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Light-emitting copolymers of cyano-containing PPV-based chromophores and a flexible spacer

M.R. Pinto[a], B. Hu[a], F.E. Karasz[a,*], L. Akcelrud[b]

[a]*Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA*
[b]*Departamento de Quimica, Universidade federal do Paraná, Curitiba 81531-900, Brazil*

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Abstract

Conjugated–non-conjugated alternating block copolymers containing cyano-modified distirylbenzene units as emitting chromophores were synthesized via Knoevenagel and Wittig reactions; the non-conjugated block was an alkylene spacer. The polymers were differentiated with respect to the location of the cyano groups in the chromophoric block (double bond or phenylene ring). When photoluminescence and electroluminescence spectra of these materials were compared with those of a similar structure without the cyano group, a strong bathochromic effect was observed. A more pronounced red shift and a higher electroluminescence efficiency was observed in the polymer with the cyano group attached to the aromatic ring. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Light-emitting polymers; Light-emitting polymeric devices; Cyano PPV derivatives

1. Introduction

The use of polymer-based materials in light-emitting diodes (LEDs) has brought about an increase in research in the field of conjugated polymers in recent years [1–3]. Numerous polymer structures containing PPV-related chromophores as main-chain [4–6], side-chain [7–9] or combined main- and side-chain [10] attached groups have been produced for LED applications.

Color tuning can be accomplished by several means, including substitution in the chromophore with appropriate choice of electron donor or acceptor groups, since these changes will affect the band gap [11]. To obtain high efficiency in electroluminescence it is also necessary to match the closest possible positive and negative charge injection into the device. It has been typically found that electron injection is more difficult than hole injection and this has led to the use of low work function cathode metals such as calcium, unstable under atmospheric conditions. Polymers with intrinsically high electron affinity are therefore highly desirable, since they reduce the barrier for electron injection. Substitution with electron withdrawing groups such as cyano, increases the electron affinity of the emitting layer chromophore, thus making possible the use of more stable electrodes such as aluminum. Cyano-substituted PPVs showed solid state photoluminescence efficiency considerably higher (50%) in comparison with PPV (27%) prepared by the sulfonium ion precursor [12].

Cyano-substituted PPV structures have been developed in which the cyano group is attached to the vinylene moiety and alkoxy groups (such as OC_6H_{13}) are substituents to the phenyl ring to provide solubility. The synthesis [13], the theoretical investigations of the effect of derivatization [11], the effects of the inclusion of alkoxy-substituted thiophene groups in the repeating unit or replacing the phenyl ring [14], the emission mechanism in solution and in the solid state using time-resolved spectroscopy [15,16], and the effects of the substitution on chain packing and optical properties of 2,5 alkoxysubstituted cyano PPVs have all been reported [17]. Studies in connection with hole transport layers such as PPV in multilayer devices [12] and silicon base anodes have also been carried out [18]. Materials emitting from blue to red have been produced [19–21].

We report on a new class of cyano-substituted light-emitting polymers, in which the chromophores are isolated from each other through a flexible non-conjugated spacer. This strategy has been used previously in several cases [22–28]. Copolymerization improves polymer solubility in organic solvents and decreases crystallinity, enhancing the

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* Corresponding author. Tel.: +1-413-545-4783; fax: +1-413-253-5295.
E-mail address: fekarasz@polysci.umass.edu (F.E. Karasz)

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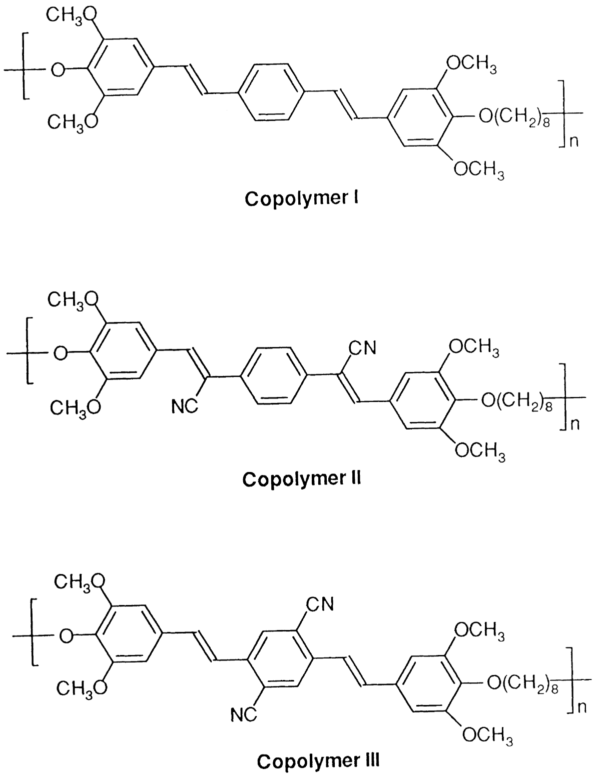


Fig. 1. Cyano-substituted Copolymers **II** and **III**, and the non-substituted reference Copolymer **I**.

properties of the film formed from spin coating or self-assembling related processes. It is also a convenient way to confine conjugation, increasing the band gap and generating a blue-shifted emission spectrum. In general, compounds with relatively shorter conjugation lengths have higher photoluminescence quantum yields, producing higher electroluminescence quantum yields. Copolymerization also brings about molecular dilution of the emitting centers, decreasing self quenching probabilities.

