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New imides based on perylene and siloxane derivatives

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Di- and poly- imides containing perylene and siloxane moieties have been prepared by reaction of 3,4,9,10-perylenetetracarboxylic dianhydride with an excess of α,ω-bis(aminopropyl)di- and oligodimethylsiloxanes, that differ by siloxane sequence length in quinoline, as a solvent. The product solubility increases with the siloxane segment length. When 3,4,9,10-perylenetetracarboxylic dianhydride:siloxane derivative molar ratio was 1:1, polyimides were formed. By partial replacement of 3,4,9,10-perylenetetracarboxylic dianhydride with 4,4′-(hexafluoroisopropylidene)diphthalic anhydride, the solubility of the resulting polyimide was improved. All structures were verified by proton nuclear magnetic resonance and infrared spectroscopy. The surface topography of the products processed as films was investigated by Atomic Force Microscopy. The photophysical properties in correlation with the structure were studied.

1. Introduction

Perylene derivatives have attracted much attention for potential applications in organic molecular electronics. Of particular interest is their use as light emitting and electrochromic materials [1]. An important class of perylene derivatives is formed by perylene-containing imidic compounds [2]. Like perylene, the derived diimides (PDI) are an important representative class of n-type semiconductors that form some of the most environmentally and thermally stable materials that can be used in nonlinear optical devices, electrochromic or smart windows, photoresists, optical modulators and valves, imaging materials, in solar energy conversion, nanoelectronic devices, and transistors. Most of these properties and applications are related to the facile reduction of PDI derivatives, giving a relatively stable radical anion species [2]. The electron acceptor character is a common property of aromatic diimides and arises from the strong electron-withdrawing power of the imide groups [3]. PDI are also excellent candidates for creating a self-organized molecular electronic material, and they are one of few n-type organic semiconductor systems that have demonstrated high charge carrier mobilities in thin film devices and structures perhaps because they have strong π–π interactions which can facilitate self-organization [4,5]. However, most of the studied perylene imides are insoluble, and therefore the preparation of thin layers is carried out by the vapor deposition method [6,7]. The alternative method of blending low molecular weight perylene imides with polymers to prepare smooth films has the inherent problem of phase separation. On the other hand, soluble low molecular perylene imide dyes can be obtained by introducing long and bulky substituents at the 1, 6, 7, 12 positions and/or at the imide nitrogen atoms [7]. Core-perfluoroalkylated perylene diimides and naphthalene diimides containing different functional side chains on the imide nitrogen atoms were prepared and their solubility proved to depend on the size of the groups attached to the nitrogen atoms [8].

The approaches to synthesize copolymers containing perylene moieties were also reported in the literature. Oligomers or polymers with end-capped perylene monoimides (polysiloxane [2], polyfluorene and polyindenofluorene [9–12]), copolymers having perylene diimides incorporated in the polymer chain [7,13–21] or graft copolymers (perylene monoimide side chains on a polyfluorene [9]), as well as more sophisticated architectures such as dendrimers [22,23] or H-bond self-assemblies containing perylene were synthesized.

As in the case of PDI, perylene-containing polyimides also showed poor solubility dissolving only in highly polar solvents, such as, m-cresol or concentrated H_2SO_4 because of the strong π–π stacking between perylene moieties. Therefore, improving the polyimide solubility is desired [14]. The main possibilities to attain this are either introduction of the bulky substituents at the imide nitrogen [24] or at the carbocyclic scaffold [25] or copolymerization with other monomers. Different combinations of monomers were approached to prepare polyimides. For example, a mixture of perylene

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dianhydride (PDA) and 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) was reacted with aromatic diamines containing 4,4′-diaminetriphenylamine and 4,4′-methylenedianiline [26]. Some aliphatic/aromatic poly(Schiff base)s were obtained from the polycondensation reaction of diaminoperylene with some different aromatic dialdehydes [13].

The Suzuki polycondensation reaction has been used to synthesize copolymers consisting of alternating oligo(*p*-phenylene vinylene) (OPV) donor and PDI acceptor chromophores or donor-acceptor copolymers that consist in oligo(*p*-phenylene vinylene) main chain with pendant perylene diimides [21,27].

Recently, perylene-containing random copolyimides with different ratios of diaminododecyl perylene tetracarboxylic dianhydride and 6FDA have been demonstrated to have improved solubility. The copolyimides with a low percentage (less than 20% of total dianhydrides) of perylene become highly soluble in conventional solvents, such as, $CHCl_3$, CH_2Cl_2, or THF [14].

Copolymers consisting of polyethylene and perylenediimide dyes have also been prepared. Optical characterization of the copolymers with UV–vis absorption and photoinduced absorption spectroscopy reveals that the optical and electronic properties of the perylenediimide moieties are not significantly affected by incorporating them into the polymer chain [15].

Two series of copolyimides, poly(quinoxaline perylene diimide)s and poly(quinoxaline perylene diimide ether)s, carrying quinoxaline units and varying amounts of substituted perylene diimides in the main chain have been synthesized. The incorporation of varying amounts of perylene diimides with different substitution patterns allowed the control of fluorescence wavelength and intensity in solution and in thin films [7].

In this paper, we report the synthesis of both perylene-containing diimides and polymides by using siloxane diamines. 6FDA was used as a dianhydride co-monomer. The aim was to prepare soluble polyimides and to investigate the effect of the perylene content and siloxane presence on the optical properties.

