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3-Hexyl Tetra-Substituted Sesquithienylene−Phenylene Polyazomethines with High Molecular Weight. Mechanistic Considerations

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ABSTRACT: The synthesis and characterization of copolymers constituted by the periodic alternation of six thienylenic and two phenylenic moieties linked by azomethine groups are reported. The azeotropic polycondensation used for this preparation yields higher molecular weight but sterically more disordered copolymers. By ^{1}H NMR experiments syn and anti isomers at imine linkages were evidenced. Mechanistic considerations on the different synthetic routes followed in polyazomethine preparation imply the lack of a polar control on the formation of the syn isomer. The capability of the substituents to rotate around the C−N bond of the intermediate is related to the overall bulkiness of the molecules. Due to their molecular weight, optical quality films were obtained either free-standing or spin-coated from tetrachloroethane solutions. The solid-state aggregation was investigated by XRD techniques, indicating for properly annealed samples some liquid crystal character, in agreement with microscopy observations; in fact a smectic or nematic arrangement was detected as a function of syn content. A proper control of anti/syn content in the copolymer allows a noticeable tuning in the photoluminescence spectra.

Introduction

Polymers having imine groups inside the chain have been the object of several works since 1923[1] to study mostly their thermal stability and the electrical properties of metal chelated products.[2] More recently thermotropic liquid crystal[3] and semiconducting materials[4] based on polyazomethines have been prepared; finally the synthesis of new stable systems received remarkable impetus from their relevant optoelectronic properties.[5,6]

The preparation and characterization of a series of *n*-hexyl-substituted polyazomethines, constituted by the regular alternation of *n*-thienylene (T) (*n* = 3, 6, 8) and phenylene (B) moieties, have been reported in the preceding paper[7] (hereafter referred to as paper 1). These polymers as well as the related polyazines can find an application in electronic and photonic devices such as LEDs, FETs, and wave guides.[7−9]

In paper 1 we have shown that, according to the experimental conditions, the formation of two different isomers at the imino linkage occurs. This fact strongly affects the structural order, the thermal properties, and, among the optical properties, the photoluminescence of the materials. To our knowledge this is the first example evidenced in polyazomethine systems; albeit other authors[5,6] presented ^{1}H NMR spectra of polyazomethines, from which one could derive the anti/syn presence.

The chemical structure of poly(3,3″,4‴,3‴″-tetrahexyl-α-sexithienylene-azomethine-1,4′-biphenylene-azomethine) (T6B2) is shown in Figure 1 for clarity.

In the same figure the chemical structures of poly(3,3″-dihexyl-α-terthienylene-azomethine-1,4′-biphenylene-azomethine) (T3B2) and of poly(3,3″,4‴″,3‴‴-tetrahexyl-α-octithienylene-azomethine-1,4′-biphenylene-azomethine) (T8B2) are shown. In the following the analog of T3B2 without hexylic groups is indicated as T3B2U, whose chemical structure is reported in Figure 1 too.

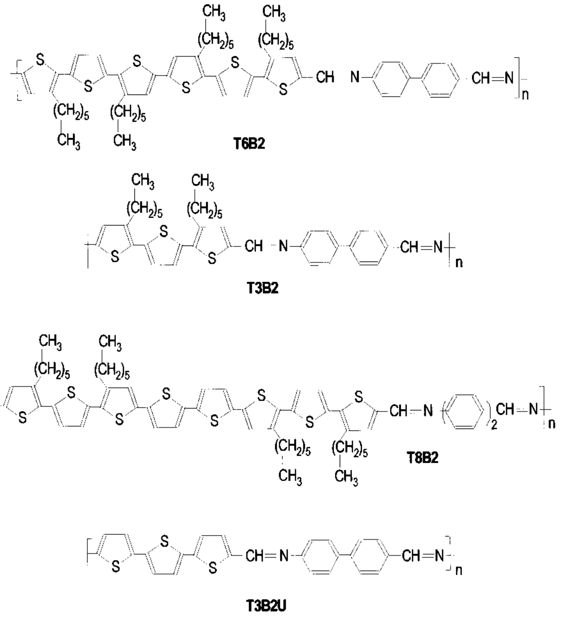


Figure 1. Molecular structure of polymers.

Moreover the model compounds α-terthienylene-azomethine-1,4′-biphenylene (MT3B2U), α-terthienylene-azomethine-1,4′-biphenylene-azomethine-α-terthienylene (MT3B2T3U), 5-bromo-3,3″-dihexyl-α-terthienylene-azomethine-1,4′-biphenylene-azomethine-5″-bromo-3,3″-dihexyl-α-terthienylene (MBrT3B2T3Br), and 5-formyl-3,3″,4‴,3‴″-tetrahexyl-α-sexithienylene-azomethine-1,4′-biphenylene-azomethine-5‴″-formyl-3,3″,4‴,3‴″-tetrahexyl-α-sexithienylene (MAT6B2T6A) have also been prepared, and their chemical structures are shown in Figure 2.