In the copolymers described below the cyano groups are attached either to the vinylene group (Copolymer **II**) or to phenyl ring (Copolymer **III**), as shown in Fig. 1. A non-cyano substituted reference structure (Copolymer **I**) was also prepared for comparison [22–25]. Copolymers **II** and **III** were synthesized using the Knoevenagel and Wittig routes, respectively, as briefly shown in Scheme 1. Copolymer **III** is the first light-emitting polymer with a cyano group attached to the phenyl ring reported so far.

2. Experimental section

Chloroform and tetrahydrofuran were refluxed over 4,4′-methylenebis(phenyl isocyanate) (MDI) and distilled prior to use. Methanol was dried with molecular sieves and distilled prior to use. 1,4-Phenylenediacetonitrile, 4-dimethylaminopyridine, 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), 1,3-dicyclohexylcarbodiimide (DCC), 2,5-dibromo-1,4-dimethylbenzene and triphenylphosphine were purchased from Aldrich and were used without further purification. All others reagents and solvents from commercial sources were used as received.

2.1. Characterization

FTIR spectra were recorded on an IBM IR3x type 913X spectrometer equipped with Nicolet PC/IR operation software. Cast films obtained from evaporation of polymer solutions in chloroform over a KBr cell were used for this purpose. ^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were taken on a Varian DPX300 spectrometer. GPC measurements were taken in a system composed of a WATERS 500 Pump, injector U6K, a WATERS 410 Differential Refraction Index detector, and a series of three Ultrastyragel columns with a porosity of 10^4, 10^3 and 10^2 Å and calibrated against polystyrene standards. THF solutions of the polymer samples were filtered through a Millipore membrane with a porosity of 0.45 μm just before injection. The elemental analysis was performed by the University of Massachusetts at Amherst Microanalytical Laboratory. Thermal transitions were determined using a Perkin–Elmer DSC-7 series differential scanning calorimeter. Solid state absorption spectra were taken using a UV–Vis Perkin–Elmer Lambda 9 UV–Vis–NIR spectrometer and solid state photoluminescence spectra were taken using a Perkin–Elmer LS50B Luminescence Spectrometer. Thin films used for spectroscopic measurements were obtained from casting polymer solutions at a concentration of 10^{-4} M onto quartz windows.

2.2. EL device fabrication and measurements

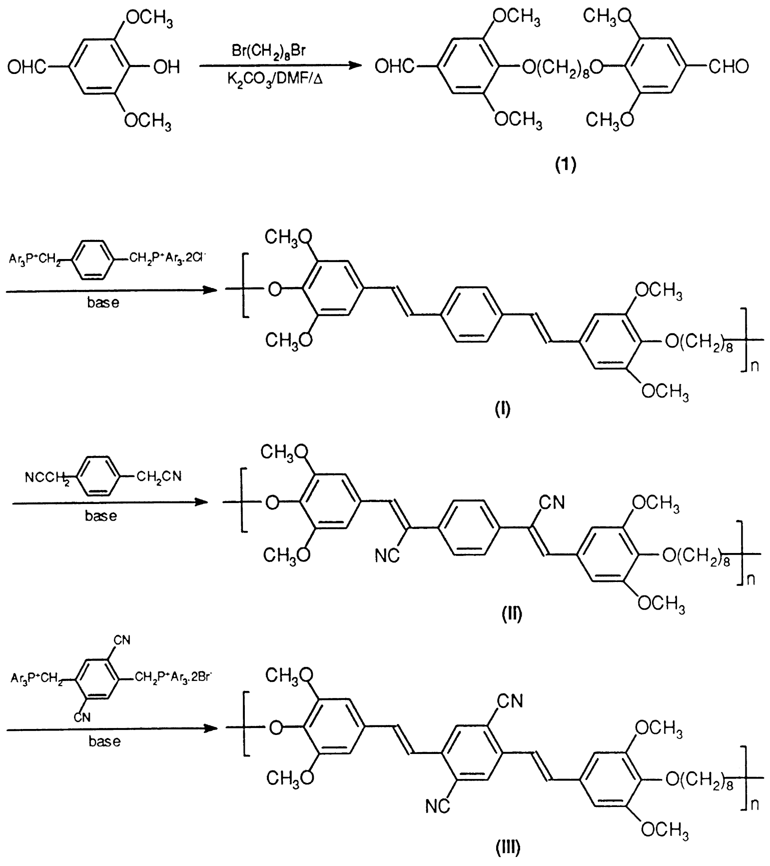
Chloroform solutions of the polymer samples, at a concentration of 20 mg/ml, were filtered through a Millipore membrane with a pore size of 0.2 μm. The solutions obtained were spin cast onto commercial ITO electrodes forming films with 80–90 nm thick. After evaporation a thin calcium layer was vacuum deposited over the substrate at a pressure below 10^{-7} Torr, and aluminum was subsenquently deposited the same way in order to prevent the anode from oxidation and improve the mechanical integrity of the device for the measurements. All the device preparation and measurements were performed under dry argon in a dry box.

