Contributions of Nonconjugated Spacers to Properties of Electroluminescent Block Copolymers

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CONTRIBUTIONS OF NONCONJUGATED SPACERS TO PROPERTIES OF ELECTROLUMINESCENT BLOCK COPOLYMERS

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ABSTRACT

Six electro-optically active alternating block copolymers consisting of short substituted phenylene vinylene sequences interspersed with optically inert oligomethylene blocks were synthesized using a Wittig condensation scheme. In this study, the focus was on the effect of the aliphatic spacer length, which was systematically varied from two to twelve methylene units. The copolymers were soluble in standard organic reagents and were characterized by NMR, FTIR, elemental analysis, GPC, UV-vis, and DSC. The vinylene groups in the conjugated blocks were isomerized into the all-*trans* form by refluxing in toluene with catalytic iodine. The electroluminescent spectra of the six copolymers were similar and displayed a maximum around 465 nm. The EL efficiency of the single-layer LEDs fabricated with the copolymer chromophores was a function of the length of the nonconjugated spacer blocks; copolymers with longer spacers yielded higher-efficiency devices.

INTRODUCTION

Copolymers containing conjugated and nonconjugated blocks have been studied in terms of their electro-optical properties such as electrical conductivity [1, 2], nonlinear optical properties [3], and electroluminescent (EL) properties [4-6], and compared to those in fully-conjugated polymers such as polyacetylene (PA), poly(p-phenylene) (PPP), and poly (p-phenylenevinylene) (PPV) [7-9]. Many polymers of this design are intrinsically soluble, have good film-forming and mechanical properties, and are suitable for fabrication of devices [9-11]. They also offer extra degrees of freedom in molecular design for specific properties. For example, it has been shown that by systematically varying the structure of the conjugated blocks, it is possible to obtain copolymers that display photolumines-cence (PL) and EL over the whole visible spectrum [5, 11, 12].

This contribution focuses on the synthesis and the electroluminescent and other properties of a series of alternating copolymers containing identical conjugated blocks in which the length of the interspersed nonconjugated methylene spacer groups is systematically varied from two to twelve units. In earlier work we briefly described properties of these systems with two methylene block lengths, namely three and eight [13]. The ether bonds which link the blocks are not affected by the post-synthesis *cis-trans* isomerization of the vinylene groups; the final copolymers have the required all-*trans* configuration in the vinylene moieties and this modification thereby overcomes a previously reported problem in the isomerization of similar copolymers containing ester linkages [14].

