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Polymer Vol. 37 No. 7, pp. 1059–1064, 1996
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0032-3861/96/$15.00 + 0.00

polymer papers

Poly(3-butyl-*co*-3,4-dibutylthiophene) copolymers: a new series of conjugated materials with a different energy-gap

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We have prepared a series of soluble polyalkylthiophenes in which it is possible to modulate continuously the electronic properties such as the conjugation length and the energy-gap. The copolymerization of 3-butylthiophene and 3,4-dibutylthiophene units in well defined ratios leads to materials with optical properties depending on the composition of the chain. Using size exclusion chromatography (s.e.c.) and n.m.r. techniques we have found that the copolymer average composition is in good agreement with the composition of the co-monomer feeds at the polymerization start. The optical characterization was performed with u.v.–visible absorption and Raman spectroscopy and this allowed us to monitor the conjugation length properties of the copolymers.

(Keywords: synthesis; copolymers; polyalkylthiophenes)

INTRODUCTION

During the last two decades the demand for new polymers has been driven by a need for 'functional materials' with electrical, optical and magnetic properties. These sophisticated materials are designed specifically for particular application in electronics, communication, or information technologies.

Among the macromolecules with interesting electronic properties, thiophene-based polymers are the subject of many studies[1] as materials for electrical and electronic applications, and for non-linear optics. In particular, polythiophenes have been proposed as components in energy storage applications[2,3], in electrochromic devices[4,5], and in electrochemical sensors[6].

The modification of the chemical structure of polythiophenes yields materials with various electronic characteristics, but also with improved stability and processability. Soluble polyalkylthiophenes show an interesting electrochromism in the visible spectral region[7] and the modulation of the backbone conjugation length, obtained with modification of the chemical structure, can produce materials suitable for applications in display-devices and electrochromic window technology.

The planarity of the backbone is a characteristic of conjugated polymers which favours a maximum overlap between the π orbitals of the monomeric units; the presence of a substituent group on the monomer produces an increase of the steric hindrance of the unit and may cause a departure from planarity of the main polymeric chain. The distortion of the conjugated backbone due to the steric interaction between adjacent monomers produces a decrease of the π orbital overlap and consequently a shortening of the effective mean conjugation length leading to a blue shift of the electronic absorption spectra.

Polyalkylthiophene chains in the solid state are mainly in an ordered phase (smectic or crystalline) where segments of four–five rings have the *trans* planar conformation of polythiophene[8,9]. The presence of the alkyl chain in the ring 3 position does not affect directly the π electronic structure of the thiophene backbone, but leads to solvatochromic and thermochromic effects. An order–disorder transition of the side chains induces interring rotations decreasing the effective mean conjugation length[10].

With this in mind, we have synthesized a series of alkyl-substituted polythiophenes in which it is possible to modulate continuously the electronic properties by tuning the conjugation length and the energy-gap of the main chain. The inclusion in a polyalkylthiophene chain of substituted units with strong steric repulsion toward adjacent rings can produce a local deviation from planarity with interruption or decrease of the π orbital overlap, that affects the mean conjugation length of the chain. The copolymerization of 3-alkylthiophene and 3,4-dialkylthiophene monomers leads to conjugated macromolecules having electronic properties depending on the monomeric composition of the chains. In this paper we report the synthesis and the characterization of

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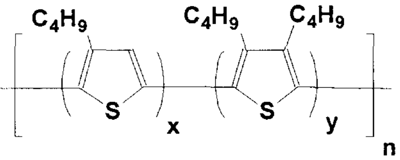

Scheme 1

conjugated copolymers (see *Scheme 1*) with different percentages of 3-butylthiophene and 3,4-dibutylthiophene units, having various energy-gap and diverse colour in the visible spectral range. These copolymers are processable materials with electrochromic properties suitable for application in optical devices[11].

EXPERIMENTAL

Both 3-butylthiophene (MBT) and 3,4-dibutylthiophene (DBT) monomers have been synthesized following the literature[12]. The copolymer series has been produced via chemical oxidation with $FeCl_3$ in chloroform[13] starting from mixtures of mono- and di-butylsubstituted thiophene monomers in well defined ratio. The copolymers prepared in this way (yields of about 90–95%) have been poured into methanol and washed several times, and then have been extracted in a Soxhlet apparatus with methanol in order to remove the residual oxidant and the oligomers. The copolymers have been dissolved in chloroform and precipitated in a solution of hydrazine (1% in volume) in methanol to eliminate traces of the catalyst. The purified copolymers are coloured powders that tone off from dark red (poly-3-butylthiophene) to white (poly-3,4-dibutylthiophene).