2.3. Synthesis of monomers

The dialdehyde 1,8-bis(4-formyl-3,5-dimethoxyphenyleneoxy)octane [22–25] (**1**) and 2,5-bis(bromomethyl)-1,4dicyanobenzene [29] (**2**) were synthesized according to procedures described in Refs. [22] and [26], respectively.

*2.3.1. 2,5-dicyano-1,4-xylylene-bis(triphenylphosphonium bromide) (**3**)*

A solution of 2.7 g (8.6 mmol) of **2** and 7.8 g (30 mmol)



Scheme 1.

of triphenylphosphine in 200 ml of toluene was mechanically stirred and refluxed for 8 h under nitrogen.The white solid obtained was vacuum filtered, dissolved in methanol, and precipitated with anhydrous ether. The product was further purified by two successive crystallization steps from methanol–ethyl ether mixtures and dried under high vacuum.

Yield	4.9 g (68%)
^{1}H NMR (CDCl$_3$)	$\delta = 7.87$ (m,30H), 7.5 (s,2H), 5.88 (d,4H)
^{13}C NMR (CDCl$_3$)	$\delta = 143.6$, 136.2, 134.5, 131.3,130.4, 117.2, 116.0, 115.5
$C_{46}H_{36}Br_2N_2P_2$	Calc.: C 65.89 H 4.33 Br 19.06 N 3.34 P7.39 Found: C 64.72 H 4.52 Br 18.57 N 3.26 P 7.02
IR (KBr)	3051, 3015, 2860, 2229, 1635, 1585, 1483, 1437, 1395,1340, 1317, 1298, 1248, 1188, 1163, 1109, 1028, 995,918, 900, 850, 819, 748, 719, 686, 652, 621, 596, 540, 503.

2.4. Synthesis of the copolymers

2.4.1. Poly[oxy-1,8-octanediyloxy-(2,5-dimethoxy-1,4-phenylene)-1,2-ethanediyl-1,4-phenylene-1,2-ethenediyl-(2,5-dimethoxy-1,4-phenylene)] (Copolymer **I**)

This polymer was synthesized as described elsewhere [22–25]. See Table 1.

^{1}H NMR (MeOH-d$_4$)	$\delta = 10.13$ (s), 7.49 (s,4H), 7.04 (d,4H), 6.74 (s,4H), 4.07 (t,4H), 3.90 (s,12H), 1.77 (m,4H), 1.47 (m,4H0, 1.37 (m.4H)
^{13}C NMR (MeOH-d$_4$)	$\delta = 153.67$, 137.41, 136.57, 132.77, 128.61, 127.53, 126.75, 103.72, 73.64, 64, 56.17, 30.12, 29.45, 25.85
IR (KBr)	1421, 1342, 3024, 2934, 2853, 1716, 1579, 1512, 1502, 1464, 1456,1321, 1236, 1128, 1039, 991, 956, 925, 829, 669, 646, 628, 528

Table 1
Structural characterization of the polymer samples

Copolymer	M_w ($\times 10^{-3}$)	M_n ($\times 10^{-3}$)	M_w/M_n	T_g (°C)	Maximum absorption (nm)	Maximum PL emission (nm)	Maximum EL emission (nm)
I	26.5	7.9	3.3	87.9	356	453	474
II (Method A)	–	–	–	83.2	383	505	–
II (Method B)	14.6	82.	1.8	75.3	379	497	505
III	6.2	4.8	1.3	67.2	383	533	558

*2.4.2. Poly[oxy-1,8-octanediyloxy-(2,5-dimethoxy-1,4-phenylene)-(2-cyano-1,2-ethanediyl)-1,4-phenylene-(1-cyano-1,2-ethenediyl)-(2,5-dimethoxy-1,4-phenylene)] (Copolymer **II**)*

2.4.2.1. Method A A solution of 1.42 g (3.0 mmol) of **1** and 0.47 g (3 mmol) of 1,4-phenylenediacetonitrile in 30 ml of a mixture of anhydrous methanol and THF in a 50:50 ratio was placed in a Schlenk flask and vacuum degassed, then stirred under a gentle flow of nitrogen.1.4 ml (6 mmol) of a 25 wt% solution of sodium methoxide in methanol was added dropwise using a long steel needle and a syringe. The reaction turned dark green and a slurry was produced in a few minutes. After 15 min, the reaction was quenched by the addition of 200 ml of methanol acidified with 5 ml of concentrated hydrochloric acid. The polymer obtained was purified by successive precipitations until no color was observed in the mother liquid. The sample was dried in a vacuum oven at room temperature for 48 h. Yield: 1.59 g (89%). See Table 1.

