HETEROCYCLES, Vol. 68, No. 1, 2006, pp. 137 – 149. © The Japan Institute of Heterocyclic Chemistry
Received, 25thJuly, 2005, Accepted, 28th October, 2005, Published online, 1st November, 2005. COM-05-10525

CONVENIENT SYNTHESIS AND PHYSICOCHEMICAL PROFILE OF NEW DERIVATIVES OF PYRIMIDINE

Joanna Cabaj,[a] Jacek Doskocz,[a] Jadwiga Sołoducho*[a], and Antoni Chyla

[a] Institute of Organic Chemistry, Biochemistry and Biotechnology, Department of Chemistry, Wrocław University of Technology, Wybrzeze Wyspiańskiego 27, 50-370 Wrocław, Poland
[b] Institute of Physical and Theoretical Chemistry, Department of Chemistry, Wrocław University of Technology, Wybrzeze Wyspiańskiego 27, 50-370 Wrocław, Poland

jadwiga.soloducho@pwr.wroc.pl

Abstract - A synthesis of linear oligoheterocycles based on the substituted pyrimidines are described. The desired compounds have been accomplished by the variation of the original Pinner synthesis in which the aliphatic nitrile reacted with hydrogen chloride to give imino ester. These compound reacted with ammonia gas to give amidine. Chalcones in reaction with amidines give bis(phenyl)pyrimidines. The bis(phenyl)pyrimidines reacted with 3,4-ethylenedioxy-2-trimethyltinthiophene or 2-trimethyltinthiophene in the presence of $Pd(PPh_3)_2Cl_2$ or $Pd(PPh_3)_4$ as catalyst to give designed compounds. In this work are presented also some electrochemical measurements using Langmuir – Blodgett technique in mono- and binary systems.

INTRODUCTION

Conjugated polymers such as polyacetylenes, polyphenylenes, polythiophenes have been extensively studied, and many important electrical and optical properties have been discovered. [1] Consequently, there is considerable interest in the preparation and purification of these materials. A few years ago, we reported on the synthesis of a 1,4-bis(pyrrol-2-yl)arylenes.[2-4] This new synthetic route opens up a number of

opportunities for the synthesis of derivatized, potentially soluble and processable pyrrole, thiophene and 3,4-ethylenedioxythiophene containing polymers.

With our ongoing interest in precursors of conducting materials, a synthesis of linear oligoheterocycles based on substituted pyrimidines are presented. We report on the synthesis of novel symmetric bis-thiophene or bisethylenedioxythiophene, derivatives based on pyrimidines. By contrast, the interest in thiophene [5] or 3,4-ethylenedioxythiophene,[6] is more recent. For these reasons, the development of practical and efficiently methods for the synthesis of pyrimidine derivatives remains an area of current interest. The protocol of obtaining bis(thiophene)- and bis(ethylenedioxythiophene)pyrimidines can be used to the synthesis of various bis(thienyl)heterocyclic derivatives.

In many electronic applications the concentration of chromophore is important as well as the knowledge of the LB film architecture.

In this paper we undertook also the study of formation of single and two component Langmuir and LB films of synthesized alkylheteroaromatic molecules.

RESULTS AND DISCUSSION

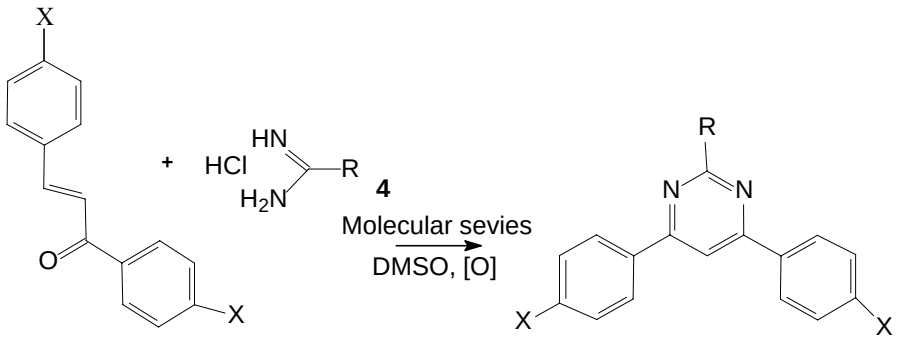
Synthesis of 4,6-bis-(4-halogenephenyl)-2-alkylpyrimidines

Even though the synthesis of pyrimidines has been extensively studied, their preparation by the reaction of amidines with chalcones has been neglected. In our cause, for the preparation of pyrimidines block we make the most three methods: Wais *et al*.,[7] P. D. Jones *et al*, [8] and Dodson *et al.* [9] as it was reported earlier. [10]

For the preparation of 4,6-bis-(4-halogenephenyl)-2-alkylpyrimidines was applied a literature method which is based on easily accessible starting materials. Wais *et al.* [7] described the preparation of pyrimidines by the oxidative coupling of chalcones with acetamidine or benzamidine in DMSO or its mixtures with toluene or xylene in the presence of molecular sieves in elevated temperatures. Yields were reported between 20% and 70%. [7]

Condensations of chalcones (**1a,b,c)** with amidine hydrochloride (**4**) in hot (80 °C) DMSO (Scheme 1) were followed by column chromatography purification to give the corresponding 4,6-bis-(4-halogenophenyl)-2-alkylpyrimidines (**5**). About preparation these compounds we wrote earlier. [10]