This paper reports both on the properties of high-molecular-weight polyazomethines and on the mechanism of isomer formation considering solvent, the pH of the reaction solution, the nucleophile power of the

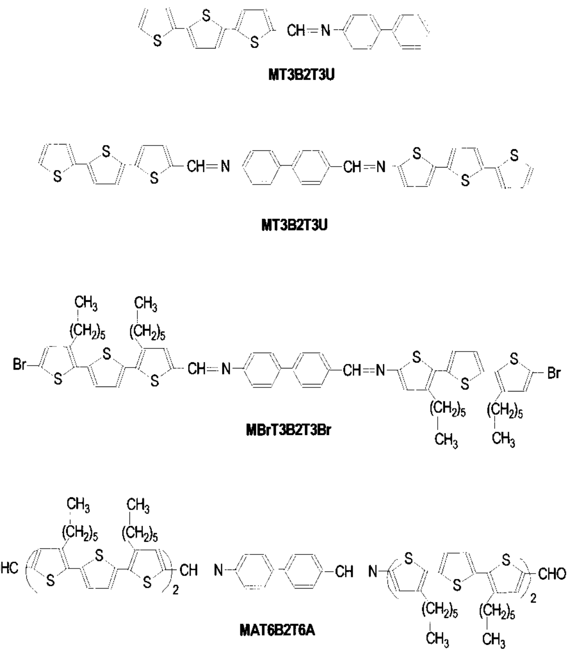


Figure 2. Molecular structure of model compounds.

growing chain, and other parameters. Among them it seems that the steric hindrance of the substituents on the C−N linkage of the intermediate is not the key factor determining the anti/syn formation, while the overall molecular size plays a relevant role in governing the isomer ratio, as displayed by comparison of model compounds and polymers.

Among the properties we have considered, the increased molecular weight of the polymers enhances the processability of the materials; in fact free-standing films can be obtained. Finally the photoluminescence range is tunable as a function of anti/syn content.

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), 1,2-dimethyl-2-imidazolidinone (MI, 98% Aldrich), hexamethylphosphoramide (HMPA, 99% Aldrich), and the water-absorbing reagent—lithium chloride (99% Aldrich)—were used as received.

Both dimethylformamide (DMF, Aldrich) and dimethyl sulfoxide (DMSO, Aldrich) were distilled under nitrogen over calcium hydride. Tetrachloroethane (TCE, Carlo Erba) and the perdeutero solvent (DTCE, Merck) were used as purchased.

Silica gel 60 (Merck) 230−400 mesh was used in flash cromatography purification.

Among the polycondensation monomers (1,1′-biphenyl)-4,4′-diamine (hereafter referred to as benzidine) 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**), and 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 10 and used after drying.

Model Synthesis. Preparation of MT3B2U. 5-Formyl-2,2′:5′,2″-terthiophene (0.123 g; 4.4 × 10^{-4} mol), 0.075 g (4.4 × 10^{-4} mol) of 4-aminobiphenyl, and 0.084 g (4.4 × 10^{-4} mol) of *p*-toluenesulfonic acid were dissolved in DMSO (130 mL) and heated at 120 °C during 17 h in a nitrogen stream. By adding water containing Na_2CO_3, the Shiff base was precipitated and was separated by filtration. It was crystallized from ethanol/chloroform, 2/1, and checked by TLC (solid phase, Merck RP18; eluent, hexane/methylene chloride, 1/4). Yield ~30%. Higher yields (90%) were obtained using chloroform at 60 °C during 18 h. FTIR (cm^{-1}): 1611 (imine group), 1482, 795 (thiophene ring), 1580 (substituted benzene ring). Mp = 234 °C (at 2°/min). ^1H NMR δ (ppm): 8.57 (imino linkage), 7.75−7.0 (aromatic region).

Preparation of MT3B2T3U. This model compound was prepared according to the conditions reported in ref 11.

Preparation of MBrT3B2T3Br. The synthesis of this compound was performed as described below for the T6B2 polymer in a solution of 1,2-dimethyl-2-imidazolidinone. The yield of the product, after purification on a silica gel column (eluent, CH_2Cl_2/hexane, 1/1), was equal to 55%. MS(EI): *m*/*z* 1195 [M^+]. UV−vis: λ_{max} 420 nm ($CHCl_3$). FTIR (cm^{-1}): 1610 (imino group); 1457, 829 (thiophene ring), 1586 (substituted benzene ring). ^1H NMR δ (ppm): 8.55 (2H, s, azomethyne protons), 7.68 (2H, d, J = 8.3 Hz, phenylenic protons), 7.37 (2H, s, thienylenic), 7.32 (2H, d, J = 8.3 Hz, phenylenic protons), 7.22 (2H, d, J = 3.4 Hz, thienylenic), 7.06 (2H, d, J = 3.4 Hz, thienylenic), 6.94 (2H, s, thienylenic), 2.84−2.70 (8H in two m, CH_2 α-thiophene), 1.74−1.58 (8H in two m, CH_2, β-thiophene), 1.46−1.26 (12H, m, CH_2), 0.92−0.87 (12H, m, CH_3).

