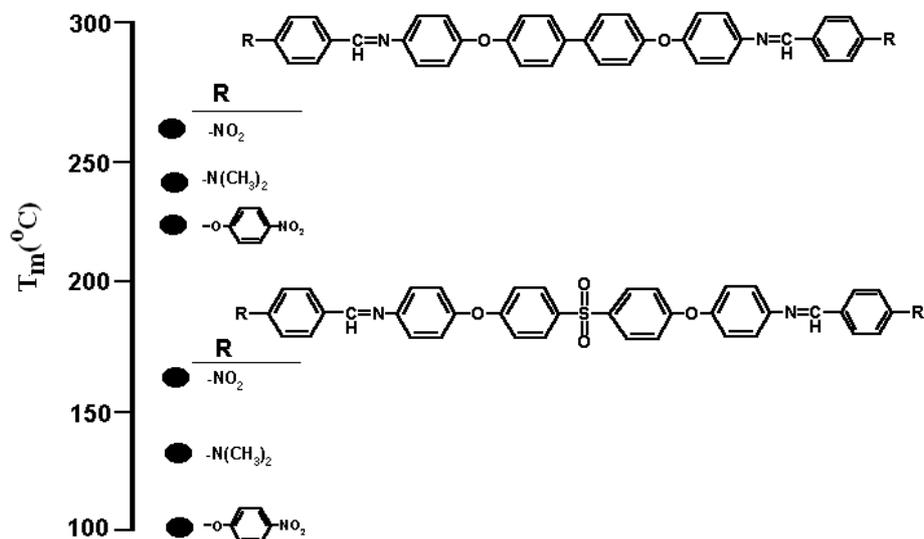


Fig. 7. Dependence of solid-to-mesophase transition temperature on structure type, for series (4) and (5).

As can be seen in Figure 7, the sulfone group in the **MCS** series led to lower melting temperatures in comparison with the values observed for the **MCD** series. The molecular modeling of both the MCS and the MCD model compounds shows a kinked structure for the MCS compounds compared to the MCD compounds, whose geometry is almost linear, which is fully in agreement with the transition temperatures (Figure 8).

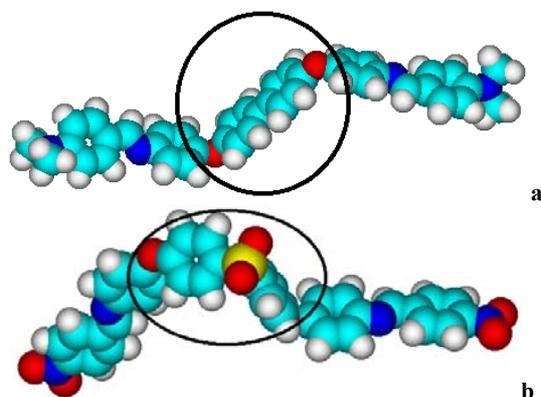


Fig. 8. Simulation of a) MCD and b) MCS structures.

#### 4.7. EFFECT OF COPOLYMERIZATION ON LIQUID CRYSTALLINE PROPERTIES

The effectiveness of kinked units diarylsulfone and bisphenol A, respectively, in reducing the crystalline melting point of the synthesised poly(azomethine-ether-

sulfone)s, is greatly enhanced if the chain is modified by units incorporated in random positions along its length. The destruction of chain periodicity inhibits crystallization, markedly reducing both crystallinity and melting point, without necessarily leading to any additional loss of mesogenicity and reduction in upper transition temperature. A phase diagram of temperature against composition is shown in Figure 9.

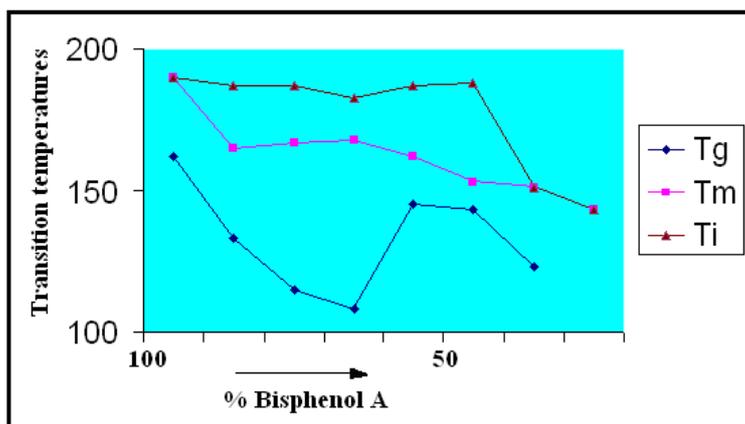


Fig. 9. Variation of transition temperatures with composition.

