SELF-ORGANISED FILMS OF POLYIMIDES CONTAINING PERYLENE DISCOTIC MESOGENS

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The synthesis of polyperyleneimides derived from a mixture of 3,4,9,10-perylenetetracarboxylic dianhydride and hexafluoroisopropylidene diphthalic anhydride with diamines containing oxadiazole rings is described. The ability of these polyimides to self-organize into supramolecular architectures was investigated. The formation of columnar phases was demonstrated by differential scanning calorimetry (DSC), polarized light microscopy (POM) and wide angle X-ray diffractions (WXRD) measurements. The morphology of the obtained supramolecular assembly was intuitively reflected in AFM images showing that the polymers are organized into self-assembled well-ordered building blocks that form supramolecular rod-like structures which tend further to aggregate into bigger rods having a lamellar structure.

INTRODUCTION

Perylene tetracarboxylic diimides (PTDCI) represent a class of highly thermostable n-type semiconductors exhibiting relatively high electron affinity among large band-gap materials. They have characteristic intense light absorption in the visible region and exhibit intense fluorescence with quantum yield reaching almost 100% in solution. The fluorescence emission can be tuned from blue to red by varying the substitution pattern of the perylene core.[1] The photocharge generation and electron transport properties of low molecular weight perylene imides have been successfully demonstrated by applying these materials in photovoltaics[2-5] light-emitting diodes[6,7] xerography,[8] and field-effect transistors.[9] Self-assembly of PTCDI derivatives into various nanostructures, including nanobelts, nanotubes, and nanofibers, has been extensively studied.[10-12] The construction of materials through self-assembly and self-organization processes, in which molecules associate spontaneously into ordered molecular and supramolecular aggregates as a result of noncovalent interactions and/or entropic factors, is

becoming one of the primary frontiers of materials research. In order to achieve this goal, several strategies, such as π-π interactions, H-bonding, metal-coordination, charge-assisted H-bonding and ionic self-assembly are available.[13-16]

On the other hand, polyimides are thermally stable polymers that exhibit good mechanical properties, low dielectric constant, low coefficient of thermal expansion and high radiation resistance. Since the first commercial polyimide-Kapton was produced by DuPont, polyimides have been extensively used in microelectronics, photonics, optics and aerospace industries.[17,18] However, research using polyimides containing perylene in optoelectronic fields can rarely be found so far,[19,20] which may be due to the poor solubility of perylenediimide polymers in common organic solvents. Therefore, the design and preparation of soluble poly(peryleneimide)s, to give satisfactory processability of products without a perceptible loss of favorable properties, is an important problem in the chemistry of heat resistant polymers. Being known that the introduction of flexible groups or/and certain supplemental heterocycles into the backbone of fully aromatic polymers can lead to soluble products,[21,22] a

