# Synthesis and Characterization of 3-Hexyl Multisubstituted Thienylene−Phenylene Polyazomethines

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*Received May 7, 1997; Revised Manuscript Received December 9, 1997*

ABSTRACT: The synthesis and characterization of the series of polymers constituted by the periodic alternation of thienylenic and phenylenic moieties linked by azomethines groups are reported. The chemical structures were determined by $^1$H NMR, FT-IR, mass, and GPC analyses; while the electronic properties in the neutral state were studied by UV−vis spectroscopy in both solution and the solid state. Thermal characterizations, performed on the polymer series, using TG and DSC analyses indicated stability up to 400 °C and no melting point also due to a postpolymerization process. The solid-state aggregation was investigated by XRD spectroscopy, revealing for the six-thienylenic-ring term a semicrystalline arrangement, after a proper annealing together with a nematic mesophase at temperatures higher than 180 °C.

## Introduction

In recent years polythiophene (PT) and its derivatives have been the subject of a large amount of studies resulting in the preparation of suitable materials for many applications in electronic devices such as LEDs, FETs (field effect transistor), and so forth[1−3]

Aside from polyaniline, which has been studied since 1985, recently polymers with double-bonded nitrogen atoms in the polymer chain have attracted major consideration. In fact both polyazines and polyazomethines have been prepared by several groups.[4−7]

Aiming to prepare organic multiple-quantum-wells, we have already prepared and studied a series of polyazomethines, evidencing an electronic confinement; however we did not succeed in definitely showing their superlattice behavior.[7a,8,9] These materials have low molecular weight (MW) and a certain solubility either in strong acids or by complexation with Lewis acids.

On the basis of calculations in the tight-binding approximation[10] and the VEH approach[11] on block conjugated copolymers, the quantum size effect in such systems was predicted provided that both wells and barriers have adequate length. In this view we prepared a series of copolymers with increasing length of the wells (thienylenic sequence). Moreover recent results shown by Jenekhe[12] indicate that strong interchain interactions due to the chain aggregation in bulk materials prevent the observation of multiple-quantum-wires/wells.

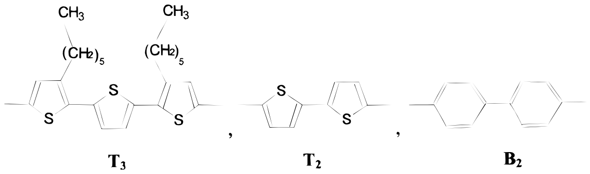
We therefore prepared the series of analogous alkyl-substituted polymers with the joint aims of decreasing the interchain interaction and varying the size of the well, to reach intrachain confinement.

Actually, since our wells are segments of thienylenic rings, it turns out that materials constituted by a sequence of thienylenic residues equal to or larger than six are difficult to manage without substitution expecially in the preparation of a copolymer.

Here we report on the synthesis and characterization of a series of multi-hexyl substituted polyazomethines constituted by three, six, or eight thienylenic units regularly alternated with biphenylenic moieties (see Chart 1). In the following paper some mechanistic considerations on this polycondensation will be reported, definitely accounting for the presence of a different configuration at imine linkages.[13]

### Chart 1

Polyazomethines
P1= $(T_3CH{=}NB_2N{=}CH)_n$
P2= $(T_3T_3CH{=}NB_2N{=}CH)_n$
P3= $(T_3T_2T_3CH{=}NB_2N{=}CH)_n$



Indeed other substituted polyazomethines have been prepared based either on phenylene[5a,b,14] or on thienylene and phenylene residues, specifically a copolymer of a terthienylene substituted on the inner ring with 1,4-diaminophenylene.[7b]

## Experimental Section

All reactions involving air- and water-sensitive materials were performed in dried glassware under nitrogen.

**Materials and Measurements.** Polymerization solvents, *N*-methyl-2-pyrrolidone (NMP, 99% Aldrich), hexamethylphosphoramide (HMPA, 99% Aldrich), and the water-absorbing reagent-lithium chloride (99% Aldrich)- were used as received.

The NMR solvents deuterated tetrachloroethane (DTCE; 99.5% Merck) and $CDCl_3$ (99.95%, Merck) were used without any purification.

Among the polycondensation monomers (1,1′-biphenyl)-4,4′-diamine was obtained from its hydrochloride (99% Fluka) by dissolution in water and reprecipitation in aqueous ammonia; then it was stored under nitrogen.

5,5″-Diformyl-3,3″-dihexyl-2,2′:5′,2″-terthiophene (**I**), 5,5′′′′′-diformyl-3,3″,4‴,3′′′′′-tetrahexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′-sexithiophene (**II**), 5,5′′′′′′′-diformyl-3,3″,4′′′′′,3′′′′′′′-tetrahexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′:5′′′′′,2′′′′′′:5′′′′′′,2′′′′′′′ -octithiophene (**III**) were prepared according the routes described in ref 15 and used after drying.

**Polymer Synthesis.** All the polymers were prepared by solution polycondensation in a dry mixture of HMPA and NMP (20 + 20 mL) containing 1 g of lithium chloride.

S0024-9297(97)00642-6 CCC: $15.00

**Table 1. Polymer Preparation from Dialdehydes and a Diamine**[a]

| HOCTnCHO | $H_2NB_xNH_2$ | polyazomethine | soluble in $CHCl_3$ | residue in $CHCl_3$ |
|---|---|---|---|---|
| **I** ($n = 3$) | $B_2$ | P1 | 70 | 30 |
| **II** ($n = 6$) | $B_2$ | P2 | 60 | 40 |
| **III** ($n = 8$) | $B_2$ | P3 | 60 | 40 |

[a] T and B are specified in Chart 1.