The molecular weight distribution (*MWD*) of the copolymers was obtained with a modular size exclusion chromatography (s.e.c.) system Waters (Milford, MA). The s.e.c. system consisted of a 600E pump, a 717 autosampler, a 410 differential refractometer and a 490E u.v.–visible detector. The column set was composed of four Waters Ultrastyragel (10^5–10^4–10^3–500 Å pore size). The experimental conditions consisted of: tetrahydrofuran as a mobile phase continuously sparged with helium, 35°C temperature, 1 ml min^{-1} flow rate, a sample concentration of 0.5 mg ml^{-1} and a 200 μl injection volume. The calibration curve, polynomial third-order fit, was constructed by 14 narrow *MWD* polystyrene standards with the molecular weight ranging from 162 to 3.28×10^{-6} g mol^{-1}.

The n.m.r. experiments were performed on a VARIAN UNITY 500 spectrometer operating at $f = 499.98$ MHz for ^{1}H. Chemical shifts are given with respect to TMS (tetramethylsilane). All reported n.m.r. experiments were carried out at temperature stabilized at 298 K in $CDCl_3$ solution.

The u.v.–vis–n.i.r. study was performed with a Varian 2400 Instrument. Raman spectra of cast films were obtained on a Bruker IFS 66 + FRA 106 FTIR spectrometer exciting with the 1064 nm line of a Nd-YAG laser.

RESULTS AND DISCUSSION

The presence of hindered units in the poly-3-alkylthiophene chain increases the torsion angle between consecutive rings and forces the backbone in this region out of planarity resulting in a decrease of the conjugated segment length. We have chosen 3,4-dialkyl substituted thiophene as the unit with strong steric hindrance, and we have copolymerized it with 3-alkylthiophene in different ratio. The copolymerization of mono and dialkyl substituted rings is an easy route to produce materials with different properties, and it is an effective strategy to tune the energy-gap and the electronic absorptions in the visible spectral range (i.e. the colour) of the polymers (see *Table 1*).

Table 1 Composition, electronic absorption maxima and energy-gap of copolymers in chloroform solution

Copolymer	x/y[a]	λ_{max} (nm)	E_g (cV)[b]
P1	10/0	430	2.3
P2	9/1	421	2.3
P3	7/3	400	2.4
P4	5/5	378	2.5
P5	1/3	339	2.6
P6	0/10	321	3.2

[a] Copolymer composition from monomer ratio at the polymerization start

[b] From the onset of the electronic absorption

Table 2 Composition and molecular weight of copolymers

Copolymer	x/y (from monomer ratio)	x/y (from n.m.r.)	M_w[a]
P1	10/0	9.4/0.6	64,000
P2	9/1	8.2/1.8	78,000
P3	7/3	6.5/3.5	60,700
P4	5/5	5.2/4.8	121,000
P5	1/3	1.1/3.8	44,000
P6	0/10	0/10	46,000

[a] By s.e.c. using u.v. detector at the absorption maximum

Molecular weight distribution

The effective knowledge, by conventional s.e.c., of the *MWD* of polythiophenes copolymer presents two main problems. Firstly, the molecular weight is relative to a polystyrene calibration not to a true polythiophene calibration. Secondly, random copolymer macromolecules can differ from each other in both molecular weight and composition, then we cannot assume that fractionation will be based solely on molecular weight. Thus the molecular weight values obtained in such a characterization are nominally not effective.

Several papers[14] have shown, by means of on-line or off-line light scattering characterization, that the nominal molecular weight for poly(3-alkylthiophene) homopolymer obtained by s.e.c. with a polystyrene calibration is very close to the effective value. In *Table 2* we have reported the M_w values obtained from the signal of the u.v. detector at the absorption maximum.