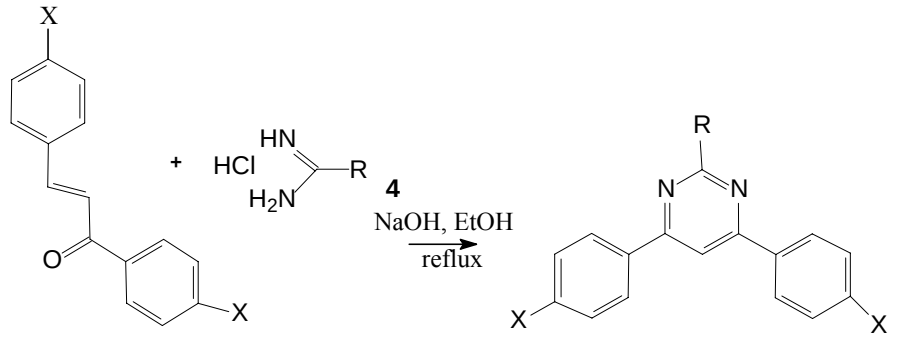
Thus the different heterocycles (**5a-c**) were also prepared by the reaction of the above chalcones with an alcoholic solution of amidines containing sodium hydroxide solution to give corresponding 2-alkyl-4,6-diphenylpyrimidines (**5a-c**). That very useful methodology (Scheme 2) was modelled after work done by P. D. Jones *et al*., and was used for preparation of bis(pyrimido)pyrimidines. [8]



1a,b,c; X=Cl,Br,I **5a,b,c,c'; R=C_3H_7, C_7H_{15},$C_{11}H_{23}$**

Scheme 1

In this way we were able to isolate 2-alkyl-4,6-diphenylpyrimidines (**5a-c**) with high yield.

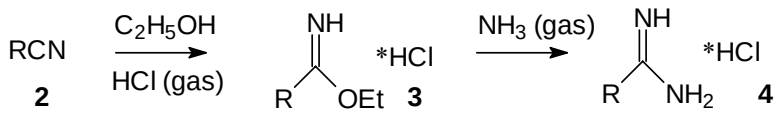


1a,b,c; X=Cl,Br,I **5a,b,c,c'; R=C_3H_7, C_7H_{15},$C_{11}H_{23}$**

Scheme 2

The synthesis of chalcones was carried out using the general method developed by Babler. [11]

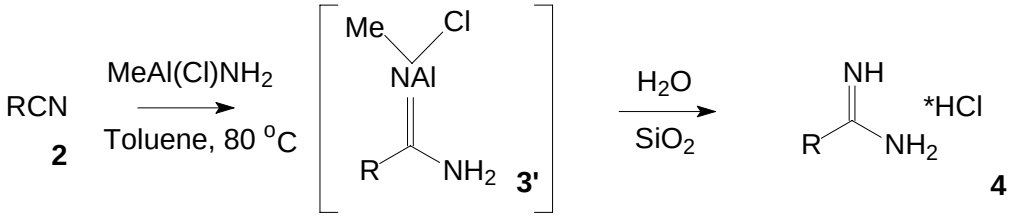
The preparation of alkylamidine hydrochloride (**4**, Scheme 3) was achieved by adaptation of procedure [12] previously reported for several lower aliphatic amidines. Thus nitrile (**2**) was treated with hydrogen chloride in EtOH to afford the imino ester (**3**) which was without further purification, converted into amidine (**4**)**,** by treatment with ammonia in EtOH at -70 °C. The amidines (**4**) were isolated as their hydrochloride salts with 79%-85% yields.



2,3,4 a,b,c; R= C_3H_7, C_7H_{15}, $C_{11}H_{23}$

Scheme 3

In another way, [13] the alkylnitriles were efficiently converted to the corresponding amidines in a one step by reaction with methylchloroaluminum amide (Scheme 4). The aluminum reagent originally developed by Weinreb, [14] was conveniently prepared by the addition of NH_4Cl to commercially available trimethylaluminum and the intermediate Al complex that formed during the intermediate reaction was gently hydrolyzed by the water adsorbed on silica gel.



2,3',4a,b,c: R=C_3H_7, C_7H_{15}, $C_{11}H_{23}$

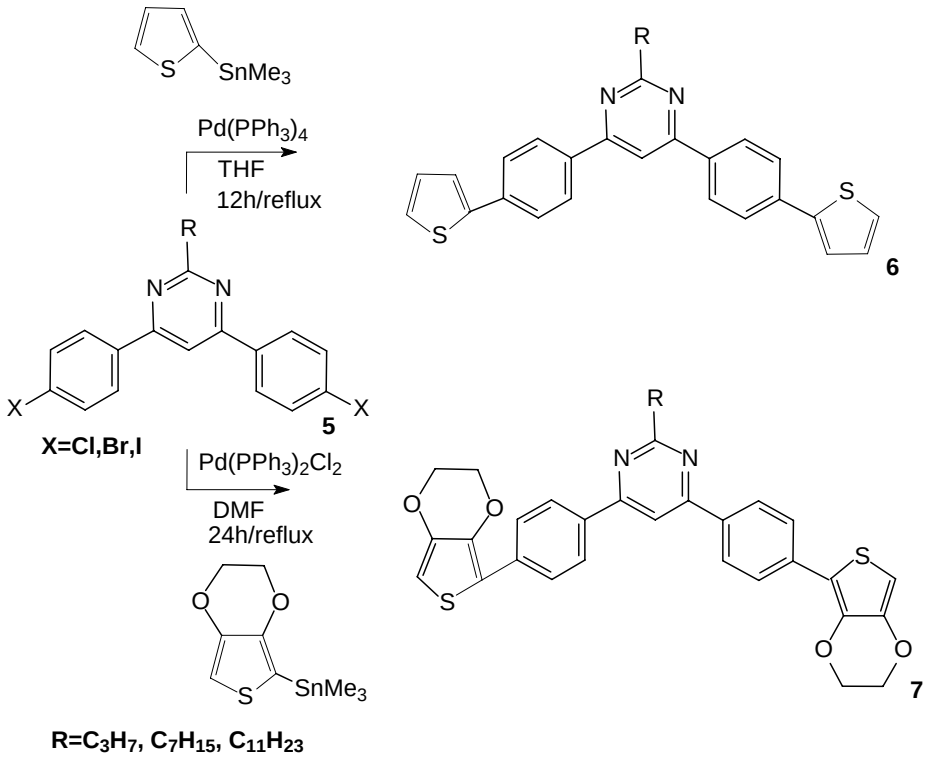
Scheme 4

Comparing these two methods for preparation amidines (**4**) from nitriles (**2**), in our case, standard Pinnner procedure [15] is more effective.