**I** (0.105 g, $2.23 \times 10^{-4}$ mol) or 0.199 g of **II** ($2.23 \times 10^{-4}$ mol) or 0.234 g ($2.23 \times 10^{-4}$ mol) of **III** together with 0.041 g ($2.23 \times 10^{-4}$ mol) of diamine was used. The mixture was stirred at 130 °C for 25 h. During the reaction, the medium was an homogeneous solution whose color changed from orange (**I** and **II**) to red for P1 and P2 and from red (**III**) to dark red for P3. The polymer P1 was collected by precipitation in 400 mL of methanol in order to remove the residual **I** and LiCl. Polymers P2 and P3 were precipitated by pouring the solutions in 400 mL of hot acetone and washed several times with the same solvent in order to remove traces of **II** and **III**, which are insoluble in methanol but soluble in acetone, cold for **II** and hot for **III**. P2 and P3 were subjected to a further washing with methanol to remove LiCl, and all the polymers were then purified by an overnight extraction with refluxing methanol in a Soxhlet apparatus and subsequently with chloroform, thus obtaining chloroform-soluble and -insoluble fractions, whose amounts depended on the thienylenic ring number of the parent dialdehyde. After the excess chloroform was removed by using rotary evaporation, P1, P2, and P3 polymers were reprecipitated with methanol using centrifugation and filtration to eliminate the solvents.

The weight fractions were calculated after drying the materials at 70−80 °C in a vacuum overnight.

FTIR spectra were recorded on a Bruker IFS 48 instrument; DSC experiments were performed on a Perkin-Elmer DSCII apparatus. UV−vis spectra were obtained using a Varian-Cary 2400 instrument; optical microscopic observations were carried out on a Reichert microscopy apparatus coupled with a Mettler FP5 hot stage. $^1H$ NMR spectra were obtained on Bruker 270-MHz and DMX 500-MHz spectrometers.

XRD experiments were carried out with a Siemens D-500 computer-controlled apparatus, with Soller slits and a graphite monochromator (002 direction), using Cu K$\alpha$ radiation.

GPC measurements were carried out on a Waters SEC system consisting of a 600E pump, a 717 autosampler, a 410 differential refractometer, and 490 UV detectors. The column was a Ultrastyragel Waters (100 Å pore size).

MALDI measurements were performed on the HP G2025A MALDI-TOF system (Hewlett-Packing, Palo Alto, Ca), operating in positive linear mode, equipped with a LeCroy 9350AM oscilloscope. Ions formed by a pulsed UV laser beam (nitrogen laser $\lambda = 337$ nm) were accelerated at 28 keV. For all the experiments $\alpha$-hydroxycinnamic acid was used as a matrix (100 mm in methanol/water 50/50 v/v).

Samples were dissolved in tetrachloroethane ($10^{-5}$ M); 1 $\mu$L of the matrix solution was deposited on a golden-plated sample holder and dried under vacuum. One microliter of the sample solution was deposited on the top of the matrix layer and dried under vacuum before introduction into the mass spectrometer. External calibration was made using the HPG2053A protein standard solution and daily controlled.

Raman scattering measurements were obtained using a Bruker IF66+FRA100 Fourier Transformer spectrometer exciting with the 1064-nm line of a Nd:YAG laser at room temperature. Photoluminescence has been measured with a double monochromator with a GaAs photomultiplier exciting with the lines of an $Ar^+$ ion laser, at room temperature.

## Results and Discussions

The polycondensation reaction gave almost quantitative yields of materials, which were partially soluble in chloroform, as reported in Table 1.

The polymers have been characterized by FTIR analysis, as reported in Figure 1. The spectra show, aside from the typical vibrations of alkylic side chains, the characteristic bands of groups already found in unsubstituted polymers.[8] Namely, the carbonyl-group band is observed at 1664 $cm^{-1}$ (C=O stretching), indicating the low degree of polymerization attained; the absorption of the imine linkage (C=N stretching) at 1610 $cm^{-1}$ is also detected. Moreover, for the series P1−P3 the relative increase of the peak attributed to CH out-of-plane deformation of $\alpha$-linked thienylene moieties in the range 791−798 $cm^{-1}$ can be observed.

As already found in the unsubstituted polyazomethine series,[8] upon treatment with either strong or Lewis acids, a complexation reaction takes place. In Figure 2 the FTIR spectra of P2 treated with acids (*p*-toluenesulfonic acid, $FeCl_3$, and $H_2SO_4$) are reported. Broad absorption bands attributed to $^+N-H$ stretching are present in the 2500−2600-$cm^{-1}$ range in the spectra of these protonated polymers (see Figure 2A and C). All the spectra show a dramatic modification of the 1000−1400-$cm^{-1}$ region due to the formation of strong infrared active (IRAV) bands, mapping the doping process.[16] Moreover in all the spectra there appears a drift in the 4000−2000-$cm^{-1}$ range, indicative of bipolaron formation,[7a] stronger in the $FeCl_3$-treated P2 sample, due to a higher doping level.

The P1 sample could not be doped either with acids or with $I_2$; this finding is related to the impossibility of short thienylenic segments supporting charged species.

In Figure 3 the electronic absorption spectra of the polymer series in $CHCl_3$ solution are shown. The intense peak close to 2 eV is due to the $\pi-\pi^*$ transition of thienylenic segments; another weak and broad absorption, characteristic of polythienylenic systems,[17] appears at 4.4−4.6 eV, and its intensity increases along the series; finally a very weak shoulder is detectable at ~5.5 eV together with another absorption around 6 eV, both likely due to phenylene segments.

It is noteworthy that the weak peak due to the individual thienylenic ring is centered at different energies with respect to those of unsubstituted oligomers[9] and dialdehydes[15] because of conjugated imine linkages, while the peaks attributed to phenylenic blocks well match the absorptions of biphenylene. In Table 2 the derived values of the absorption maximum and $E_g$ are reported; a clear trend (lower energies) is evident on increasing the number of thienylenic residues in the copolymer (increased conjugation pathway).