2. Experimental

2.1. Materials

1,3-Bis(aminopropyl)tetramethyldisiloxane, (AP_0), supplied by Fluka (b.p. = 142 °C/11.5 mmHg, $d_4^{20} = 0.905$) was used as received. α,ω-Bis(3-aminopropyl)oligodimethylsiloxanes (AP) having two different average number molecular weights (1185 and 3357 estimated from ^{1}H NMR spectra) were synthesized according to the known procedure [28] by the bulk equilibration reaction of octamethylcyclotetrasiloxane (D_4) with 1,3-bis(aminopropyl)tetramethyldisiloxane in the presence of the tetramethylammonium hydroxide (TMAH) as a catalyst. 4,4′-(Hexafluoroisopropylidene) diphthalic anhydride, 6FDA, $M = 444$, m.p. 243–245 °C 3,4,9,10-Perylenetetracarboxylic dianhydride (PDA) (Aldrich), p.t. 350 °C, $M = 392.32$. Quinoline (Merck), $d_{25}^4 = 1.09$, m.p. = −15 °C. Zinc acetate, $Zn(CH_3COO)_2 \cdot 2H_2O$, $M = 219.5$.

2.2. Equipments

Fourier transform infrared (FTIR) spectra were recorded using a Bruker Vertex 70 FTIR spectrometer. Analyses were performed in the transmission mode in the range 400–4000 cm^{-1} at room temperature with a resolution of 2 cm^{-1} and accumulation of 32 scans. The samples were incorporated in dry KBr and processed as pellets in order to be analyzed.

The proton magnetic resonace (^{1}H NMR) spectra were acquired in $CDCl_3$ at 25 °C with a Bruker Avance DRX 400 MHz spectrometer operating at 400.13 MHz for ^{1}H. The spectrometer was equipped with a 5 mm four nuclei, direct detection z-gradient probehead. Chemical shifts are reported in ppm and are referenced to chloroform $\delta^1H = 7.26$ ppm.

UV–VIS absorption spectra were recorded on an Analytik Jena SPECORD 200 spectrophotometer using 1 cm quartz cuvettes. Fluorescence spectra were obtained by means of a Perkin Elmer LS55 luminescence spectrometer under ambient conditions. For the emission spectra an excitation wavelength of 490 nm was used since all derivatives have strong absorptions at this wavelength.

A Scanning Probe Microscope SOLVER PRO-M, NT-MDT, Russia was used to evaluate the surface topography and morphology of the samples that could be processed as films. Drop cast films were prepared from the solution 1% w/v in proper solvents. By slow solvent evaporation, the concentration gradually increases and favors self-organization in thermodynamically stable structures [4].

2.3. Procedure

2.3.1. Synthesis of perylene diimides (PDI1, PDI2, PDI3, Scheme 1)

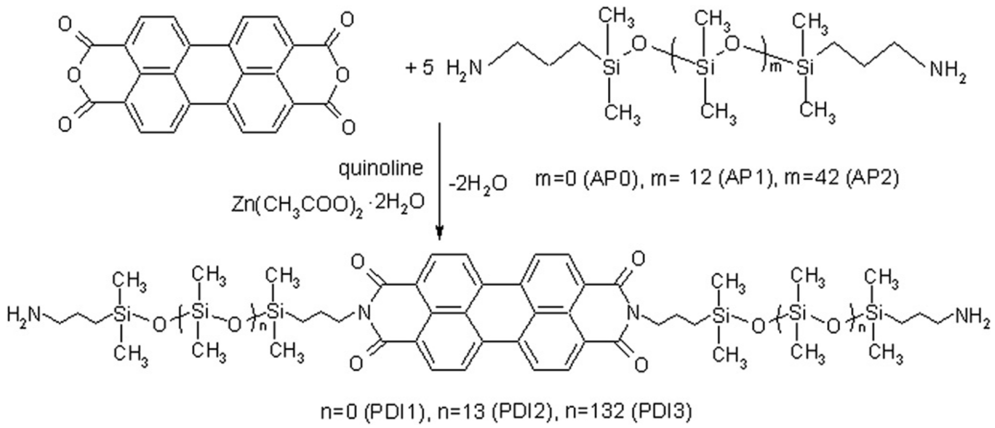
Siloxane diamine AP0 (0.124 g, 0.5 mmol), AP1 (0.568 g, 0.5 mmol) or AP2 (1.678 g, 0.5 mmol) was dissolved in 20 mL quinoline at room temperature under magnetic stirring in a two-necked, flat-bottom flask, equipped with reflux condenser. Then, zinc acetate dihydrate (0.002 g, 0.01 mmol) was added. The temperature was increased at 100 °C and PDA powder (0.0392 g, 0.1 mmol) was added stepwise. The mixture was stirred at this temperature for 4 h, after that the temperature was increased to 160 °C and kept in these conditions for 8 h. After this time, the mixture was cooled to room temperature, and poured into methanol (300 mL). The precipitated solid was filtered, repeatedly washed with methanol and dried. Products were obtained as dark red powder (PDI1), or flexible films (PDI2 and PDI3) depending on the siloxane sequence length.