In our case, we found that alkylamidines will condense readily with ketones to give 6-alkyl-substituted 2,4-diphenylpyrimidines according to procedures described by Dodson for preparation triphenylpyrimidine. [9]

Synthesis of bis-(phenylthienyl)pyrimidines and bis-(phenylethylenedioxythiophene)pyrimidines

The synthesis of bis-(phenylthienyl)pyrimidines (**6**) was accomplished by the reaction of 4,6-bis-(4-halogenophenyl)pyrimidines (**5**) with 2-metallated thiophene (Scheme 5) according to the literature procedure (our previous experience) for the preparation of bis-(thienyl)tetrazine derivatives.[16]



Scheme 5

The synthesis of 2-alkyl-4,6-bis-[phenyl-4-(2-{3,4-ethylenedioxythiophene}]pyrimidine was carried out as outlined in Scheme 5, where a Stille coupling reaction was employed to couple 3,4-ethylenedioxy-2-trimethylthinthiophene [16] (Scheme 5) with 2-alkyl-4,6-bis-(4-halogenephenyl)pyrimidine to give compound (**7**), (Scheme 5).

Aggregation properties of designed compounds

Based on our previous experience for derivatives of *N*-alkylcarbazoles [17] and also for bis-(pyrrolyl)fluorene, [18] in this work we presented an aggregation effects in LB films for obtained new compounds. Since the Langmuir-Blodgett technique allows for controlled, layer-by-layer deposition of ordered molecular films on solid substrates, the films formed by this method are expected to find a potential applications in sensoric, photonic or photoelectronic devices.

To obtain Langmuir films the synthesized compounds: 2-propyl-4,6-bis-[phenyl-4-(2-{3,4-ethylenedioxythiophene})]pyrimidine (P3DT), 2-undecyl-4,6-bis-[phenyl-4-(2-{3,4-ethylenedioxy-thiophene})]pyrimidine (P11DT), 2-propyl-4,6-bis-[phenyl-4-(2-thiophene)]pyrimidine (P3T), 2-undecyl-4,6-bis-[phenyl-4-(2-thiophene)]pyrimidine (P11T) were dissolved in chloroform (Aldrich, HPLC grade). Concentrations of solutions were maintained to *ca*. 1 mg/mL.

The films of desired composition were formed by dropwise spreading of diphenylpyrimidine derivatives solutions, with or without docosanoic acid - DA, octadecylpyrrole - ODP, dimiristilphosphatidilocholine - DMPCh and octadecylthiophene – ODT used as film facilitators.

Figures 1-4 show the π-A isotherms of investigated binary systems of P3DT, P11DT, P11T and P3T. Although pure P3DT and another pyrimidines derivatives form good Langmuir films their LB films are not very stable because the transfer occurs under a relatively low surface pressure. The surface pressure π is generally considered to be equal to the reduction of the pure liquid surface tension by the film, i.e. $\pi = \sigma_0 - \sigma$, where σ_0 is the surface tension of the pure liquid and σ is the tension of the film covered surface.

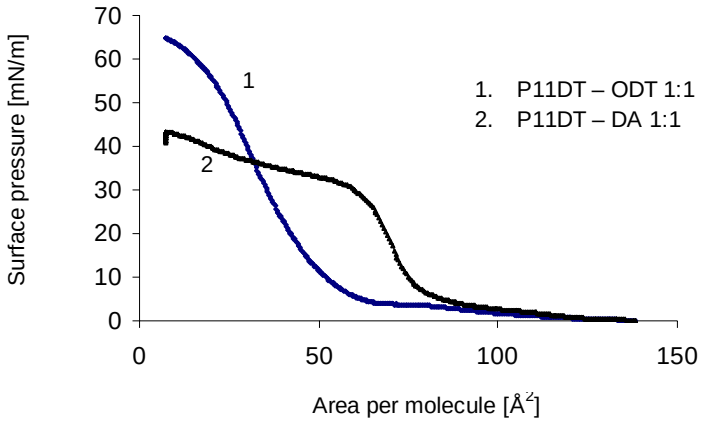


Figure 1 π - A Isotherms of P11DT in binary complexes

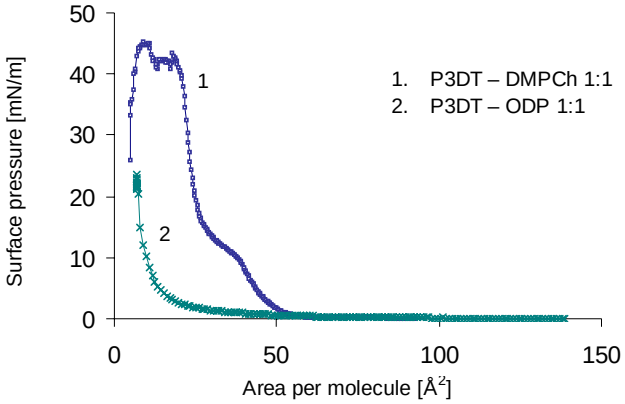


Figure 2 π - A Isotherms of P3DT in binary complexes

Comparison of Figures 1 – 2 shows that by building of the binary systems one can obtain higher surface pressures and therefore closer packing. It is clear that DMPCh , ODT and DA facilitates the process of packing the most effectively.