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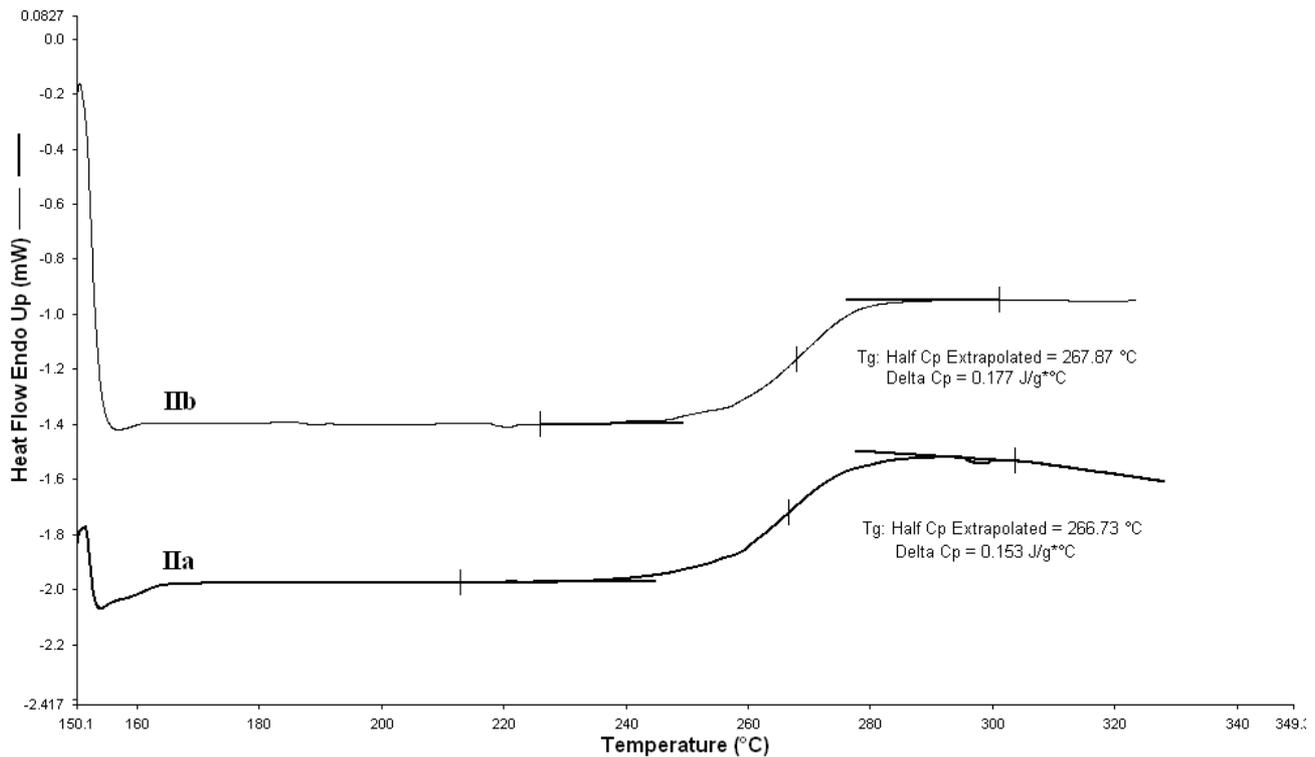
combined approach was undertaken through the synthesis of copoly(peryleneimide)s containing oxadiazole rings and flexible groups such as ether or hexafluoroisopropylidene.

In this contribution we report the synthesis of organosoluble polyperyleneimides containing oxadiazole rings and their morphology and thermotropic behaviour in solid state as investigated by optical polarized microscopy (POM), differential scanning calorimetry (DSC), X-ray diffraction and atomic force microscopy (AFM).

RESULTS AND DISCUSSION

The copolyimides studied here are based on two dianhydrides, one containing perylene unit and another one containing hexafluoroisopropylidene group and various aromatic diamines containing preformed oxadiazole ring. One-step polycondensation reaction of one diamine with a mixture of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), and 4,4'-(hexafluoroisopropylidene)-diphthalic dianhydride (6FDA) in a solution of N-methylpyrrolidinone (NMP) with LiCl, yielded copolyimides **I**, **II** and **III** after heating at high temperature.[23] Their structures are shown in Scheme 1.

The copolyimide **Ia** precipitated during imidization and therefore we increased the proportion of 6FDA until a soluble polymer was obtained. The same procedure was applied to copoly(perylene-imide)s **II**, since a mixture 1:1 PTCDA:6FDA gave a copolyimide that precipitated during heating.

It is known that conventional aromatic poly(peryleneimide)s are insoluble in easily accessible and safe organic solvents, being soluble only in *m*-cresol, due to the rigid nature of perylenediimide unit which dictates the overall

shape of the corresponding macromolecules and thus facilitates the strong interchain interactions, and due to the compact aggregation of the polymer chains which occurs during imidization that is carried out at high temperatures.[24] Our copoly(peryleneimide)s are soluble in a convenient aprotic amidic solvent which is NMP, at a concentration of 0.5-1% due to the presence of flexible 6F groups and oxadiazole rings in the macromolecular structure that introduce a deviation from the linearity of the chain and disturb the tight packing of the polymer chains.