In the electronic absorption spectra of $FeCl_3$-treated P2 samples the appearance of two peaks centered at about 1.6 and 0.8 eV is assigned to the doping process, namely polaron formation.[18a]

Raman characterizations have been performed both in solution (carbon disulfide) and on solid films. The presence of side chains enlarges the peak attributed to the C=C stretching of the thienylenic portion with the appearance of two shoulders and causes a new peak to appear at lower energy. As shown in Figure 4, the ratio between the intensity of the C=N stretching at 1563 $cm^{-1}$ and that of the C=C stretching of the thienylenic part decreases in the series T6B2 prepared by coupling,[8] T6B2 by polycondensation,[18b] and P2, in accordance with the increased molecular weight through the series. The peak close to 1500 $cm^{-1}$, related to vibrational confinement within the thienylenic blocks of the copoly-

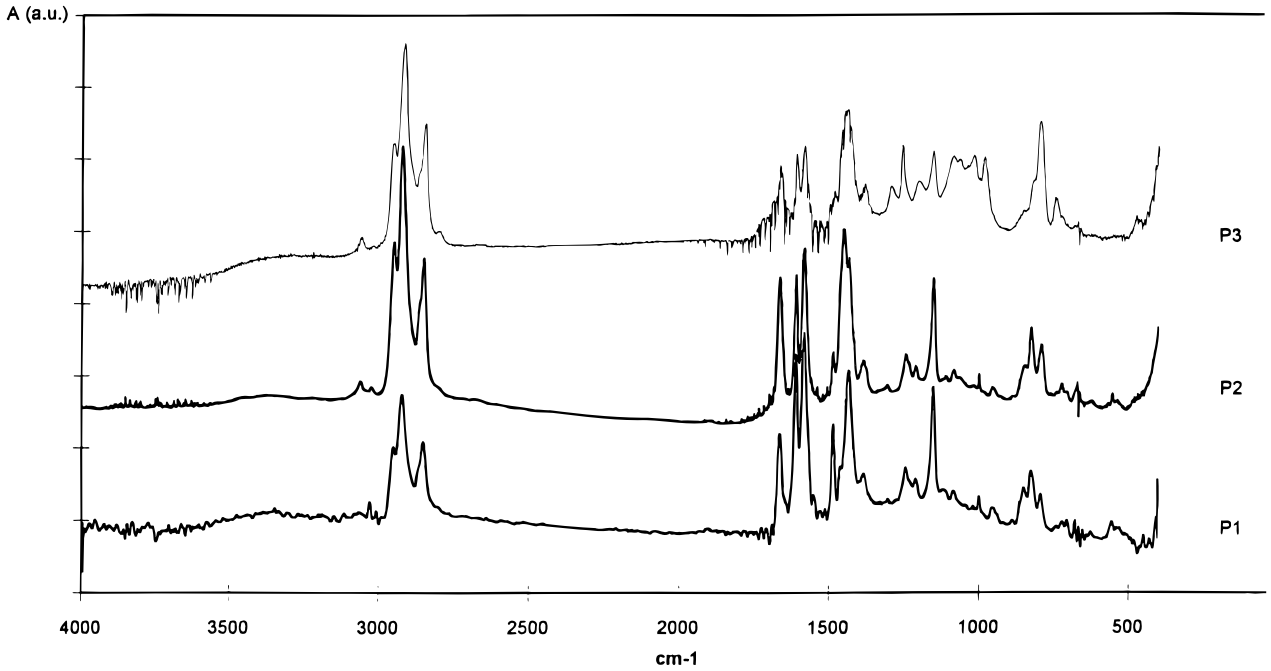


**Figure 1.** FTIR spectra of P1, P2, and P3.

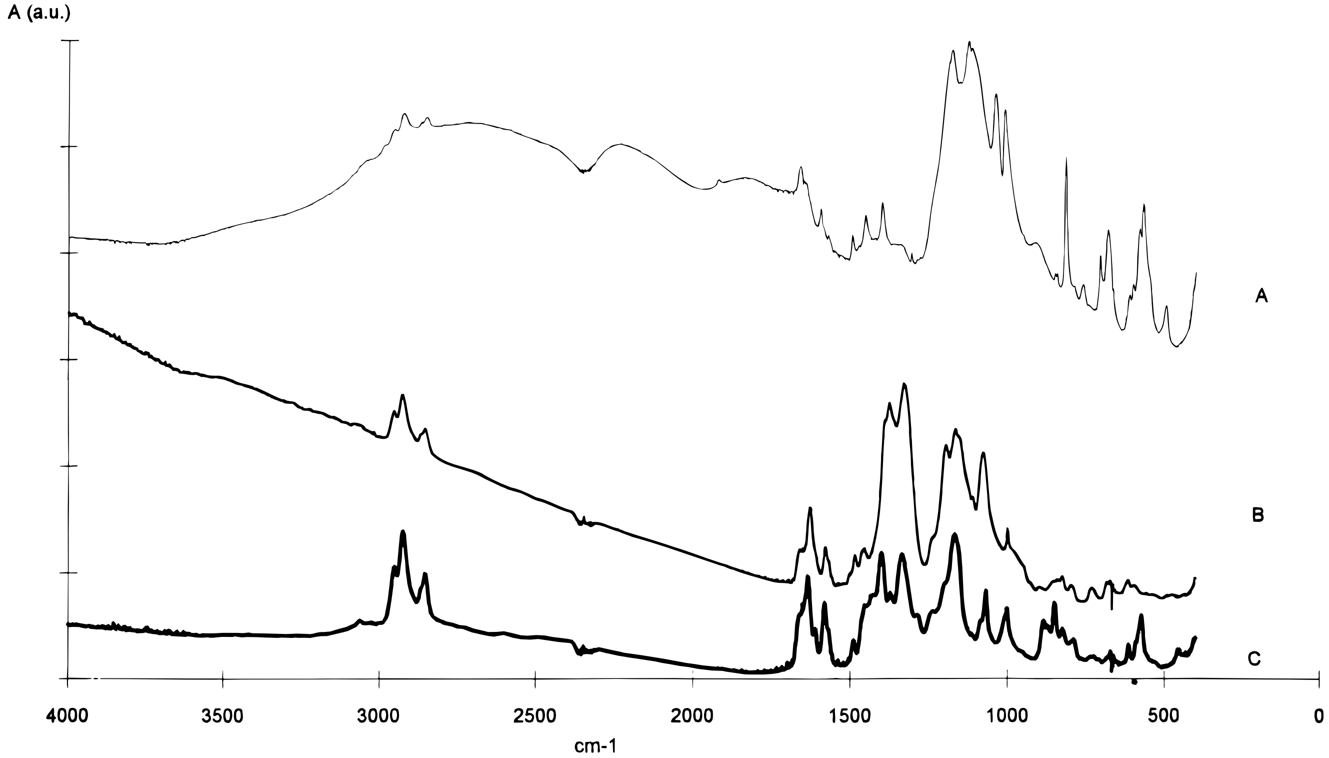


**Figure 2.** FTIR spectra of P2 samples treated with *p*-toluenesulfonic acid (A), $FeCl_3$ (B), and $H_2SO_4$ (C).

mer, is progressively shifted toward higher energy with the increasing of the periodicity (MW), indicating an improved confinement.

Figure 5 shows the photoluminescence (PL) spectra of dilute TCE solutions of polymers P1−P3. A sensitive shift toward lower energies is observed on passing through the series, displaying PL emissions turning from blue-green to red.

Molecular characterizations of the copolymer were carried out by GPC analysis (polystyrene as a reference) and by MALDI-TOF measurements. The results are summarized in Table 3. Note that the results obtained by the two techniques are referred to specimens in different phases; in fact the former is related to solutions while the latter is performed on solid-state samples.

The differences observed are not surprising because it has recently been observed that MALDI-TOF strictly agrees with other techniques only in the case of a very narrow degree of polymerization (DP);[19] however, the values of $M_n$ are comparable and show that in all cases we are dealing with polymers having a low DP, although the derived DP values from GPC analysis show a polyazomethine, based on the terthiophene moiety, at

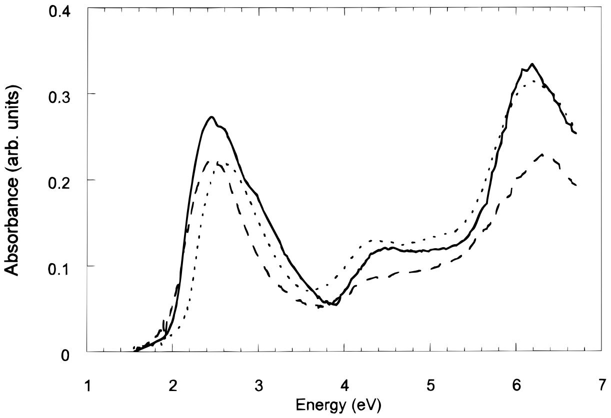


**Figure 3.** Optical absorption spectra of P1 (dotted line), P2 (solid line), and P3 (dashed line) spin-coated films, at room temperature.

**Table 2. UV−Vis Absorption Maximum and $E_g$ (solid film) for the Polymer Series (eV)**

| sample | $CHCl_3$ solution | thin film | $E_g$ |
