Synthesis and Characterization of Conjugated Polyazines and Polyazomethines Containing the Thienylene Moiety and Flexible Hydrocarbon Side Chains

Silvia Destri,[*,†] **Mariacecilia Pasini,**[†] **Corrado Pelizzi,**[‡] **William Porzio,**[†] **Giovanni Predieri,**[*,‡] **and Carlo Vignali**[§]

Istituto di Chimica delle Macromolecole del CNR, via E.Bassini 15, I-20133 Milano, Italy, Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Viale delle Scienze, I-43100 Parma, Italy, and Centro Interdipartimentale di Misure "Giuseppe Casnati", Università di Parma, Viale delle Scienze, I-43100 Parma, Italy

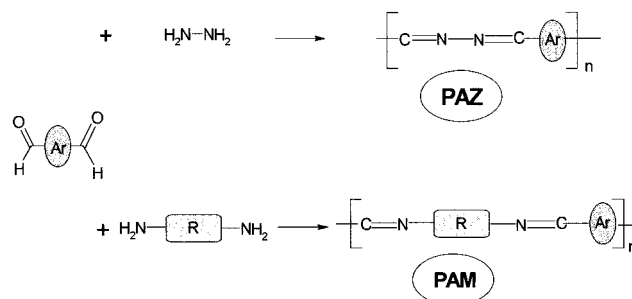*Received July 28, 1998; Revised Manuscript Received October 16, 1998*

ABSTRACT: Condensation reactions of mono- and didodecyl-substituted-2,5-diformylthiophene with hydrazine, *p*-diaminobenzene, 2,7-diaminofluorene, and 1,5-diaminonaphatalene give the corresponding polyazines (PAZs) and polyazomethines (PAMs), which have been characterized by thermal, structural, and optical analyses. The former polymers begin to decompose at 300 °C, while the latter polymers are stable up to 360 °C. All disubstituted polymers and the regioregular monosubstituted polyazines show nematic character. Disubstituted polymers display a larger conjugation with respect to monosubstituted ones. This effect has been attributed to a different conformation of thiophenic rings versus imino-linkages assumed by the polymeric backbone in the two classes of polyazines. Particular attention has been devoted to study the reactivity of mono- and disubstituted dialdehydes toward condensation with nucleophiles displaying different steric hindrance or power. Specifically the study of the reaction onset allowed us to determine the conditions to obtain regioregular monosubstituted polymers even with hydrazine, which is the less hindered and the more powerful nucleophile used.

Introduction

Two important families of conjugated polymers exhibiting interesting optical and electronic properties are those of polyazines (PAZs) and polyazomethines (PAMs), both belonging to the general class of Schiff-base polymers.[1] They are characterized by the presence of HC=N linkages, which are isoelectronic with the HC=CH groups present in many prototypical conjugated polymers such as polyacetylene and poly(*p*-phenylenevinylene).[2]

Conjugated PAZs (Scheme 1), contain direct N−N bonds because they derive from condensations of hydrazine with aromatic dialdehydes or diketones. On the other hand PAMs (Scheme 1) are the product of condensation of aromatic dialdehydes with aromatic diamines hence they are less flexible than analogous PAZs due to the presence of a stiff aromatic moiety between two subsequent nitrogen atoms. Lateral alkyl chains should be present in order to overcome the drawback of the insolubility in organic solvents, which limited the early investigations on these systems.[1e,3] Park et al., among others, inserted (*n*-alkoxide)methyl side chains on a polyazomethine backbone, improving the solubility of polymers of not too high molecular weight.[4] Conjugated PAMs, containing only phenylenic moieties, have been synthesized even in a vacuum by using chemical vapor deposition and tested as active layer or hole transport layer in electroluminescent devices.[5]

[†] Istituto di Chimica delle Macromolecole del CNR.
[‡] Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma.
[§] Centro Interdipartimentale di Misure "Giuseppe Casnati", Università di Parma.

Scheme 1

Recently, several conjugated PAMs containing different aromatic hydrocarbon moieties in the backbone and various side-group substituents have been prepared and used to investigate the effects of the molecular structure on the electronic and optical properties of conjugated polymers.[6]

Soluble PAMs in which both phenylenic and thienylenic rings constituted the polymeric backbone have been prepared in more recent years by several authors.[7] Moreover, other PAMs and PAZs containing thiophene rings have used for the preparation of optical waveguides.[8]

As regards the alkylic side chains in polymers, it is well-known that their presence modifies electronic and structural properties in polyalkylthiophenes, such an influence is relevant in both substituted PAZs or PAMs although they are more flexible of polyalkylthiophenes. This effect has been studied by Roncali[9] on thienylene−vinylene oligomers, which are comparable with oligomers containing imine linkage for both flexibility and electronic character of the double bond.

This paper deals with synthesis and characterization of PAZs and PAMs derived from a mono- or dialkyl-substituted 2,5-diformylthiophene with the aim to study the influence of this substitution on the optical and electronic properties.

We have found that the effect of one or two alkylic chains is already appreciable on the reactivity of the starting dialdehyde; in fact, by choosing the proper reaction conditions, regioregular PAZ polymers can be obtained.

Finally, the comparison among the NMR data in solution for PAZs and related model compounds, has permitted to understand the relationship between polymer conformations and number of side chains in the thiophene ring.

Experimental Section[23]

Materials. Analytical grade solvents, the catalysts LiCl and CF_3COOH, hydrazine, 1,4-phenylendiamine, 3,4-dibromo-thiophene (Aldrich), 2,7-diaminofluorene, and 1,5-diamino-naphthalene (Fluka Chemika) were commercial product and used as received. 2,5-Diformyl-3-dodecylthiophene (**D**) was prepared as reported in ref 7.

Preparation of the building blocks. 2,5-Diformyl-3,4-didodecylthiophene has been prepared as follows in two steps.

3,4-Didodecylthiophene. $C_{12}H_{25}Br$ (24 mmol) in dry Et_2O (10 mL) was added dropwise over 1 h to a stirred suspension of Mg (26.8 mmol) in the same solvent (10 mL) kept at 0 °C, under nitrogen atmosphere. The reaction mixture was stirred overnight at room temperature and then, after dilution with Et_2O (75 mL), was added dropwise over 1 h to an ethereal solution (100 mL) containing 3,4-dibromothiophene (10.4 mmol) and [Ni(dppp)Cl₂] (0.104 mmol). The orange-brown solution was heated at reflux for 18 h and then poured onto an excess of water. The organic layer was collected and dried, the solvent was eliminated by using a rotary evaporator, and the 3,4-didodecylthiophene was then purified by flash chromatography using hexane as eluent (yield 46%).