^{1}H NMR (MeOH-d_4)	$\delta = 7.73$ (s,4H), 7.50 (s,4H), 7.22 (s,4H), 4.06 (t,4H), 3.92 (s,12H), 1.76 (m,4H), 1.29 (m,4H), 1.28 (m,4H)
^{13}C NMR (MeOH-d_4)	$\delta = 153.94$, 143.12, 140.35, 130.28, 128.93, 126.79, 118.54, 109.36, 107.30, 56.64, 74.11, 30.51, 29.76, 26.15
IR (KBr)	3165, 2936, 2853, 2212, 1691, 1577, 1502, 1464, 1423, 1387, 1331, 1251, 1234, 1128, 1066, 1014, 918, 839, 748, 682, 663, 642, 526

2.4.2.2. Method B To a solution of 2.37 g (5.0 mmol) of **1** and 0.78 g (5.0 mmol) of 1,4-phenylenediacetonitrile in 20 ml of anhydrous tetrahydrofuran was added, in one step and with stirring, 3.09 g (15 mmol) of 1,3-dicyclohexylcarbodiimide (DDC). The system was vacuum degassed and purged under a flow of nitrogen. After complete dissolution of the DDC, 1 ml of 4-dimethylaminopyridine was added to the reaction mixture. The reaction proceeded for 14 h when a clean-cut peak in the region of 15 000 g/mol was observed in GPC curves. Then, gentle reflux was applied for 10 min. and the reaction was quenched by pouring the mixture into a large amount of methanol. The polymer produced was treated in the same way as above. Yield: 2.11 g (71%). See Table 1.

*2.4.3. Poly[oxy-1,8-octanediyloxy-(2,5-dimethoxy-1,4phenylene)-1,2-ethanediyl-(2,5-dicyano-1,4-phenylene)-1,2-ethenedyl-(2,5-dimethoxy-1,4-phenylene)] (Copolymer **III**)*

A solution of 2.37 g (5.0 mmol) of **1** and 4.05 g (5.0 mmol) of **3** in 50 ml of a mixture of anhydrous tetrahydrofuran and methanol in a proportion of 90:10 was added to a Schlenk flash, vacuum degassed and then stirred under a gentle flow of nitrogen. Then, 3 ml (20 mmol) of 1,8-diazabiciyclo[5.4.0]undec-7-ene (DBU) was added in small aliquots so that each addition was made after an almost complete color change in the reaction media from red to yellow was observed. After complete addition of the base, the reaction was left overnight and was quenched by dissolving the mixture into a large amount of methanol. After three steps of purification by precipitation, the polymer was dissolved in chlorobenzene and isomerized to the all-*trans* configuration by refluxing with a catalytic amount of iodine for 4 h in the absence of light and under nitrogen. Further purification steps were performed in the same way as above. Yield: 1.43 g (48%). See Table 1.

^{1}H NMR (MeOH-d_4)	$\delta = 10.14 >$ (s), 8.02 (s, 2H), 7.26 (m, 4H), 6.79 (s, 4H), 4.02 (t, 4H), 3.91(s, 12H), 1.75 (m, 4H), 1.45 (m, 4H), 1.38 (m, 4H)
^{13}C NMR (MeOH-d_4)	$\delta = 191.14$, 153.92, 139.0, 135.29, 130.81, 129.78, 122.95, 117.51, 104.58, 73.70, 56.27, 30.12, 29.40, 25.74.
IR (KBr)	30.14, 2936, 2851, 2228, 1689, 1631, 1579, 1504, 1464, 1421, 1385, 1329, 1240, 1184, 1126, 1041, 956, 912, 858,817, 615, 528.

3. Results and discussion

3.1. Polymer synthesis

Scheme 1 shows the synthetic routes used to produce the polymers with cyano groups in the chromophoric block. Copolymer **I** which has been previously synthesized [22–25] in our laboratories represents the reference structure for comparison with the new polymers.

Two different approaches were employed to obtain Copolymer **II**. In the first (Method **II**A) a Knoevenagel-type condensation was used in the conditions commonly reported i.e. a strong base is used in a mixture of solvents at 50°C [18,19].Thus, soldium methoxide in a 1:1 v/v mixture of methanol and tetrahydrofuran at 25°C was used. Under these conditions, crosslinking occurred during the reaction and/or the purification. This can be seen in the IR spectrum of Fig. 2 (and is discussed in Section 3.2). Moreover, it was noted that the molecular weght increased on aging, in solution or in the solid state,and some insoluble material was observed during subsequent solubilization. These results were attributed to a Michael-type addition between active methylene end groups and the vinylene groups in the polymer, since the effect was observed even in samples stored in the dark under inert atmosphere and refrigeration. This effect was not found in the results reported for this type of reaction and can be explained by the steric hindrance provided by bulky *ortho* substituents in the aromatic ring, which were necessary for solubilization since the polymers were fully conjugated.These findings prompted us to use milder conditions to obtain Copolymer **II**, as described in Method B.