All the synthesized copolymers contain perylene unit, a polyaromatic mesogenic core, which has the tendency to form columnar phases because of the strong π-π interactions. Additionally, these copoly(peryleneimide)s contain oxadiazole mesogenic core which also has the ability of self assembling in supramolecular architectures. The ability to form columnar phases was checked by DSC, POM and WXRD measurements.

The differential scanning calorimetry (DSC) curves of copoly(peryleneimide)s **I-III** were recorded during a heating-cooling-heating cycle at a heating rate of 10ºC/min. All the studied polymers show in the first DSC scan a broad weak endothermic peak and, in the second heating scan, a trace inflection corresponding to the glass transition. Only **IIa** shows a second endothermic peak in the first heating scan. Such weak transitions are characteristic of liquid crystalline perylene-containing polyimides due to the strong interactions between the perylene moieties.[25] The glass transition temperatures, as measured in the second heating scan, of these polymers are in the range of 227-268°C. Representative DSC curves are shown in Fig. 1.

I : Ar = –

I a: x : y : z = 2 : 1 : 1
I b: x : y : z = 3 : 1 : 2
I c: x : y : z = 4 : 1 : 3

II : Ar = –⟨⟩–O–

II a: x : y : z = 2 : 1 : 1
II b: x : y : z = 3 : 1 : 2

III : Ar = –⟨⟩–O–

III: x : y : z = 2 : 1 : 1

Scheme 1 – Structures of polyimides containing perylene and oxadiazole moieties.

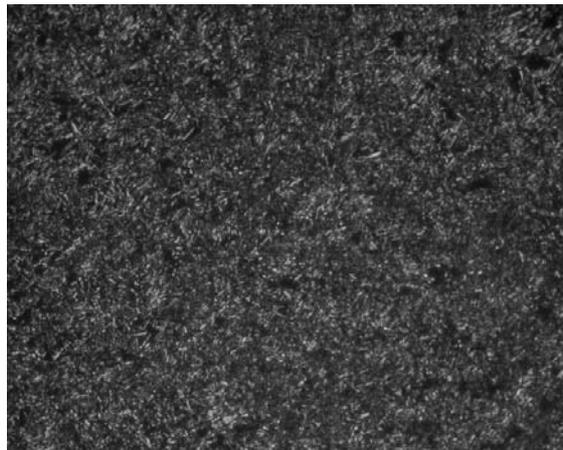Fig. 1 – DSC curves of polymers **IIa** and **IIb**.

Fig. 2 – POM image of the birefringent molten of copolyimide **Ia.**
(first heating scan, 350ºC, 40x, polarized light).

POM measurements show for all the samples a slight birefringence in solid state indicating a degree of crystalinity. All the studied polymers show a birefringent molten at the temperatures corresponding in DSC thermograms to the broad endothermic peak. A representative POM image is shown in Fig. 2. The polymers **Ib**, **Ic** and **III** form viscous molten, while the copolyimides **Ia, IIa** and **IIb** show more fluid birefringent molten. By cooling, all the polymer samples form a birefringent and homogeneous glass which can not be scratched by a spatula, as observed in polarized and non-polarized light. The isotropisation was not observed up to 350ºC.

In order to investigate the structural changes which take place in DSC and POM measurements, X-ray diffractograms of copolymer powders were recorded at temperatures corresponding to different phase regions.

All the samples show similar X-ray patterns consisting in an amorphous halo in the range 10–30º (2 theta degree), and five sharp peaks situated around 9.4º, 11.08º, 12.34º, 24.5º, 27.3º (2 theta degree). A diffuse weak halo was

registered in the region 3.5°–7.5° (2 theta degree), too. This XRD pattern indicates the presence of what we define as a semicrystalline state, which was formed during solution polycondensation reaction. The diffraction position and peaks shape seem to be independent of the diamine monomer type and monomers ratio used in the polymers synthesis, the main difference between the XRD diffractograms being in the diffraction intensity (Fig. 3a). This means that the intermolecular forces which control the orientation and molecular packing into the samples are generated by almost the same rigid segments.