2,5-Diformyl-3,4-didodecylthiophene (DD). Under nitrogen atmosphere, a hexane solution (9.6 mmol, 4.6 mL) of *n*-butyllithium was added over 10 min to a mixture of TMEDA (9.6 mmol) and 3,4-didodecylthiophene (4.8 mmol) in dry hexane (45 mL). The orange solution was stirred for 30 min at 40 °C and then refluxed for 2 h more. After addition of dry THF (45 mL), the solution was cooled at −70 °C. An excess of DMF dry (16.2 mmol) was added dropwise under nitrogen over 15 min. The reaction mixture was left to reach room temperature and the obtained solution was poured into a 3.7% aqueous HCl solution (400 mL), under vigorous stirring and kept below 0 °C. After neutralization with sodium hydrogen carbonate, the organic layer was extracted several times with Et_2O and dried with sodium sulfate. The product **DD** was purified by flash chromatography using hexane−THF (95:5) as eluent mixture (yield 53%); mp 30 °C. MS (CI): m/z 476 [M]⁺. FTIR (cm⁻¹): 1658 (CO stretching). UV−vis: λ_{max}(CHCl₃) 310 nm. ¹H NMR (CDCl₃), δ: 10.11 (s HCO, 2H), 2.90 (t, αCH₂, $J = 8$ Hz, 4H), 1.59 (m, βCH₂, 4H), 1.42−1.26 (m, $\gamma−\omega CH_2$, 36H), 0.88 (t, CH₃, $J = 6.9$ Hz, 6H). ¹³C NMR (CDCl₃), δ: 183.0 (HCO, 2C), 151.4 (α-C thiophenic ring, 2C), 143.1 (β-C thiophenic ring, 2C), 31.7−22.5 (C side chain).

Preparation of Model Compounds. Synthesis of MM. **DD** (0.52 mmol) in ethanol (10 mL) was added dropwise to a stirred solution of hydrazine (26 mmol) in ethanol (10 mL). The solution was left stirring at room temperature for 4 h, under nitrogen flux and light repaired. The yellow bis-(hydrazone) **HH** was obtained by cooling the solution (−20 °C) and recovered by filtration (yield 73%); decomposition at ≈40 °C. MS (CI): m/z 505 [M + 1]⁺. FTIR (cm⁻¹): 3359, 3212 (N−H₂ stretching), 1593 (C=N stretching), 1467 (C=C_arom stretching); UV−vis: λ_{max}(CHCl₃) 367 nm. ¹H NMR (CDCl₃), δ: 7.88 (s, H−C=N, 2H), 5.47 (br, NH₂, 4H), 2.52 (t, αCH₂, 4H), 1.46 (m, βCH₂, 4H), 1.26 (m, $\gamma−\omega CH_2$, 36H), 0.88 (t, CH₃, 6H).

An excess of formylthiophene (0.92 mmol) was added to a stirred solution of hydrazone (0.37 mmol) dissolved in ethanol (25 mL). Some drops of trifluoroacetic acid were added to the solution that turns from yellow to red color with precipitation of a red powder. The mixture was left at room temperature, under stirring, for 4 h, and then it was cooled in freezer. The product **MM**, a red powder, was filtrated and recrystalized in ethanol (yield 70%); mp 119 °C. MS (CI): m/z 693 [M + 1]⁺. FTIR (cm⁻¹): 1604 (C=N stretching), 1468 (C=C_arom stretching). UV−vis: λ_{max}(CHCl₃) 459 nm. ¹H NMR (CDCl₃), δ: 8.83, 8.81 (s H−C=N, 2H), 7.5 (d, H_3 outer thiophene, $J = 5.0$ Hz, 2H), 7.45 (d, H_5 outer thiophene, $J = 3.4$ Hz, 2H), 7.14 (dd, H_4 outer thiophene, $J = 5.0$ and 3.4 Hz, 2H), 2.72 (t, αCH₂, $J = 7.5$ Hz, 4H), 1.56 (m, βCH₂, 4H), 1.27 (m, $\gamma−\omega CH_2$, 36H), 0.88 (t, CH₃, $J = 6.8$ Hz, 6H).

Synthesis of M. A procedure very similar to the previous one provides a white-yellow bis(hydrazone) **H** (yield 66%); mp ≈63 °C. MS (CI): m/z 337 [M + 1]⁺. FTIR (cm⁻¹): 3337, 3186 (N−H₂ stretching), 1600 (C=N stretching), 1467 (C=C_arom stretching). UV−vis: λ_{max}(CHCl₃) 342 nm. ¹H NMR (CDCl₃), δ: 7.88, 7.76 (2s, H−C=N, 2H), 6.78 (s, thiophenic, 1H), 5.48 (br, NH₂, 4H), 2.56 (t, αCH₂, 2H), 1.54 (m, βCH₂, 2H), 1.24 (m, $\gamma−\omega CH_2$, 18H), 0.87 (t, CH₃, 3H).

The reaction under the conditions used for **MM** of this hydrazone with formylthiophene gives the red powder model compound **M** (yield 40%). MS (CI): m/z 525 [M + 1]⁺. FTIR (cm⁻¹): 1603 (C=N stretching), 1468 (C=C_arom stretching). UV−vis: λ_{max}(CHCl₃) 437 nm. ¹H NMR (CDCl₃), δ: 8.82, 8.67 (2s, H−C=N, 2H), 8.77 (s, H−C=N outer, 2H), 7.5 (d, H_3 outer thiophene, $J = 5.0$ Hz, 2H), 7.45 (d, H_5 outer thiophene, $J = 3.4$ Hz, 2H), 7.27 (s, H_4 inner thiophene, 1H), 7.13 (dd, H_4 outer thiophene, $J = 5.0$ and 3.4 Hz, 2H), 2.72 (t, αCH₂, $J = 7.5$ Hz, 4H), 1.56 (m, βCH₂, 4H), 1.27 (m, $\gamma−\omega CH_2$, 36H), 0.88 (t, CH₃, $J = 6.8$ Hz, 6H).

Polymerization. Polymeric Schiff bases were prepared starting from 2,5-diformyl-3-dodecylthiophene and 2,5-diformyl-3,4-didodecylthiophene with hydrazine and different aromatic diamines giving PAZs or PAMs, respectively.

Regioregular Polymer PD1-1. Polycondensations between hydrazine and 2,5-diformyl-3-dodecylthiophene have been carried out under different experimental conditions; using the procedure described below, we obtained a regioregular polymer.