A second source of discrepancy, between effective and nominal values of molecular weight, is more insidious. Particularly it is important to establish the composition heterogeneity of the copolymers. For these reasons we have used for every s.e.c. run two on-line detectors, in all three signals: a refractive index detector, and a u.v.–visible detector at two wavelengths, 254 nm (thiophene

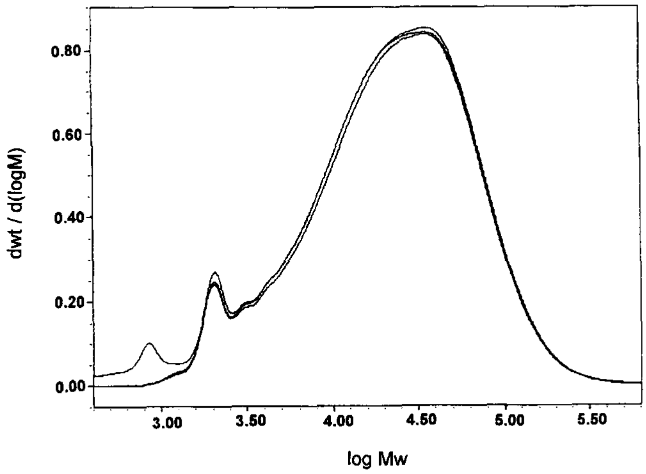

Figure 1 Comparison of molecular weight distribution obtained with RI detector and u.v. absorption detector at 380 and 254 nm for the sample P5

ring absorption) and the absorption maximum of the copolymer chains. Significant difference in the *MWD*s obtained from the three signals would mean composition heterogeneity of the copolymer. *Figure 1* shows the *MWD*s obtained from the three signals (detectors RI and UV at 254 nm and at the absorption maximum) for P5 sample (see *Table 2*). In such a figure we can see a substantial superposition of the MWDs, except for the oligomer range. We argue that compositional variations are negligible and the fractionation is, to a good approximation, based on molecular weight. The weight-average molecular weights M_w obtained however are nominal, not effective, but the comparison in molecular weight between the sample are nevertheless significant.

Copolymer composition

The ^{1}H n.m.r. spectra of the copolymer series are given in *Figure 2*. Represented are the regions of aromatic hydrogen and of the CH2 protons in the α position