The d-spacing calculated with Bragg's law by using the measured diffraction angle and the relative intensities observed in X-ray diffraction patterns for the synthesized copolyimides are enclosed in Table 1.

Usually, as confirmed by X-ray diffraction of several single crystals, the perylene mesogen units exhibit flat π-systems, which are arranged in stacks showing a parallel orientation of the neighboring, cofacially stacked perylene cores at a distance between 3.34 and 3.55 Å.[26,27] In the case of X-ray diffraction pattern of our polymers, the π-π stacking of the perylene cores gives two peaks at 24.5° and 27.3° (2 theta degree) situated above the diffuse halo, which indicates that the columns are slightly disordered and can slide past each other. The calculated d-spacing for these reflections corresponding to the intracolumnar disk-disk distance among the perylene mesogenes is 3.72 Å and 3.36 Å respectively; these values are very close to the distance of 3.35 Å which was found in graphite.[28, 29] The close contact of the perylene π-systems may lead to the good charge conduction. The explanation for this close stacking into perylene columns could be the rigid imide rings which restrict the rotation and enhance the interactions of perylene discs to stabilize the columns by facilitating face-to-face packing motifs.
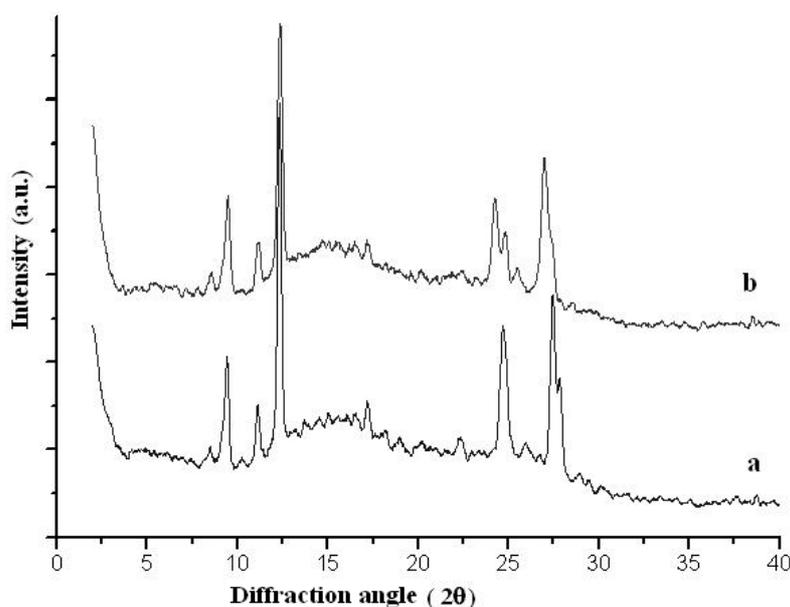
Fig. 3 – X-ray powder diffraction pattern of polymer **Ia** at room temperature (a) and at high temperature (b).

Table 1

The intensities (**I**) of the peaks observed in X-ray diffraction patterns for the studied copolyimides