Method B was based on very mild polycondensation

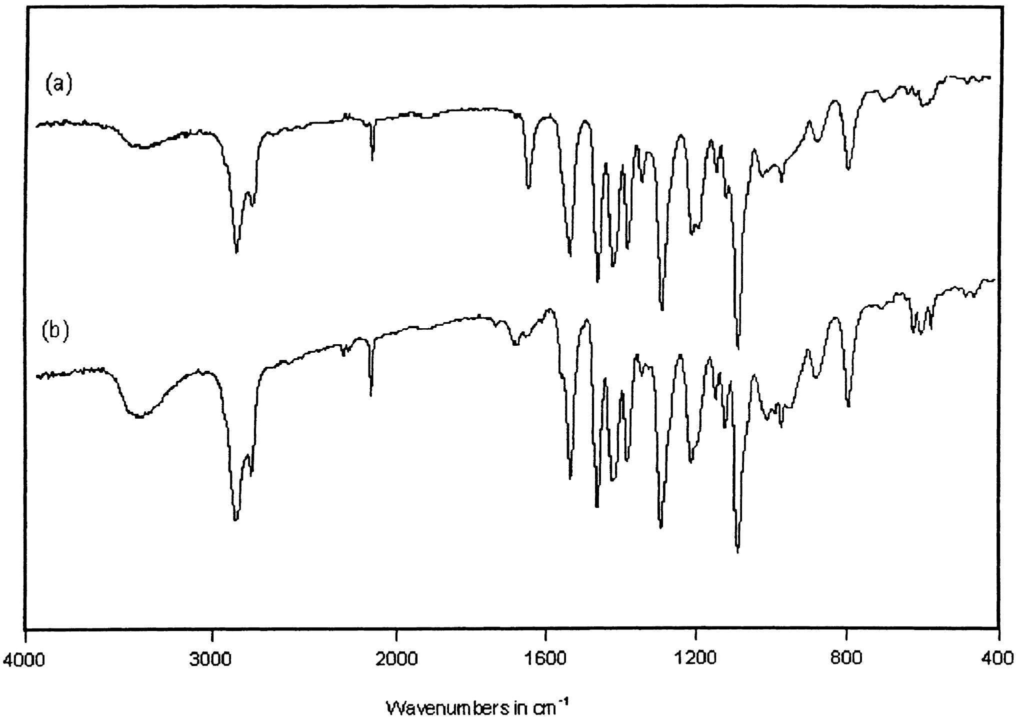


Fig. 2. FTIR spectra of cast films of Copolymer **II** obtained by (a) method A and (b) method B. See text.

conditions. The reaction was carried out in tetrahydrofuran at room temperature and promoted by 4-dimethylaminopyridine (DMAP) as a base and 1,3-dicyclohexylcarbodiimide as a condensing agent. The increase in molecular weight was followed by SEC as the reaction proceeded. After 14 h at room temperature, a clean-cut peak appeared in the region corresponding to the molecular weight of 8000–14 000 g/mol. After purification it was shown by ^{1}H NMR that no side reactions took place to any significant extent. Polymers obtained using this method showed good photoluminescence spectra reproducibility. The improved performance of this method can be explained by the fact that DCC may halt the condensation reaction during aldol formation, due to the possibility of an adduct formation, thus leading to undesirable Michael additions. At the end of the polymerization reaction any adduct formed between DCC and the aldol functions [30,31] was, if necessary, destroyed by a gentle reflux of the reaction mixture.

The Wittig-type polycondensation, used to synthesize Copolymer **III**, was easily accomplished by the reaction between the dialdehyde and the ylide, which was formed in situ from the reaction between 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and the corresponding phosphonium salt. A polymer with molecular weight of 6000 g/mol was obtained in a few hours at room temperature. The polymer was isomerized to all-*trans* configuration by refluxing the polymer solution in toluene with a catalytic amount of iodine.

The Wittig polymerization carries advantages over the Knoevenagel polymerization, since in the former there is no possibility of crosslinking reactions, and as a result the probability of structural defects is lower. The Wittig reaction is favored by the enhanced acidity of the methylenic protons of the phosphonium salt, caused by the presence of the two electron withdrawing cyano groups. Consequently, weaker bases, such as tertiary amines, can be used to promote ylide formation without affecting the cyano and aldehyde groups, both of which are sensitive to strong basic media. This is therefore a good synthetic strategy for the production of cyano-containing PPV-like structures.

3.2. Structural and thermal characterization of the polymers

Data from the GPC analysis are shown in Table 1. As mentioned above the molecular weight of the Knoevenagel polycondensation polymers was controlled by the reaction time or by the polymer solubility.The two Wittig polycondensation polymers, Copolymers **I** and **III** showed quite different molecular weghts This can be attributed to the difference in monomer reactivity, since the polymer with the lower molecular weight resulted from the less reactive cyano-substituted ylide which seemed to be relatively stable, even in the presence of a small amount of protic solvent added to the reaction medium.The molecular weight of the polymer obtained by Knoevenagel polycondensation via Method A was not determined due to problems in obtaining a clear solution in tetrahydrofuran.

DSC curves of the polymer samples showed only second-order transitions, characterized as the T_g transitions, during heating steps at 20°C/min (Table 1). No apparent