The homopolymer based on DCDFS and mesogenic core M2 at the left of the diagram is PAES2, which is not liquid crystalline. The effect of the introduction of bisphenol A kinked groups is to decrease the melting point, this effect being more pronounced for an increasing proportion of bisphenol A *versus* mesogenic bisphenol. Between 10 and 50% bisphenol A, the system becomes thermotropic in a temperature range of about 20°C. The non-regular insertion of bisphenol A units into the macromolecules achieves a reduction in  $T_m$  of around 25°C [24]. The bisphenol A and diphenylsulfone units produce a “kink effect” and add a “length effect” due to their shorter length than that of azomethinic mesogenic core. They determine a reduction in  $T_m$  because they are shorter than the mesogenic cores, and the long range periodicity and hence crystallizability of the macromolecules are impaired. Comparing the transition temperatures of the PAES2 to CoPAES2, we can conclude that the random copolymerization is the major factor in determining the reduction in melting point.

#### 4.8. SEMICONDUCTING PROPERTIES

Because the PAES1 and CoPAES1 polymers provided the lowest optical energy gap (UV-measurements), they were the subject of a study on electrical properties. Electrical conductivity was measured on thin films deposited on the

glass substrates from DMF solutions. In order to obtain polymeric films with stable structures, the samples were successively heated after preparation and cooled within a certain temperature range, corresponding to their thermal stability [25]. While the polyethersulfone is considered an insulator, having electrical conductivity of about  $10^{-16}$  ( $\Omega^{-1}\text{cm}^{-1}$ ), the studied polymers showed a high increase in electrical conductivity, with values of  $10^{-8}$  ( $\Omega^{-1}\text{cm}^{-1}$ ). Additionally, it was observed that the polymeric films had a better electrical conductivity after this thermal treatment than the untreated polymeric films (Table 4).

Table 4

Semiconducting properties

Sample code	d ( $\mu\text{m}$ ) <sup>a</sup>	T <sub>max</sub> (°C) <sup>b</sup>	$\sigma_c$ ( $\Omega^{-1}\text{cm}^{-1}$ ) <sup>c</sup>	$\sigma_T$ ( $\Omega^{-1}\text{cm}^{-1}$ ) <sup>d</sup>	rms <sub>C</sub> (nm) <sup>e</sup>	rms <sub>T</sub> (nm) <sup>f</sup>
PAES1	1.84	210	$1.1 \times 10^{-8}$	$81.5 \times 10^{-8}$	49.7	78.7
PAES170/30	1.58	225	$4.6 \times 10^{-8}$	$25 \times 10^{-8}$	77.08	5.6
PAES150/50	1.05	215	$1.25 \times 10^{-8}$	$8.1 \times 10^{-8}$	303.4	154.4
PAES130/70	0.38	205	$0.24 \times 10^{-8}$	$7.68 \times 10^{-8}$	159.4	1.66

<sup>a</sup>film thickness; <sup>b</sup>upper temperature of thermal treatment; <sup>c</sup>electrical conductivity at room temperature; <sup>d</sup>electrical conductivity after heat treatment; <sup>e</sup>surface roughness of untreated films; <sup>f</sup>surface roughness of treated films

Usually, electrical performance depends strongly on film morphology and crystallinity. High film crystallinity and order and strong crystalline domain connectivity ensure the best conditions for charge transport. Polarized optical microscopy (POM) observations of the thermally treated and untreated films reveal a strong birefringence for the treated film of the PAES1 polymer and an isotropic state for the treated films of the others (CoPAES1 50/50, CoPAES1 70/30, CoPAES1 30/70), while untreated films have a weak birefringence. Morphological characterization through atomic force microscopy (AFM) of both treated and untreated film surface reveals that in all cases the substrate surface was completely covered. While the untreated films presented grainy morphology with high surface roughness, the treated film of sample PAES1 (with liquid crystalline structure) exhibited connected grains forming a percolation lattice, with an improved connectivity among domains, *versus* untreated PAES1 film. Treated films of samples CoPAES1 50/50, CoPAES1 70/30, CoPAES1 30/70 (with isotropic structure) presented more homogeneous morphology with lower surface roughness *versus* untreated films (Figure 10).