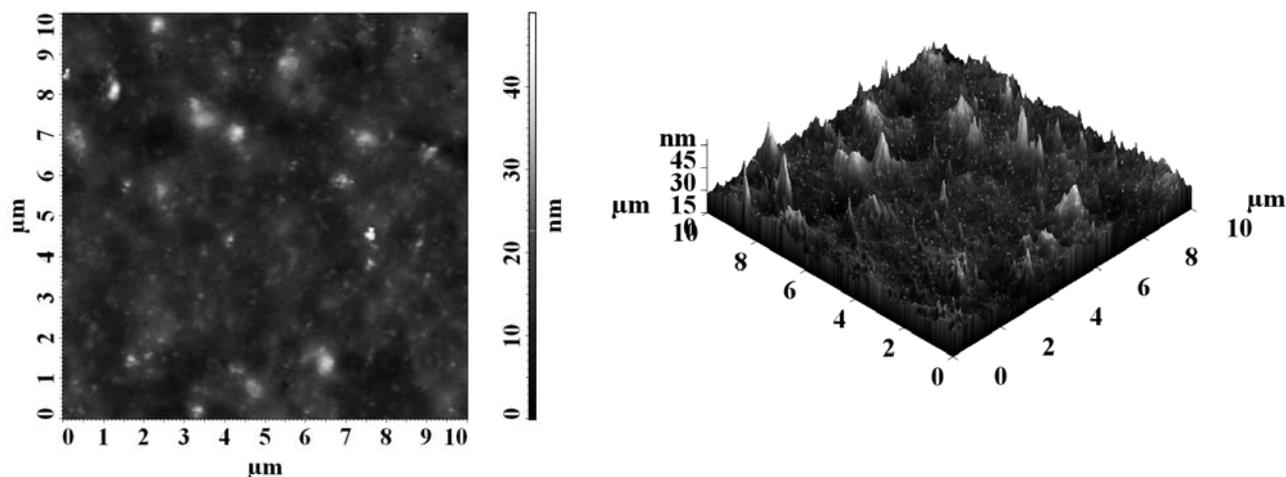| 2 theta	d (Å)	I (%)					
		Ia	**Ib**	**Ic**	**IIa**	**IIb**	**III**
9.4	9.43	102	80	54	58	31	69
11.1	8.02	75	67	49	53	28	57
12.2	7.21	247	166	101	106	44	142
24.6	3.72	121	87	65	74	30	87
27.4	3.36	138	90	60	66	28	90

Fig. 4 – AFM images of polyimide film **IIa** (left: 2D image, right: 3D image).
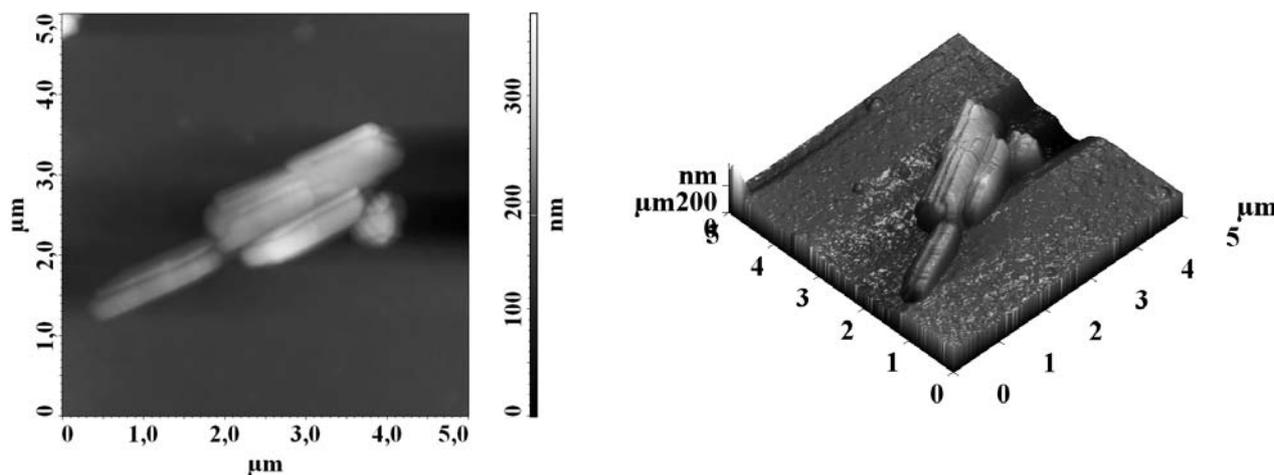

Fig. 5 – AFM images of nanorods formed in polyimide film **III** (leff: 2D image; right: 3D image).

