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Synthesis and characterization of semiconductor polymers having different phenylene–vinylene conjugation lengths

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Abstract We have synthesized phenylene–vinylene (PV) polymers containing segments with different conjugation lengths interspaced by random distributed aliphatic segments. Infrared (IR) and ultraviolet–visible (UV–vis) spectroscopies, hydrogen nuclear magnetic resonance (^{1}H NMR) spectrometry and differential scanning calorimetry (DSC) were used to characterize the prepared copolymers' structures. Polymers molecular weights were determined by gel permeation chromatography (GPC). The effect of polymer structure and composition on emission properties was studied by fluorescence (PL) spectroscopy under different irradiation wavelength. The emission energy shift due to segments with longer conjugation lengths was minor owed to the low polymerization degree achieved.

Introduction

The photo-physical properties of conjugated poly(p-phenylenevinylene) (PPV) have been studied due to their good charge transport properties and mechanical resistance in applications as active layer in light-emitting devices (LED).

The exciton singlet quantum confinement is observed in polymers with segments having different conjugation degrees (n), for small n ($n < 10$) [1–3], separated by non-conjugated segments. According to Marletta [4], in these materials the migration of energy occurs by Foster mechanism, phenomenon in which the excitation energy tends to migrate toward longer conjugation length (with smaller band gap energy) [5, 6].

One advantage of quantum confinement arrangement by conjugation rupture is the increasing emission quantum efficiency of these polymers. This increase occurs due to the decreasing exciton mobility, which decreases the probability of exciton singlet migration to quenching sites, such as chain ends, impurities and other defects [3, 7, 8]. In this context, studies on the effects of phenylene–vinylene (PV) conjugation lengths and conjugation fraction on charge delocalization and mobility along PPV chains have been recently addressed by molecular models [9, 10].

The conjugation confinement can be controlled through the insertion of aliphatic inactive spacers in the polymer backbone [11, 12]. Additionally, these spacers increase the solubility and mechanical flexibility of polymers.

This contribution focuses on the synthesis and the luminescent and other properties characterization of a series of random copolymers containing segments with different conjugation lengths interspaced by non-conjugated segments with eight methylene groups. The copolymers were synthesized by polycondensation using the same method reported by Karasz [12], with minor modifications (Fig. 1).

The materials were prepared from different molar ratios x:y between the comonomers dialdehydes, 1,4-terephthaldehyde (**1**) and 1,8-bis(4-formyl-2,6-dimethoxyphenoxy)octane (**2**) (Fig. 1), in order to get structures with a

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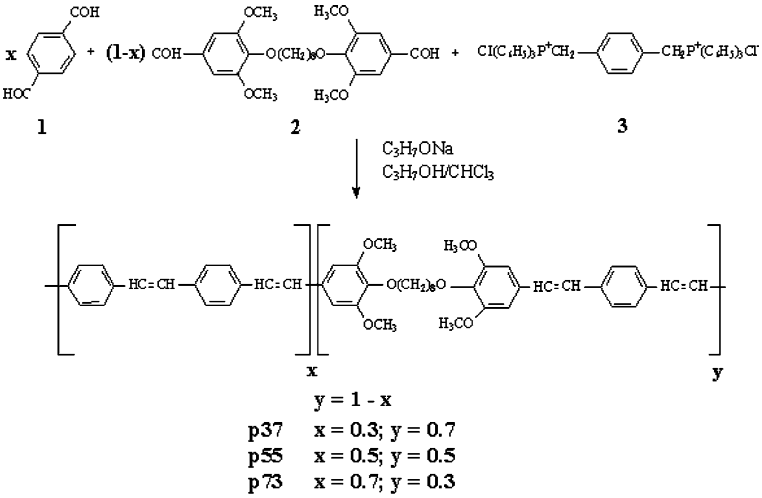


Fig. 1 Synthesis of Copolymers with different conjugation lengths via Wittig rote

random size distribution of conjugated segments or chromophores and the properties were correlated to the different *x*:*y* ratios.

Experimental

The statistical copolymers were synthesized by polycondensation reaction of 1,4 (methyltriphenylphosphonium)benzene dichloride **(3)** with 1,4-terephthaldehyde **(1)** and 1,8-bis (4-formyl-2,6-dimethoxyphenoxy)octane **(2)** (Fig. 1).