The alternating block copolymer concept using an oligomethylene spacer and a phenylene vinylene-related chromophore has also been studied by Hay *et al.* [15], who obtained PL spectra from copolymers in which the number of methylene groups was varied. Burn et al. used a similar conjugated/non-conjugated structure as a side group chromophore; the length of the methylene spacer block was not varied, however [16]. Herrema *et al.* [5] synthesized a series of multiblock alternating copolymers containing soft block oligosilylene units and hard block oligo-thiophene units of variable length. The spectroscopic results showed a pronounced effect of the oligosilylene length on the absorption and fluorescence spectra and on PL efficiency of the copolymers, in contrast to the present results. These effects were attributed to $\pi-\sigma$ interaction of the thiophene units with the oligosilylene blocks. This also results in spectroscopic differences between these block copolymers and the corresponding chromophoric model compounds.
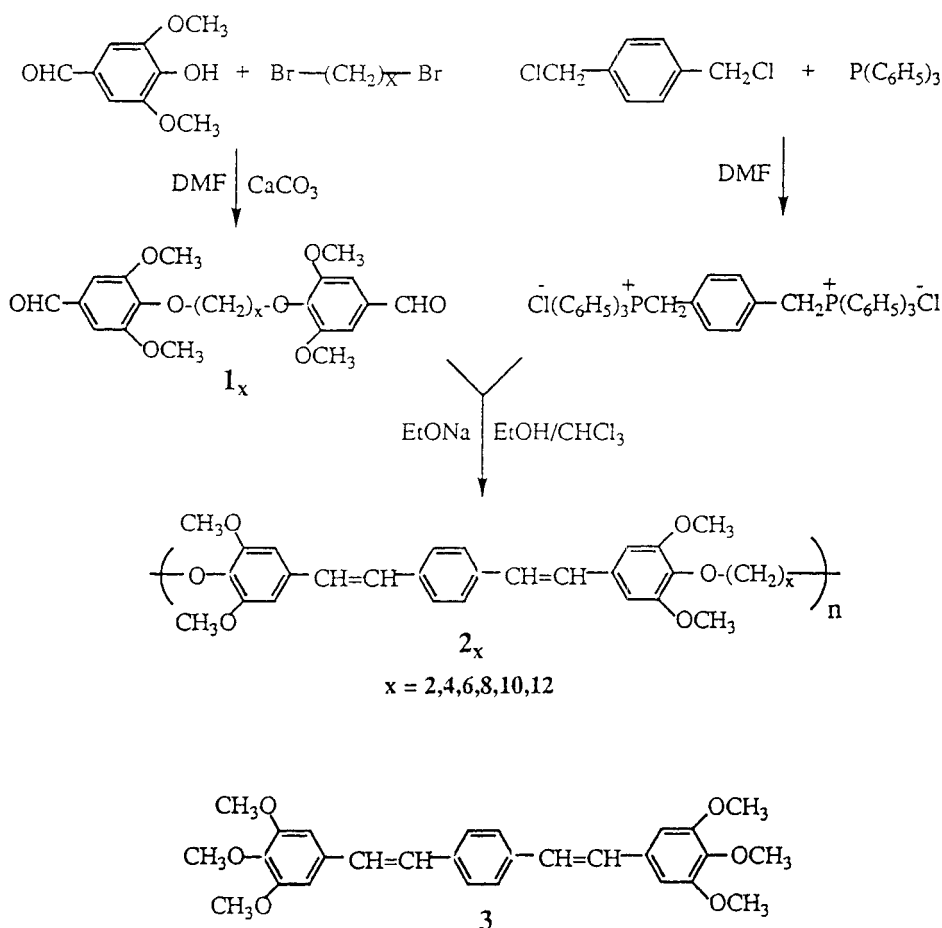
Figure 1. Synthetic route and structures of dialdehydes (1_2 through 1_{12}) and block copolymers (2_2 through 2_{12}); model structure 3.

EXPERIMENTAL

The synthetic scheme is shown in Figure 1. The characterization of the resulting copolymers was by means of GPC, FTIR, NMR, UV-vis, DSC, and elemental analysis.

Syntheses of Dialdehyde Monomers

Synthesis of 1,2-bis(4-formyl-2,6-dimethoxyphenoxy)butane, compound 1_4: A solution of 3.64 g (0.02 mol) of 3,5-dimethoxy-4-hydroxybenzaldehyde and

TABLE 1. Yields, Melting Points, and Elemental Analyses of the Dialdehyde Monomers

| Monomer | Yield (%) | Melting Point (°C) | Elemental Analysis | | | |
| | | | C | | H | |
			Calc.	Found	Calc.	Found
1_2	41	188-189	C 61.53	61.48	H 5.68	5.66
1_4	63	153-155	C 63.15	63.15	H 6.26	6.47
1_6	95	89-90	C 64.56	64.26	H 6.77	6.75
1_8	79	87-88	C 65.81	65.43	H 7.22	7.20
1_{10}	87	86-87	C 66.91	66.48	H 7.62	7.71
1_{12}	95	77-78	C 67.90	67.73	H 7.98	8.02

2.16 g (0.01 mol) of 1,2-dibromobutane in 150 mL of DMF was stirred and heated to 60°C while 3.0 g (0.022 mol) of potassium carbonate was added slowly. After the addition, the solution was stirred and kept at 60°C overnight; the mixture was then poured into 2 L of distilled water. After 2 hours, the precipitate was collected and dried in air at ambient temperature and then recrystallized from EtOH/water (5/1). The yield of 1_4 was 2.6 g (63%) with a melting point of 153° to 155°C.

The other dialdehydes, 1_2 through 1_{12}, were synthesized in the same way from corresponding starting materials. The yields, melting points, and elemental analyses are listed in Table 1.