PDI1. Yield 0.068 g (80%); FTIR (KBr, cm^{-1}): 3383, 3302, 3092, 2954, 2926, 2873, 1696; 1658, 1256, 1052, 795; Anal. (%) Calcd. for $C_{44}H_{60}N_4O_6Si_4$: C, 61.9; H, 7.0; N, 6.6; Si, 13.1; Found C, 63.1; H, 8.1; N, 5.9; Si, 14.1; ^{1}H NMR (400 MHz, $CDCl_3$), ppm δ: −0.2–0.2 (bs, 24H), 0.48–0.53 (m, 4H), 0.63–0.67 (m, 4H), 1.42–1.49 (m, 4H), 1.67–1.88 (bs, 4H), 2.65 (t, 4H, 6.8 Hz), 3.84–4.10 (bs, 4H), 7.01–8.60 (m, 8H). **PDI2**. Yield 0.176 g (67%); FTIR (KBr, cm^{-1}): 3119, 2963, 2905, 1698, 1660, 1261, 1096–1021, 799; Anal. (%) Calcd. for $C_{96}H_{216}N_4O_{32}Si_{30}$: C, 41.5; H, 7.8; N, 2.0; Si, 30.2; Found C, 40.3; H, 7.1; N, 2.1; Si, 29.8; ^{1}H NMR (400 MHz, $CDCl_3$), ppm δ: 0.07–0.21(bs, 186H), 0.53 (t, 4H, 8.7 Hz), 0.70 (t, 4H, 7.6 Hz), 1.50 (bs, 4H), 1.78 (bs, 4H), 2.48–2.52 (m, 4H), 4.17–4.19 (m, 4H), 7.52–8.71 (m, 8H). **PDI3**. Yield: 0.459 g (65%); FTIR (KBr, cm^{-1}): 3109, 2964, 2907, 1698, 1661, 1262, 1096–1020, 799; Anal. (%) Calcd. for $C_{572}H_{1644}N_4O_{270}Si_{268}$: C, 33.7; H, 8.1; N, 0.3; Si, 36.8; Found C, 36.0; H, 8.0; N, 0.7; Si, 33.8; ^{1}H NMR (400 MHz, $CDCl_3$), ppm δ: 0.08 (bs, 1608H), 0.51–0.56 (m, 4H), 0.70 (t, 4H, 8.5 Hz), 1.50 (bs, 4H), 1.78 (m, 4H), 2.20–2.40 (m, 4H), 4.17–4.19 (t, 4H,7.7 Hz), 7.42–8.39 (m, 8H).

2.3.2. Synthesis of perylene based polyimides (PPI1, PPI2, Scheme 2)

The above described procedure was applied to prepare polyimides but 0.1 mmol siloxane diamine was used for 0.1 mmol PDA and NMP was used as a solvent. The products as dark red powders were obtained in about 80% yields.

PPI1. Yield 0.086 g (80%); FTIR (KBr, cm^{-1}): 3093, 2953, 2873, 2802, 1696, 1655, 1253(s), 1049, 794; ^{1}H NMR (400 MHz, $CDCl_3$), ppm δ: 0.06–0.19 (m, 12H), 0.67 (m, 4H), 1.50–1.87 (m, 4H), 4.08 (m, 2H), 8.18–8.68 (m, 8H). **PPI2**. Yield 0.114 g (80%); FTIR (KBr, cm^{-1}): 3098, 2962, 2905, 2802, 1698, 1657, 1260, 1088–1017, 796 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$), ppm δ: 0.01–0.21 (bs, 63H), 0.71 (bs, 4H), 1.76 (bs, 4H), 4.14 (bs, 2H), 7.54–8.56 (m, 8H).



Scheme 1.

2.3.3. *Synthesis of perylene based copolyimides (PCPI, Scheme 3)*

Siloxane diamine AP_0 (0.248 g, 1 mmol) was solved in NMP (20 mL) at room temperature under magnetic stirring in a two-necked, flat-bottom flask, equipped with reflux condenser. Then, zinc acetate dihydrate (0.02 g, 0.1 mmol) and PDA powder (0.078 g, 0.2 mmol) were added. The mixture was stirred at 80 °C for 1 h, and then at 120 °C for 4 h. After cooling to room temperature, 6FDA (0.359 g, 0.8 mmol) was added and the mixture was heated at 120 °C for 2 h. The red clear solution was cooled at 80 °C and poured into 250 mL acetone with vigorous stirring. The precipitate was collected by filtration, washed with methanol and dried under vacuum. This was labeled as fraction PCPIa. From the washing methanol, fraction PCPIb was recovered. Both fractions showed as dark red powders.