Hydrazine (3.2 mmol) was added dropwise to a solution of **D** (3.2 mmol) dissolved in ethanol (40 mL). Some drops of trifluoroacetic acid were added before heating the solution to reflux for 24 h. During the heating a red compound precipitated. The polymer was extracted using a Kumagawa apparatus with methanol and chloroform. Average molecular mass (GPC determination), $M_w = 32.4 \times 10^3$ with a dispersity (η) of 3.3. Anal. Calcd for the polymer PD1 of infinite length, $C_{18}H_{28}N_2S$: C, 71.05; H, 9.21; N, 9.21; S, 10.53. Found: C, 70.84; H, 9.38; N, 9.24; S, 11.17. FTIR (cm⁻¹): 2923 (C−H stretching), 1599 (H−C=N stretching). UV−vis: λ_{max}(CHCl₃) 492 nm. ¹H NMR (CDCl₃), δ: 8.83, (s, 5-HC=N, nearer from the side chain, 1H), 8.68, (s, 2-HC=N, farther to the side chain, 1H), 7.29, (s, ring H_4, 1H), 2.78 (m, αCH₂, 2H), 1.65 (m, βCH₂, 2H), 1.27 (m, $\gamma−\omega CH_2$, 18H), 0.87 (t, CH₃, 3H). ¹³C NMR (CDCl₃) aromatic region, δ: 148.5, 141.6, 136.8, quaternary carbons; 134.3, $^1J(^{13}C,^1H) = 168$ Hz ternary carbon; 155.6 ^1J $(^{13}C,^1H) = 172$ Hz 5-imine carbon; 154.5, $^1J(^{13}C,^1H) = 172$ Hz 2-imine carbon.

Polymer PDD1. All the polymerization reactions have been carried out following a procedure similar to that described below for polymer **PDD1**.

PDD1-1. D (0.29 mmol) and hydrazine (98%, 0.29 mmol) were dissolved in ethanol (20 mL) under stirring. Some drops of trifluoroacetic acid were added, and the solution was heated at reflux. After 10 min a red precipitate was formed, which dissolved by adding chloroform (10 mL). The mixture was heated at reflux for 24 h, then was cooled and poured into an aqueous solution of sodium hydrogen carbonate. The precipitate was recovered by filtration, while the solution was extracted with chloroform and evaporated. The precipitate and

Table 1. Reaction Conditions and Solubility Data for the Synthesized Polymers

aldehydes	diamine	polymer	solvent	catalyst, time/h	solubility
D	1	**PD1-1**	EtOH	CF$_3$COOH, 24	A
DD	1	**PDD1-1**	EtOH/CHCl$_3$ 2/1	CF$_3$COOH, 24	A
DD	1	**PDD1-2**	EtOH/CHCl$_3$ 2/1	CF$_3$COOH,[b] 24	A
DD	1	**PDD1-3**	toluene	CF$_3$COOH, 24	A
D	2	**PD2-1**	toluene	−, 24	A,B
DD	2	**PDD2-1**	toluene	−, 24	A,B
DD	2	**PDD2-2**	DMF	LiCl, 48	A,B
DD	2	**PDD2-3**[a]	toluene	−, 36	A,B
DD	2	**PDD2-4**[a]	EtOH/CHCl$_3$ 1/1	−, 36	A,B
DD	2	**PDD2-5**[a]	hexane/CHCl$_3$ 1/1	−, 36	A,B
D	3	**PD3**	toluene	−, 24	
DD	3	**PDD3**	toluene	−, 24	
D	4	**PD4**	toluene	−, 24	
DD	4		toluene	−, 24	

[a] Reactions performed under nitrogen flux, light repaired, with degassed solvents and dry reagents. A = CHCl$_3$, toluene; B = THF, CH$_2$Cl$_2$. [b] Added at reflux.

the solid were dried together under vacuum and fractionated using a Kumagawa extractor with methanol and chloroform.

PDD1-2. The acid was added at reflux and a red precipitate was recovered by filtration after cooling and neutralization of the solution with sodium hydrogen carbonate. This precipitate was soluble only in chloroform. $M_w = 27.5 \times 10^3$ with η of 1.8. Anal. Calcd for the polymer **PDD1** of infinite length, C$_{30}$H$_{52}$N$_2$S: C, 76.27; H, 11.02; N, 5.93; S, 6.78. Found: C, 75.64; H, 9.92; N, 6.00; S, 3.70. FTIR (cm^{-1}): 2923, 2852 (C−H stretching), 1593 (H−C=N stretching), 1465 (C=C ring stretching). UV−vis: λ_{max}(CHCl$_3$) 515 nm. ^{1}H NMR (CDCl$_3$), δ: 8.82, (s, HC=N, 2H), 2.72 (m, αCH$_2$, 4H), 1.57 (m, βCH$_2$, 4H), 1.5−1.2 (m, $\gamma-\omega$CH$_2$, 36H), 0.88 (t, CH$_3$, 6H).

PDD1-3. The reaction solvent was toluene, the acid was added at reflux, and it was not necessary to use chloroform because there was no precipitate.

Polymer PDD2. Polycondensation between *p*-diaminobenzene and **DD** was carried out under different experimental conditions; the procedure described below concerns the sample **PDD2-3**; nevertheless, it applies also to the other samples, with the modification reported in Table 1 (see Results and Discussions).

In a 100 mL two-necked round-bottomed flask, equipped with a magnetic stirrer and a refrigerator, **DD** (0.26 mmol) and *p*-diaminobenzene (0.26 mmol) were dissolved in toluene. The orange mixture was heated at reflux for 36 h then was cooled and the solvent eliminated by rotary evaporator. **PDD2-3** average molecular mass (GPC determination), M_w, is 45.8×10^3 with η of 2.1. Anal. Calcd for the polymer **PDD2** of infinite length, C$_{36}$H$_{56}$N$_2$S: C, 78.77; H, 10.28; N, 5.1; S, 5.8. Found: C, 77.39; H, 11.15; N, 5.08; S, 4.88. FTIR (cm^{-1}): 2924, 2853 (CH stretching), 1590 (C=N stretching), 1490, 1463 (C=C ring stretching), 849, 803, 719 (CH out-of-plane bending). UV−vis: λ_{max}(CHCl$_3$) 475 nm. ^{1}H NMR (CDCl$_3$), δ: 8.67 (s, HC=N, 2H),7.29 (s, aromatic ring, 4H), 2.77 (m, αCH$_2$, 4H), 1.58 (m, βCH$_2$, 4H), 1.26 (m, $\gamma-\omega$CH$_2$, 36H), 0.87 (t, CH$_3$, 6H). ^{13}C NMR (CDCl$_3$), δ: 151.1 (HCN, 2C), 150.1 (α-C thiophenic ring, 1C), 147.5 (C1 phenylenic ring, 1C) 140.9 (β-C thiophenic ring, 2C), 122.4 (C orthophenilenic ring, 2C), 31.7−22.5 (C side chain).

In the case of **PDD2-2**, after cooling some water was added and the product was extracted with chloroform.