Polymerization

Synthesis of poly[oxybutyleneoxy-(2,6-dimethoxy-1,4-phenylene-1,2-eth-enylene-1,4-phenylene-1,2-ethenylene-3,5-dimethoxy-1,4-phenylene)], compound 2_4: To a stirred solution of 1.68 g (0.004 mol) of 1_4 and 2.80 g (0.004 mol) of 1,4-xylylene-bis(triphenylphosphonium chloride) in 100 mL of anhydrous ethanol and molecular sieve-dried chloroform (3/1), a solution of 0.23 g (0.01 mol) Na in 15 mL of anhydrous ethanol was added dropwise at ambient temperature. After the addition, the mixture was stirred for 4 hours and then 5 mL of 2% hydrochloric acid was added. The paste-like product, collected on the wall of the flask, was thoroughly washed with ethanol/water (3/1) to remove the by-products (triphenyl-phosphine oxide and NaCl). After drying, the product was isomerized to the all-*trans* configuration by refluxing for 4 hours in toluene in the presence of a catalytic

TABLE 2. Yields, T_g's, M.W.s, M.W.D.s and Elemental Analyses of Copolymers

Copolymer	Yield (%)	T_g(°C)	M.W.[a] $(M_w) \times 10^4$	Dispersity	Elemental Analysis			
					C		H	
					Calc.	Found	Calc.	Found
2_2	91	123	2.3	4.2	73.0	72.3	6.13	6.20
2_4	85	103	2.6	1.8	73.8	72.8	6.60	6.75
2_6	86	83	6.3	3.0	74.4	73.6	7.02	7.26
2_8	89	68	3.4	2.0	75.0	74.0	7.40	7.46
2_{10}	86	67	4.3	2.3	75.5	74.7	7.74	7.88
2_{12}	85	53	3.6	2.0	76.0	75.2	8.05	8.23

[a]Relative weight average molecular weights obtained from GPC measurement calibrated with PS standards.

amount of iodine. After removal of the toluene, the product was dissolved in 30 mL of chloroform and the solution was used to cast a film on a clean glass plate pretreated with dichlorodimethysilane. The solvent was evaporated, and the dried film peeled off the glass and further dried *in vacuo* at 40°C for one week to give 1.67 g of a yellow polymeric product.

The other copolymers, compounds 2_2 to 2_{12}, were synthesized in the same way from the corresponding dialdehydes and the bisphosphonium salt. The yields, GPC molecular weights, glass transition temperatures, and elemental analyses, are listed in Table 2.

A model compound, *trans, trans,* 1,4-bis[2-(3,4,5-trimethoxy-phenyl)-ethenyl]-benzene, 3 (Figure 1) was synthesized as discussed previously [17].

Characterization

FTIR spectra were obtained on an IBM IR/3X Type 913X FTIR spec-trophotometer equipped with Nicolet PC/IR Operation software. UV-vis spectra were recorded on an IBM 9420 spectrophotometer. ^{1}H NMR spectra ($CDCl_3$) were recorded using a Varian XL-300 spectrometer and chemical shifts were referred to TMS. ^{13}C NMR ($CDCl_3$) spectra were recorded on a Varian XL-200 spectrometer and chemical shifts were referred to TMS. Elemental analyses were performed by the Microanalysis Laboratory at the University of Massachusetts at Amherst. GPCs were performed using THF as solvent on a Waters model 500 with a Waters 416 Differential Refractometer and Waters Data Module 730. Polystyrene standards
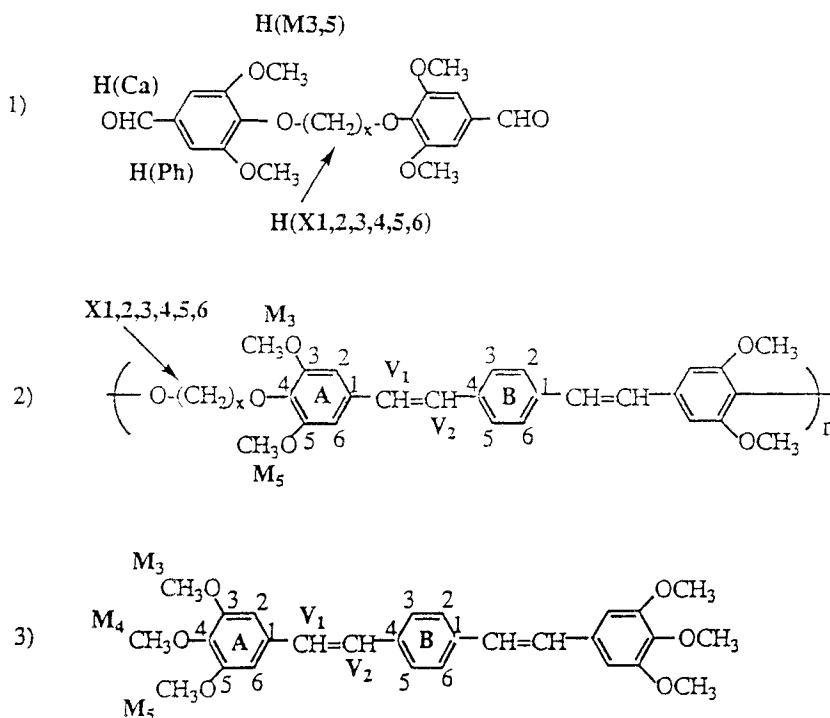
Figure 2. Atom numbering scheme used in NMR assignments for the dialdehydes (**1**), model compounds (**2**), and copolymers (**3**).