The monomers **(2)** and **(3)** were prepared according to the literature [12–14] and **(1)** were purified by recrystallization in methanol before polymerization.

Polymerization

Synthesis of polymer **p37**: a solution of 0.299 g of Na in 3.74 mL of anhydrous propanol-2 was added drop wise at room temperature to a stirred solution of 0.215 g (1.6 mmol) of **(1)**, 1.776 g (3.74 mmol) of **(2)** and 3.739 g (5.35 mmol) of **(3)** in 100 mL of anhydrous propanol-2 and molecular sieve dried chloroform (1/1). After the addition, the mixture was stirred for 24 h and then 5 mL of aqueous 2% hydrochloric acid was added. The collected product was thoroughly washed with ethanol/water (3/1) to remove by-products (triphenyl-phosphine oxide and NaCl). The solid polymer was dried in a vacuum oven at 0.2 mmHg pressure for1 week. The yield of **p37** was 0.528 g (52.83%).

The product was isomerized to the all-trans configuration by refluxing for 4 h in toluene in the presence of a catalytic amount of iodine. After removal of the toluene, the product was dissolved in 10 mL of chloroform and the solution was slowly added to 70 mL of methanol to purify the copolymer by precipitation. The material was dried in a vacuum oven at 0.2 mmHg pressure for 1 week.

The synthesis of copolymers **p55** e **p73** followed the same copolymer **p37** route, the difference was in the proportion between comonomers **(1)** and **(2)**. Moreover, in the **p55** polymerization sodium ethanoxide was added in the reaction system instead of sodium propanoxide.

Characterization of polymers

^{1}H NMR spectra were recorded on a Varian XL-200 spectrometer. The samples were dissolved in $CDCl_3$; chemical shifts shown were referred to TMS. The IR spectra were obtained on a Nicolet Magma-IR 560 spectrophotometer equipped with Nicolet PC/IR operation software. Molar mass and polydispersity were determined by gel permeation chromatography (GPC) using a Waters HPLC equipped with two columns in series, PLgel mixed-B and PLgel mixed-C. About 10 µL of each sample solution at 1 wt.% in THF was injected and GPC measurements were carried out in tetrahydrofuran at 1 mL/min. and monodisperse polystyrene samples were used as standards. The UV and Photoluminescence spectra were recorded on a Varian Cary 50Conc and Varian Eclipse spectrophotometer, respectively. Chloroform solutions of samples at 1.25×10^{-5} M were poured in 10 mm square quartz cuvet for UV and fluorescence spectroscopies. DSC measurements were performed on a Shimadzu DSC50 previously calibrated with Indium. Samples of 10–20 mg were encapsulated in Al pan and submitted to analysis from –50 °C to 200 °C. The heating rate was set at 20°C/min under nitrogen atmosphere.

Results and discussion

The polymerization reactions were performed according to monomers relative concentrations as shown in Table 1. Yields of PPV synthesis are typically high, approaching

Table 1 Monomers relative concentrations and reaction yields

	Monomer 1	Monomer 2	Monomer 3	Polymer	Yiels
p37	0.215 g	1.775 g	3.739 g	0.528 g	52.83%
p55	0.562 g	1.988 g	5.859 g	2.499 g	79.75%
p73	0.315 g	0.477 g	2.337 g	0.558 g	37.82%

100% for some derivatives [11]. However synthesis of alternating copolymers presenting conjugated non-conjugated structure is reported to present low yield [13]. The statistical polymer here prepared in a propanol-2/chloroform mixture presented higher yields compared to those reactions carried out in ethanol/chloroform [13].

The gel permeation chromatography (GPC) (Table 2) showed that the copolymers molar mass is in the range 2,930–8,100 g/mol, which is close to those reported in the literature (3,000–10,000 g/mol [15]).

Polymer **p37** presented a comparatively higher molar mass among the prepared copolymers; the result is attributed to the higher solubility in the reaction medium provided by the higher proportion of aliphatic blocks in the backbone. Karazs et al. [16] observed the same solubility effect in similar reactions. When the polymer is not soluble and precipitation do occur during the reaction, the Wittig polycondensation leads to polymers having lower molar mass, which can be explained by the limited growth of chains as solid precipitate.

In this case, the use of propanol instead of ethanol as co-solvent in the polymerization process probably aided increasing the molar mass. The lower M_w of **p55**, in which polymerization sodium ethanoxide was used, confirms this. This result for **p5**5 indicates an incomplete polymerization reaction, with limited formation of chromophores.