|---|---|---|---|
| P1 | 2.77 | 2.64 | 2.07 |
| P2 | 2.70 | 2.50 | 2.0 |
| P3 | 2.65 | 2.45 | 1.95 |

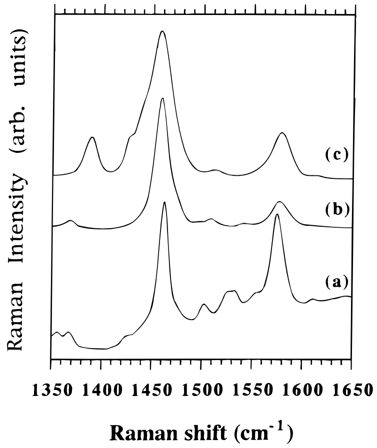


**Figure 4.** Raman spectra of T6B2 (cast film) prepared by coupling (a), polycondensation (b), and P2 (c). Excitation wavelength 1064 nm, at room temperature.

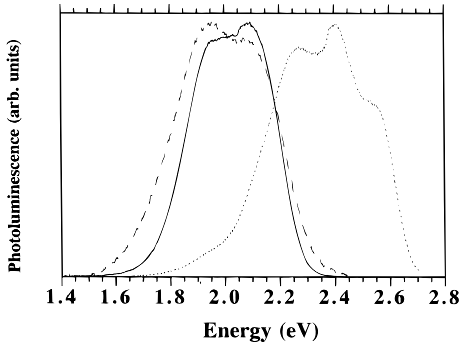


**Figure 5.** Photoluminescence of P1 (dotted line), P2 (solid line), and P3 (dashed line) tetrachloroethane solutions at room temperature.

**Table 3. GPC and MALDI-TOF Analyses on Polymers**

| | Mn | Mw | DP |
|---|---|---|---|
| | GPC (refractometer detector) | | |
| P1 | 10300 | 21000 | 12 |
| P2 | 3700 | 7100 | 4 |
| P3 | 4300 | 15300 | 4 |
| | Mass (Matrix-Assisted Laser Desorption Ionization) | | |
| P1 | 6700 | | 9 |
| P2 | 7000 | | 7 |
| P3 | 3700 | | 4 |

higher molecular weight than that one recently reported.[7b]

**Thermal Characterizations.** DSC and TG analyses were performed on crude polymer samples. The polymers are stable up to almost 400 °C; at this temperature a weight loss of less than 5% is evident, except for syn-rich samples, where the loss is more pronounced (8% loss).[14] Over this limit an increasing loss is detected up to 500 °C, where almost 50% of the pristine sample has been lost. A similar behavior was observed in unsubstituted polymers;[7a] hence, the presence of alkyl side chains does not seem to influence the polymer stability. DSC findings are more complex; in fact two endothermic peaks are detected. The first—onset at 62 °C—is attributable to a glass transition, that is, to alkyl side-chain disordering already found in comb-like systems;[20] the second—broad and showing the onset at 181 °C—is interpreted as mesophase formation (see XRD analysis below). The ratio between the energies involved in the first and second endothermic processes, about 0.1, is quite consistent with this attribution. The optical microscopy observations are in agreement with these findings; in fact the progressive alkyl chain motions result in thermochromic effects, especially near 180 °C, while no melt is evident up to 300 °C. On the other hand it must be noted that in polymeric systems having flexible side chains the endothermic peak, attributable to melt, is weak as compared with other transitions (i.e. mesophase) or even undetected.[20]

The attempt to detect the melting point after a proper annealing process at different temperatures (200 °C or 300 °C) failed, possibly due a postpolymerization process already found in polyazomethine systems,[21] as detected from the disappearance of C=O stretching (1663 $cm^{-1}$) in the FTIR spectrum.