(Polymer Laboratories Ltd., UK) were used in calibration. DSC measurements were carried out on a Perkin-Elmer DSC-7 calibrated with indium. The temperature was scanned at a rate of $20°C/min$ under nitrogen.

EL Device Fabrication and Property Measurements

The EL fabrication and EL and other spectroscopic measurements were performed using the same procedures described previously [18-20]. EL spectra were recorded at room temperature in an argon atmosphere.

RESULTS AND DISCUSSION

Figure 2 records the atomic labelling for all component structures investigated. Table 3 shows the assignment in the ^1H NMR spectra for the dialdehyde

TABLE 3. ^{1}H NMR Chemical Shifts (ppm) of the Dialdehydes in CDCl$_3$

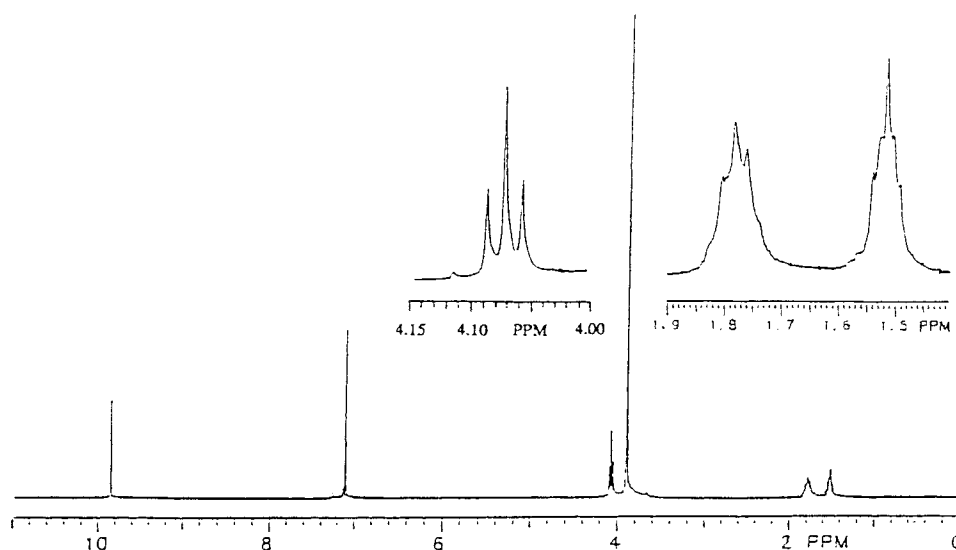| H	1_2	1_4	1_6	1_8	1_{10}	1_{12}
H(Ca)	9.86	9.85	9.86	9.86	9.85	9.86
H(Ph)	7.11	7.11	7.11	7.12	7.11	7.12
H(M3,5)	3.88	3.89	3.90	3.91	3.90	3.91
H(X1)	4.43	4.13	4.07	4.06	4.05	4.07
H(X2)		1.97	1.79	1.75	1.75	1.76
H(X3)			1.52	1.46	1.43	1.44
H(X4)				1.36	1.31	1.28
H(X5)					1.31	1.28
H(X6)						1.28

Figure 3. ^{1}H NMR spectrum of dialdehyde monomer 1_6 in CDCl$_3$ solution with expanded fine structures of X1, X2, X3 (Table3).

monomers 1_x, which confirms the molecular structure of these compounds. As an example, the 1_6 spectrum is shown in Figure 3.