Analyzing the AFM, POM and semiconducting data, some interesting correlations can be established. Thus, in the case of the PAES1 sample, whose thermally treated film has an ordered structure in the mesophase state, a high increase in electrical conduction was noticed (about 74 times).

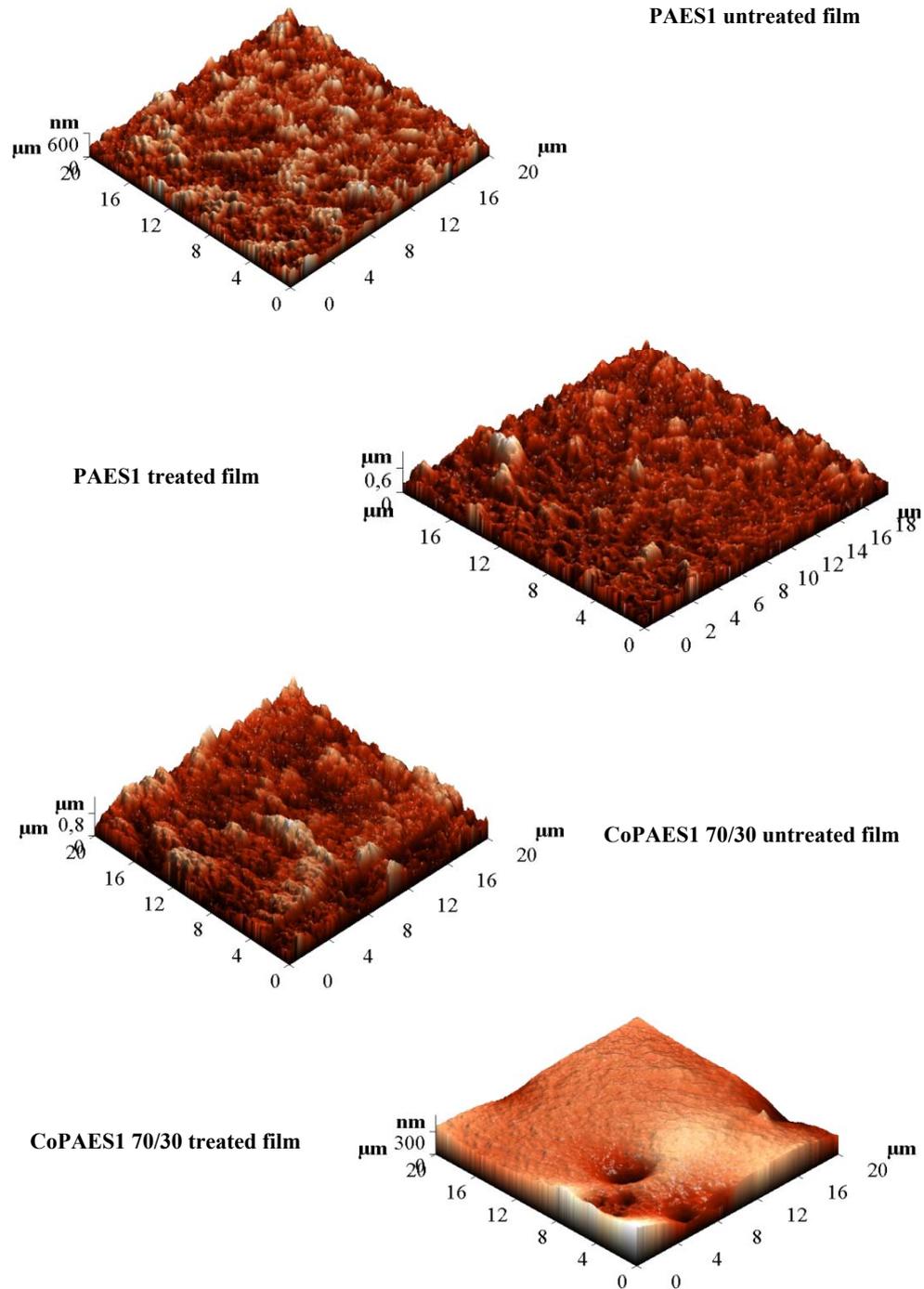


Fig. 10. Surface film morphology of PAES1 and PAES1 70/30.