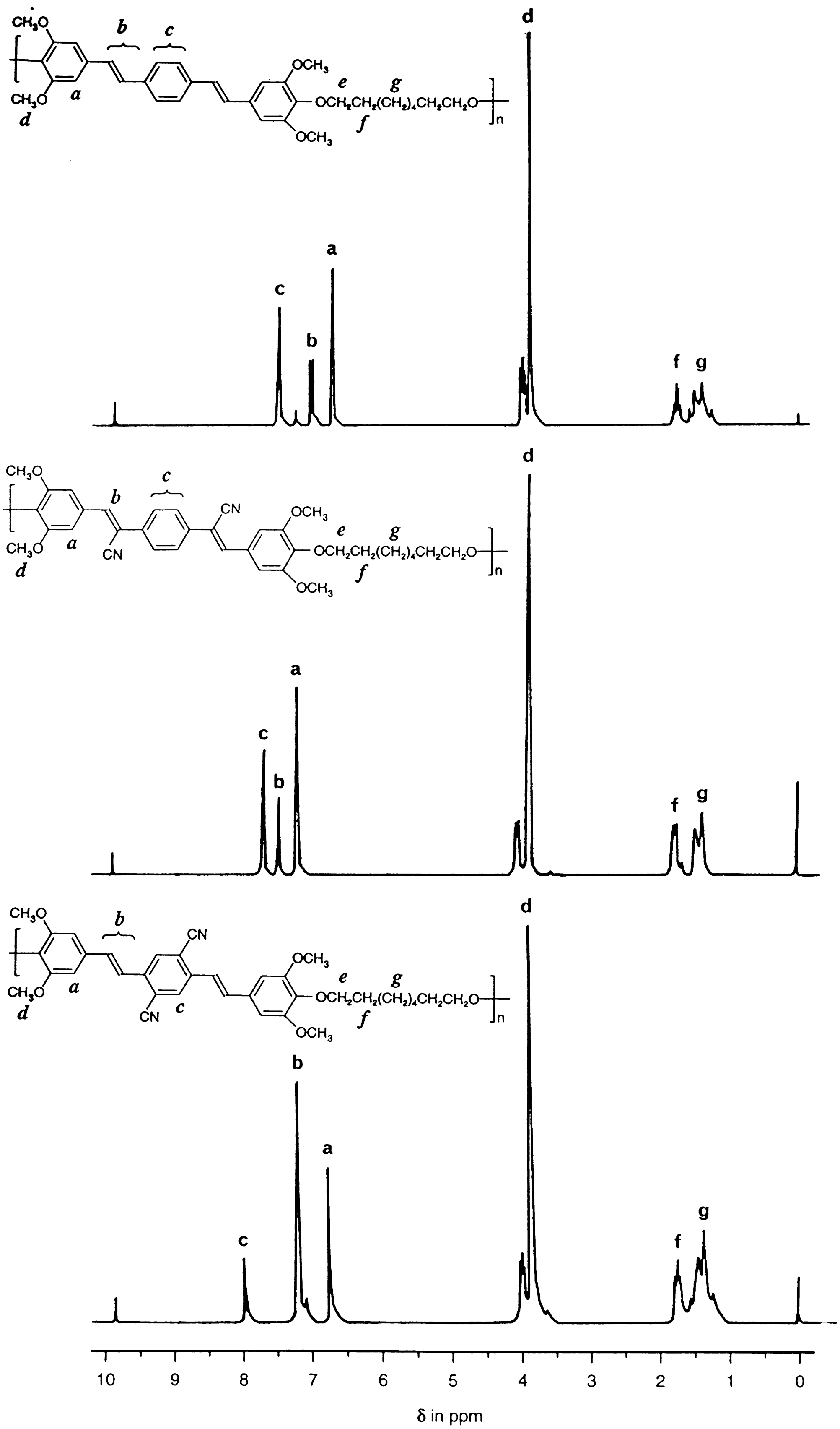


Fig. 3. ^1H NMR spectra, $CDCl_3$, of the copolymers.

crystallization was observed after annealing the samples above their T_g for 24 h. The somewhat low values of these transitions are associated with the thermal motion of the alkylene soft blocks. The T_g values increased with increasing molecular weight and it may be that the molecular weight of Copolymer **II-A** which could not be measured by GPC experiments, lies between those of Copolymer **I** and Copolymer **II-B**.

In the FTIR spectra of the three copolymer samples (Fig. 2) a peak was found in the 920–960 cm^{-1} region assigned to the out-of-plane vibration of the *trans*-vinylene groups of the chromophore. A strong peak centered at 2212 cm^{-1} assigned to the cyano groups was present in Copolymers **II** and **III**. Also, a small peak at 1701 cm^{-1} was found in all samples, and was assigned to the aldehyde terminal groups. By comparing the FTIR spectra of the polymers obtained from Knoevenagel-type polycondensation under different reaction conditions, i.e. Methods A and B, it can be seen from Fig. 2 that Method A produces a polymer with some structural defects, as indicated by the presence of multiple peaks observed in the 1690–1710 cm^{-1} region.They can be assigned to carboxylic groups produced by hydrolysis of the cyano groups or by a Canizarro reaction of the aldehyde terminal groups promoted by the strong basic conditions used in this method.

In the aromatic regions of the ^{1}H NMR and ^{13}C NMR spectra, all samples showed only three peaks (Fig. 3). Two of these peaks were assigned to aromatic protons and the other one to the *trans*-vinylene protons. The *cis*-vinylene protons, which can be observed in the region 6.5–7.0 ppm for non-isomerized Wittig-type polymers, were not be observed indicating complete isomerization. In the Knoevenagel polymer samples, the vinylene proton was at centered at 7.2–7.3 ppm and the other peaks were assigned to the aromatic protons. A very small peak at 10.1 ppm, attributed to the terminal aldehyde groups, could be observed in the low molecular weight samples of Copolymers **II-B** and **III**. ^{13}C NMR data showed good agreement with the structures synthesized, although the Knoevenagel polymer spectra showed very small multiple peaks in the aromatic region in addition to the main structure-related peaks.