In the case of **PDD2-4** and **PDD2-5** when a precipitate started to form chloroform was added dropwise until the complete solubilization of the solid.

The general experimental procedure described above was applied to the synthesis of other polymers derived by the condensation of **D** or **DD** with different aromatic diamines.

PD3. D (0.25 mmol) reacted with 2,7-diaminofluorene (0.25 mmol) in 20 mL of toluene to afford an orange insoluble powder.

PDD3. DD (0.30 mmol) reacted with 2,7-diaminofluorene (0.30 mmol) in 30 mL of toluene to afford a red insoluble powder.

PD4. D (0.25 mmol) reacted with 1,5-diaminonaphthalene (0.25 mmol) in 20 mL of toluene to afford a red powder.

FTIR spectra were recorded on a Nicolet 5PC spectrometer, while UV−vis spectra were obtained using a Kontron instrument Unikron 860.

DSC and TG experiments were performed on Perkin-Elmer instruments, a Delta Series TGA 7 thermobalance, and a DSC 7 calorimeter, respectively.

For melting point determinations a Galleramp (0-300) instrument was used and mass spectroscopic measurement were carried out on a Finningan SSQ 710 quadrupole.

XRD experiments were carried out with a Siemens D-500 computer controlled apparatus, with Soller slits and a graphite monochromator, using Cu Kα radiation.

GPC measurements were carried out on a Waters SEC system consisting of a pump, a 717 autosampler, a 410 differential refractometer, and 490 UV detectors. The column was a Ultrastyragel Waters (100 Å pore size).

NMR measurements were carried out on a Bruker AMX400 spectrometer at 295 °K. Typical acquisition parameter for 1D experiments were a 200 ppm spectral window for ^{13}C spectra with 32K size, a 45° pulse width, and a recycle delay of 1.5 s.

For NOESY experiments a set of 512 time increment spectra were collected, with zero-filling to 1024 points. A total of 24 transients per spectrum were used with relaxation delay of 3 s, while the mixing time was 0.4 s for **PD1-1** or 0.8 s for **D**.

Results and Discussion

Synthesis of the Polymers. Two series of new conjugated aromatic polyimines were prepared by solution polymerization of different aromatic diamines (*p*-diaminobenzene, 2,7-diaminofluorene, and 1,5-diaminonaphthalene) and hydrazine, with **D** and **DD** respectively following the general reaction pathway depicted in Scheme 2.

Polycondensations were carried out under different experimental conditions as summarized in Table 1.

The resulting polymers are soluble in common organic solvents, as shown in Table 1, with the exception of **PD3**, **PDD3**, and **PD4** having too stiff a polymeric backbone. Attempts to obtain the analogous of **PD4** with **DD** by varying the experimental conditions were unsuccessful, in fact even after 24 h of reflux the greater part of the starting reagents was recovered.

Characterization of Molecular Structure. The proposed polymer structures were derived from ^{13}C NMR and ^{1}H NMR, FTIR, and GPC data. The assignment of the chemical shifts of all resonances (excluding $\beta-\omega$ protons of the dodecyl chains) in the spectra of the more representative polymers are listed in Table 2.

In the spectrum of **PDD1-2**, as expected, only one peak at 8.82 ppm, due to the all equivalent imine protons,

Scheme 2

D for R=H and DD for R= $C_{12}H_{25}$

$H_2N—R'—NH_2$= 1, 2, 3 and 4
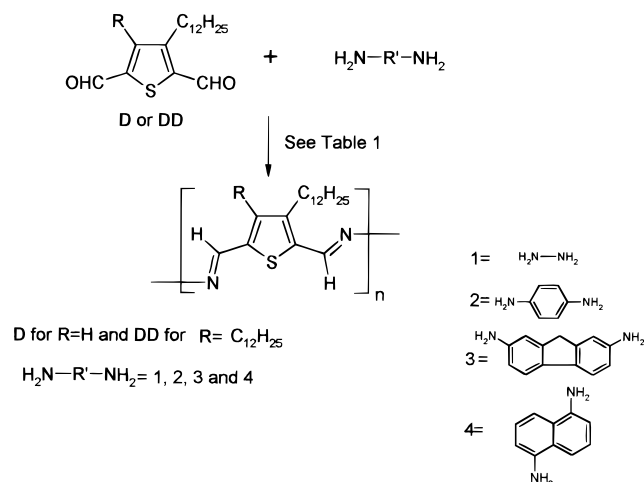
Table 2. Assignment of Chemical Shifts (ppm) of ^1H NMR Spectra of Polymers in CDCl$_3$

species	aldehyde	imine	phenylene	αCH$_2$	thiophene
PD1-1		8.83, 8.68		2.78	7.29
PDD1-2		8.82		2.72	
PD2-1		8.65, 8.52	7.25	2.87	7.25
PDD2-3		8.67	7.29	2.77	
PDD2-4	10.08	8.66	7.28	2.79	

is present (apart from the series of peaks due to the aliphatic chains). In the case of monododecyl polyazine derived from **D** (**PD1**), the situation should be more complex because of the intrinsic asymmetry of the dialdehyde which can lead to different enchaiments (head−head, head−tail, and tail−tail).

In fact the ^1H NMR spectrum of the **PD1** polymer described in ref 7, aside from the main peaks, exhibits other signals in the range 8.1−8.4 ppm due to imine protons and around 7 ppm due to the thiophenic proton attributable to monomeric units in irregular enchaiments. Nevertheless, in the case of regioregular polymer **PD1-1**, described here, there are only two peaks, due to the imine protons at 8.83 (nearer to the side chain) and at 8.68 ppm (farther from the side chain), and only one peak for thiophene proton.

The corresponding PAM polymers with *p*-diaminobenzene present the same situation with an additional peak at 7.25 ppm due to the phenylenic protons. The resonance peak at about 10 ppm, detected only in a few polymers, is attributed to terminal aldehyde. This is consistent with the presence of a small peak due to the C=O groups in the Fourier transform infrared (FTIR) spectrum of these compounds.

In fact, the absorption bands over 1650 cm^{-1} due to this group are very strong in the dialdehydes, while they are reduced in intensity, or even disappear, in the polymers.

At the same time a new strong absorption band at about 1590 cm^{-1} appears consistently with the formation of the imine linkage. The bands at 1460 cm^{-1} are due, both in polyazomethines and, in polyazines, to thiophene ring stretching (C=C). In the former polymers, another band attributed to phenylene residue appears at 1490 cm^{-1}; the bands around 840 cm^{-1}, stronger in the case of the polymers with aromatic diamine, are characteristic of the aromatic C−H out-of-plane deformations.