For the CoPAES1 70/30 and CoPAES1 50/50 samples, whose treated films are amorphous, but have a better homogeneity *versus* untreated films, a slight increase in electrical conductivity was observed (about 5 times). In the case of the CoPAES1 30/70 sample, whose treated film is amorphous, but has a high homogeneity against the untreated film, medium increases of the electrical conduction were produced (about 32 times). We conclude that ordered films have better charge transport properties than amorphous films, and the amorphous film homogeneity plays an important role in improving electronic conduction.

## 5. CONCLUSIONS

A new type of polyazomethines, which we have named poly(azomethine-ether-sulfone)s, were synthesised. The new polymers, incorporating diphenyl sulfone or diphenylsulfone and bisphenol A units as kinking groups and mesogenic azomethinic cores, have good solubility, thermal stability and mesomorphic behavior. Additionally, they have semiconducting properties in films. The comparative study of treated and untreated films clearly shows the improvement of charge transport properties of ordered films *versus* amorphous films. Also, amorphous films have better charge transport properties when film continuity is higher.

Our results demonstrate that, with the help of self-assembling processes, it is possible to obtain complex surface patterns even with simple linear molecular bricks.

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## REFERENCES

1. ALY K., KHALAF A.A., ALKSKAS I.A., *Liquid crystalline polymers VII. Thermotropic liquid crystalline poly(azomethine-ether)s containing dibenzylidene derivatives in the main chain*, Eur. Polym. J., 2003, **39**, 1035–1044.
2. BARBERA J., ORIOL L., SERRANO J. L., *Hydroxy-functionalized liquid-crystalline poly(azomethines I. Synthesis, characterization and structure-mesogenic behaviour relationship*, Liquid Crystals, 1992, **12** (1), 37–47.
3. BARON M., *Definitions of basic terms relating to low-molar-mass and polymer liquid crystals*, Pure Appl. Chem., IUPAC, ISSN: 0033-4545, 2001, **73**, 845–895.
4. CATANESCU O., GRIGORAS M., COLOTIN G., DOBREANU A., HURDUC N., SIMIONESCU C.I., *Synthesis and characterization of some aliphatic – aromatic poly(Schiff base)s*, Eur. Polym. J., 2001, **37**, 2213–2216.
5. COZAN V., MARIN L., BRUMA M., *Preparation and study of new phenolic azomethine compounds*, Rev. Roum. Chim., 2005, **50** (7–8), 641–648.
6. DESTRI S., PORZIO W., MARIN L., DAMACEANU D., BRUMA M., *New thermotropic oligomers designed for FET applications*, J. Optoelectron. Adv. Mater., 2007, **9** (5), 1337.