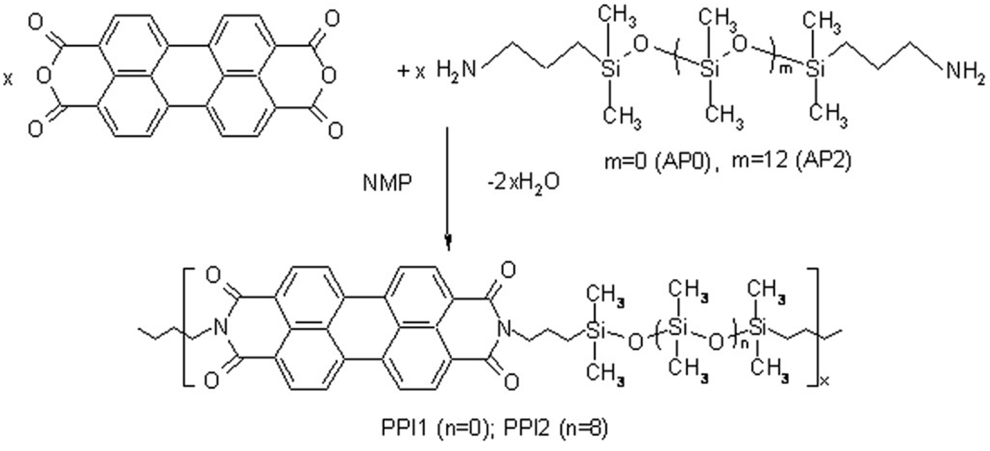
PCPIa. Yield 0.260 g (40%); FTIR (KBr, cm^{-1}): 3092–3070, 2954, 2878, 2800, 1721, 1696, 1658, 1254, 1189, 1055(s), 795; ^1H NMR (400 MHz, $CDCl_3$), ppm δ: PCPIa: 0.03–0.20 (m, 24H), 0.54–0.56 (m, 4H), 0.59–0.75 (m, 4H), 1.66 (m, 4H), 1.85 (m, 4H), 3.66 (m, 4H), 4.05–4.21 (m, 4H), 7.50–8.64 (m, 8H), 7.75–7.89 (m, 6H). **PCPIb**. Yield 0.195 g (30%); FTIR (KBr, cm^{-1}): 3110–3079, 2954, 2899, 2879, 1721,1699, 1660, 1256, 1191, 1066, 796. ^1H NMR (400 MHz, $CDCl_3$), ppm δ: −0.02–0.19 (m, 24H), 0.52–0.56 (m, 4H), 0.60–0.75 (m, 4H), 1.66 (m, 4H), 1.87 (m, 4H), 3.64–3.68 (m, 4H), 4.06–4.16 (m, 4H), 7.75–7.89 (m, 6H), 7.76–8.64 (m, 8H).

3. Results and discussions

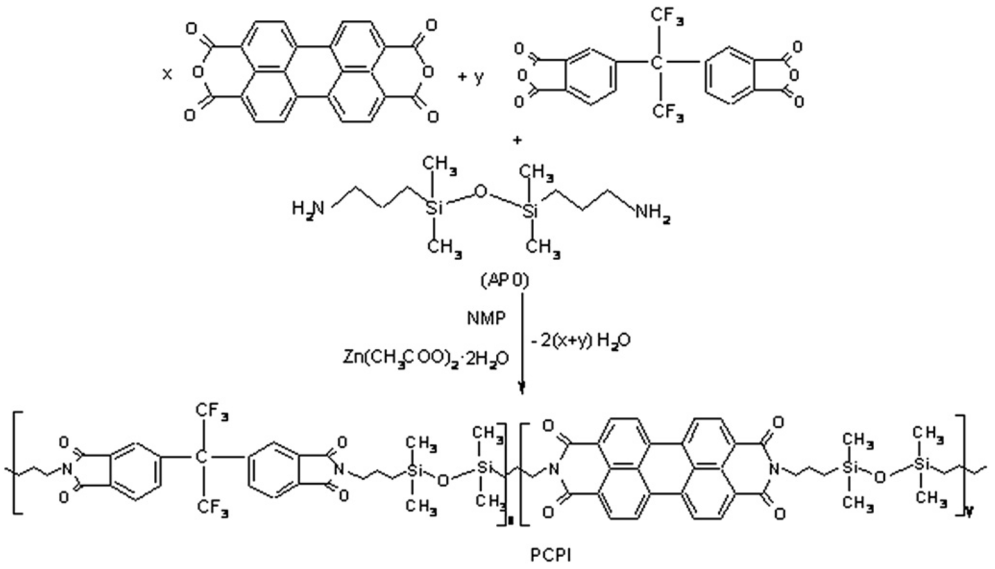
3.1. *Perylene diimides (PDI1, PDI2, PDI3)*

In order to prepare perylene-siloxane diimides, PDA was reacted with high excess of siloxane diamine (PDA:AP = 1:5 molar ratio). Three siloxane diamines having different chain lengths were used (Scheme 1).

Reaction occurred in solution under two heating stages and in the presence of a catalyst. The choice of the solvent for such a reaction depends on the reactivity of the amine. Reaction temperatures between 160 and 180 °C and solvents such as quinoline or molten imidazole are necessary in the case of using less reactive aromatic amines. Quinoline was selected as the solvent for this series employing aliphatic aminosiloxanes. Zinc acetate was used as catalyst since this type of catalyst has the ability to solubilize the anhydride [21]. The reactions were conducted for 4 h at 100 °C and 4 h at 160 °C. The imide formation was first verified by FTIR spectroscopy. The anhydride band at 1772.5 cm^{-1} from PDA dissapears from the FTIR spectrum and two new bands appear at 1696 and 1657 cm^{-1} assigned to 6-membered imidic C=O asymmetric and symmetric stretching. The presence of the siloxane unit was proven by the bands at 1255 (Si–CH_3), 1052 (SiOSi) and 794 cm^{-1} (Si–CH_3). The intensity



Scheme 2.



Scheme 3.

ratio of the imide/siloxane bands decreased as the siloxane sequence length increases.

One purpose of attaching siloxane moieties to the perylene was to obtain diimides with improved solubility as compared with simple wholly organic substituted examples. In the case of polyimides based on perylene and aliphatic diamines it was found [29] that the number of carbons in diamines must to be greater than 5 in order to obtain partially soluble polyimides in m-cresol, for example. In our case using siloxane derivatives is expected to improve solubility both due to attached siloxane-aliphatic chain of different lengths and to siloxane itself that hinders intermolecular interactions. Indeed, it was observed that, the solubility of the resulted PDIs strongly depends on the siloxane length. While the PDIs based on siloxane oligomers proved to be soluble in some of the common solvents (DMF, $CHCl_3$, ethyl acetate, THF, etc.), that based on the disiloxane was only partially soluble in chloroform although the diamine backbone contains 9 atoms (6C, 2Si, O).