Tables 4 and 5 summarize ^{1}H and ^{13}C NMR chemical shifts of the copolymers 2_x and of the low molar mass model compound 3. The results are consistent

TABLE 4 . ^{1}H NMR Chemical Shifts (ppm) of the Copolymers and Model Compound in CDCl$_3$

| H	Model	2_2	2_4	2_6	2_8	2_{10}	2_{12}
H(A2,6)	6.76	6.73	6.75	6.75	6.74	6.75	6.74
H(B2,3,5,6)	7.51	7.50	7.50	7.51	7.50	7.50	7.50
H(V1)	7.05	7.04	7.04	7.04	7.04	7.04	7.04
H(V2)	7.04	7.03	7.03	7.03	7.02	7.02	7.02
H(M3,5)	3.93	3.89	3.90	3.91	3.90	3.91	3.90
H(M4)	3.88						
H(X1)		4.37	4.07	4.01	3.99	3.99	3.99
H(X2)			1.98	1.81	1.77	1.77	1.76
H(X3)				1.56	1.47	1.45	1.44
H(X4)					1.38	1.33	1.29
H(X5)						1.33	1.29
H(X6)							1.29

with those reported for the analogous polyester-containing copolymers [14]. Figures 4 and 5 show representative spectra for copolymer 2_6. The assignment of the chemical shifts verifies the molecular structure of the copolymers and confirms the *trans* configuration in the vinylene groups.

Figure 6 shows the FTIR spectrum of (a) the dialdehyde 1_{10} and (b) the copolymer 2_{10}. The C=O stretching can be clearly identified at 1696 cm^{-1} in (a) together with the aldehydic C-H stretch at 2760 cm^{-1} (arrows, Figure 6); their intensities are decreased in the spectrum of the copolymer (b), and a new peak assigned to the out-of-plane breathing mode of *trans* C=C at 965 cm^{-1} appears. This is in agreement with results published previously for the Wittig polymerization of similar copolymers [2].

DSC measurements indicate that neither a melting peak nor any first order transition attributed to liquid crystal behavior could be observed in the heating and cooling cycle of the copolymers in the 0° to 220°C range. A characteristic glass transition discontinuity was seen in the DSC traces for all copolymers; Figure 7 shows the glass transition temperatures (T_g) as a function of the chain length of the

TABLE 5. ^{13}C NMR Chemical Shifts (ppm) of the Copolymers and Model Compound in $CDCl_3$

Carbon	Model	2_2	2_4	2_6	2_8	2_{10}	2_{12}
C(A1)	133.1	132.9	132.8	132.8	132.7	132.7	132.7
C(A2,6)	103.8	103.8	103.7	103.7	103.6	103.6	103.6
C(A3,5)	153.5	153.5	153.7	153.6	153.6	153.6	153.6
C(A4)	138.0	137.4	137.4	137.3	137.3	137.3	137.3
C(V1)	128.6	128.6	128.6	128.5	128.5	128.5	128.5
C(V2)	127.7	127.7	127.5	127.5	127.4	127.4	127.5
C(B1,4)	136.6	136.6	136.6	136.5	136.5	136.5	136.5
C(B2,3,5,6)	126.8	126.8	126.8	126.7	126.7	126.7	126.7
C(M3,5)	56.1	56.2	56.2	56.1	56.1	56.1	56.1
C(M4)	60.9						
C(X1)		71.8	73.2	73.6	73.6	73.6	73.6
C(X2)			26.6	30.1	30.0	30.1	30.1
C(X3)				25.7	25.8	25.8	25.8
C(X4)					29.4	29.4	29.5
C(X5)						29.5	29.6
C(X6)							29.6
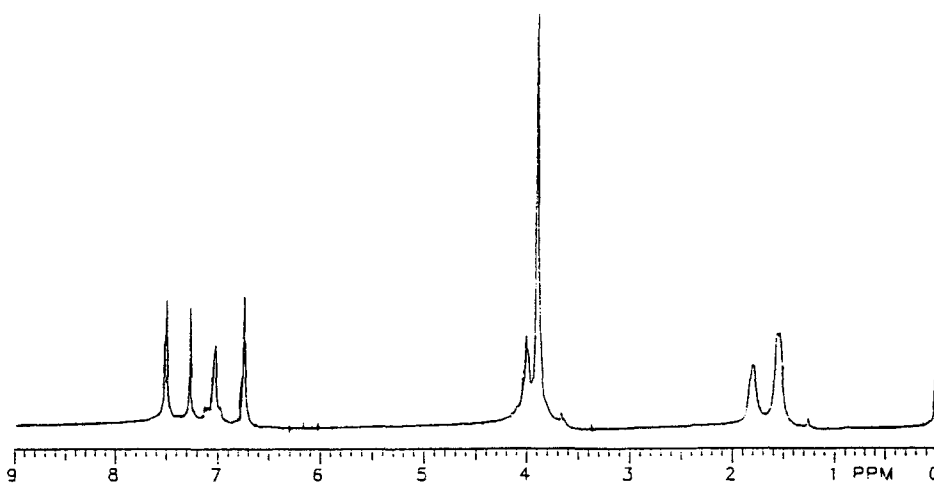
Figure 4. ^1H NMR spectrum of copolymer 2_6 in $CDCl_3$ solution; see Table 4.
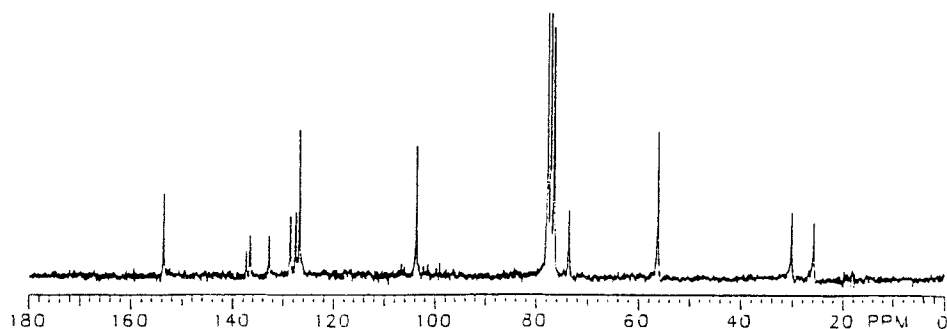
Figure 5. ^{13}C NMR spectrum of copolymer 2_6 in $CDCl_3$ solution; see Table 5.