Preparation of MAT6B2T6A. The synthesis of this compound was performed according to the conditions reported for the previous preparation. The yield was about 10%. FTIR (cm^{-1}): 1613 (imine group); 1664 (carbonyl group); 1446, 827 (thiophene ring); 1580, 793 (para-substituted benzene ring). UV−vis: λ_{max} = 457 nm ($CHCl_3$). ^1H NMR δ (ppm): 9.85 (2H, s, CHO), 8.55 (2H, s, HC=N), 7.67 (4H, d, J = 8.4 Hz, phenylenic proton), 7.61 (2H, s, thienylenic proton), 7.36 (2H, s, thienylenic proton), 7.34 (4H, d, J = 8.4 Hz, phenylenic proton), 7.27 (2H, d masked by chloroform, thienylenic proton), 7.24 (2H, d, J = 3.6 Hz, thienylenic proton), 7.141 (2H, d, J = 3.8 Hz, thienylenic proton), 7.137 (2H, d, J = 3.8 Hz, thienylenic proton), 7.05 (4H, s, thienylenic proton).

Polymer Synthesis. Preparation of T3B2U. 5,5″-Diformyl-2,2′:5′,2″-terthiophene (0.05 g; 1.7 × 10^{-4} mol) and 0.03 g (1.63 × 10^{-4} mol) of benzidine were put together with 5 mg of LiCl and degassed three times. A mixture of the solvents HMPA and NMP (4 + 4 mL) was added under nitrogen, and the reaction solution was heated while stirring at 100 °C in order to impart solubility to the aldehyde, which does not completely dissolve. A fine red-orange precipitate began to form in a short period together with a red solution; hence, after 15 h at 100 °C, water was added to stop the reaction and to precipitate all the polymer. The powder was filtered and handled as described elsewhere,[11] obtaining 0.065 g of an unsoluble polymer, the FTIR spectrum of which shows a great number of aldehydic groups that cannot be attributable to the starting product, which was completely consumed, as determined by TLC of a methanol solution from Soxhlet extraction.

For the polymerization in DMSO with acid catalysis, see ref 11.

T6B2 Synthesis. The polymer has been prepared by polycondensation both in solution using azeotropic conditions (A) and in melt (B), according to the conditions reported in Table 1.

(A) The conditions for the polycondensation of T6B2 in HMPT/NMP as well as of T3B2 and T8B2 in the same solvent have been reported in paper 1. T6B2 polymers were synthesized also in 1,2-dimethyl-2-imidazolidone (MI) (runs 3−5), DMF (run 6), and DMSO (run 7), in all cases with addition of toluene.

In a typical example of polymerization, 0.3 g (3.38 × 10^{-4} mol) of dialdehyde, 0.063 g (3.46 × 10^{-4} mol) of benzidine, 1.5 mL of MI, and 3 mL of toluene were charged into a 25-mL two-necked round-bottomed flask, equipped with a magnetic stirrer, a nitrogen line, and a Dean−Stark trap with a condenser.[12] While stirring and with a stream of nitrogen, the flask was placed in a bath heated to 120 °C. Toluene and water were distilled off as an azeotrope and collected in the

Table 1. Polycondensation Experiments of Different Monomers with Benzidine

runs	sample	solvent[a]	temp (°C)	time (h)	$CHCl_3$ solubility	NMR solvent	avg DP[b]	syn/anti ratio[c]
1a	T3B2	HMPA-NMP	130	25	+	DTCE	7	0.21–0.19
1b					–	TDF	13–14	0
2	T6B2	HMPA-NMP	130	25	±	TDF	5–6	0.09–0.09
3a		MI	120	4	+	DTCE	>60	0.34–0.36
3b	T6B2	MI			–	DTCE	25	0.20–0.21
4a	T6B2	MI	120	4	+	DTCE	60	0.25–0.24
4b		MI			–	DTCE	25	0.26–0.20
5	T6B2	MI	80	15	+	DTCE	8–9	0.33
6	T6B2	DMF	120	4	+	DTCE	7	0.28–0.30
7a	T6B2	DMSO	125	4	+[d]	DTCE	5	0.23–0.21
7b					–[d]	DTCE	2	0.27–0.23
8a	T6B2		250–260	1	+	DTCE	7–8	0.35–0.33
8b					–	DTCE	5–6	0.34–0.30
9	T8B2	HMPA-NMP	130	13	±	CS_2	4–5	0.19–0.15
10	T8B2	HMPA-NMP	130	15	±	TDF	4–5	0.20–0.17
11	T3B2U	HMPA-NMP	100	20		DNM[e]	15	<0.02
12	T3B2U	DMSO	120	6		DNM[e]	4–5	~0.05

[a] The solvent label is reported in the Experimental Section. [b] Values from NMR determination by comparing the ratio between the signal of the proton of the aldehydic group and that of the proton of the azomethine residue. [c] The determination was carried out by comparing the area of the peaks assigned to the protons of imine residues in the two conformations (first value) with the area of the peaks due to phenylenic protons adjacent to the azomethine moiety (second value). [d] Solubility in acetone. [e] Solutions in deuterated nitromethane (DNM) of unsubstituted samples were obtained by complexation with $GaCl_3$ under nitrogen atmosphere.

trap during 15 min. The solution was held at this temperature for 4 h. After cooling, the reaction solution was mixed with chloroform and poured in methanol. After filtration and drying, the polymer was dissolved in cold TCE. The part insoluble in TCE was extracted with chloroform, giving a residue (**1**) and an extract, which was precipitated in methanol (**2**). The part soluble in TCE was precipitated in methanol and also extracted with chloroform, giving a residue (**3**) and an extract, again precipitated in methanol (**4**). All fractions were dried in a vacuum, yielding the following: **1**, 204 mg; **2**, 6 mg; **3**, 33 mg; **4**, 65 mg.