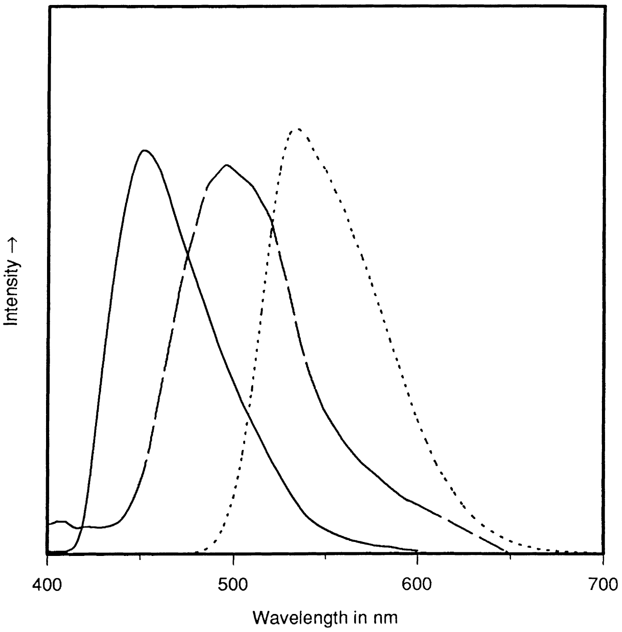


Fig. 4. Photoluminescent spectra of neat thin films cast onto quartz windows: (—) copolymer **I** (– – –) copolymer **II** and (···) copolymer **III**. Spectra were arbitrarily scaled to facilitate comparison. Samples were excited at 390 nm.

3.3. Absorption and photoluminescence properties

3.3.1. Solid state absorption and PL spectra

The solid state photoluminescence spectra of the copolymers are shown in Fig. 4. They were obtained from solid thin films cast onto glass plates and with excitation at 390 nm. Copolymer **I** showed a characteristic blue emission at 453 nm. The introduction of the cyano groups into this structure brought about a large bathochromic effect. Copolymer **II** emitted at 497 nm, while Copolymer **III** showed a greenish-yellow emission at 533 nm. Solutions of this copolymer in apolar solvents are visibly fluorescent even when observed in a brightly lit room.

The energy level of the conduction band is lowered by increasing the electron affinity of the polymer, and since cyano groups lower the LUMO energy, a corresponding shift of the emission towards longer wavelengths is expected. In the case of poly(cyanoterephthalylidene)s the LUMO band is lowered by 0.9 eV and the HOMO band by 0.6 eV relative to PPV, causing the emission to change from greeenish yellow to red [12].

Another feature of Coplymers **II** and **III** is the presence of methoxy electron donating groups, which induce strong permanent dipoles affecting the donor–acceptor strengths of the OCH_3 and CN groups. These dipoles increase the electron density in the chromophoric block and consequently bring about a decrease of the energy of the excited state. Therefore the relaxational decay produces lower frequency emission. In fact, the absorption spectra of the cyano-based polymers showed a π–π^* transition at lower frequencies than Copolymer **I**, as it can be seen in the absorption spectra shown in Fig. 5.

This effect is more pronounced in Copolymer **III** where the two methoxy substituents and the two electron withdrawing CN substituents are attached to separate aromatic rings. Moreover, the CN groups are one π system away in relation to Copolymer **II**. This difference in electron density is reflected in different chemical shifts in the NMR as it can be seen from the location of peaks a, b and c in Fig. 3, which represent the protons in the OCH_3 substituted ring in the vinyl bond and in the middle ring respectively.If $\Delta\delta_a$, $\Delta\delta_b$ and $\Delta\delta_c$ are the corresponding displacements of peaks a, b and c of Copolymers **II** and **III** in relation to the reference

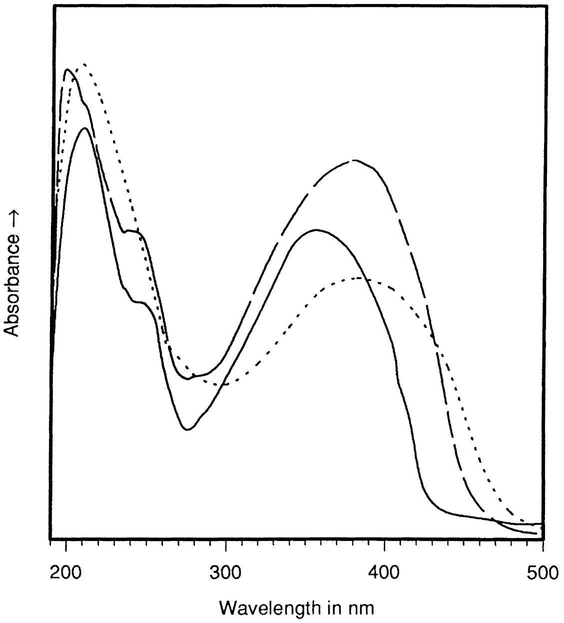


Fig. 5. Solid state absorption spectra of neat thin films cast onto quartz windows: (—) Copolymer **I**; (– – –) Copolymer **II** and (···) Copolymer **III**. Spectra were arbitrary scaled to facilitate comparison.

copolymer, it can be observed that $\Delta\delta_a$, $\Delta\delta_b$ and $\Delta\delta_c$ for Copolymer **II** are approximately the same ($\Delta\delta_a = 0.48$ ppm, $\Delta\delta_b = 0.46$ ppm and $\Delta\delta_c = 0.24$ ppm), whereas the presence of the cyano group in the aromatic ring (Copolymer **III**) induces a major change in line a ($\Delta\delta_c = 0.53$ ppm), a small shift in line b ($\Delta\delta_b = 0.25$ ppm) and a negligible effect in line c ($\Delta\delta_c = 0.05$ ppm) showing that in Copolymer **III** the effect of charge delocalization is much higher than in Copolymer **II**.