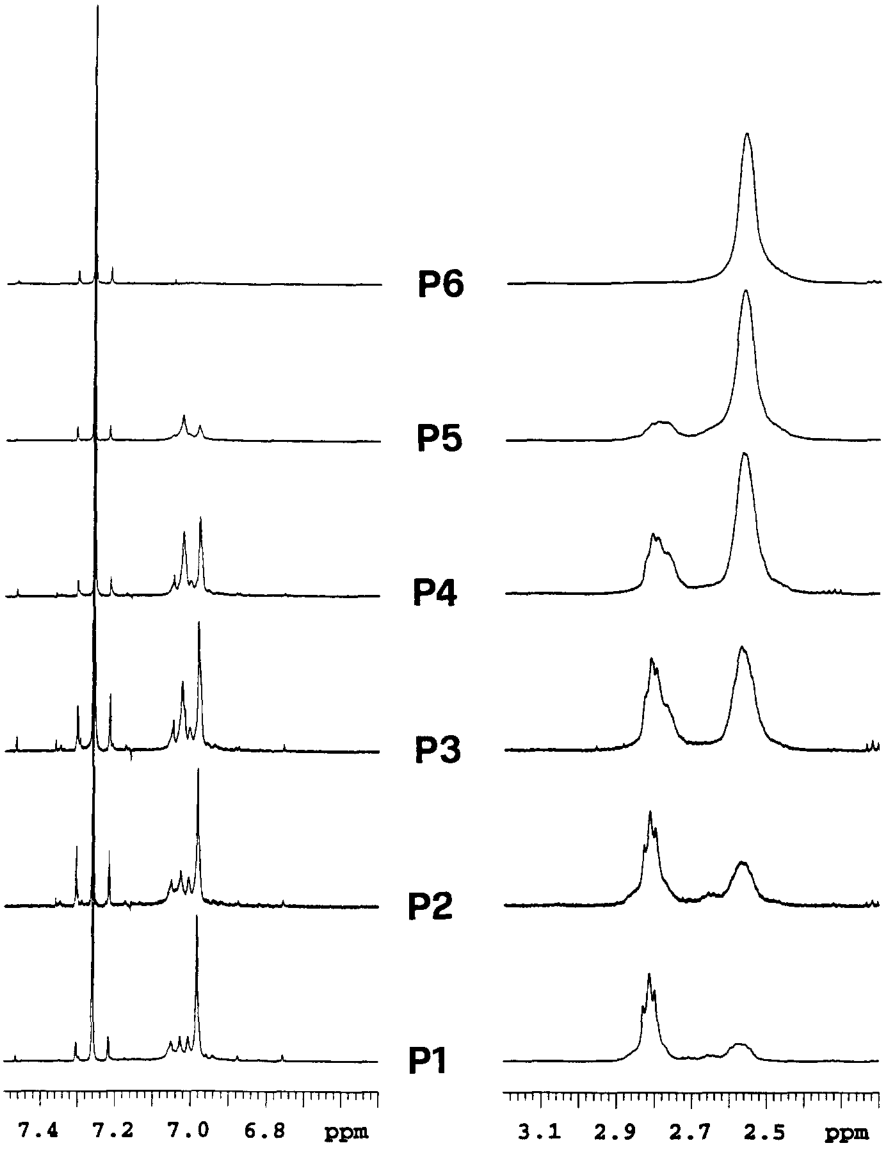

Figure 2 ^{1}H n.m.r. spectra of the copolymer series: shown are the aromatic region (left) and the resonance of the CH_2 in α position on the alkyl chain (right)

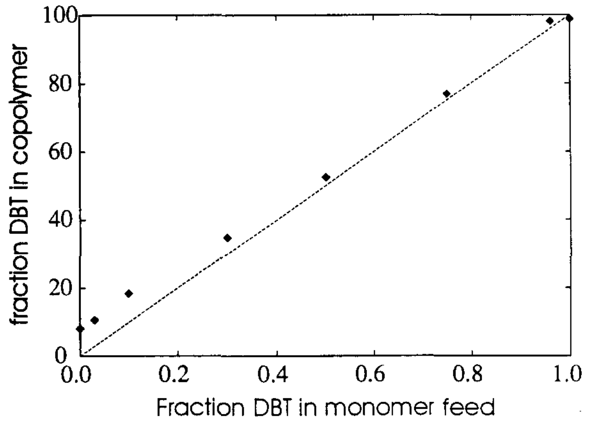

Figure 3 The composition of the copolymers, expressed as the fraction of dibutylthiophene (DBT) determined by n.m.r. spectroscopy, as a function of the composition of the monomer feed at the polymerization start

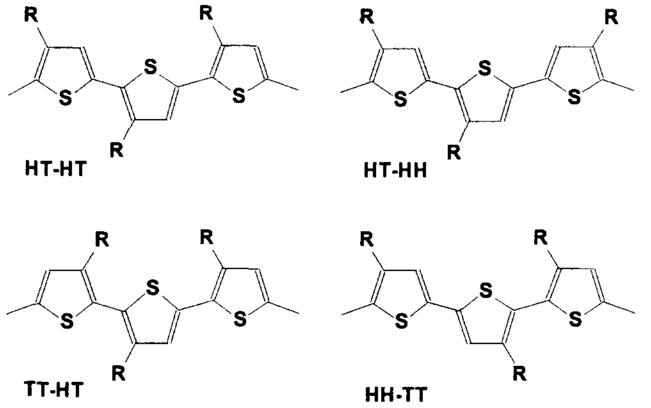

Figure 4 The four different environments for a monosubstituted thiophene unit: the regular enchainment head–tail HT–HT and the three irregular ones HT–HH, TT–HT and HT–TT