(B) Dialdehyde (0.128 g; 1.44×10^{-4} mol) and 0.026 g (1.43×10^{-4} mol) of benzidine were melted together in a condensation tube, while stirring, under a strong flow of nitrogen at 250 °C for 1 h. Polymer formation took place in a few minutes. After the polymeric mixture was cooled, it was dissolved in chloroform (12 h). The soluble part was precipitated in methanol; the other part was finally solubilized in TCE at 60 °C. Both the fractions were extracted with chloroform. The yield was about 87%, 0.115 g being the part insoluble in $CHCl_3$ and 0.019 g the soluble one.

FTIR spectra were carried out on a Bruker IFS 48 instrument; DSC experiments were performed on a Perkin-Elmer DSC2 apparatus. The instruments used for all the optical characterizations, namely UV–vis, photoluminescence, and microscopy, were described in ref 7. ^1H NMR spectra were obtained on Bruker 270-MHz and 500-MHz apparata.

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

Results

Samples of different kinds of T6B2 have been prepared by condensation of the corresponding dialdehyde and benzidine using different experimental conditions, which are reported in Table 1 together with those of the polycondensation of the other two alkyl-substituted and one unsubstituted α,ω dialdehydes with the same diamine. The T6B2 polymers were characterized by FTIR, UV–vis, and ^1H NMR spectroscopies in order to determine exhaustively their chemical structure, as already detailed in paper 1.

Depending on the preparation and fractionation conditions, the UV–vis maxima range from 480 to 502 nm for spin-coated or free-standing films and from 440 to 455 nm for chloroform solutions. In FTIR spectra the intensity of the C=O stretching at 1664 cm^{-1} largely varies as a function of the molecular weight. Specifically in samples 3a and 4a, this peak is hardly detectable, in agreement with NMR findings (see below).

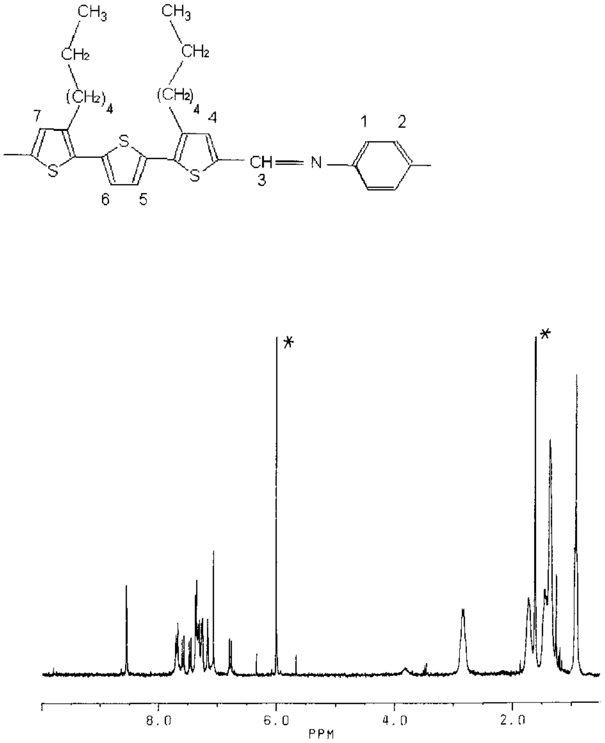


Figure 3. 270-MHz ^1H NMR of T6B2 in deutered tetrachloroethane. In the inlet the atom numbering is reported for clarity.

The complete determination of the molecular structure on the basis of the ^1H NMR spectrum has already been carried out in paper 1. However in Figure 3 the whole ^1H NMR spectrum of T6B2 (4a sample) in DTCE is reported, to evidence that the peak at 9.81 ppm, attributed to the aldehydic proton (end chain), is hardly detectable. The intensity of peaks at 8.54–8.55 ppm, attributed to azomethinic protons, is largely variable according to the preparation conditions; from the ratio between their integrated area, the percentage of the two