The diimide formation was also verified by using ^1H NMR spectra recorded for freshly prepared samples. New signals assigned to the protons from the silicon-attached amino-aliphatic moiety that is involved in the imide formation, $-Si-CH_2-CH_2-CH_2-N<$ could be seen in ^1H NMR spectra of the PDI1−PDI3 samples. They are shifted to lower field compared to their counterparts in the starting diamines (Table 1). Presence in ^1H NMR spectra of the signals corresponding to the aliphatic protons adjacent to the imidized and primary amines, respectively, with approximately the same intensities, proves the diimides, PDIs, formation with the sequence AP-PDA-AP.

Perylene diimides are known as compounds able to self-organize by $\pi-\pi$ interactions [4]. However in our case due to the high difference in polarity, a high tendency to form micelles was observed by AFM studies (Fig. 1). This depends on the nature of the solvent and the siloxane segment length. Thus, the AFM images of the PDIs films cast from ethyl acetate show the changes in the surface morphology as siloxane chain length increases (Fig. 1a−c). Clear spherical siloxane domains of about 10 nm high and a few hundered nanometers in diameter can be seen in the case of the samples containing the longest siloxane moieties (Fig. 1c,d). The morphology also changed depending on the casting solvent nature (Fig. 1c,e−g).

3.2. Perylene based polyimides and copolyimides (PPI1, PPI2, PCPI)

By using a molar ratio 1:1 between PDA and siloxane diamine (AP0 and AP2) in NMP, the reaction was directed towards the formation of polyimides (Scheme 2).

FTIR spectra indicated the imide groups formation by the presence of the imidic C=O bands at 1696 and 1654 cm^{-1} in PPI1 and 1698 and 1956 cm^{-1} in PPI2.

In these examples (PPI1 and PPI2) only signals assigned to protons from the imidized $-Si-CH_2-CH_2-CH_2-N<$ moieties could be identified in the ^1H NMR spectra. The absence of proton signals corresponding to the primary aliphatic amines in the spectra indicates the formation of the polyimidic structure. The proton

Table 1
Chemical shifts of the protons from diimides as compared with the corresponding diamines.

Assigned protons	Chemical shift, ppm					
Sample	AP0	PDI1	AP2	PDI2	AP3	PDI3
$-Si-CH_3$	0.02	−0.2−0.2	0.03−0.06	0.07−0.21	0.07−0.13	0.08
$-Si-CH_2-$	0.45−0.49	0.63−0.67	0.49−0.53	0.68−0.72	0.51−0.55	0.69−0.73
		0.48−0.53[a]		0.51−0.55[a]		0.51−0.56[a]
$-Si-CH_2-CH_2-$	1.37−1.45	1.67−1.88	1.40−1.43	1.78	1.42−1.50	1.78
		1.42−1.49[a]		≈1.50[a]		≈1.50[a]
$-Si-CH_2-CH_2-CH_2-N-$	2.63	3.84−4.10	2.65	4.17−4.19	2.67	4.17−4.19
		2.64−2.70[a]		2.48−2.52[a]		2.20−2.40[a]
Aromatic		7.01−8.60		7.52−8.71		7.42−8.39

[a] Chemical shifts of the protons from the terminal groups.