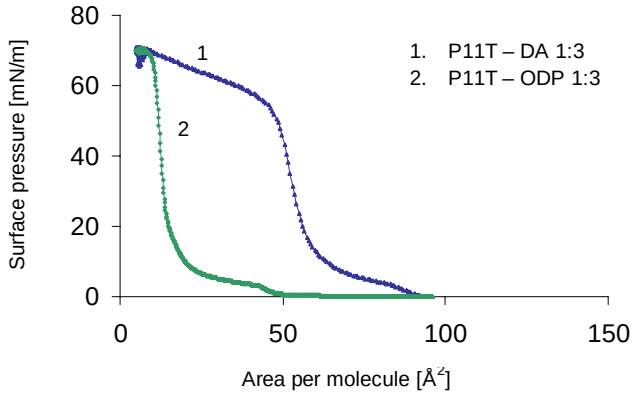


Figure 3 π - A Isotherms of P11T in binary complexes

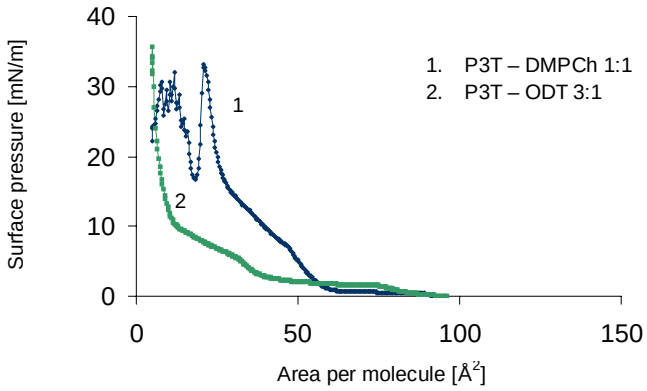


Figure 4 π - A Isotherms of P3T in binary complexes

From our experience (Figures 3 and 4) one can conclude that good facilitators for P3T and P11T were docosanoic acid, octadecylpyrrole and octadecyltiophene. These compounds in the best way improve packing and LB films architecture.

But in our case the deposited LB films in binary system with docosanoic acid (DA) are completed and high quality what is confirmed by additivity of UV-VIS spectra (Figure 5).

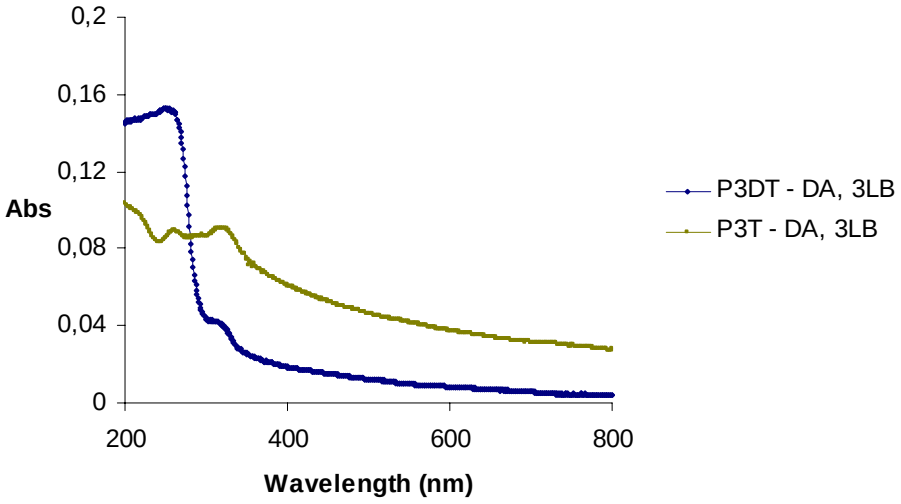


Figure 5 UV-VIS spectra of 3 LB films of P3DT – DA and P3T – DA complexes

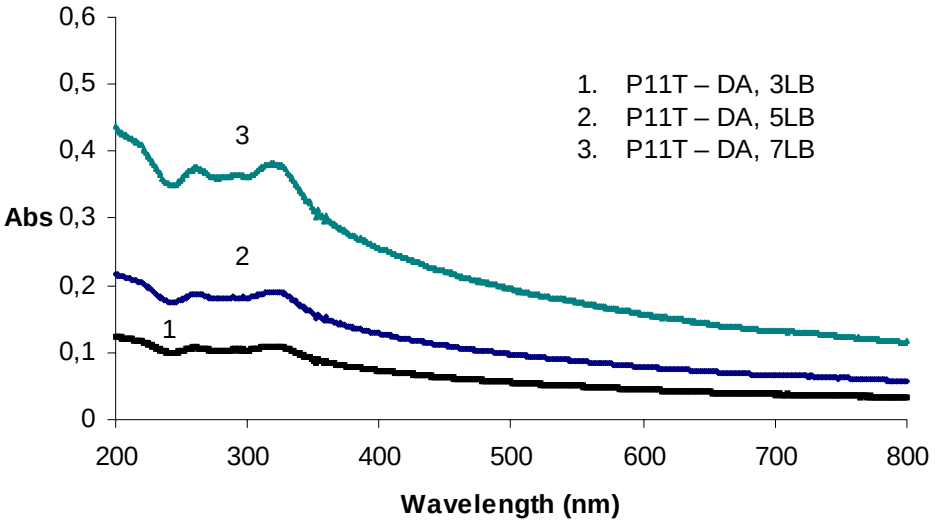


Figure 6 UV-VIS spectra of 3,5,7 LB films of P11T-DA complex

In Figure 7 a computer-optimized model of P3DT and P3T molecules are presented. If an average plane of all aromatic rings (hydrophilic part of molecule) laid almost flat on the water an aliphatic chain of "free" molecule would be elevated by 36 ^{0}. In such an arrangement calculated area per molecule equals *ca.*110 Å^2 for P3DT and 90 Å^2 for P3T, what is close to values also found from π - A isotherms (130 for P3DT and 100 for P3T).