In the small angle region the polymers showed only a diffuse weak halo which reflects the disordered liquid character of the statistic chains connecting the perylene cores. Due to the fact that in macromolecular chain perylene cores are separated from each other by chain units with different lengths, the regular repetitions of these columnar layers is hindered. The broad halo (3–7°, 2 theta degree) corresponds to a polydispersity of the intercolumnar distances in the range of 30–13 Å and reflects the statistical disposition of the perylene cores columns.

Compared to related semiflexible perylene-containing polyimides, our polymers show in X-ray difractograms a broad wide angle halo centered at 15.7^o, 2 theta degree. The calculated value of spacing corresponding to the broad wide angle halo is around 5.7 Å and it is attributed to the liquid like correlation of the disordered chain units. The reflections in the middle angle region (9.4^o, 11.08^o, 12.34^o, 2 theta degree) correspond to the distances of 9.43, 8.02, 7.21 Å. Taking into account that the supramolecular architecture is dictated by π-stacking of the perylene cores and excluding the ordering of the other mesogenic segments, by analogy with rod-like mesogens, we attributed these distances to the tilted perylene discs.[30,31] This fact indicates that the columnar stacks have various orientations.

The XRD pattern of the polymer samples at the temperature corresponding to the end of the thermal transition (Tg), as it was observed in DSC thermogram, shows some changes with respect to the room temperature diffractogram. Since all polymers showed similar features, only the X-ray diffractogram of polymer **Ia** is reproduced as a representative example (Fig. 3b). It can be seen that after heating, the peaks from the wide-angle region shifted slightly to smaller angles and a new reflection in the wide-angle region appeared. These features suggest a decrease of the attractive forces among perylene units, due to the increase of

thermal energy and thus of the conformational disorder of single tetrahedral coordinated C atom and of O atom. The columnar structure of the semicrystalline state is retained by virtue of strong π-π perylene interactions and chain rigidity, but there is one component of rotational disorder and poor translational movement of chain segments, especially for the polymers **Ia**, **IIa** and **IIb**. After cooling the reflections position became similar to XRD pattern before heating. These scarce changes of the XRD patterns are similar to other results reported in literature for perylene-containing polymers,[32] and reflect the strong interactions among perylene mesogens.

In conclusion, the X-ray measurements indicate that the supramolecular architecture of the semicrystalline copolyimides consist in columns of perylene units arranged face-to-face, with different orientations and without intercolumnar correlations. These perylene columns are statistically distributed into amorphous part of the sample. This conclusion is consistent with AFM images, as will be discussed later.

The good solubility makes the present polymers potential candidates for practical applications in spin-coating and casting processes. Very thin films having the thickness in the nanometer range were deposited by spin-coating technique onto glass plates, by using diluted solutions of polymers **I**, **II** and **III** (concentration of 1%). The quality and the morphology of these films were studied by atomic force microscopy (AFM). These spin-coated copolymer films are self-organized into vertically segregated structures as can be seen in AFM images (Fig. 4).

The solid-state packing behavior of these copolymers was hypothesized based on their aggregation characteristics in solid state,[33] and the morphology of the obtained supramolecular assembly was intuitively reflected in AFM images (Fig. 5), showing a well-ordered 1D crystalline arrangement. These images of the very thin cast film of the copolyimides show that the polymers are organized into self-assembled well-ordered building blocks that form supramolecular rod-like structures which tend further to aggregate into bigger rods having a lamellar structure, as can be seen in Fig. 5. These aggregates mainly result from the π-π stacking interactions of perylenediimide units.

EXPERIMENTAL

Monomers

2,5-Bis(*p*-aminophenyl)-1,3,4-oxadiazole, 2,5-bis[4-(*p*-aminophenoxy)phenylene]-1,3,4-oxadiazole, and 2,5-bis[4-

(*m*-aminophenoxy)phenylene]-1,3,4-oxadiazole were prepared according to published procedures.[34-36]

Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and hexafluoroisopropylidene-diphthalic anhydride (6FDA) have been purchased from Aldrich and used as received.