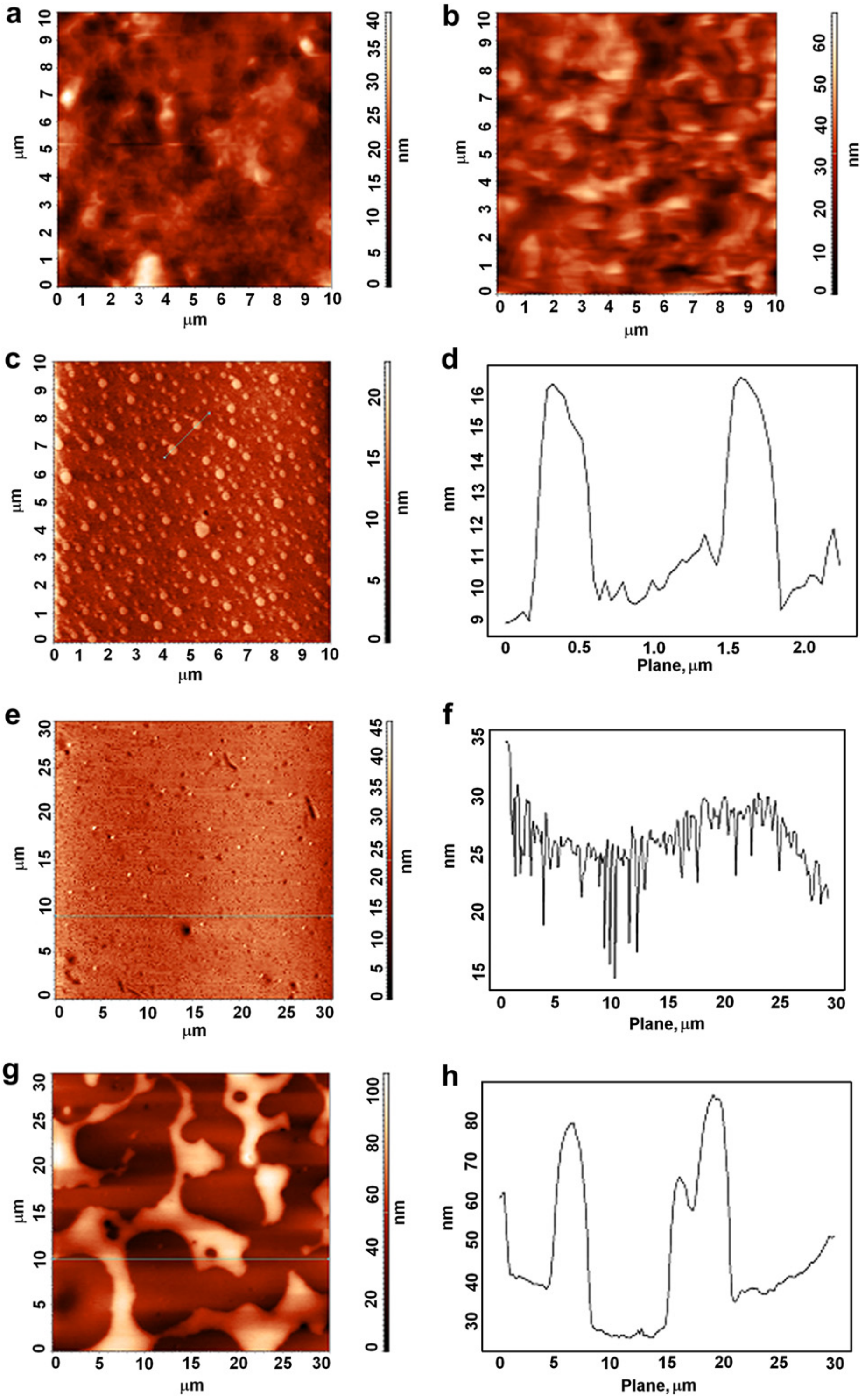


Fig. 1. AFM images illustrating the change in the surface morphology of the diimides as siloxane moiety length increases in different solvents: a – PDI1 in ethyl acetate; b – PDI2 in ethyl acetate; c – PDI3 in ethyl acetate; d – surface profile for PDI3 in ethyl acetate; e – PDI3 in hexane; f – surface profile for PDI3 in hexane; g – PDI3 in THF; h – surface profile for PDI3 in THF.

chemical shifts for the two prepared polyimides are listed in Table 2.

Interesting surface morphologies were visualized by AFM in the case of these polyimides. Thus, the polyimide PPI1 film obtained from chloroform solution shows a fibrilar organization (Fig. 2a). The fibers arranged in different topologies (straight, curves, crosses, knots, rings) seem to have about 50 nm width, maximum 25 nm height and a few μm in length. This organization is assigned to a π-stacking

Table 2
Chemical shifts of the protons from polyimides.

Assigned proton	Chemical shift, ppm	
Sample	PPI1	PPI2
$-\mathrm{Si}-\mathrm{CH}_3$	0.06–0.19	0.01–0.21
$-\mathrm{Si}-CH_2-$	0.67	0.71
$-\mathrm{Si}-\mathrm{CH}_2-CH_2-$	1.50–1.87	1.76
$-\mathrm{Si}-\mathrm{CH}_2-\mathrm{CH}_2-CH_2-\mathrm{N}-$	4.08	4.14
Aromatic	8.18–8.68	7.54–8.56

Table 3
Chemical shifts of the protons from copolyimides.

Assigned protons	Chemical shift, ppm	
Sample	PCPIa	PCPIb
$-\mathrm{Si}-\mathrm{CH}_3$ (PDA)	0.03–0.20	−0.02–0.19
$-\mathrm{Si}-CH_2-$ (PDA)	0.59–0.75	0.60–0.75
$-\mathrm{Si}-\mathrm{CH}_2-CH_2-$ (PDA)	1.85	1.87
$-\mathrm{Si}-\mathrm{CH}_2-\mathrm{CH}_2-CH_2-\mathrm{N}-$ (PDA)	4.05–4.21	4.06–4.16
Aromatic (PDA)	7.50–8.64	7.76–8.64
$-\mathrm{Si}-\mathrm{CH}_3$ (6FDA)	0.03–0.20	−0.02–0.19
$-\mathrm{Si}-CH_2-$ (6FDA)	0.54–0.56	0.52–0.56
$-\mathrm{Si}-\mathrm{CH}_2-CH_2-$ (6FDA)	1.66	1.66
$-\mathrm{Si}-\mathrm{CH}_2-\mathrm{CH}_2-CH_2-\mathrm{N}-$ (6FDA)	3.66	3.64–3.68
Aromatic (6FDA)	7.75–7.89	7.75–7.89

process. It seems that the presence of the short flexible siloxane sequence in PPI1 structure allows manifestation of this tendence of the perylene moiety.

In THF, the fibrilar structure is significantly altered. Instead, the polyimide PPI2 having a longer siloxane sequence has manifested a strong tendency to micellization, both in DMF, but especially when the film was cast from THF solution (Fig. 2b). Slightly elongated spheres having width of about 1 μm and maximum height of 0.8 μm can be seen on such AFM image. However, these spheres seem to be also arranged along curved lines similar to those observed in Fig. 2a.

Unfortunately, the solubility of the reaction products was still low. Therefore, in other experiments, perylene was mostly replaced with other dianhydride, 6FDA, to obtain copolyimides PCPIs (Scheme 3). It is known that the presence of the hexafluoroisopropylidene bridge improves the solubility of the derived polyimides due to the low intermolecular interactions. A molar ratio AP0:PDA:6FDA = 1:0.2:0.8 was used. The reaction occurred in NMP as a solvent and in presence of zinc acetate as a catalyst.