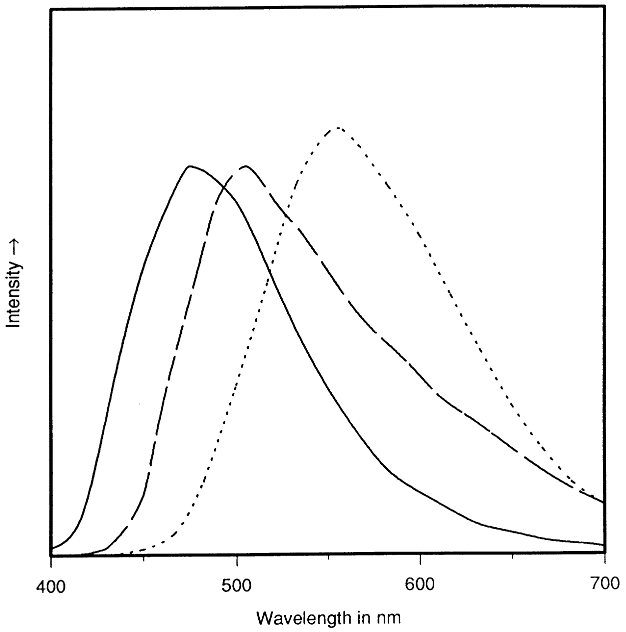


Fig. 6. Electroluminescence spectra of: (—) Copolymer **I**; (– – –) Copolymer **II-B** and (···) Copolymer**III**. Spectra were arbitrary scaled to facilitate comparison.

3.4. Electroluminescent properties

Fig. 6 compares the electroluminescence spectra of Copolymers **I**, **II** and **III**. The intensities of the spectra were normalized in order to facilitate comparison of the emission properties of each sample. The spectra of all samples were wider and slightly red-shifted in relation to the corresponding solid state PL spectra. This is probably due to interactions between the chromophores and ITO at the polymer–electrode interface. In fact, PL spectra taken directly from the devices were consistent with the respective EL spectra.Copolymer **II** showed a low-intensity emission, centered at 505 nm. One of the factors that contributed to this is the solubility associated with this structuture. Conversely,the Copolymer **III** device showed good performance and a yellow emission centered at 553 nm could be observed in a well-lit room. Fig. 7 shows the emission intesity and input current as a function of applied voltage for Copolymer **III**. At a 13 V applied forward bias the device turns on, and the current function showed a close relation with the output emission intensity. This indicates a balanced charge injection and a facile charge recombination.

4. Conclusions

Block copolymers containing a methylene-based spacer and cyano-substituted PPV segments were prepared for the first time. The cyano groups were located in the vinylidene bond (Copolymer **II**) or in the aromatic ring (Copolymer **III**). Copolymer **II** was prepared via a Knovenaegel route

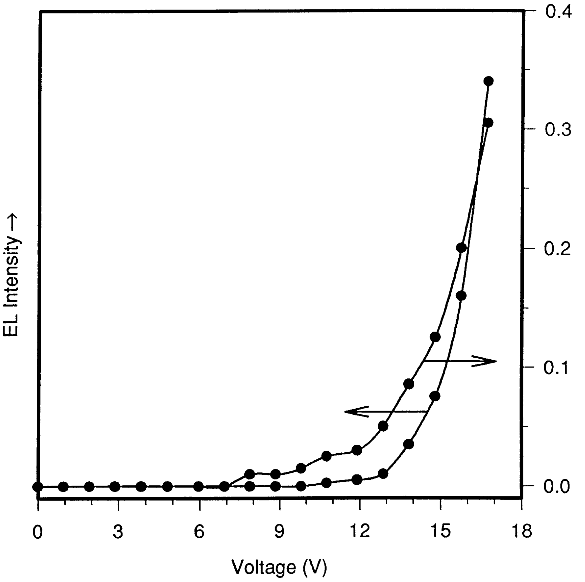


Fig. 7. Emission intensity and current density vs applied forward bias plot for copolymer **III** LED.

and Copolymer **III** was made using a Wittig reaction.The latter process afforded a more perfect structure, whereas there was a possibilty of side reactions in the former.

The photophysical properties of these materials were compared to those of the corresponding non-substituted product (Copolymer **I**).The PL and EL spectra of the new polymers showed a red shift in relation to the non-substituted copolymer. This was attributed to the increase in the electron dispersion brought about by the enhanced polarization.Copolymer **II** showed a bright yellow EL emission centered at 558 nm.

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