**NMR Experiments.** To attain the complete determination of the molecular structure, $^1H$ NMR spectra were recorded in different solvents and at different fields. In Figure 6 the proton spectrum of T6B2 (P2 sample) in $CS_2$ at 270 MHz is reported as an example. The peaks centered at 1.24, 1.5−2.0, and 3.08 ppm are attributed to aliphatic side-chain protons (methyl, the first signal, and methylenes, the others, respectively), while that at 10.05 ppm is attributed to the aldehydic proton of the end chain (proton **a** in the figure). The peaks at 8.75−8.72 ppm are assigned to the azomethinic proton in anti or syn configurations: in particular the ratio between the integrated areas of the signals due to azomethinic and aldehydic protons gives an approximate molecular weight in good agreement with GPC measurements (see Table 3). Moreover the signal at 7.77 ppm in $CS_2$—peak 11 in Figure 6—has an area comparable to that of the aldehydic proton; therefore, it should be related to the polymeric end unit.

A complete assignment in the aromatic region was achieved by performing a 2D DQF-COSY experiment at 500 MHz in DTCE. In this different solvent a very good signal resolution was attained: specifically the thienylenic proton signals centered at 7.14, 7.23, and 7.26 ppm can be explained only taking into account the low degree of polymerization. This unexpected number of signals is actually due to the effect played by the formyl group at the end unit.

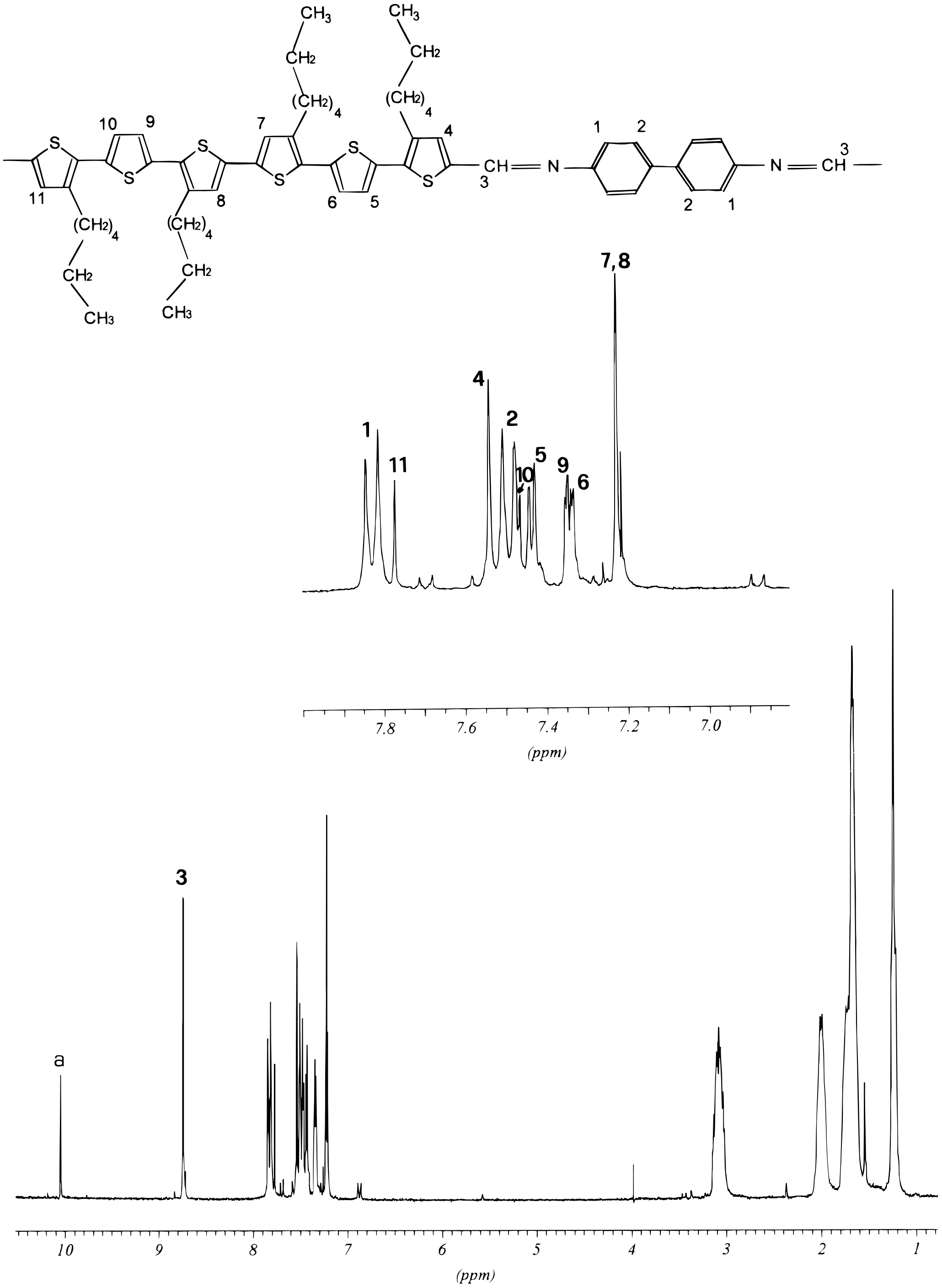


**Figure 6.** $^1$H NMR of P2 polymer in $CS_2$. In the inlet the expansion of the aromatic proton area is reported for clarity.