By adding perylene first in the diamine solution, a diimide PDI like those presented in Scheme 1 is thought to form. This will compete with free siloxane diamine in the reaction with subsequently added 6FDA to result copolyimide PCPI.

Two fractions, PCPIa and PCPIb, were separated differing by their solubility in methanol. The copolyimides structures were proved in both cases by FTIR spectrometry. The C=O stretching bands of the 6FDA at 1853 and 1779 cm^{-1} and those at 1772 and 1760 cm^{-1} from PDA are absent in the spectra of the polyimides. The 6FDA-imide band can be seen at 1721 cm^{-1} while PDA-imide bands appear at near 1696 and 1656 cm^{-1}. The C–F stretching band is also present in the spectra of the polyimides at 1190 cm^{-1}.

However examination of the IR spectra of the two fractions of the copolyimide PCPI, leads to the conclusion that the highly soluble fraction (PCPIb) contains mostly 6FDA-derived imide, while in the other fraction (PCPIa) are more visible PDA-imide bands.

In ^{1}H NMR spectra both fractions show peaks at the same chemical shifts (Table 3) but the ratios between the two sequences types are different. An estimation based on the ratio of the integrals of the characteristic peaks for $-\mathrm{Si}-\mathrm{CH}_2-CH_2-$ (PDA) at 1.85–1.87 ppm and for $-\mathrm{Si}-\mathrm{CH}_2-CH_2-$ (6FDA) at 1.66 ppm led to values for the molar composition of the two copolyimides fractions, PDA/6FDA: PCPIa –0.8; PCPIb-0.2.

The main properties and applications suitable for these structures are based on electron transfer. The optical properties of PDIs, PPIs and PCPI derivatives were studied by electronic absorption and

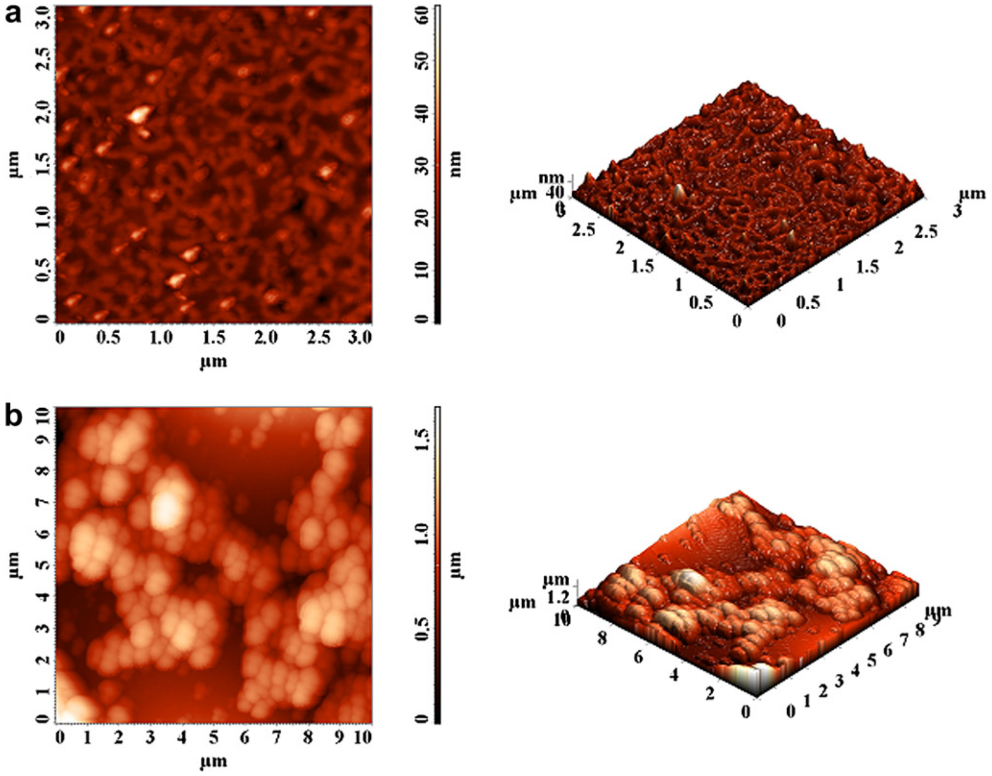


Fig. 2. Topographic images for: a – PPI1 films obtained from solution in CHCl$_3$; b – PPI2 films obtained from solution in THF.

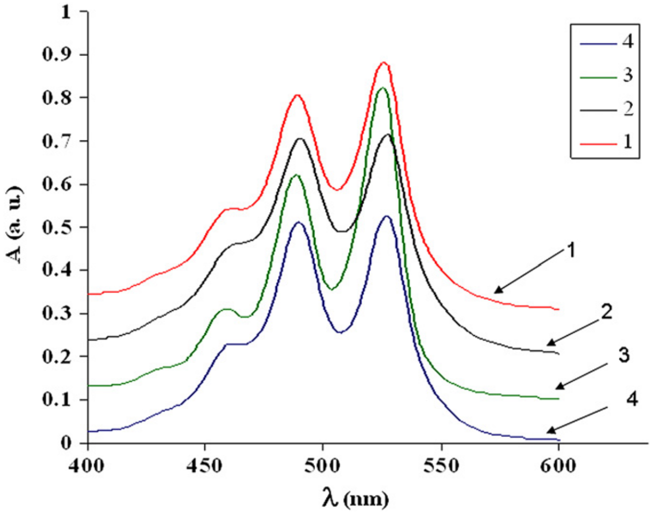


Fig. 3. Electronic absorption spectra of perylene derivatives in chloroform: 1-PDI1 (21.9 mg/l); 2-PDI3 (90.8 mg/l); 3-PPI1 (20.2 mg/l); 4-PCPIb (58.1 mg/l).