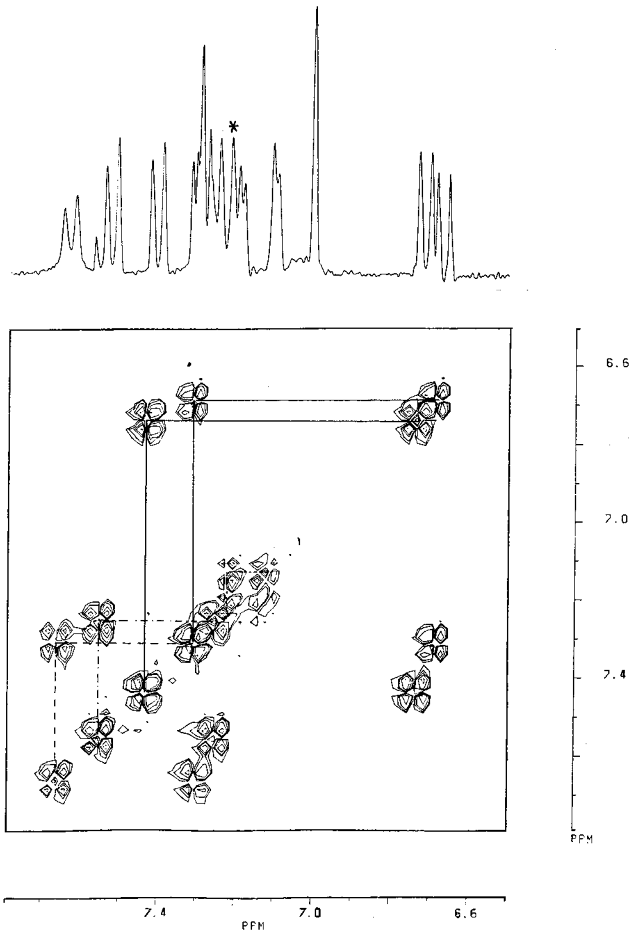


Figure 4. 270-MHz 2D DQF-COSY spectrum of T6B2 in deuterated tetrachloroethane.

isomers present in the polymer (anti/syn) is derived. In the spectra of samples 5−7 and those of 3b and 4b, where the peak at 9.81 ppm is observed, the ratio between its area and that of the azomethinic protons gives an approximate M_n (see Table 1).

Here even more than in the spectrum of the P2 polymer reported in paper 1, the assignment of the peaks in the range 6.5−8 ppm (the aromatic region) is not achievable on the basis of the 1D spectrum only, due to the great number of signals detected; therefore, a 2D DQF-COSY spectrum has been recorded (see Figure 4). The bidimensional spectrum clearly shows the correlations among the signals, allowing us to assign all the peaks due to phenylene and thienylene protons, as reported in the top of Figure 4. Following the numbers shown in the Figure 4 model, protons 1 feel the configuration of the imine linkages adjacent to the biphenylene residue, so four different diads (anti-anti, 7.6/7.25 ppm; anti-syn, 7.55/7.25 ppm; syn-anti, 7.40/7.25 ppm; syn-syn, 7.30/6.65 ppm), the first one being always the predominant one, are observed, corresponding to the possible configurations of the two double bonds in the repeating unit. The assignment of protons 4−7, belonging to thienylene rings, has been reported in paper 1.

In the spectra of samples with lower molecular weight the peak at 7.56 ppm, visible also in the 2D DQF-COSY spectrum of Figure 4, can be attributed to proton 4 on the thienylene holding the carbonyl end group.[7]

As described in the previous paper, we observed that thermal treatments on T6B2 samples resulted in an improvement of the crystallinity. This effect was particularly remarkable in the case of samples having an amount of syn configuration at the azomethine moiety lower than 15% (from NMR determination), as shown in Figure 9 of paper 1, where the XRD spectra of pristine and annealed at 200 °C samples are shown. On the contrary, a sample with 33% syn configuration, subjected to a proper annealing and slowly cooled (0.2 °C/min), from amorphous tends to a partial crystallization into a mesophase, as shown in Figure 5. This arrangement is nematic or smectic as a function of anti versus syn configuration content in the polymer; namely, samples having a higher content of syn configuration tend to assume a nematic arrangement. From the peak width an average value of the crystallite size (∼420 Å) of this sample was derived, corresponding to a coherence along the interdigitation direction of ∼24 unit cells, larger than the value derived in the 3D phase of the polymer.[7] This observation confirms a general trend found in polythienylene systems, namely a major microhomogeneity of samples in the mesophase with respect to samples in a 3D arrangement.[13]

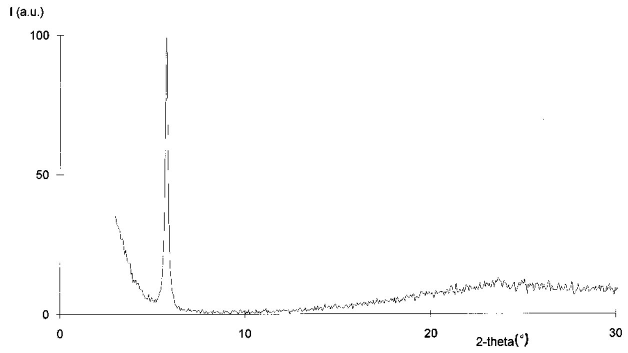


Figure 5. XRD of T6B2—syn-rich sample—annealed at 200 °C (see text).

Because of the coincidence of the mesophase peaks ($d = 15.5$ and 5.14 Å) with the effects found in samples showing a 3D arrangement—see the spacings with an asterisk in Table 2 of the related paper—we cannot rule out the copresence in the pristine sample of two phases, one 3D and the other mesomorphic. On the other hand attempts to improve the degree of order in syn-rich samples, aiming to obtain a 3D isolated phase, failed, possibly either due to partial postpolymerization or because of in-chain disorder (see paper 1).

Optical microscopy analysis indicates a progressive color change of the polymer samples (red to orange) together with a softening, typical of liquid crystal behavior, but neither Schlieren patterns nor evident melting have been detected.