nonconjugated spacer blocks. The observed glass transition in these copolymers results from the onset of motion in the flexible methylene blocks with the T_g's modified by the presence of the rigid aromatic anchoring units; the monotonic decrease is consistent with a phase separation characteristic of segmental block copolymers containing chemically dissimilar rigid and soft blocks.

The UV-vis absorption spectra of the six copolymers are qualitatively identical with maximum absorption at 372 nm in chloroform solution and in the solid state.

The EL spectrum of copolymer 2_{10} is shown in Figure 8. The emission is in the blue region with a maximum intensity at 465 nm. No vibronic structure can be seen. The spectra of the other copolymers in the series are qualitatively the same, indicating that the luminescence originates strictly in the conjugated blocks. The functional independence of the EL spectra on spacer block length in these copolymers agrees with the findings of Hay *et al*. [15]. Photoluminescent spectra of the copolymers are similar to the EL with maximum intensity at 465 nm.

Figure 9 shows the internal quantum efficiency of single-layer devices using the copolymers, as a function of the length of the nonconjugated spacer in an ITO/copolymer/Al configuration. It is seen that copolymers containing longer spacers give rise to higher efficiency. For the copolymer 1_{10}, the internal quantum efficiency reaches a value of 0.03%, about 10 times that reported for PPV in the same device configuration. Such enhanced efficiency resulting from the introduction of nonconjugated spacers has also been observed when spacers were randomly distributed in the backbone of PPV [4]. It is clear that the phase separation of the nonconjugated (spacer) and conjugated blocks leads to a confinement of excitons
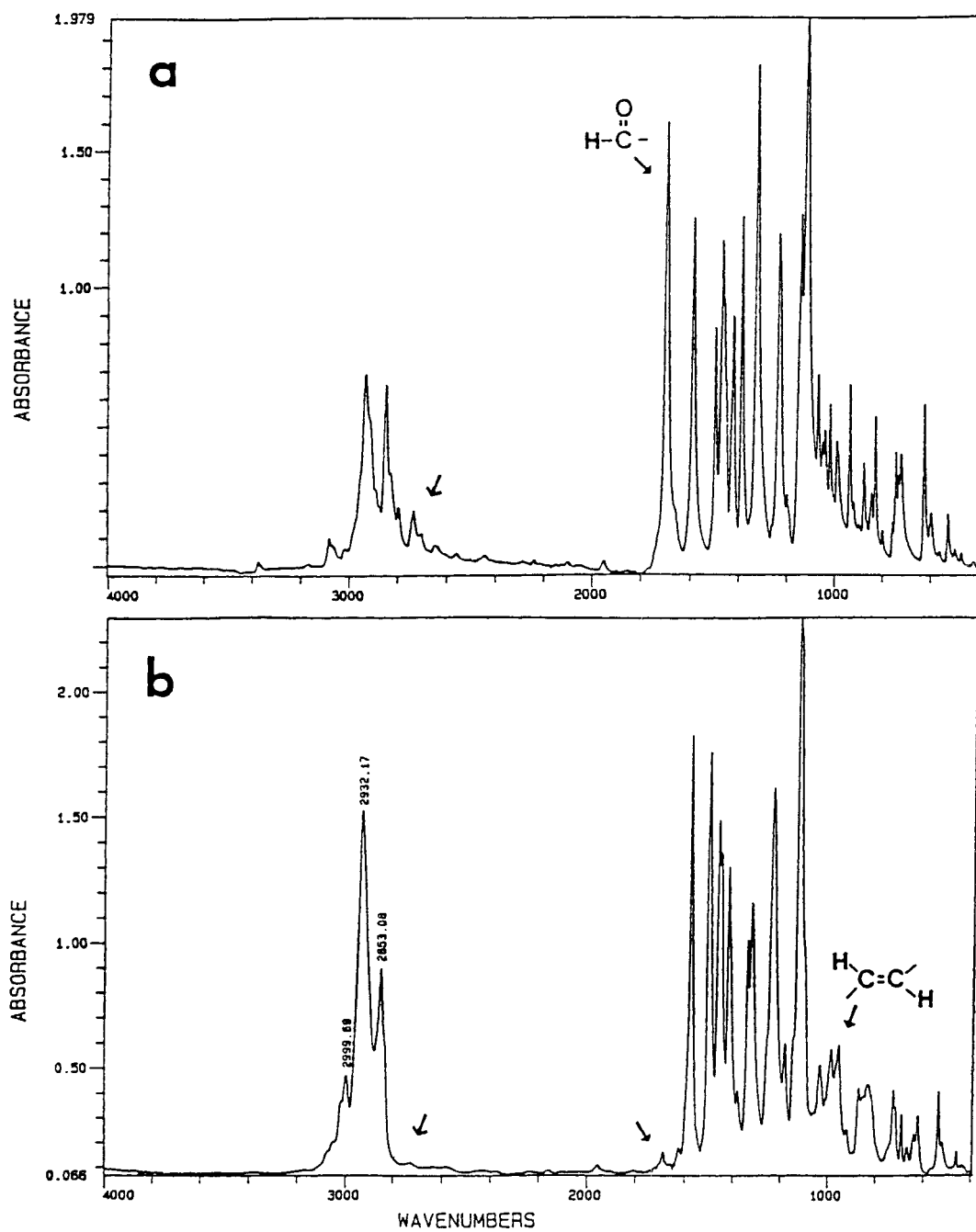
Figure 6. IR spectra of dialdehyde 1_{10} (a) and copolymer 2_{10} (b); see text.
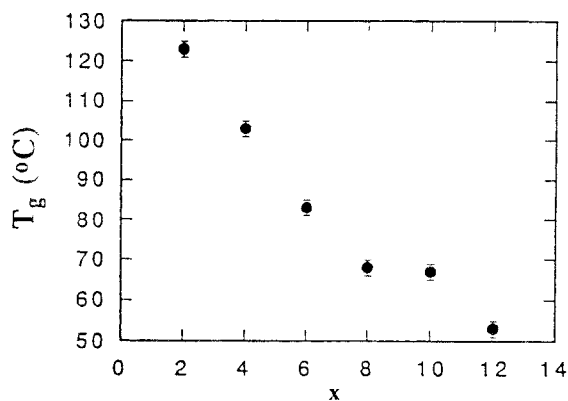
Figure 7.   Glass transition temperature of copolymers as a function of spacer block length.
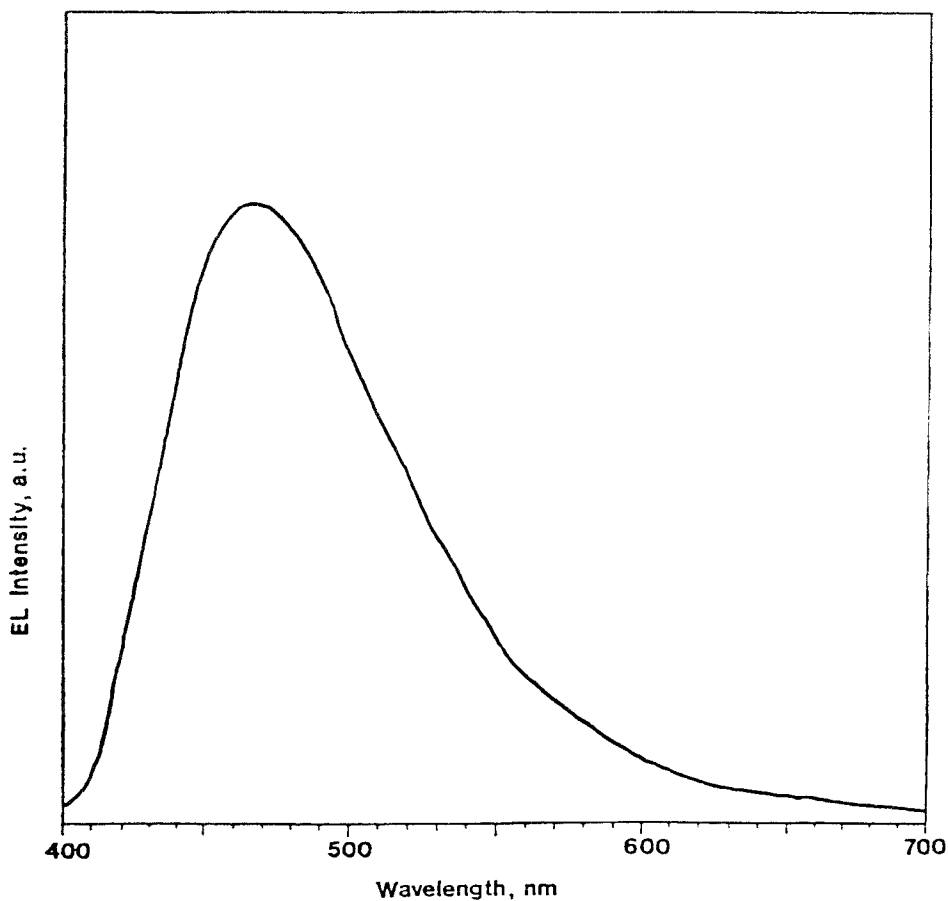