The reduced molar mass of **p73** was expected, because this polymer is poorly soluble in chloroform, but easily soluble in 1,2,4-trichlorobenzene. According to Klavetter et al. [11], in synthesis of similar statistical polymers, only copolymers with more than 40% of flexible segments groups are readily soluble in organic solvents.

Figure 2 shows the FTIR spectra of the synthesized copolymers. A band at 960 cm^{-1} implies the formation of trans-vinylene [12, 14], while the absorption at 1,680 cm^{-1} indicates the existence of the aldehyde groups in the chain ends. This strong band is an evidence of the formation of short polymer chains.

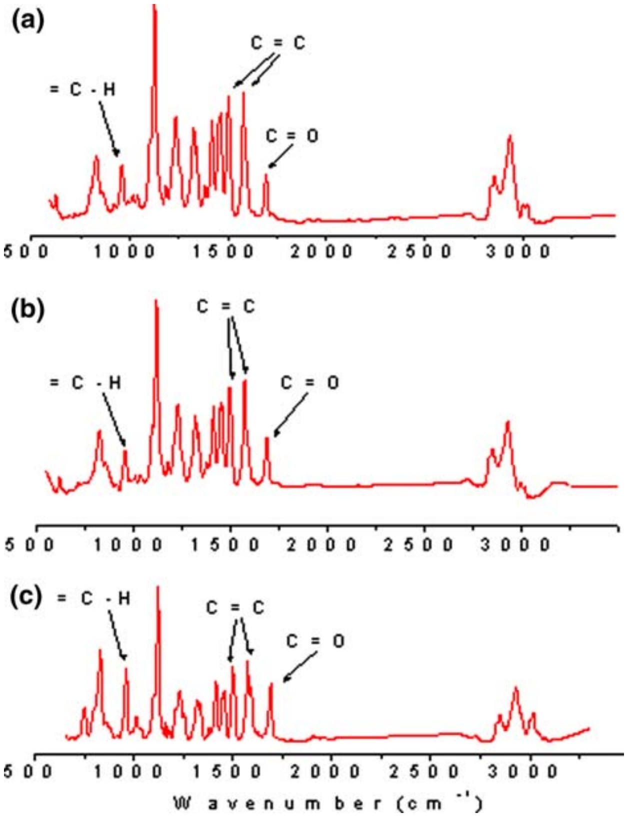


Fig. 2 Copolymers infrared (IR) spectra: (**a**) p37, (**b**) p55 and (**c**) p73

The ^{1}H NMR spectra of the copolymers were compared to the conjugated non-conjugated alternating copolymer (CNCP) [14], having defined conjugated segment with 2½ PV units (equivalent to $n = 1$, see Fig. 3), isolated by an 1,8-dioxyoctamethylene unit (Table 3). It is possible to observe that the equivalent peaks in the different copolymers presented nearly the same chemical shifts (±0.01 ppm), confirming the similarity of the molecular structures of the segments.

Besides those peaks reported on Table 3, other peaks are additionally observed in the prepared copolymers (Fig. 4) in the vinylene and aromatic hydrogen's region. Due to the multiplicity of the hydrogen–hydrogen coupling in this region, no specific hydrogen integration was possible,

Table 2 Average molar mass, polymerization degrees, polydispersities and glass transition temperatures of synthesized copolymers

Copolymers	M_n (g/mol)	x_n	M_w (g/mol)	x_w	PD	T_g
P37	2.41×10^3	3.81	8.1×10^3	12.81	3.37	63.1°C
P55	1.52×10^3	2.03	2.93×10^3	3.91	1.92	30.0°C
P73	1.56×10^3	1.53	3.15×10^3	3.08	2.02	70.1°C