The molecular weights of the soluble polymers can be estimated by GPC in THF using polystyrene as

Table 3. Electronic Absorption and Emission Maxima and the GPC Analysis Values for the Chloroform Extraction Fraction of Conjugated Aromatic Polyimines

polymer	λ_{max}, nm		$M_w \times 10^3$	η	n
	absorption	emission			
PD1-1	492	575	32.4	3.3	106
PDD1-1	511	569, 613	15.8	1.5	34
PDD1-2	515	571, 615	27.5	1.8	58
PDD1-3	404	567, 611	10.3	1.3	22
PD2-1	464	511, 530	26.8	2.5	71
PDD2-1	472	540, 570, 620	32.7	1.7	60
PDD2-2	467	546, 566, 621	28.5	7.2	52
PDD2-3	475	550, 579, 623	45.9	2.1	84
PDD2-4	472	548, 577, 618	26.0	1.6	48
PDD2-5	479	550, 575, 619	50.0	2.0	92

standards. M_w values, the polydispersity index (η) and the polymerization degree (n) for the heavy fraction extracted in CHCl$_3$ are shown in Table 3. In particular, **PDD1** and **PDD2**, which were studied in more details, show η values which are affected by solvent, catalyst presence, and reaction time and, in the case of the latter polymer also by the presence of O$_2$ or light.

The good film-forming ability of **PD2** and **PDD2** indicates that their molecular weights are reasonably high in agreement with GPC data.

Thermal and Structural Characterizations. The thermal stability of polymers was examined by TGA. The onset of thermal decomposition occurs at about 300 °C for polyazines and 370 °C for polyazomethines under nitrogen flux. However a consistent weight loss is detected at 400C° (>70%) for polyazines irrespectively of the side-chain number, while polyazomethines are more stable showing at the same temperature a corresponding weight loss of about 50%.

The lower thermal stability of polyazines results in a discontinuous profile over 150 °C, probably due to the N−N thermal cleavage, whereas polyazomethines exhibit a linear endothermic behavior until 290 °C.

By comparing **PD2** and **PDD2** polymers with analogous substituted[4] or unsubstituted[3] PAMs, it is evidenced that first the presence of aromatic ring containing sulfur decreases the stability at high temperature (residual weight at 700°C less than 20%), second the more is the number of alkylic side chains per monomeric unit, the more is the stability lowering.

Differential scanning calorimetry (DSC) analysis of the polymers PAMs and PAZs, in the range 50−290 °C, are very similar and show, in the first heating run, two endothermic peaks, one at about 60−70 °C, due to the increased mobility of the side chains, and one broad and barely detectable at about 100 °C, due to the decreased planarity of the backbone chain (melting). A quite similar behavior was observed for poly(3-alkylthiophenes).[10]

Structural analysis was done for the polymers **PD1-1**, **PDD1-2**, **PD2-1**, **PDD2-1**.

Only the X-ray powder diffraction patterns of the polymers **PDD1-2** and **PD2** revealed poor order degree. Aside from the amorphous phase, a single peak is observed corresponding in both cases to a *d* spacing near to 25 Å, already detected in poly(3-dodecylthiophene)[11] and attributed to interchain spacing. These data are consistent with the presence of a nematic mesophase, typically observed in polyazomethine systems having two configurations (syn/anti) in the backbones.[12]

Optical Characterization. The absorption and emission maximum λ_{max} values of the lowest energy $\pi \rightarrow \pi^*$
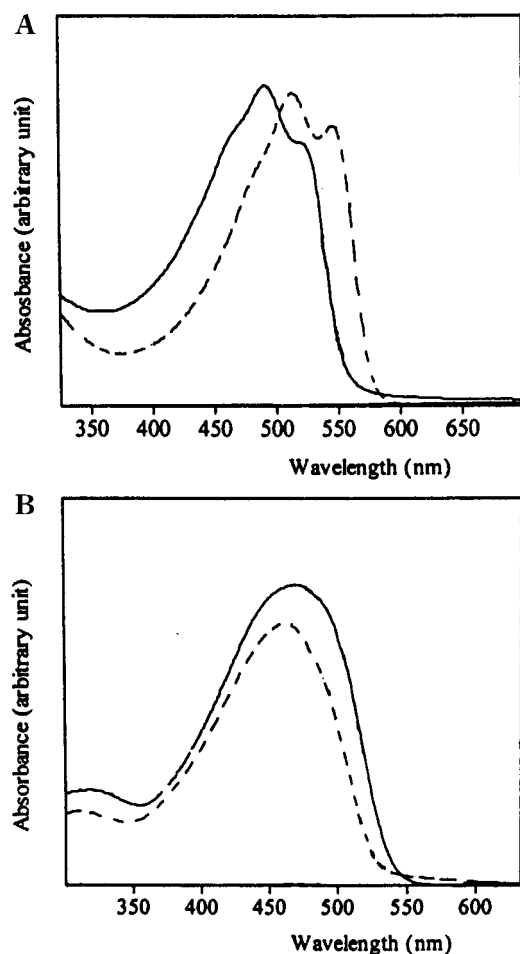
A

B

Figure 1. UV–vis spectra in CHCl$_3$ of **PD1-1** (solid line) and **PDD1-2** (dotted) polymers (A) and of **PD2-1** (dotted line) and **PDD2-5** (solid) polymers (B).

Table 4. Assignment of Chemical Shift of ^{1}H NMR Spectra in CDCl$_3$ (Chemical Shift (ppm) of Protons on Functional Groups) and Electronic Absorption Maxima

	chem shift				
species	aldehyde ^{1}H–C=O	aldehyde^a H–^{13}C=O	imine^b ^{1}H–C=N	^{1}H thio-phene^b ring	λ_{max}, nm absorption
D	10.06, 9.89	183.5, 183.1		7.62	297
DD	10.11	183.1			310
H			7.88, 7.76	6.78	342
HH			7.88		367
M			8.82, 8.67	7.27	437
MM			8.83		459

^{a} δ (2-formyl) 183.1, $^1J(^{13}C,^1H)$ = 180 Hz; δ (5-formyl) 183.5, $^1J(^{13}C,^1H)$ = 181 Hz, $^3J(^{13}C,^1H)$ = 3.5 Hz. ^{b} Only the values of chemical shift of the protons derived by the aldehydes **D** or **DD** were reported.

PAMs exibhit noticeable luminescence. Results and quantum yields determination are the object of a forcoming publications.