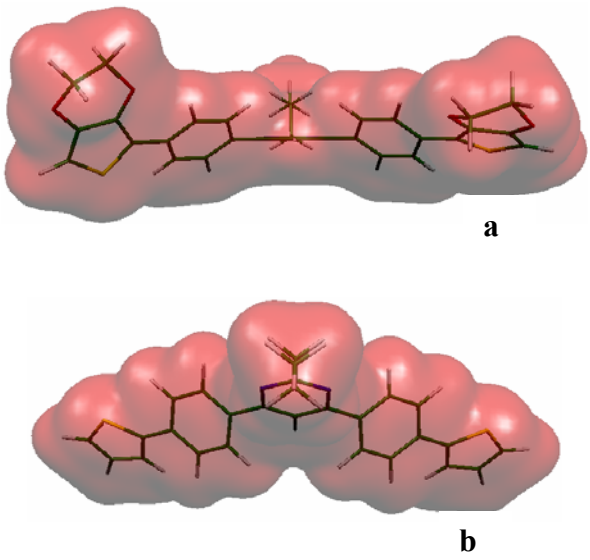


Figure 7 The computer optimized models of P3DT (a) and P3T molecule (b)

During the compression, molecules form close packed phase (liquid condensed) and in such a case both calculated and measured (from π-A isotherms), areas per molecule amount ca. 80 Å ^{2} for P3DT or 60 Å ^{2} for P3T and then 40 Å^2 for both molecules.

Octadecylpyrrole (ODP), the model amphiphile can also be used for the creation of binary systems of interest but the structures of P3DT and P11DT tend to form aggregates under the surface of subphase. During the compression, designed molecules are pressed by strongly polar ODP into the water often with solvent, forming some kind of "pocket systems" encapsulating the solvent molecules inside. In this situation value of area per molecule on the surface equals *ca.* 40 Å^2. What is seen as a kinks at P3DT-ODP and P11DT-ODP π-A isotherms. This is probably the reason that the transfer ratio observed during LB deposition of P3DT and P11DTin binary complex with octadecylpyrrole is between 1 -2.

EXPERIMENTAL

General Comments. Melting points are uncorrected. All NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 MHz (^{1}H) and 75 MHz (^{13}C) in $CDCl_3$ and DMSO- d_6, unless otherwise specified. Column chromatography was carried out on Merck Keisel gel 60 (5386) silica gel. THF was used immediately after distilling from a solution containing benzophenone/sodium. Other starting materials, reagents and solvents were used as received from suppliers.

General procedure for iminoester : ethyldodecylimino ester hydrochloride (3c):

This compound was prepared according to the literature procedure [10] from dodecanonitrile (**2c)**. Yield 76%, mp 81-82 °C (EtOH) (lit., [19] 79-80 °C).

for ethylbutylimino ester hydrochloride (3a):

The title compound was prepared similarly as compound above from butylnitrile. Yield 76%, mp 66-68

(EtOH) (lit., [20] 66-67 °C).

for ethyloctylimino ester hydrochloride (3b):

The title compound prepared similarly as compound from heptyl cyanide (octanenitrile). Yield 80%, mp 67-70 °C (EtOH). ^{1}H NMR (DMSO-d_6) δ 11.7 (s, 1H), 10.9 (s, 1H), 4.53 (q, 2H, *J*= 6.96 Hz), 2.63 (2H, *J* = 7.50 Hz); 1.68-1.58 (m, 2H,), 1.39 (t, 3H, *J* =6.92 Hz); 1.25-1.17 (m, 11H), 0.77 (t, 3H, *J*=6.97 Hz,). ^{13}C NMR δ 179.8, 70.6, 33.2, 31.6, 28.9, 28.8, 28.7, 25.6, 25.3, 22.5, 16.8, 14.0, 13.5. Anal. Calcd for $C_{10}H_{20}NO$: C, 70.54; H, 11.84; N, 8.22. Found: C, 70.35, H, 11.62, N, 8.05.

General procedure for amidines: dodecylamidine hydrochloride (4c):

This compound was prepared according to literature procedure [10] from ethyldodecylimino ester hydrochloride (**3c)** . Yield 79%, mp 127-128 °C (EtOH) (lit., [21] 128-129 °C).

for dodecylamidine hydrochloride (4c):

(conversion nitriles to amidines by Garigipati reaction)**.** [13] A 2 M solution of Me_3Al in toluene (25 mL, 50 mmol), was slowly added to a magnetically stirred suspension of 2.9 g (54 mmol) of NH_4Cl in 20 mL of dry toluene at 5°C under N_2 atmosphere. After the addition, the solution was warmed to 25 °C and stirred for 2 h until gas evolution (CH_4) had ceased. Then 5.44 g (39 mmol) of dodecanenitrile in 15 mL of dry toluene was added and the solution was heated to 80 °C for 15 h, under N_2, when TLC indicated the absence of nitrile. The reaction mixture was slowly poured into a slurry of 15 g of silica gel in 50 mL of $CHCl_3$ and stirred for 10 min. The silica gel was filtered and washed with MeOH. The filtrate and washing were combined and solvent was stipped to a residue of 15 mL which was refiltered to remove NH_4Cl. Then 10 mL of methanolic HCl (2 g, 54 mmol) was added to the filtrate followed by 400 mL of ether. The mixture was added to 150 mL of 4:1 isopropanol-acetone and stirred at 25 °C for 12 h, NH_4Cl was removed by filtration, the filtrate was stipped to 15 mL, and 300 mL of ether was added. The white solid of **7a** was filtered and dried under vacuum to yield 4.2 g, 59.6%, mp 118-119 °C. [10]

for butylamidine hydrochloride (4a):

The title compound was prepared according to Pinner's procedure, [15] similarly as compound (**3a**) from 0.1 g of ethylbutyliminoester hydrochloride. Yield 80%, mp 106-107 °C (EtOH) (lit., [22] 26-27 °C for butylamidine).

for octylamidine hydrochloride (4b):

The title compound prepared similarly as compound above from 0.1 g of ethyloctylimino ester hydrochloride. Yield 85%, mp 65-68°C (EtOH). ^{1}H NMR (DMSO-d_6) δ 8.70 (s, 2H), 8.60 (s, 1H), 2.49 (t, 2H, *J* =7.45 Hz),), 1.68-1.59 (m, 2H), 1.16 (br s, 10H), 0.77 (t, 3H *J*=8.78 Hz). Anal. Calcd for $C_8H_{18}N_2$: C, 67.54; H, 12.75; N, 19.69. Found: C, 67.40, H, 12.55, N, 19.55.