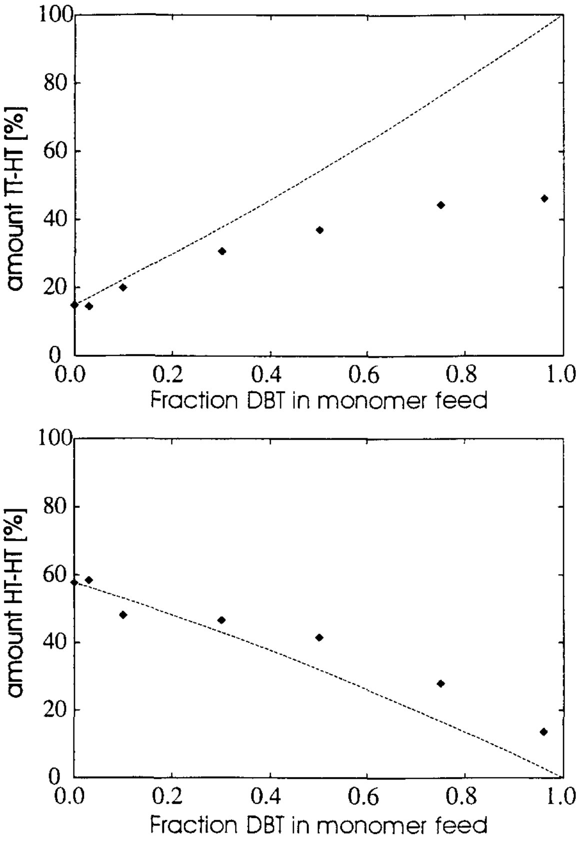

Figure 5 Fraction of HT–HT (bottom) and HT–TT (top) enchainments determined by n.m.r. spectroscopy as a function of the composition of the monomer feed at the polymerization start

(i.e. the first site on the side chain) of the thiophene rings. The n.m.r. resonance of these protons are especially sensitive to configurational disorder, as was shown previously[15–19], and can be used to estimate the ratio between monobutyl (MBT) and dibutylthiophene (DBT) units.

The first point of interest is to determine whether the average composition of the copolymers is the same as the composition of the starting monomeric mixture. The ratio of mono- and di-butylsubstituted units can be estimated by comparing the intensities of the protons in α position (originating from four hydrogen atoms of the DBT and two protons of MBT) with the intensity of the aromatic protons (originating from one hydrogen of MBT). The result is given in *Table 2* and in *Figure 3*. At first glance it seems that the composition of DBT in MBT is overestimated for those copolymers where the fraction of disubstituted thiophene, f, is low. But as the curve is continuous towards $f = 0$ (corresponding to the 3-butyl homopolymer P1 where no DBT is present) this deviation does not relate to the composition of the macromolecule.

The amplitude of the ^{13}C satellites of the proton impurities in $CDCl_3$ is comparable to the amplitude of the aromatic protons. The intensity of these lines is expected to be negligible though, as their line width is much smaller than the line width of the copolymer. This was confirmed by comparing spectra recorded with and without ^{13}C decoupling of the chloroform. The origin of the systematic deviation of the copolymer composition, as determined by n.m.r., might be accounted for by the presence of some impurity signals. In fact, the presence of 100 μmol l^{-1} of impurities, with a signal in the same region as the aromatic proton, would be sufficient account for the observed deviation.

We can therefore conclude that the copolymer composition is the same as the composition of the starting monomer mixtures.

Distribution of the defects

Using the ^{1}H n.m.r. spectroscopy it is possible to obtain information on the enchainment of the thiophene rings in the copolymer chain. The relative intensity of the lines in the aromatic region corresponds to the four possible environments an aromatic proton can have in a poly-3-alkylthiophene chain (see *Figure 4*). These resonances have been assigned unambiguously by investigation of a series of trimers[20]. This assignment corresponds well with our previous work on poly(3-decylthiophene)[21] and with the data here presented. For low amounts of monoalkyl substituted units we expect that the line corresponding to head tail–tail tail (HT–TT) environment is strongest as indeed it is.

The distribution of the defects depends on the polymerization method used. Botta *et al.*[21] found that for polymerization with $FeCl_3$ the defects are correlated in the sense that HH enchainment is preferentially

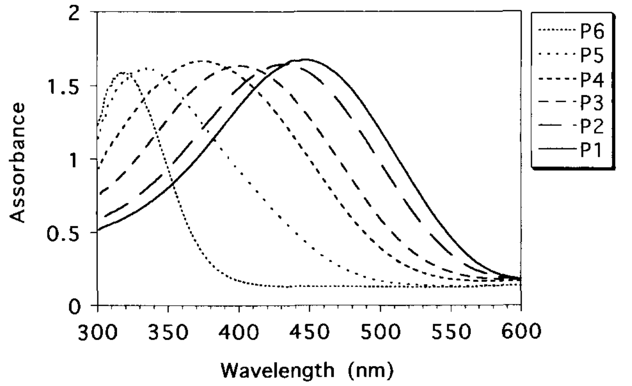

Figure 6 Electronic absorption spectra of copolymer thin films obtained with spin-coating