Reactivity and Conformational Studies. Thiophenic aldehydes are less reactive toward nucleophilic attack than other aromatic dialdehydes; in fact, the solution condensation of 1,4-diamineanthraquinone with terephthaldehyde yields a black polymer,[13] while when **D** was used with the same amine, no evidence of condensation was detected.
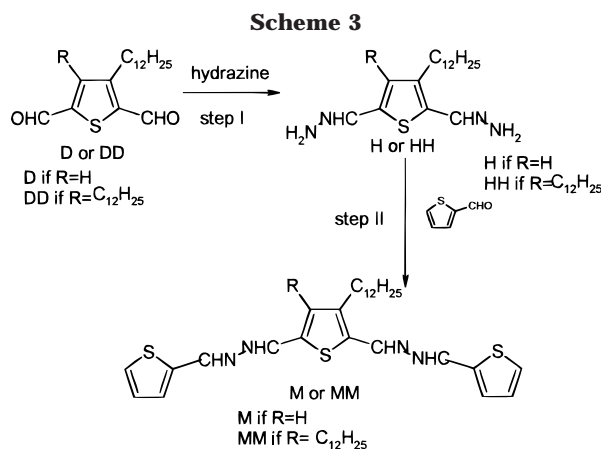
Moreover hindered aromatic diamines, such as 1,5-diaminonaphthalene, give polymers only with monosubstituted dialdehydes, while when 1,4-diaminophenylene, which is less hindered but should have comparable reactivity, was used, both the dialdehydes yield polymers in the same conditions (see Table 1).

The minimization of the steric hindrance of the diamine is achievable by using hydrazine, hence evidencing the steric and electronic contributions due to the substituted dialdehydes in discriminating **D** from **DD**. Different polymerization runs using hydrazine and **DD** point out that the reaction does not proceed without acid catalyst, while the same condensation with **D** occurs at reflux temperature without catalyst, producing oligomers of noticeable length.

Therefore it appears that, due to both steric and electronic contributions being indistinguishable, **D** is more reactive than **DD** toward the nucleophilic attack. Steric effects, due to the presence of one or two alkyl chains should play the major role, but also electronic effects could exert some influence. In fact the values of chemical shifts of ^{13}C NMR spectra of **DD** and of **D** reported in Table 4 indicate that the 3-alkyl substitution provokes a shielding effect preferentially onto formyl carbon in 2 position which exhibits the same chemical shift value (δ 183.1) of the formyl carbons of the 3,4-disubstituted species. According to these chemical shifts the reactivity of formyl group to nucleophilic attack of amines should decrease in the following order:

5-position of **D** > 2-position of **D** $\approx$

2,5-positions of **DD**
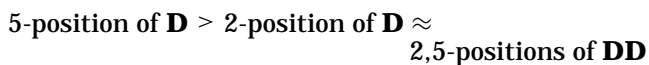
Bearing two formyl groups having different reactivity, the monosubstituted dialdehyde offers the opportunity to control this different reactivity by producing a regioregular polymer. As a confirmation, by monitoring the reaction between **D** and hydrazine by ^{1}H NMR spectroscopy, we can observe that, immediately after mixing (under kinetically controlled conditions: room temper-

transition in chloroform solution, are listed in Table 3. The wavelength values of the absorption maxima appear related to the molecular weights of the different fractions, being generally higher for larger molecular weights, i.e., for longer chromophores if the polymerization degree does not exceed 15–20 monomeric units. The optical absorption spectra of **PD1-1** and **PDD1-2** polymers are very similar in line shape and only slightly shifted to each other of about 20 nm (see Figure 1A). Polymer **PD1-1** presents a structured profile only when high regioregularities is detected by NMR analysis. The absence of structure in the absorption profiles of **PD2** and **PDD2** (see Figure 1B) has been related to both molecular weights dispersivity and bad solvent effect, while regular enchaiment has been proved by NMR analysis. The observed *blue shift* of the electronic absorption spectra for the incorporation of phenylene rings on the polymer skeleton can be explained in terms of a greater backbone planarity of **PD1** and **PDD1** polyazines as compared with the **PD2** and **PDD2** polyazometines. It has been well documented[6] that the imine linkage (CH=N) is not coplanar with the phenylene ring adjacent to nitrogen atom in Schiff base molecules. This non planar molecular structure is the result of the conjugation between the imine nitrogen lone pair electrons and the π-electrons on the *N*-phenyl ring. Differently from poly(3-alkylthiophenes) in both classes it is possible to observe a red shift for the absorption of disubstituted polymers with respect to the monosubstituted ones (see Table 3). Both PAZs and

Scheme 3

Figure 2. ^{13}C spectrum (not ^{1}H decupled), in the carbonyl region of compound **D**.

Figure 3. Molecular model of **D**.

ature and no added catalyst), the prevailing products, besides unreacted dialdehyde, come from the condensation of the 5-formyl residue; among them the simple monoazine has been recognized. A subsequent heating causes the formation of oligomers with different enchainments involving the condensation of both the formyl moieties. Finally, the addition of acid catalyst results into a nonregioregular polymer. On the other hand, by adding the catalyst at room temperature, it has been possible to prepare a polymer with a regioregularity greater than 90%, essentially constituted by the regular alternation of head-to-head and tail-to-tail enchainments.

It is well established that the alkyl chains also influence the conformation of conjugated polymers. In particular the presence of two alkyl chains onto adjacent aromatic rings provokes large distortions in polymeric backbones.[14] However, in the electronic absorption spectra of **PD1**-**1** and **PDD1**-**2** polymers (see optical characterization) the absorption maxima value of **PDD1**-**2** is shifted to longer wavelengths as already observed in 3- and 3,4-alkyl-substituted thienylene−vinylene oligomers.[9]

To throw light on the polymer conformation in solution, we synthesized molecular compounds modeling the arrangement of the polymeric backbones. The models were obtained by condensation of **D** or **DD** with hydrazine, to form the bis(hydrazones) **H** and **HH**, respectively, step I in Scheme 3, and then the bis(hydrazones) reacted with formylthiophene to give the corresponding diazines **M** and **MM**, respectively, step II in Scheme 3.

The absorption maxima values and the chemical shifts of ^{1}H NMR spectra of dialdehydes and of the model compounds are reported in Table 4. Looking at the table, it is worthwhile to note that also the absorption maximum of **DD** in UV−visible spectra is shifted toward lower energies with respect to that of **D**.