The model compound MAT6B2T6A[14] gives us the opportunity to appreciate the different deshielding effects exerted onto thienylenic protons by imine and formyl groups. Figure 7 shows an expansion of the aromatic region of the 2D DQF-COSY at 500 MHz, in $CDCl_3$.

The assignment is quite straightforward: in particular the two protons on the inner thienylenic rings result in one singlet at 7.05 ppm, and the proton on the outer ring holding the formyl group gives the singlet at 7.61 ppm, while the proton on the ring close to the imine bond brings about the singlet at 7.36 ppm.

Taking into account the model assignment, we can now analyze in detail the aromatic region of the polymer spectrum, where the same peaks appear, although at a different ratio between the thienylene close to the imine group and the thienylene near to the formyl group. In Figure 8 six doublets are observable; the correlation at 7.670/7.338 ppm corresponding to four protons belongs to the AA′BB′ spin system of the phenylene ring (1,2; $^3J_{HH} = 8.4$ Hz), while those at 7.268/7.141 ppm (10,9; $^3J_{HH} = 3.7$ Hz) and 7.240/7.137 ppm (5,6; $^3J_{HH} = 3.6$ Hz) must be attributed, the former, to the AB system of the protons of the inner thienylenic ring near to the formyl end group and, the latter, to another AB system of the protons on the thienylenic ring near to the imine residue. In the 1D spectrum the other weak doublets are due to the syn/anti isomers of the imine bond: the

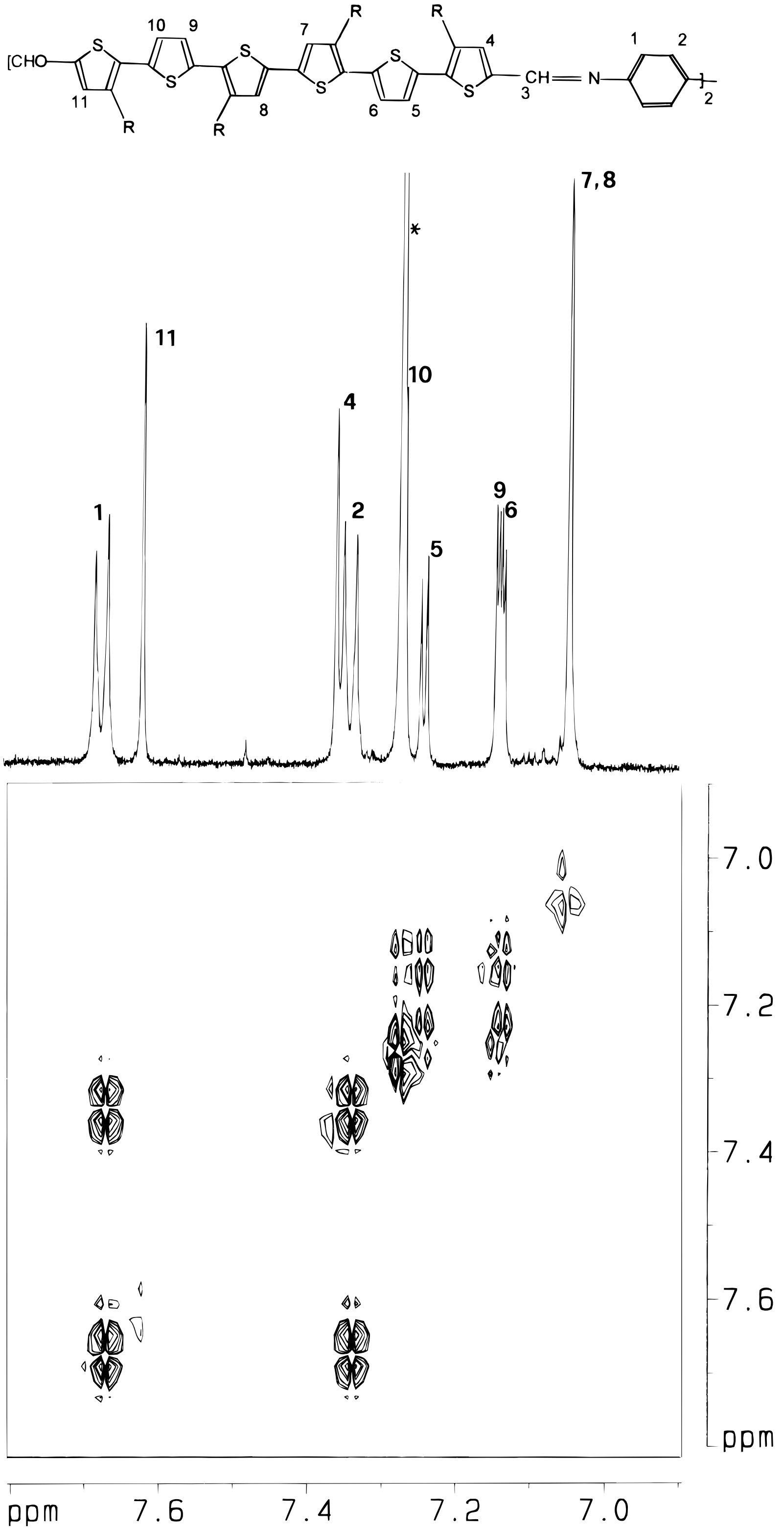


**Figure 7.** 2D DQF-COSY of model compound labeled MAT6B2T6A (see ref 19) in $CDCl_3$, the asterisk indicates the peak solvent. 2D homonuclear shift correlation with phase-sensitive mode and gradient pulses for coherent selection. Resolution enhancement functions before Fourier tranformation were used in both dimensions. Monodimensional and bidimensional spectra were acquired on a Bruker DMX 500 equipped with an INDY workstation.