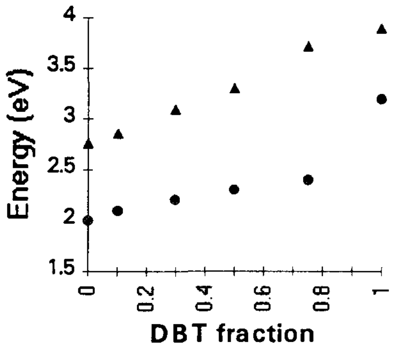

Figure 7 Plot of the energy-gap, defined as the onset of the optical transition (circles), and of the π–π^* absorption maximum (triangles) in copolymer films, as a function of the fraction of the disubstituted monomer in the copolymer

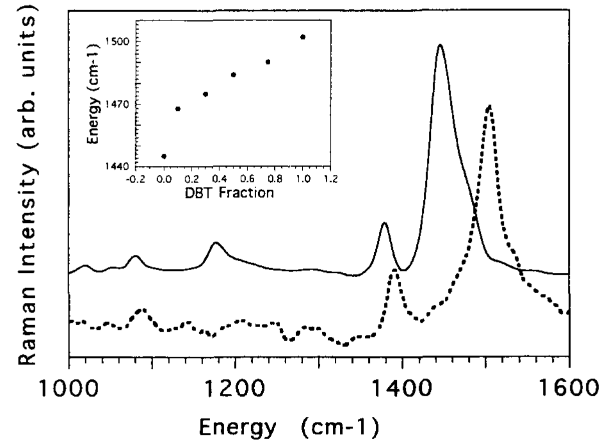

Figure 8 Raman spectra of poly-3-butylthiophene (full line) and of poly-3,4-dibutylthiophene (dashed line) obtained with a 1064 nm excitation wavelength. In the insert is the plot of the C=C stretching frequency of the copolymer series as a function of BDT fraction

followed by a TT one. The same applies to our copolymer samples. This implies that it is not possible to predict the relative intensities of the lines by a simple statistical model. It is, however, possible to derive some qualitative information from the spectra by comparing the relative intensity of the aromatic protons. The relative intensity of the lines stemming from HT–HT and HT–TT enchainments are reported in *Figure 5*. The dashed line represents the intensity that could be expected if the enchainments were random.

If there is no correlation between the MBT units it could be expected that, for a low concentration of monosubstituted monomer, the relative intensity of the HT–HT regular enchainment tends to zero and the relative intensity of HT–TT tends to 1. It can be observed that the intensity of the regular enchainment tends to 0.15 and the intensity of the irregular tends to 0.45–0.50. These are clear indications that an MBT unit is preferentially close to another MBT, this results in an inhomogeneous distribution of monosubstituted units in the copolymer chain.

Electronic absorption characterization

Figure 6 shows the u.v.–visible absorption spectra of the copolymer films reported in arbitrary scale. The absorption band corresponds to a $\pi - \pi^*$ transition whose energy and oscillator strength depends on π electron delocalization. It can be seen that the energy maximum shifts to higher energies with the increase of the DBT fraction f. In the copolymer series the intensities of the $\pi - \pi^*$ absorption, normalized with respect to the 254 nm thiophene absorption band whose oscillator strength does not vary π electron delocalization[22], decrease with f.

These features indicate that the mean conjugation length of the copolymers is decreased by increasing the fraction of DBT content in the copolymer.

As a matter of fact the steric hindrances of the dialkyl substituted monomer induce rotations between adjacent thiophene rings and may account for these results. The absorption spectrum of the P6 homopolymer suggests a 50° rotation between consecutive monomers[23].