Previous conformational studies on thiophene 2,5-dicarboxyaldehyde indicate that in solution an equilibrium mixture of the O,S,O-cis,cis (in the majority) and of O,S,O-cis,trans conformers exists,[15] the former being stabilized by a Coulombic interaction between sulfur and oxygen atoms.[16]

Considering **D** and **DD** dialdehydes, we have to take into account both steric hindrance and electronic contributions due to the alkyl chains. In **DD** the presence of two alkylic side chains should forces both the formylic groups to assume an O,S-cis conformation, forming torsion angles near to 0° between the formyl groups and thiophene ring planes, to minimize the steric hindrance. In **D** the lack of both electron donating and steric effects
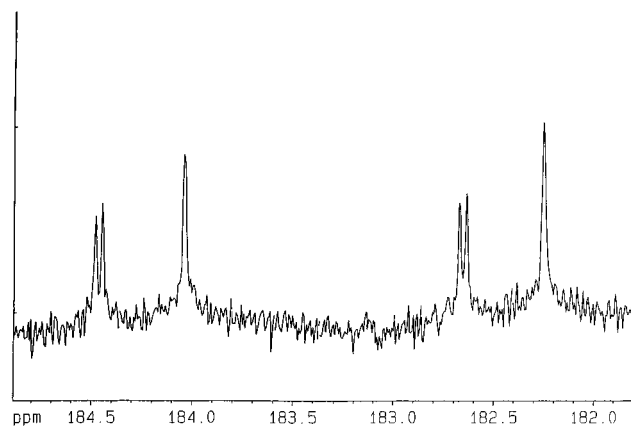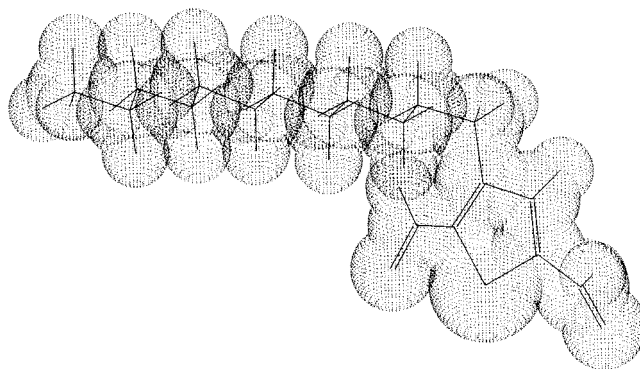
due to the alkyl chain induces the dihedral angle in the 5-position to assume a different value.

As a matter of fact, considering the ^{13}C spectrum of **D** reported in Figure 2 and the heteronuclear coupling constant $^3J_{C-H}$ measured between a formyl group in the 5-position and thiophenic hydrogen, it is possible to estimate the dihedral angle between the formyl group and thiophene ring planes.

It has been shown that vicinal heteronuclear coupling constants are related to torsion angle by a Karplus-like relationship[17] and, therefore, could give interesting conformational information in solution. Theoretical studies in conjuction with experimental data and NMR and X-ray diffraction data, have also demonstrated that several breakdowns of the Karplus equation are present due to the fact that there is not a general parametrization of this equation.[18] By considering different proposed modifications,[19−21] we calculated several dihedral angle values that could fit our NMR data.

Integration of the 2D NOESY cross-peaks led us to use qualitative distance restraints to calculate a molecular model (Figure 3) which fit our data. Again the dihedral angle measured from this model confirmed the deviation from the planarity of this fragment.

The different conformation of the formyl groups in 5 and 2 positions with respect to thiophene ring account for the absorption data of the **D** and **DD** molecules.

In ^{1}H NMR spectrum of the model compound **H** (see Scheme 3) the signal of the thienylenic proton is shifted toward higher field as compared with the same resonance in compound **D** or in the polymer. This observation allows us to infer that the imino group in the 5-position adopts a trans conformation with respect to thiophene sulfur atom in such a way that the thiophenic
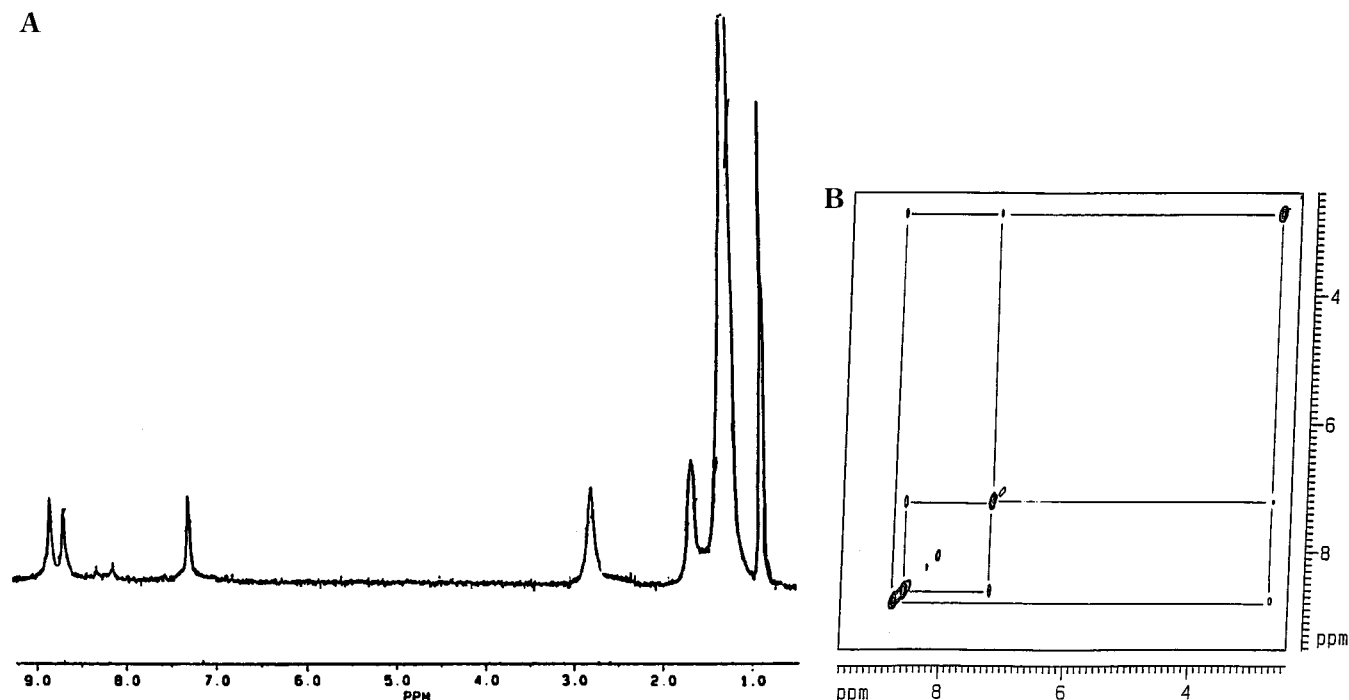
A

B

Figure 4. (A) 300 MHz ^{1}H NMR of the regioregular **PD1**-**1**. (B) 400 MHz ^{1}H NMR NOESY map of the regioregular **PD1**-**1** polymer showing 2D NOE cross-peaks connecting resonances of spatial adjacent protons.

proton experiences the shielding cone of the iminic double bond.[22] To justify the absorption data of **H** and **HH** molecules, the imine group and the thiophene ring should not be coplanar in the monosubstituted compound.