correlation observed in the 2D spectrum centered at 7.669/7.312 ppm (1,2; $^3J_{HH}$ = 8.2 Hz) belonged to the AA′BB′system in an anti configuration of the two imine bonds adjacent to the phenylene residue, while the correlation at 7.561/7.264 ppm (1′,2′; $J$ = 8.1 Hz) and that at 7.443/6.748 ppm (1″,2″; $J$ = 8.37 Hz) are assigned to both anti–syn or syn–anti configurations of the two C═N bonds of the repeating unit. At variance with the spectrum reported in the following paper,[14] no peak attibutable to phenylenic protons in a syn–syn configuration can be observed, in agreement with the mechanistic considerations there dealt with. As a

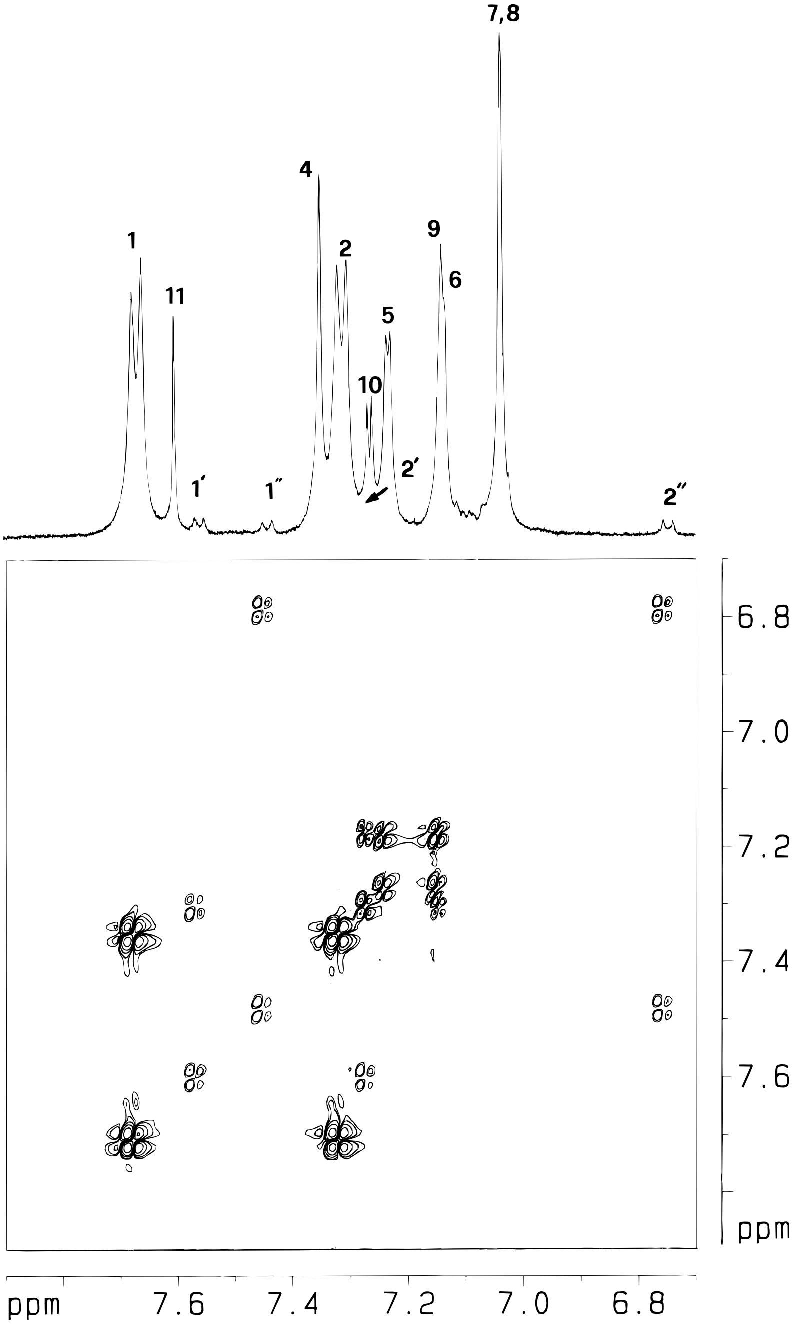


**Figure 8.** 2D DQF-COSY of P2 copolymer in DTCE. The numbering is reported in Figure 7; 1′,1″and 2′,2″indicate phenylenic protons feeling different configurations (anti/syn) of the closest azomethine bonds. 2D homonuclear shift correlation with phase-sensitive mode and gradient pulses for coherent selection. Resolution enhancement functions before Fourier tranformation were used in both dimensions. Monodimensional and bidimensional spectra were acquired on a Bruker DMX 500 equipped with an INDY workstation.

matter of fact, considering the low degree of polymerization of the sample here examined, hence a low syn content, a syn−syn sequence is highly unlikely.[14]

**XRD Experiments.** Spectra were recorded on both pristine and thermally annealed samples of the polymer series. Independently of the treatment to which the samples were subjected, the XRD profiles are generally poor, indicating a low degree of crystallinity attainable. Only the term P2 reveals a certain aptness to crystallization, after a proper thermal treatment, as shown in Figure 9; therefore, we tried to perform a structural analysis on it.

A significant variation of the *d* spacings as a function of the thermal treatment was detected, and it has been attributed either to the conformational changes of alkylic side chains or to the presence of a syn configuration at azomethine residues, which prevents a closer chain packing.[14]

As a matter of fact XRD investigations revealed the presence of a nematic mesophase at temperatures higher than 180 °C in agreement with DSC analysis.

Annealing at 200 °C for 30 min and then slow cooling (~1 °C/min) yielded a sample suitable for structural analyses.