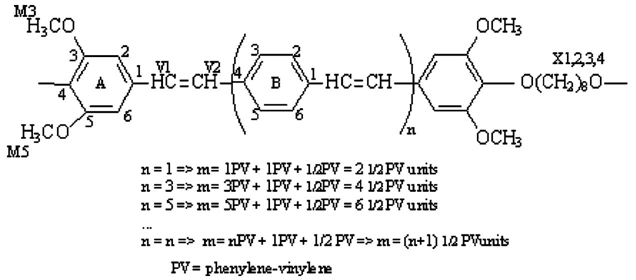


Fig. 3 Conjugated segments with *n* PV units

however, although individual assignment was not possible, the integration of the region 6.9–7.6 ppm relative to the aromatic hydrogen A2,6 (6.75 ppm) characterized the relative concentration of the inner PV hygrogens, that is $(PV)_n$. And, accordingly, a consistent increment of the multiplet area against the phenyl rings H(A2,6) was observed as a result of the higher relative content of terephthaldehyde in the polymerization feed, indicating the rise in the average length of the conjugated segments. Therefore, there is an increasing probability of finding segments with longer conjugation length when the terephthaldehyde (**1**) proportion is enlarged (Fig. 4).

Table 3 Protons chemical shifts (in ppm) of the copolymer with defined conjugation length CNCP [14] compared to those of synthesized statistical copolymers (d = doublet)

Protons	CNCP [14]	**p37**	**p55**	**p73**
H(A2,6)	6.74	6.74–6.75d	6.72–6.74d	6.72–6.74d
H(B2,3,5,6)	7.50	7.51	7.49	7.49
H(V1)	7.04	7.04	7.03	7.04
H(V2)	7.02	7.04	7.03	7.04
H(M3,5)	3.90	3.91	3.91	3.89
H(X1)	3.99	3.99	3.98	3.98
H(X2)	1.77	1.75–1.78d	1.74–1.77d	1.74–1.76d
H(X3)	1.47	1.40	1.39	1.38
H(X4)	1.38	1.40	1.39	1.38

In the absorption spectra (Fig. 5) the copolymers presented the maximum absorption at 329.0 nm, 329.9 nm and 347.1 nm for **p37**, **p55** and **p73**, respectively. This fact indicated a shift to longer wavelength according to increasing conjugation length. It is possible to observe absorption by other chromophore centers, which are revealed by the presence of shoulders in the spectra. The vibronic structure is in the spectral region correspondent to the 2½ units of PV [14], indicating a predominance of that conjugation length in the copolymers or *n* = 1, as displayed in Fig. 3.

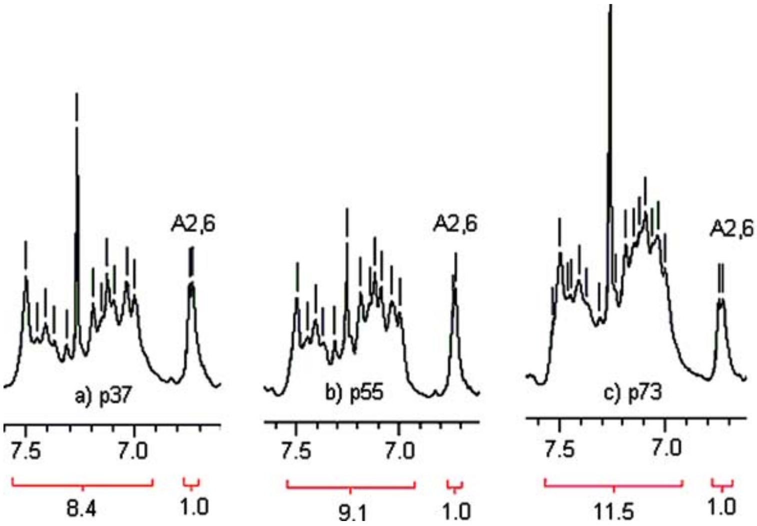
All copolymers presented photoluminescence spectra with the same maximum at 460 nm (Fig. 6), close to literature values for CNCP [14]. It shows that the synthesized copolymers have average segments of 2½ PV units due to the limited growth of chains. However, the characteristic band of each polymer is shifted to higher wavelength according to the concentration of (**1**) used in the polymerization, as longer conjugation degrees *n* would be possible.

The low polymerization degree of copolymers decreases the photoluminescence yields due to the non-radiative decay of exciton singlets at the chain ends, which will also impart low charge mobility [9, 10].

DSC analysis was performed in the range –50 °C to 200 °C. No transition was observed under –20 °C and above 120 °C, the copolymers start to undergo thermal decomposition.