Procedure for 2-undecyl-4,6-bis-(4-iodophenyl)pyrimidine [10] (5c'):

(according to Wais's procedure [7]). This compound was obtained in reaction between dodecane amidine hydrochloride (1.4 g, 6 mmol) and diiodochalcone (1.0 g, 2.2 mmol). Yield 80% (yellow crystals), mp

113-114.5 °C ($CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.02 (d, 2H, *J*=8.52 Hz), 7.75 (s, 1H); 7.42 (d, 2H, *J*=8.55 Hz), 7.19 (s, 2H), 2.99 (t, 2H, *J* = 7.70 Hz), 1.38-1.87 (m, 16H), 0.80 (t, 3H, *J* = 5.6 Hz), ^{13} C NMR δ 172.1, 163.8, 138.0, 136.9, 128.8, 109.1, 97.4, 39.7, 31.9, 29.6, 29.6, 29.5, 29.5, 29.3, 28.5, 22.7,14.1. Anal. Calcd for $C_{27}H_{32}N_2I_2$: C, 50.80; H, 5.05, N, 4.40. Found: C, 50.60, H, 5.00, N, 4.31.

Procedure for 2-undecyl-4,6-bis-(4-chlorophenyl)pyrimidine (5c):

(according to Dodsons's procedure [9]). Sodium hydroxide (0.24 g, 6 mmol) was added to a vigorously stirred solution of dodecane amidine hydrochloride (1.4 g, 6 mmol) in ethanol (30 mL). The mixture was stirred at rt for 10 min, and then dichlorochalcone (1.2 g, 4.4 mmol) was added. The reaction mixture was stirred in refluxing ethanol for 6 h with an air stream bubbled through. The cooling product precipitated and was collected by filtration. The crude product was purified by column chromatography (hexane: ethyl acetate = 2:1). The title compound was prepared similarly. Yield 1.74 g (80%), white crystals, mp 74-75 °C ($CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.03 (d, 4H, *J* = 8.52 Hz); 7.51 (s, 1H), 7.43 (d, 4H, *J* = 8.52 Hz), 3.00 (t, 2H, *J* = 7.69 Hz), 1.89-1.84 (m, 2H), 1.38-1.18 (m, 16H), 0.80 (t, 3H, *J* = 6.67 Hz), ^{13}C NMR δ 172.1. 163.6, 136.9, 135.9, 129.1, 128.5, 109.3, 39.7, 31.9, 29.6, 29.5, 29.5, 29.4, 28.6, 22.7, 14.1. Anal. Calcd for $C_{27}H_{32}N_2Cl_2$: C, 72.41; H, 6.78; N, 5.89. Found: C, 72.24, H, 6.57; N, 5.66.

Procedure for 2-propyl-4,6-bis-(4-chlorophenyl)pyrimidine (**5a**):

The title compound was prepared similarly as above from dichlorochalcone and butylamidine (**4a**). Yield 84% (yellow solid), mp 56-58 °C ($CHCl_3$). ^{1} H NMR ($CDCl_3$) δ 8.07 (d, 4H, *J* = 8.43 Hz), 7.80 (s, 1 H,), 7.47 (d, 4H, *J* = 8.45 Hz), 3.03 (t, 2H, *J*=7.44 Hz), 2.02-1.90 (m, 2H), 1.05 (t, 3H, *J* =7.32 Hz), ^{13} CNMR δ 171.8, 163.4, 136.9, 135.9, 129.1, 128.9, 128.5, 109.4, 41.6, 21.9, 14.0. Anal. Calcd for $C_{19}H_{16}N_2Cl_2$: C,66.48; H, 4.69; N, 8.16. Found: C, 66.3; H,4.50; N, 8.10.

Procedure for 2-heptyl-4,6-bis-(4-chlorophenyl)pyrimidine (**5b**):

The title compound was prepared similarly as above from dichlorochalcone and octylamidine (**4b**). Yield 85% (yellow crystals), mp 67-69 °C ($CHCl_3$). ^{1} HNMR ($CDCl_3$) δ 8.03-8.01 (m, 4H,), 8.00 (s, CH,), 7.75-7.72 (m, 4H), 2.95 (t, 2H, *J*=7.45 Hz), 1.99 (q, 2H, *J*=7.45 Hz,), 1.14-1.04 (m, 8H), 0.98 (t, 3H, *J*=7.40 Hz), ^{13} C NMR δ Anal. Calcd for $C_{23}H_{24}N_2Cl_2$: C, 69.17; H, 6.05; N, 7.01. Found: C, 69.00; H, 5.86; N, 6.85.

General procedure for bis-(phenyl-4-thiophene)pyrimidines: **2-undecyl-4,6-bis-(phenyl-4-thiophene)pyrimidine (6c):**

Thiophene (0.52 g**,** 2.1 mmol), 2-undecyl-4,6-bis-(4-chlorophenyl)pyrimidine (**5c,** 0.4 g, 1.0 mmol), and $Pd(PPh_3)_4$ (0.6 g, 0.8 mmol) were added to THF (100 mL). The mixture was stirred at 65°C overnight under nitrogen atmosphere. The THF was evaporated to give solid. The residue was purified by column chromatography (eluent: hexane/ethyl acetate, 2:1). Yield 85% (yellow-green plates), mp 199-201°C (ethyl acetate). ^{1}H NMR ($CDCl_3$): 8.13 (d, 4H, *J* = 8.31 Hz), 7.85 (s, 1H), 7. 33 (dd, 4H, $^4J_{HH}$ = 1.90 Hz, $^3J_{HH}$ = 7.50 Hz), 7.10 (d, 2H, *J* = 3.73 Hz), 2.95 (t, 2H, *J*=7.80 Hz), 1.87 (q, 2H, *J*=7.05 Hz), 1.90-1,85