7. DONALD A.M., WINDLE A.H., HANNA S., *Liquid crystalline polymers*, Cambridge University Press, Cambridge, 2006.
8. EL-HIBRI M.J., NAZABAJ J., EQUIAZABAL J.I., ARZAK A., *Poly(arylethersulfone)s*, in *Handbook of Thermoplastics* (O. Olabisi, ed.), Marcel Dekker, New York, 1997, Chapter 36, p. 893.
9. GRIGORAS M., CATANESCU C. O., *Imine oligomers and polymers*, J. Macromol. Sci. Part C – Polym. Rev., 2004, **44** (2), 131–173.
10. IWAN A., SEK D., *Processible polyazomethines and polyketanils: From aerospace to light-emitting diodes and other advanced applications*, Prog. Polym. Sci., 2008, **33** (3), 289–345.
11. LENZ R. W., *Balancing mesogenic and non-mesogenic groups in the design of thermotropic polyesters*, Faraday Discuss. Chem. Soc., 1985, **79**, 21–32.
12. LENZ R. W., JIN J.-I., *Liquid crystal polymers. 3. Thermotropic rigid aromatic copolymers with bisphenol spacers*, Macromolecules, 1981, **14** (5), 1405–1411.
13. LI C.-H., CHANG T.-C., *Thermotropic liquid crystalline polymer. III. Synthesis and properties of poly(amide-azomethine-ester)*, J. Polym. Sci. – Chem., 1991, **29** (3), 361–367.
14. MARIN L., COZAN V., *Liquid crystalline azomethines. The effect of sulfonyl group on the liquid crystalline properties*, Ann. St. Univ. Iasi, Sec. Chim, 2004, **12**, 65–70.
15. MARIN L., COZAN V., *New Thermotropic Azomethines Containing Sulfonyl Group*, Rev. Roum. Chim., 2006, **51** (7–8), 675–681.
16. MARIN L., COZAN V., BRUMA M., *Synthesis and study of new symmetric azomethine trimers containing biphenyl units*, Rev. Roum. Chim., 2005, **50** (7–8), 649–653.
17. MARIN L., COZAN V., BRUMA M., *Comparative study of new thermotropic polyazomethines*, Polym. Adv. Technol., 2006, **17** (9–10), 654–672.
18. MARIN L., COZAN V., BRUMA M., GRIGORAS V.C., *Synthesis and thermal behaviour of new poly(azomethine ether)*, Eur. Polym. J., 2006, **42**, 1173–1182.
19. MEHDIPOUR-ATAI S., *Novel thermally stable poly(sulfone ether ester imide)s*, Eur. Polym. J., 2005, **41**, 91–95.
20. MEHDIPOUR – AATAI S., SARRAFI Y., HATAMI M., AKBARIAN – FEIZI L., *Poly(sulfone ether amide amide)s as a new generation of soluble, thermally stable polymers*, Eur. Polym. J., 2005, **41**, 491–499.
21. MENON S.K., JOGANI S.K., AGRAWAL Y.K., *Macrocyclic Schiff bases and their analytical applications*, Reviews in Analytical Chemistry, 2000, **19**(5), 361–412.
22. MORMANN W., BROCHER M., *Liquid crystalline thermosets by polymerization of mesogenic azomethine based diepoxides-influence of reaction rate on phase behavior*, Polymer, 1998, **40**, 193–198.
23. PARKER D., BUSSINK J., GRAMPPEL H.T., WHEATLEY G.W., DORF E-U. OSTLINNING E., REINKING K., *Polymers, High-Temperature*, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH: Weinheim, 2002.
24. PAVEL D., MARIN L., COZAN V., CRAUS M. L., *New Poly(Azomethine-Ether-Sulfone)s. Modification by Random Copolymerization*, in *Advanced Research in Polymer Science* (Firas Awaja, ed.), Transworld Research Network, Kerala, 2006.
25. RUSU G.H., AIRINEI A., RUSU M., PREPELIȚĂ P., MARIN L., COZAN V., RUSU I., *On the electronic transport mechanism in thin films of some new poly(azomethine sulfone)s*, Acta Materialia, 2007, **55** (2), 433–442.
26. SHUKLA U., RAO K.V., RAKSHIT A.K., *Thermotropic liquid-crystalline polymers: synthesis, characterization, and properties of poly(azomethine-ester)s*, J. Appl. Polym. Sci., 2003, **88**, 153–160.

27. SIMIONESCU C., FILIP D., *Azomethine – structure polymers*, Mater. Plast., 2000, **37**(1), 42–46.
28. SUN S.-J., CHANG T.-C., LI C.-H., *Studies on thermotropic liquid crystalline polycarbonates – I. Synthesis and properties of thermotropic liquid crystalline poly(azomethine-carbonate)s*, Eur. Polym. J., 1993, **29**(7), 951–955.
29. TANAKA H., SHIBAHARA Y., SATO T., OTA T., *Preparation and thermal behavior of spin polymers and their precursors based on azomethine mesogens*, Eur. Polym. J., 1993, **2**(12), 1525–1530.
30. VASANTHI B. J., RAVIKUMAR L., *Synthesis and characterization of new poly(azomethine ester)s having phenylthiourea units*, Eur. Polym. J., 2007, **43**, 4325–4331.
31. WINDLE A.H. *Structure of Thermotropic Main – Chain Polymers*, in *Liquid Crystalline and Mesomorphic Polymers* (Shibaev V.P., Lam L., eds.), Springer-Verlag, 1994, p. 42.
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