DSC measurements carried out under nitrogen on pristine samples of T6B2 with high syn content, reported in Figure 6 top, show a very feeble peak over 200 °C attributable to the mesophase → melt transition. The endothermic ΔH, related to this transition and evaluated in 0.003 kcal/mol, is in agreement with the presence of a low-order phase. Further annealing revealed the complete disappearance of this peak, possibly due to the partial postpolymerization, as discussed in paper 1, or insufficient time of crystallization (cooling rate 1 °C/min).

The materials are thermally stable up to 400 °C; in fact TG analysis under nitrogen, shown in Figure 6 bottom, reveals that at this temperature the weight loss of the sample is only 8%.

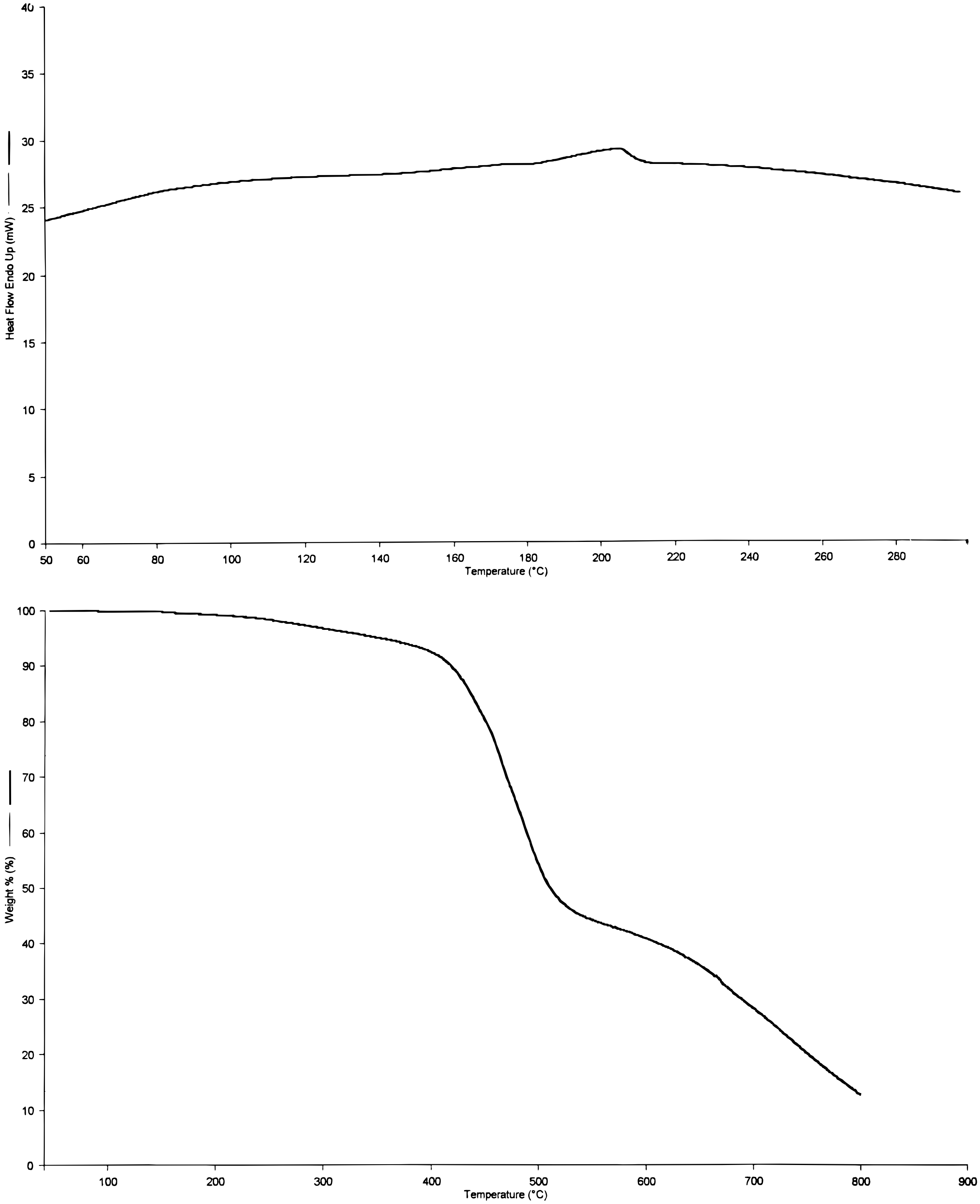


Figure 6. DSC trace (top) and TG curve (bottom) of T6B2 sample (first scan) with high syn content (see text).

These characterizations indicate that the alkyl substitution onto polyazomethinic chains has the effect of enhancing the processability, due to increased solubility and molecular weight, while the thermal stability is maintained. Concerning the crystal packing, the noticeable reduction observed—from tridimensional to mesophase (liquid crystal character) or even amorphous—is attributable to both the alkyl substitution and the introduction of a larger amount of syn configuration at the imino group. Notably the increased M_w strongly improved the mechanical properties and also the homogeneity of the sample, although it is in a less ordered mesophase (compare the average crystal size).

Because the highest syn content is observed in polymers with the highest molecular weight, to understand the mechanism of anti/syn formation, it can be useful to consider finally the results reported in Table 1 for unsubstituted T3B2 and in Table 2 for model compounds and also the results reported in Table 3 concerning oligomers of T6B2.