Distribution of conjugation length

Figure 7 shows that the energy maximum of the absorption spectra increases linearly with f, while the energy gap (defined as the onset of the absorption spectrum) exhibits a slow increase with DBT fraction and a sudden increase for f near 1. The energy maximum probes the mean conjugation length of the copolymer, and the onset of the absorption spectrum probes the longest conjugation lengths. A homogeneous distribution of the two units in the chain should produce the same variation of both energy maximum and energy gap with the increase of f. The observation reported in *Figure 7* brings support to an inhomogeneous distribution of monosubstituted units in the copolymer chain, in agreement with n.m.r. data. A similar behaviour for the energy gap has been described by dos Santos *et al.* for polyparaphenylene vinylene copolymers[24]. The authors, by employing the 'valence effective Hamiltonian technique', showed that the HOMO-LUMO gap is strongly affected by the distribution of the monomer units in the copolymer chain. An inhomogeneous intrachain distribution with formation of a low energy gap island produces a reduction in the HOMO-LUMO gap, and this accounts for the non-linear dependence of the gap experimentally observed. A theoretical investigation of the electronic structure as a function of the copolymer composition is the subject of a following paper[25].

Raman scattering also provides information on the distribution of conjugation. In monosubstituted polyalkylthiophenes the C=C stretching mode, which is strongly coupled to the $\pi-\pi^*$ transition, shows a frequency dispersion with the excitation energy which is coherently related to the distribution of conjugation lengths[26]. This mode does not shift in frequency for more than three adjacent planar rings, while it has an upper shift for a loss of backbone planarity at a short range scale.

Figure 8 shows the Raman spectra of the two homopolymers obtained in preresonance condition with a 1064 nm excitation wavelength. The C=C stretching is at 1445 $\mathrm{cm^{-1}}$ for the poly(3-butylthiophene) and at 1509 $\mathrm{cm^{-1}}$ for poly(3,4-dibutylthiophene). If the same backbone conformation is supposed, the substitution of a hydrogen with an alkyl chain may lead to a decrease of the C=C stretching frequency. Therefore the 55 $\mathrm{cm^{-1}}$ upper shift observed at 1064 nm in P6 homopolymer, is indicative of interring rotations.

The inset in *Figure 8* shows the C=C stretching frequency measured with a 1064 nm excitation as a function of the fraction of DBT content. It can be seen that there is a sudden upper shift from P1 homopolymer and P2 copolymer with 10% of DBT. This is due to the lack of backbone planarity at short scale. At a matter of fact *trans* planar thiophene segments in the P1 homopolymer do not exceed four–five consecutive rings.

CONCLUSION

The synthesis of copolymers containing both 3-butylthiophene and 3,4-dibutylthiophene units leads to conjugated macromolecules having electronic properties depending on the co-monomer ratio in the chains. We have produced a series of copolymers in which the change in the chemical composition produces a modulation of both conjugation length and energy-gap of the materials.

The copolymerization of mono- and di-alkylsubstituted thiophenes is an easy route to produce a series of processable materials with colours that tone off from red to white and with an electrochromic effect suitable for application in optical devices.

The copolymers have been synthesized via chemical oxidation with $FeCl_3$, starting from mixtures of mono and dibutyl-substituted thiophene monomers in well defined ratio.

The molecular weight distribution of the copolymers was obtained with a modular size exclusion chromatography (s.e.c.) using a refractive index detector, and a u.v.-visible detector at two wavelengths. The fractionation is based on molecular weight, the weight-average molecular weights M_w obtained however are nominal, not effective, but the comparison in molecular weights between the samples are nevertheless significant.

The n.m.r. results have permitted the determination of the average composition of the copolymer and the distribution of monoakylthiophene units in the chains. We found that the average copolymer composition is the same as the composition of the monomer feed at the polymerization start, but the monoalkylsubstituted units prefer the closeness of equal units.

The electronic absorption spectra of the copolymer films show an energy band assigned to the $\pi-\pi^*$ transition of the conjugated backbone, whose energy and intensity depends on the copolymer composition. The spectral features indicate a reduction in the effective mean conjugation length coinciding with an increase of the 3,4-dibutylthiophene fraction in the copolymer composition. The energy maximum of the absorption spectra increases linearly with f, while the energy gap (defined as the onset of the absorption spectrum) exhibits a slow increase for f close to 0 and a sudden increase for f near 1. These results support an inhomogeneous distribution of the two units in the copolymer chain.

In the Raman scattering spectra of copolymer films the frequency position of the C=C stretching band show a shift from 1442 $\mathrm{cm^{-1}}$ (poly-3-butylthiophene) to 1502 $\mathrm{cm^{-1}}$ (poly-3,4-dibutylthiophene) by varying the copolymer composition. This demonstrates that there is a loss of backbone planarity at short scale with the increase of the number of disubstituted units.

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