Polymers

Copolyimides **I**, **II** and **III** have been prepared by one-step polycondensation reaction of three different aromatic diamines with a mixture of PTCDA and 6FDA taken in different molar ratios. The reactions were carried out in NMP with 3.5% LiCl, at a concentration of 7% total solids, under nitrogen stream, at high temperatures (200-210°C). In case of the two dianhydrides with different reactivity, the less active dianhydride monomer PTCDA was added in the first stage of reaction to the solution of diamine in NMP, and then the more active dianhydride monomer 6FDA was added to achieve an even more random incorporation of the two monomer units in the polymer chain. Owing to the low solubility of PTCDA in NMP with LiCl at room temperature, higher reaction temperature is necessary to achieve better solubility. The reaction mixture was stirred and heated to 200-210°C and allowed to react for 10 h, then gradually cooled to room temperature. The generated imidization water was removed through a gentle nitrogen flow, and hence the reaction balance was moved to the formation of polyimide. The resulting dark red copolyimide solutions were poured into water to precipitate the solid polymer. The dark red polymers were washed with plenty of water and finally treated with ethanol in a Soxhlet apparatus for 1 day in order to remove the unreacted monomers and the high boiling solvent. Finally, copolyimides **I-III** were obtained as a red powder after drying in an oven, under vacuum, at 100°C for 6 h.

Preparation of polymer films

Very diluted polymer solutions in NMP with concentration of 0.5-1% were used to obtain very thin films having the thickness in the range of nanometers onto silicon wafers by casting technique. These films, as deposited, were gradually heated from room temperature up to 200°C, and kept at 200°C for 1 h. to remove the solvent. The resulting dark red coatings were used for atomic force microscopy (AFM) investigations.

Measurements

The glass transition temperature (Tg) of the precipitated polymers was determined by using a Diamond DSC Perkin Elmer calorimeter. Approximately 3 to 8 mg of each polymer were crimped in aluminium pans and run in nitrogen with a heat-cool-heat profile from room temperature to 380°C at 10°C/min. The mid-point temperature of the change in slope of the DSC signal of the second heating cycle was used to determine the glass transition temperature values of the polymers.

The polymer mesophases were investigated by observing the textures with an Olympus BH-2 polarized light microscope under cross polarizers with a THMS 600/HSF9I hot stage.

Wide Angle X-Ray Diffraction (WAXD) was performed on a Bruker D8 ADVANCE Diffractometer, using the Ni-filtered Cu-Kα radiation (λ=0.1541 nm). A MRI-WRTC–temperature chamber (with nitrogen inert atmosphere) and a MRI-TCPU1-Temperature Control and Power Unit were used. The working conditions were 36 kV and 30 mA. All the

diffractograms were investigated in the range 1.5÷40° (2 theta degrees), at different temperatures. Initial samples for X-Ray measurements were powders obtained directly by polycondensation. All diffractograms are reported as observed.

The quality of very thin films as-deposited on silicon plates was investigated by atomic force microscopy (AFM) using a Scanning Probe Microscopy Solver PRO-M, NT-MDT equipment made in Russia, in semi-contact mode, semi-contact topography technique.

CONCLUSIONS

Ternary copolyimides containing perylene and oxadiazole moieties were processed into very thin films and their morphology and self-assembling ability were investigated. The copolymer films contain various ratios of perylene unit – a polyaromatic mesogenic core which has the tendency to form columnar phases because of the strong π-π interactions. This feature was checked by DSC, PLM and WXRD measurements. The data showed that the supramolecular architecture of the semicrystalline copolyimides consists in columns of perylene units arranged face-to-face, with different orientations and without intercolumnar correlations, being statistically distributed into the amorphous part of the polymer sample. Supramolecular assembly was reflected in AFM images, as well, showing a well-ordered 1D crystalline arrangement: the polymers are organized into self-assembled well-ordered building blocks that form supramolecular rod-like structures which tend further to aggregate into bigger rods having a lamellar structure.

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