On the other hand, the Schiff base model **M** (see step 2 of Scheme 3) and the corresponding polymer **PD1**-**1** should show a N,S,N-cis,cis conformation, with a deviation from coplanarity between the imino group and the thiophene ring lower than that observed in **D**. This accounts both for the electronic absorption spectra, from where a larger effective conjugation length is deduced, and for the ^{1}H NMR NOESY data of regioregular **PD1**-**1**, reported in Figure 4, in which the integrated volumes of the 2D cross-peaks of the protons are similar to those of compound **D**.

Conclusions

Polyazines and polyazomethines containing mono- and didodecylthiophene have been synthesized and characterized. The different reactivity of formyl groups in 2- and 5-positions allows us to control the reaction conditions to obtain a highly regioregular polymer with monoalkyl-substituted thiophene.

Conformational studies performed on polyazines indicated for the monododecyl polymer indicated that the imino group plane far from the alkylic chain and thiophene ring plane are tilted, hence accounting for a reduced overall conjugation length of this polymer with respect to the didodecyl polymer.

Therefore we must infer that the steric and inductive effect of alkyl chain onto the C(thiophene)−C(imino) bond results into an hampered rotation of formyl moiety, enhancing the planarity of the polymer, i.e., the overall conjugation.

References and Notes

(1) (a) Kossmehl, G. *Handbook of Conducting Polymers;* Marcel Dekker: New York, 1986; p 386. (b) Euler, W. B. *Handbook of Organic Conductive Molecules and Polymers;* Nalwa, H. S., Ed.; John Wiley & Sons: New York, 1997; Vol. 2, p 719. (c) Morgan, P. W.; Kwolek, S. L.; Pletcher, T. C. *Macromolecules* **1987**, 20, 729−739. (d) Millaud, B.; Strazielle, C. *Polymer* **1979**, 20, 563−570. (e) Destri, S.; Porzio, W.; Dubitsky, Y. *Synth. Met.* **1995**, 75, 2536−2540. (f) Amari C.; Pelizzi C.; Predieri G.; Destri S.; Porzio W. *Synth. Met.* **1995**, 72, 7−12.

(2) (a) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. *Phys. Rev. Lett.* **1979**, 42, 1698−1701. (b) Curan, S.; Stark-Hauser, H.; Roth, S. *Handbook of Organic Conductive Molecules and Polymers;* Nalwa, H. S., Ed.; John Wiley & Sons: New York, 1997; Vol. 2, p 1. (c) Karasz, F.; Kapistrain, J. D.; Gagnon, D. R.; Lenz, R. W. *Mol. Cryst. Liq. Cryst.* **1985**, 118, 327−333. (d) Kwarnström, C.; Ivaska, A. *Handbook of Organic Conductive Molecules and Polymers;* Nalwa, H. S., Ed.; John Wiley & Sons: New York, 1997; Vol 4, p 487.

(3) Yang, C.-J.; Jenekhe, S. A. *Chem. Mater.* **1991**, 3, 878−887.

(4) Park, S.-B.; Kim, H.; Zin, W.-C.; Jung, J. C. *Macromolecules* **1993**, 26, 1627−1632.

(5) (a) Weaver, M. S.; Bradley, D. D. C. *Synth. Met.* **1996**, 83, 61−66. (b) Fischer, W.; Stelzer, F.; Meghdadi, F.; Leising, G. *Synth. Met.* **1996**, 76, 201−204.

(6) Yang, C.-J.; Jenekhe, S. A. *Macromolecules* **1995**, 28, 1180−1196.

(7) (a) Wang, C.; Shieh, S.; LeGoff, E.; Kanatzidis, M. G. *Macromolecules* **1996**, 29, 3147−3156. (b)Olinga, T. E.; Destri, S.; Botta, C.; Porzio, W.; Consonni, R. *Macromolecules* **1998**, 31, 1070−1078.

(8) Amari, C.; Pelizzi, C.; Predieri, G.; Destri, S.; Porzio, W.; Einsiedel, H.; Menges, B.; Mittler Neher, S. *J. Mater. Chem.* **1996**, 6, 1319−1324.

(9) Elandaloussi, E. H.; Frère, P.; Richomme, P.; Orduna, J.; Garin, J.; Roncali, J. *J. Am. Chem. Soc.* **1997**, 119, 10774−10784.

(10) Bolognesi, A.; Porzio, W.; Zhuo, G.; Ezquerra, T. *Eur. Polym. J.* **1996**, 32, 1097−1103.

(11) Chen, S. A.; Ni, J. M. *Macromolecules* **1992**, 25, 6081−6086.

(12) Destri, S.; Khotina, I. A.; Porzio, W. *Macromolecules* **1998**, 31, 1079−1086.

(13) El-Sheikeil, A. G.; Hamid, S. M. K.; Alì, D. A. *Polym. Bull.* **1997**, 39, 1−7.

(14) Daust, G.; Leclerc, M.; *Macromolecules* **1991**, 24, 455−459.

(15) Huckerby, T. N. *Tetrahedron Lett.* **1971**, 38, 3497−3500.

(16) Scrowston, R. M. *Thiophene and its derivatives;* Gronovitz, S., Ed.; J. Wiley & Sons: New York, 1986; Vol. III, Chapter III, pp 342−343.

(17) Aydin, R.; Loux, G. P.; Günter, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 449. Lemieux, R. U.; Nagabushan, T. L.; Paul, B. *Can. J. Chem.* **1972**, *50*, 773−776. Delbaere, L. T. J.; James, M. N. G.; Lemieux, R. U. *J. Am. Chem. Soc.* **1973**, *95*, 7866−7875. Hamer, G. K.; Balza, F.; Cyr, N.; Perlin, A. S. *Can. J. Chem.* **1978**, *56*, 3109−3115.

(18) Parella, T.; Sànchez-Ferrando, F.; Virgili, A. *Magn. Reson. Chem.* **1997**, *35*, 30−34.

(19) Tvaroška, I.; Mazeau, K.; Blanc-Muesser, M.; Lavaitte, S.; Driuez, H.; Taravel, F. R. *Carbohydr. Res.* **1992**, *229*, 225−231.

(20) Tvaroška, I.; Hiricovìni, M.; Petràkovà, E. *Carbohydr. Res.* **1989**, *189*, 359−362.

(21) De Marco, A.; Zetta, L.; Consonni, R.; Ragazzi, M. *Tetrahedron* **1988,** *44*, 2329−2338.

(22) Mathieson, D. W. *Nuclear Magnetic Resonance for Organic Chemists*; Academic Press: London, 1967; pp 31−32.

(23) For nomenclature of compounds see Schemes 2 and 3.

MA9811932