(m, 16H). 0.80 (t, 3H, *J*=7.70 Hz). ^{13}C NMR δ 183.1, 162.7, 138,7 135.1, 130.9, 130.8, 128.7, 128.2, 122.0, 112.9, 38.1, 29.6, 29.5, 29.3, 29.3, 22.6, 14.5. Anal. Calcd for $C_{35}H_{38}N_2S_2$: C, 76.34; H, 6.95; N, 5.08. Found, C, 76.05; H, 6.70; N, 4.90.

for 2-propyl-4,6-bis-(phenyl-4-thiophene)pyrimidine (6a):

The title compound was prepared similarly as above from 2-propyl-4,6-bis-(4-chlorophenyl)pyrimidine (**5a**). Yield 90.5% (yellow-green plates), mp 124-126 °C (ethyl acetate). ^{1}H NMR ($CDCl_3$): 8.15 (d, 4H, *J*=8.31 Hz), 7.79 (s, 1H), 7.73 (d, 4H, *J* = 8.29 Hz), 7. 33 (dd, 4H, $^4J_{HH}$ = 1.90 Hz, $^3J_{HH}$ = 7.50 Hz), 7.10 (d, 2H, *J* = 3.73 Hz), 2.95 (t, 2H, *J*=7.80 Hz), 1.7 (q, 2H, *J*=7.05 Hz), 0.80 (t, 3H, *J*=5.70 Hz). ^{13}C NMR δ 162.7, 138,7 135.1, 130.9, 129.8, 128.7, 128.2, 122.9, 41.2, 18.1, 14.5. Anal. Calcd for $C_{27}H_{22}N_2S_2$: C, 73.96; H, 5.06; N, 6.39. Found, C, 73.80; H, 4.95; N, 6.20.

for 2-heptyl-4,6-bis-(phenyl-4-thiophene)pyrimidine (6b):

The title compound was prepared similarly as above from 2-heptyl-4,6-bis-(4-chlorophenyl)pyrimidine (**5b**). Yield 88.8% (yellow-green plates), mp 144-146 °C (ethyl acetate). ^{1}H NMR ($CDCl_3$):8.12 (d, 4H, *J* = 8.32 Hz), 7.85 (s, 1H), 7.74 (d, 4H, *J*=8.20 Hz), 7. 33 (dd, 4H, $^4J_{HH}$ = 1.90 Hz, $^3J_{HH}$ = 7.50 Hz), 7.10 (d, *J*=3.75 Hz, 2H,), 2.95 (t, 2H, *J*=7.51Hz), 1.85 (q, 2H, *J*=7.20 Hz), 1.40-1.30 (m, 8H), 0.83 (t, 3H, *J*=6.98 Hz). ^{13}C NMR δ 182. 161.4, 139.2, 135.1, 134.7, 131.0, 129.5, 128.9, 121.5, 112.5, 38.5, 32.1, 31.5, 29.7, 21.5, 14.7. Anal. Calcd for $C_{31}H_{30}N_2S_2$: C, 75.28; H, 6.11; N, 5.66. Found, C, 75.06; H, 6.00; N, 5.55.

General procedure for bis-(phenyl-3,4-ethylenedioxythiophene)pyrimidines: for 2-undecyl-4,6-bis-[phenyl-4-(3,4-ethylenedioxythiophene)]pyrimidine (7c):

3,4-Ethylenedioxy-2-trimethyltinthiophene (prepared from 3,4-ethylenedioxythiophene according the literature procedure, [6] 0.64 g, 2.1 mmol), 2-undecyl-4,6-bis-(4-chlorophenyl)pyrimidine (**5c**), and $Pd(PPh_3)_2Cl_2$ (0.6 g, 0.8 mmol) were added to DMF (100 mL). The mixture was stirred at 100°C overnight under a nitrogen atmosphere. The DMF was evaporated to give solid, which was purified by column chromatography (eluent: hexane/ethyl acetate, 2:1). Yield (80%), yellow-green plates, mp 212 °C (ethyl acetate). ^{1}H NMR ($CDCl_3$); 8.10 (d, 4H, *J*=8.50 Hz), 7.70 (s, 1H); 7.50 (d, 4H, *J*= 7.05 Hz), 6.20 (s, 2H), 4.60-4.80 (m, 8H), 2.75 (t, 2H, *J* =7.80 Hz), 1.60 (q, 2H, *J*=7.05 Hz), 1.20-1.30 (m, 16H), 0.80 (t, 3H, *J*=7.50 Hz). ^{13}C NMR δ 1731.7, 163.7, 141.9, 136.6, 135.8, 129.2, 128.4, 109.4, 97.5, 64.7, 38.1, 41.4, 29.6, 29.6, 29.3. 29.4, 29.1, 28.5, 14.5. Anal. Calcd for $C_{39}H_{42}N_2O_4S_2$: C, 70.25; H, 6.35; N, 4.20. Found, C, 70.00; H, 6.05; N, 4.05.

for 2-propyl-4,6-bis-[phenyl-4-(3,4-ethylenedioxythiophene)]pyrimidine (7a):

The title compound was prepared similarly as above from 2-propyl-4,6-bis-(4-chlorophenyl)pyrimidine (**5a**). Yield 88.6% (yellow-green solid), mp 144-146 °C (ethyl acetate). ^{1}H NMR ($CDCl_3$), 8.09 (d, 4H, *J* =8.66 Hz), 7.80 (s, 1H), 7.47 (d, 2H, *J* = 8.65 Hz), 6.3 (s, 2H), 4.16 (s, 8H), 3.03 (t, 2H, *J*=7.46 Hz), 1.96 (q, 2H, *J*=7.48 Hz), 1.05 (t, 3H, *J*=7.37 Hz). ^{13}C NMR δ 171.8, 1631.6, 141.8, 136.9, 135.9, 129.1, 128.5,

109.3, 99.6, 64.7, 41.6, 21.8, 14.1. Anal. Calcd for $C_{31}H_{26}N_2O_4S_2$: C, 67.14; H, 4.72; N, 5.02. Found, C, 66.95; H, 4.70; N, 4.85.