The absorption and photoluminescence spectra of differently prepared T6B2 are also presented in Figure

Table 2. Preparation of Model Compounds

	sample	solvent	temp (°C)	time (h)	NMR solvents	syn/anti ratio[b]
I	MT3B2U	DMSO	120	7	DTCE	0
II	MT3B2T3U	DMSO	120	12	DNM[a]	0.03
III	MBrT3B2T3Br	MI	120	4	DTCE	<0.03
IV	AT6B2T6A	MI	120	4	CDCl3	0

[a] Solutions in deuterated nitromethane (DNM) of unsubstituted samples were obtained by complexation with $GaCl_3$ under nitrogen atmosphere. [b] As determined from the NMR spectrum by estimation of the ratio between the two signals of the proton of the imine linkage.

Table 3. Syn/Anti Ratio versus Temperature in Polyazomethine T6B2 Samples

sample	temp (°C)	time (min)	yield (%)	syn/anti ratio[a]
T1	130	30	5	0.13
T2	140	30	46	0.16
T3	150	30	46	0.25

[a] Estimated from NMR diads of azomethine- and phenyl-coupled protons (see text).

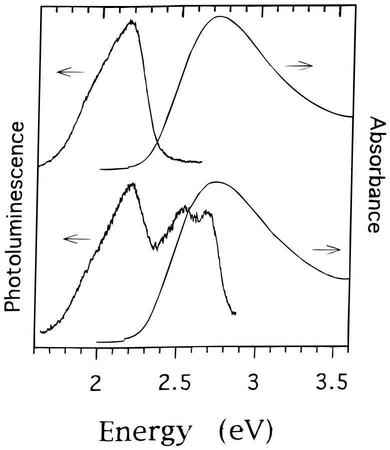


Figure 7. Electronic absorption and photoluminescence spectra of T6B2 samples with different anti/syn content.

7. The absorption spectra of samples with 8% or 33% syn content do not differ from one another, but a dramatic change in the PL profile of samples having larger syn content is evident; namely, a new component at higher energies appears. Therefore, by controlling the anti/syn ratio in the copolymer a wide tunability of the emission is achievable.

These observations are related to different torsion angles of phenylenic and thienylenic residues around the imine linkage in the ground state of anti and syn configurations. This difference results in a different planarity of the excited state for anti and syn isomers.[14]

A detailed study of the optical properties of these copolymers has recently been published.[15]

Discussion

Other authors have prepared analogous polyazomethines with only phenylene[5] or phenylene and thienylene[6] moieties, but the presence of the syn isomer was never recognized, although a large number of unassigned peaks was present in the NMR spectra. Therefore this report and the previous one are the first example of a complete assigment of ^1H NMR spectra in both azomethine and aromatic regions. In fact the proton in the imino group can be in two different configurations (anti/syn), and phenylenic protons close to the nitrogen atom feel the effect of such configurations, which, on the contrary, do not seem to affect the nearest proton of each thienylenic segment. This fact gives rise to distinct singlets for azomethine anti and syn protons and to different doublets for phenylene protons. Particularly, because the latter are between two azomethine groups and influenced by both, they can be affected by anti-anti (7.6/7.25 ppm), anti-syn (7.55/7.25 ppm), or syn-anti (7.40/7.25 ppm) and syn-syn (7.30/6.65 ppm) situations (see Figure 4). At this point two major observations emerge:

(1) only high-molecular-weight copolymers show syn/syn diads, while in the 2D DQF-COSY NMR spectrum of low-molecular-weight T6B2 samples no syn/syn diads are observed;[7]

(2) the situations anti-syn and syn-anti determine different bendings of the polymeric backbone, that is, chemical environments along the chain resulting in two distinct chemical shifts for the configurations. Accordingly (see above), photoluminesce data on these copolymers account for these observations.

Considering first the T6B2 polymer, prepared in different experimental conditions (see Table 1), and then other substituted[7] and unsubstituted[11] polymers and model compounds (see Tables 1 and 2), it is possible to get an insight into the mechanism governing the imine formation.

This two-step reaction consists of a nucleophilic addition on the carbonyl group, followed by a catalyzed dehydration of a tetrahedral intermediate.[16] Benzidine molecules have two distinct nucleophile groups which cannot react simultaneously; so indicating benzidine and thienylenic dialdehyde with $H_2NB_2NH_2$ and $HCOT_6CHO$, respectively, the first compound formed is $H_2NB_2N{=}CHT_6CHO$ (see Scheme 1).

Scheme 1

primary attack: $H_2NB_2NH_2 + HCOT_6CHO \longrightarrow H_2NB_2N{=}CHT_6CHO$

secondary attack: $H_2NB_2N{=}CHT_6CHO + HCOT_6CHO \longrightarrow H_2NB_2N{=}CHT_6CH{=}NB_2T_6CHO$

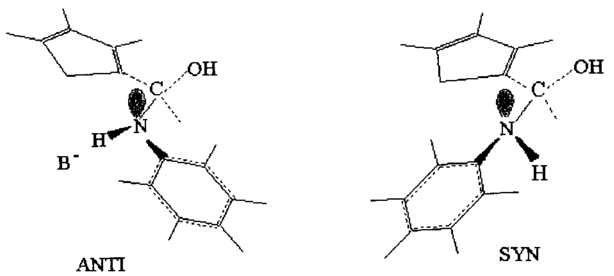
The first attack of benzidine is easier than the second one because the amino group of $H_2NB_2NH_2$ is a stronger and more basic nucleophile than the amino functionality in $H_2NB_2N{=}CHT_6CHO$.[16a] Hence, with the latter nucleophile, a concerted mechanism could be preferred, but the pH of the medium should be not strongly acidic in order to prevent the protonation of amino groups still present.[16] It should be recalled that during all the polycondensation we are dealing with reactions which either are the first attack of benzidine or are quite similar to the second attack of benzidine.