Figure 8.   EL spectrum of copolymer 2_{10} at room temperature in argon atmosphere.
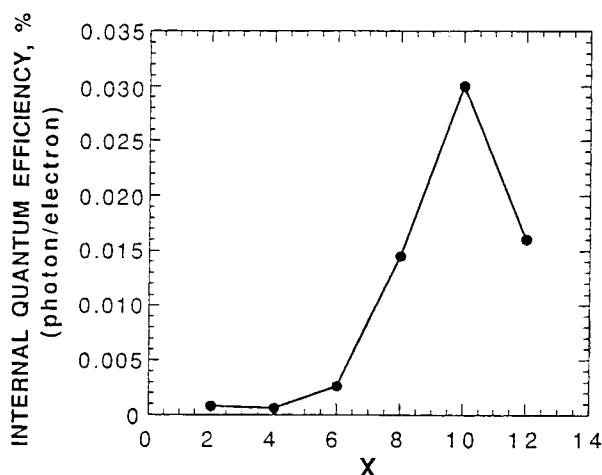
Figure 9. Internal quantum efficiency of ITO/copolymer/Al device as a function of spacer block length.

and generally accounts for the enhancement of EL efficiency. When the soft spacers are short, phase separation is relatively incomplete and provides a less complete confinement of excitons. Therefore, there is a greater energy loss due to exciton migration and consequent non-radiative decay processes. For longer soft spacers, the phase separation and domain formation is more complete and creates a tighter confinement of excitons leading, therefore, to a lower energy loss. The decrease in efficiency observed for the longest spacer is related to the near ambient T_g of 2_{12}, which diminishes the performance as the chromophore temperature is increased during the imposition of the electric field.

CONCLUSION

Six copolymers with well-defined uniform conjugated and nonconjugated alternating blocks were synthesized and characterized. They are intrinsically soluble and have excellent film-forming properties, yielding transparent, free-standing films. The electroluminescent spectra of the copolymers lie in the blue region and show the same features. A dependence of EL efficiency on the length of the nonconjugated spacer blocks in a single-layer diode configuration was observed.

ACKNOWLEDGEMENT

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