On the basis of the structural investigations on polythiophene,[22] poly(3-alkylthiophene),[20 b,c−23] and unsubstituted T3B2[24] and T6B2[25] polymers, we attributed the mid-2$\theta$-range to lateral packing (equatorial peaks) and the low-angle region to side-chain arrangement (interdigitation in comblike systems). By assuming

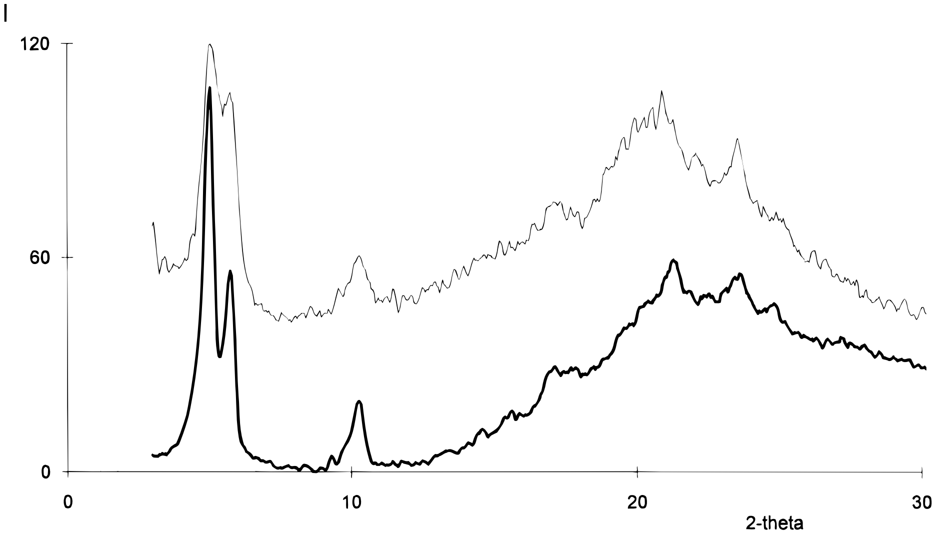


**Figure 9.** XRD of P2 polymer as synthesized (top) and after an annealing at 200 °C (bottom).

**Table 4. Unit Cell Parameters of P2 Polymer in the Assumption of Pseudo-orthonormal Axes and XRD *d*-Spacings (Å)[a]**

| | |
|---|---|
| *T* (°C) | 25 |
| *a* (Å) | 17.20(5) |
| *b* (Å) | 4.25(2) |
| *c* (Å) | 37.0(1) |
| | 90(2)° |
| $d_c$ ($Z = 2$) (g·cm$^{-3}$) | 1.26 |

| reflection | $D_{obs}$ |
|---|---|
| 100 | 17.2 |
| 101 | 15.5[b] |
| 200 | 8.6 |
| 303 | 5.14[b] |
| 010 | 4.25 |
| 112 | 4.02 |
| 210/211 | 3.78 |

[a] Due to insufficient data and the variety of *d*-spacings as a function of the thermal treatment, in the determination of the present unit cell three more very broad and weak peaks were not taken into account. [b] These diffraction effects could be attributed to a different mesophase readily developed by thermal annealing of samples containing large amounts of the syn conformation at the azomethine residue; see text.

conventional bond distances and angles, we adopted a reasonable model for the P2 polymer, that is, an antiplanar conformation for adjacent thienylene residues and an extended planar conformation for alkylic side chains, while for the azomethine residue the two possible conformations (syn/anti) were considered.

Using MACROMODEL,[26] it was possible to evaluate a tentative molecular model suitable to indexing all the diffraction intensities as listed in Table 4.

From the derived unit cell a density value (1.26 g·cm$^{-3}$) close to the observed one—1.24 g·cm$^{-3}$, measured by a flotation method—was calculated. This observation is in agreement with the value (1.26 g·cm$^{-3}$) found for thienyl-based polyazomethine.[7b]

This structural attribution is similar to the one already published for thienyl-based polyazomethine,[7b] albeit in the present case the repeating unit spacings could not be directly observed due to the amount of disordered material.

The aptness of the P2 term for crystallization is comparable to similar behavior observed in poly(3-alkylthiophene)[20b,c] and is attributed to a peculiar width/length ratio of the polymer.

From the peak width an average value of crystallite size (∼220 Å) was derived, corresponding to a coherence along the interdigitation direction of ∼15 unit cells, a value remarkable on considering the in-chain syn/anti configurations, hence the copresence of different chain bending.

## Conclusions

The preparation and characterization of a series of soluble polyazomethines in which a modulation of high- and low-energy-gap segments is present, with different well lengths, are reported. The alkyl side chain insertions allow us to increase the molecular weight of all the polymeric terms and the well size up to eight thienylenic moieties, nevertheless the main-chain interaction is not enough hampered. Despite the attempt to reduce such interaction, using blends in PMMA or sol-gel in siloxane or blends in biphenyl (which represents the high-gap segment in the copolymer[12]), we could not definitely clarify their multiple-quantum-well nature by examining PL and photoluminescence excitation (PLE) spectra of very diluted blends. Moreover the presence of two configurational situations (syn/anti) of the imino linkage in the polymeric chain is observed for the first time. In the series only the P2 term displays any aptness for crystallization upon proper thermal treatment, which could be related to an optimal length/width ratio of the polymer, as already observed for poly(3-alkylthiophene) systems.[20b,c]

From optical characterizations on P2, the first term of the series which supports charged species, the increased electronic confinement as a function of the enhanced degree of polymerization appears evident. By the modulation of well length, the photoluminescence tuning along the overall range of the visible is obtained.

Since phenylene-based polyazomethine was prepared by deposition in high or ultrahigh vacuum,[14,27] we plan to prepare these polymers also in such a way; their synthesis via the usual chemical route will allow us to compare the behavior of samples prepared by different ways with respect to both electronic and optical properties.

**Acknowledgment.** This research has been partially supported by Italian Oriented Project “Materiali Innovativi” of C.N.R. and by HCM-SELMAT project of EEC.

We are also indebted to Dr. L. Zetta for NMR discussions. We also thank Dr. R. Mendichi and Mr. A. Schieroni for GPC measurements and Dr. D. Favretto for MALDI-TOF analysis.

## References and Notes

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MA970642F