Figure 7 shows the glass transition temperatures (T_g) for copolymers **p37** and **p73**, which were close to that of CNCP [14]. The presence of greater conjugated fraction induces the raise of the polymer T_g. The copolymer **p55**

Fig. 4 Spectra region showing the multiplets of phenyl rings and vinylic doublet in the conjugated segments along with the A2,6 phenyl ring hydrogens for the copolymers



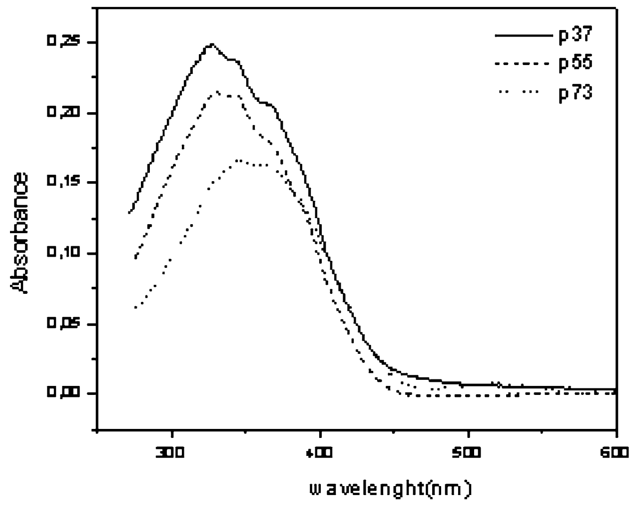


Fig. 5 UV–vis spectra of synthesized copolymers

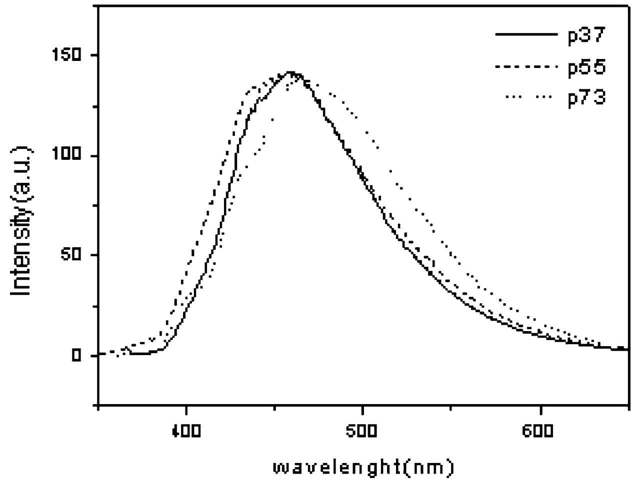


Fig. 6 Fluorescence spectra of synthesized copolymers

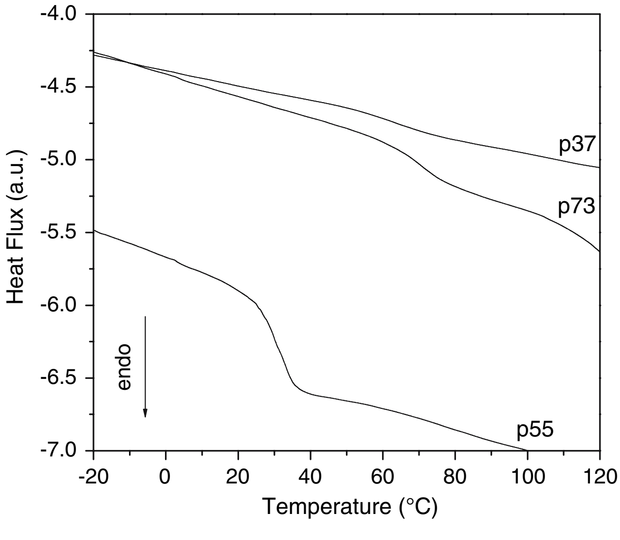


Fig. 7 DSC curve showing glass transition temperatures of copolymers: 63 °C (p37), 30 °C (p55) and 70 °C (p73)

presented an unexpected low T_g, which can be attributed to its lower polymerization degree, as its IR spectrum has shown relatively higher content of aldehyde groups.

Conclusion

The synthesis of the statistical segmented PV polymers carried out in propanol-2/chloroform mixtures resulted low yields and molar masses. The use of propanol/chloroform reaction medium was compared to the conventional ethanol/chloroform, and higher reaction yields were observed for the former.

It was possible to observe the absorption and emission band shifts due to the longer conjugated segments. For a more detailed study of Foster mechanism it is necessary to prepare copolymers with higher polymerization degree in order to get a representative distribution of the different chromophores.

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