The tetrahedral intermediate can exist in different conformers which evolve to syn or anti isomers. Molecular mechanics calculations on these conformational isomers, using the Hyperchem program,[17] indicate that the anti situation is clearly preferred; however, the energy difference among them is small enough to account for the presence of other isomeric situations, although in different proportions.

The experimental conditions of the polymerization, particularly the pH of the medium, the temperature, and the overall size of the molecule, strongly affect the anti/syn ratio, and it is rather difficult to discriminate among them.

The polymerization of substituted T6B2 was always carried out in slightly basic conditions assured by the

Chart 1

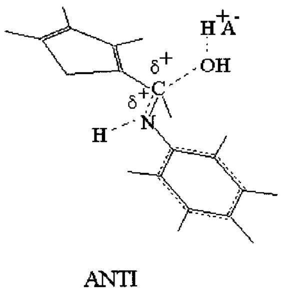


presence of excess of benzidine. Considering Chart 1, in which the two possible mechanisms of dehydration are shown, a tentative rationalization can be carried out.

In run 2 of Table 1, LiCl shifts the equilibrium reaction toward polymer formation without making it faster; in this situation the basicity of the medium promotes the anti isomer, implying that the nitrogen deprotonation is concerted with elimination of hydroxide ion, giving rise to an anti bimolecular elimination. The intermediate in a conformation favorable to the syn isomer has the possibility in terms of time and overall size of the molecule to rotate. Consequently a polyazomethine with the highest amount of anti isomer (90%) but not the highest molecular weight is prepared.

When the reaction rate increased, always in a basic medium, as in the azeotropic (runs 3−7) or melt (run 8) polymerizations, the second step, formation of the imino linkage, is probably faster than that in run 2 conditions and both the mechanisms (bimolecular elimination from the anti isomer and monomolecular elimination from the syn isomer) take place (the percentage of the syn isomer varies in these runs from 10 to 35). In the latter case the nitrogen proton can act like an acid for the hydroxide ion in order to eliminate water in a syn periplanar conformation, as these two ions are in a closer proximity than those in an anti periplanar conformation (see Chart 1).

Chart 2



Moreover we mention that, to prepare unsubstituted T3B2 and T6B2 and the models **I** and **II**, an acid-catalyzed polycondensation was used. In this case the breakdown of the carbinolamine intermediate occurs by means of expulsion of water, involving the development of some positive character on the carbonyl carbon and the nitrogen atom in the transition state, as shown in Chart 2. So it will be facilitated by the electron donor substituent on both the thienylenic and phenylenic rings. Hence in the second attack of the benzidine reaction to form model compounds **II**, **III**, and **IV** of Table 2, as well as in all the other similar steps of polymerization, the dehydration tends to become slower, allowing the transition of the intermediate evolving to syn into the intermediate evolving to anti to occur.

This finding results almost completely in the anti isomer for model compounds, while for the polymers the anti/syn ratio depends on the molecular weight. To completely understand the anti/syn formation in the condensation reaction, steric effect should also be taken into account. In fact it is noted that the highest molecular weight polymers are always the most disordered ones, due to anti/syn content. This result can be partially explained with an increased solubility of the disordered compounds, but it is necessary to consider that, as the macromolecule grows, the overall bulkiness of the group which must rotate in the intermediate in order to produce the anti isomer increases. Actually in the intermediate leading to Shiff bases (see models **II**, **III**, and **IV**) the overall bulkiness makes the rotation around the C−N linkage quite easy and the almost complete isomerization syn → anti occurs. As the molecule size increases, the rotation of the C−N bond implies more energy; hence, the isomerization is not complete. This reason can explain that the syn content ranges from 3% at most in the model compounds, independently of the side chain present, to 30% in the polymers.

A further evidence of the relevance of bulkiness is derived from the experiments with increasing temperature (Table 3). As the temperature rises, the molecular weight increases, and the syn/anti ratio also increases.

Moreover the steric hindrance of the bulky groups on both carbon and nitrogen atoms of the intermediate does not appreciably change with the variation of the number of the thienylene rings and also the presence of side chains.

Conclusions

The polycondensation reaction to yield alkyl-substituted polyazomethines has been widely studied, definitely determining different configurations (anti/syn) at the imino group, typically occurring in polyazomethine preparation but up to now never recognized. Mechanistic considerations, quite in agreement with experimental data, allow us both to explain the anti/syn formation and to control their ratio.

By a proper variation of the polycondensation conditions, and hence the anti/syn ratio, it is possible to prepare stable, processable, polyazomethines high-molecular-weight showing some liquid crystal character, which are suitable for optoelectronic applications. Specifically a valuable tunability in the emission spectrum is achievable.

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