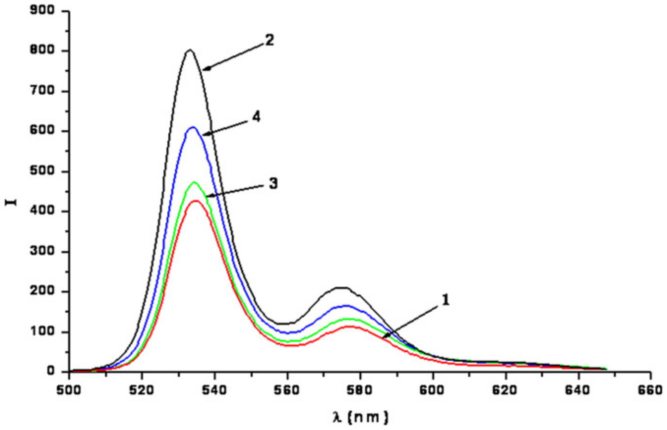


Fig. 4. Representative fluorescence spectra of perylene derivatives in chloroform: 1-PDI1 (4.2 mg/l); 2-PDI3 (17.6 mg/l); 3-PPI1 (4.39 mg/l); 4-PCPIb (10.1 mg/l).

fluorescence spectroscopy. The absorption spectra of these derivatives in chloroform are depicted in Fig. 3 and some optical data are presented in Table 4.

As can be seen from Fig. 3, the electronic absorption spectra displayed absorption bands between 450 and 550 nm due to the perylene diimides chromophore [30–32]. The vibronic structure of the absorption bands corresponds to a $\pi - \pi^*$ electronic transition of the perylene chromophore. The longest absorption band is assigned to a S_0–S_1 transition of perylene diimide along the long axis. A second absorption band was observed at lower wavelength (490 nm) which corresponds to S_0–S_2 transition where the transition dipole moment is along the short axis [32,33]. Generally, the maximum wavelength of absorption band of the perylene derivatives is dependent on the substitution pattern of the perylene core and on the interaction of chromophore moieties [9,34]. Within the three series of perylene derivatives, diimides (PDI1, PDI2, PDI3), polyimides (PPI1, PPI2), copolyimide (PCPIb), under study the electronic absorption spectra are practically identical (Table 4) as shape and vibronic fine structure. The similarity in band shape indicated that no perylene diimide dimer or other aggregates are formed in solution in the measurements conditions. The fine vibration structure was maintained in perylene copolymers having the same absorption spectrum with perylene polyimide. In addition, these facts show that the planarity and rigidity of the perylene diimide core was unaffected by the length of siloxane chain.

Solutions of all of the perylene derivatives in chloroform exhibit a bright yellow fluorescence in daylight. The emission band also shows a vibronic structure (Fig. 4) with two peaks at about 535 and 575 nm, respectively and a shoulder at 630 nm, which correspond to the emission of the perylene diimide units. There is good mirror image symmetry between the UV–VIS absorption and the emission spectra implying that the fluorescence is due to the perylene diimide unit with a Stokes shift of about 9 nm, which is of the same order of magnitude of other perylene diimides containing polymer chains [35]. In both absorption and emission spectra the optical intensity increased with chromophore concentration and no bands due to the formation of chromophore aggregated were found in the spectra. Although the spectra of the perylene derivatives (1-PDI1, 2-PDI3, 3-PPI1, 4-PCPIb) are almost similar, the relative intensity of the emission bands differs from that of the absorption bands.

Table 4
The main electronic absorption and fluorescente data for the prepared imide derivatives.

Sample	λ_{max} (nm)	λ_{em} (nm)
PDI1	460sh; 490; 526	535; 577; 630sh
PDI2	460sh; 490; 526	536; 576; 630sh
PDI3	460sh; 488; 526	533; 575; 630sh
PPI1	460sh; 490; 528	535; 576; 630sh
PPI2	460sh; 490; 526	534.5; 576; 630sh
PCPIb	465sh; 490; 526	534; 576; 630sh

For diimides, the emission intensity increases with the increase of the siloxane chain length. With increasing siloxane chain length, the fine structure of the three absorption bands of perylene derivatives does not modify, suggesting that no $\pi - \pi^*$ interactions occur between adjacent perylene compounds.

4. Conclusions

Three types of imidic compounds based on perylene and siloxane derivatives have been prepared. The syntheses were directed to diimides or polyimides formation by selection of appropriate reactant ratios and the reaction conditions. The solubility of the formed structures strongly depends on the siloxane sequence length and increased even more through introduction of the perfluoro unit (6FDA) in the polyimide structure. Self-organization forms from micelles to fibers were revealed depending on the number and length of the siloxane sequences and the nature of the solvent. All structures showed optical properties that were emphasized by electronic absorption and fluorescence spectroscopy. These are conferred mainly by the perylene sequence and are less influenced by the overall structure of the compound. Thus the spectral pattern preserved modifying only the intensity of the bands in dependence of the concentration of the chromophore in structure.

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