for 2-heptyl-4,6-bis-[phenyl-4-(3,4-ethylenedioxythiophene)]pyrimidine (7b):

The title compound was prepared similarly as above from 2-heptyl-4,6-bis-(4-chlorophenyl)pyrimidine (**5b**). Yield 88.6% (yellow solid), mp 182-184 °C (ethyl acetate). ^{1}H NMR ($CDCl_3$): 8.00 (d, 2H, *J* = 8.80 Hz), 7.70 (s, 1H); 7.35 (d, 4H, *J*=8.50 Hz), 6.40 (s, 2H); 4.40-4.30 (m, 8H), 2.85 (d, 2H, *J*=7.45 Hz), 1.64 (q, *J*=7.45 Hz, 2H), 1.20-1.35 (m, 8H), 0.87 (t, 3H, *J*= 7.30 Hz). ^{13}C NMR δ 172.0, 163.1, 142.0, 137.0, 135.9, 129.1, 128.7, 109.2, 99.3, 64.2, 41.7, 38.0, 31.1, 30.5, 29.1, 22.0, 14.5. Anal. Calcd for $C_{35}H_{34}N_2O_4S_2$: C, 68.8; H, 5.61; N, 4.58. Found, C, 67.90; H, 5.45; N, 4.49.

General procedure for LB deposition

The binary systems of composition 3:1, 1:1 and 1:3 were maintained by resulting molar composition of the deposition mixture. The π-A isotherms were measured by means of commercial LB trough (KSV, System 5000), using Pt hydrophilic Wilhelmy plate, on high purity water at 295 K. The compression rates in our experiments ranged between 25 and 100 mm/min, depending on rigidity of the films. LB films were prepared by means of vertical emerging and dipping of the substrate at the surface pressure of around 15 mN/m.

CONCLUSIONS

Continuing our previous efforts, we have developed a practical strategy for preparation of 4,6-bis(phenyl)-, bis(phenylthiophene)- or bis(phenylethylenedioxythiophene)pyrimidines. The diphenylpyrimidines reacted with 3,4-ethylenedioxy-2-trimethyltinthiophene in the presence of $Pd(PPh_3)_2Cl_2$ or 2-trimethyltinthiophene in presence of $Pd(PPh_3)_4$ as catalysts to give the designed compounds. For reaction of condensation bis(halogenephenyl)pyrimidines with thiophene or 3,4-ethylenedioxythiophene derivatives we used bis-chloro-, bis-bromo-, bis(iodophenyl)pyrimidines, and the yields of reactions were almost similar, but the most reactive is bis-bromo derivative of biphenylpyrimidine. The aggregation results allow to suppose that materials achieved from bis(phenylthiophene)-, and bis(ethylenedioxythiophenephenyl)pyrimidines mixed with substances facilitating the film building, may give stable and good quality Langmuir and Langmuir-Blodgett films of desired composition and be promised candidate for electronic and sensoric devices or other application (medical diagnostic).

ACKNOWLEDGEMENTS

This work was facilitated in part by Wroclaw University of Technology Grant and Polish Science Foundation - KBN, Grant No PBZ-KBN-098/T09/2003.

REFERENCES

1. T. A. Skotheim, L. R. Elsenbaumer, and J. R. Reynolds, *Handbook of Conducting Polymers,* 2nd ed. New York, 1998.
2. G. A. Sotzing, J. R. Reynolds, A. R. Katritzky, J. Sołoducho, S. Belyakov, and R. Musgrave, *Macromolecules*, 1996, **29**, 1679.
3. J. Sołoducho, *Tetrahedron Lett.,* 1999, **40**, 2429.
4. J. Sołoducho, Sz. Roszak, A. Chyla, and K. Tajchert, *New J. Chem*., 2001, **25**, 1175.
5. A. Afzali, T. L. Breen, and C. R. Kagan, *Chem. Mater*., 2002, **14***,* 1742.
6. J. Cao, J. W. Kampf, and M. D. Curtis, *Chem. Mater.,* 2003, **15**, 404.
7. A. L. Wais, V. M. Shyrina, and V. P. Mamaev, *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk.,* 1975, **6**, 144 (Russ.) (C*hem. Abstr.,* 1975, **84**, 105528r).
8. P. D. Jones, and T. E. Glass, *Tetrahedron Lett.,* 2001, **42**, 2265.
9. R. M. Dodson, and J. K. Seyler, *J.Org. Chem.,* 1951, **16**, 461.
10. A. R. Katritzky, J. Soloducho, and S. Belyakov, *ARKIVOC*, 2000, **1**(**1**), 46.
11. J. H. Babler, *Synth. Commun*., 1982, **12**, 839.
12. A. Dinculescu, *Rom. Pat.* 59061 (Cl. CO7C123/00), 07 Jul 1975 (*Chem. Abstr*., 1978, **88**, 169615g).
13. R. S. Garigiparti, *Tetrahedron Lett.*, 1990, **31**, 1969.
14. J. I. Levin, E. Turos, and S. M. Weinreb, *Synth. Commun*., 1982, **12***,* 989.
15. A. Pinner, *Ann. Chem*., 1897, **297**, 221.
16. J. Sołoducho, J. Doskocz, J. Cabaj, and Sz. Roszak, *Tetrahedron,* 2003, **59**, 4761.
17. J. Sołoducho, J. Cabaj and A. Chyla, *Pol. Pat*. P 369 384, 2004.
18. J. Sołoducho, and A. Chyla, *Pol. Pat*. P 362 188, 2003 (Biul.Urz. Pat., 2004, **6**, 53).
19. E.E. George, and J.B. Polya, *Chem. Ind.,* 1979, **9**, 316.
20. H. J. Shine, and A. K. M. Mansurul-Hoque, *J.Org. Chem.,* 1988**, 53**, 4349.
21. P. Eitner, and H. Wetz, *Ber.,* 1893, **26***,* 2840.
22. R. F. Lambert, and C. E. Kristofferson, *J. Org. Chem.,* 1965, **30**, 3938.