Light-Emitting Polymers with Pendant Chromophoric Groups.
1. Poly(stilbenyl-*p*-methoxystyrene)

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ABSTRACT: An electroluminescent polymer in which the chromophoric pendant groups are attached to a nonconjugated main chain, poly(stilbenyl-*p*-methoxystyrene), has been synthesized by a Williamson condensation of poly(*p*-acetoxystyrene) and *p*-(chloromethyl)stilbene. Characterization was carried out by NMR, FTIR, DSC, and elemental analysis. When used as the active layer of a light-emitting diode, emission was observed with a spectral maximum at 450 nm.

Introduction

Light-emitting diodes (LED's) based on organic materials have attracted attention in the past few years because of their scientific interest and potential applicability in display and other technologies. When compared to their inorganic counterparts, a perceived advantage is based on the possibility of constructing large-area visible light emitting displays. A variety of organic low-molar-mass materials have been used for LED fabrication, and in principle there is available a wide selection of emission colors. However, crystallization of the organic layers, thereby compromising interfacial contacts, and the relatively high voltages required to inject charge carriers into low-molar-mass organic materials are limiting factors in the use of such devices. Recent advances including vacuum deposition of amorphous transport layers separating polycrystalline emitting materials from the electrodes[1–5] or dispersing the chromophores in a polymeric matrix, e.g., poly(methyl methacrylate) or polycarbonate,[6,7] in a solid solution have partially circumvented these problems. Nevertheless, the fabrication of bright, efficient, electroluminescent devices particularly with blue emission remains difficult, and an appropriate combination of emissive and transport layers to achieve an efficient device is highly desirable.[5]

The use of intrinsically emitting polymers has been the most obvious way to improve structural stability in these devices. Conjugated polymers in particular have been widely used as the emitting layers in LED's because π electrons can be easily removed or injected forming ion-radicals (polarons) without affecting σ bonds responsible for the polymer's physical integrity. Besides having to provide both charge transport and high efficiency for electroluminescence, such semiconducting polymers need to be processible using well-established techniques for film deposition such as spin casting or dip coating. As most highly conjugated materials show poor solubility in common solvents, approaches to using conjugated polymers have involved strategies such as the use of a processible precursor,[8] the attachment of solubilizing side groups,[10,11] the use of solubilizing spacers between the conjugated segments, or a combination of these strategies.

When a low molecular weight emitter is used, the color of the emitted light is established *a priori*; but for electroluminescent polymers, the emission color depends on the structural features of the macromolecule. The first reported electroluminescent polymer, poly(*p*-phenylenevinylene) (PPV), a green-blue emitter, was prepared from a soluble precursor.[8] The energy gap in PPV has been chemically modified, for example, by the partial elimination of precursor leaving groups, thereby providing a red or blue shift in the band gap, achieved by interrupting the conjugation along the chain.[9–11] Attachment of alkoxy groups, as in poly[(2,5-dialkoxyphenylene)vinylene], causes a red shift of 0.4 eV[10,11] with respect to PPV, whereas poly[(2-methoxy-5-(2′-ethylhexoxy)-1,4-phenylene)vinylene][11] (MEH–PPV) showed a yellow-orange emission peaking at 2.1 and 1.9 eV.[12,13] LED's prepared with soluble alkyl derivatives of polythiophene have also been prepared with red-orange emission;[14–18] a red hue was obtained with poly(cyanoterephthalylidene)s,[19] and blue emission was obtained using poly(9,9-dialkylfluorene)s.[18,20,21] LED's constructed with several layers of PPV and PPV derivatives with different band gaps provide a range of colors varying from red to yellow-green.[22] This latter strategy can only give red-shifted emissions from the highest energy emitter.

Confinement of the effective conjugation has proved to be an efficient means for blue shifting the spectrum, because the conjugated emitters can allow charge carriers to form, but not to diffuse along the chain. This electronic localization results in a large π–π^* band gap which decreases with conjugation length. The conjugation confinement can be achieved by tailoring the polymer structure in various ways: inserting meta linkages or imposing steric distortions in the main chain as in fully aromatic polyphenylenes[23,24] or separating the emitting units by nonconjugated spacers as in conjugated–nonconjugated block copolymers (CNCP's).[25] In the latter, the confinement of resonance within the aromatic blocks was proved by noting the independence of the photoluminescence spectra on the length of the spacer.[26,27]

Previous results reported by our group showed that changing the aromatic group from a *p*-phenylene to a *p*-thienylene residue in conjugated blocks of a $[-\mathrm{PPV}-\mathrm{O(CH_2)}_n\mathrm{O}-]_m$ type structure[28] causes band gap shifts

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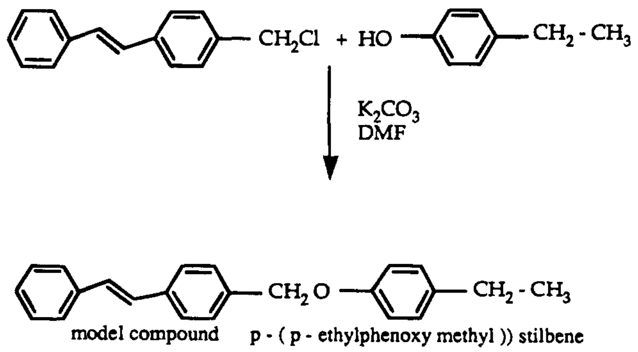
Scheme 1



in which the emission changed from blue to yellow. We also demonstrated that by extending the conjugation length of the chromophore of the CNCP's it was possible to red shift the UV absorption and the photo- and electroluminescence spectra.[29]

In this contribution, we describe the synthesis of a novel electroluminescent polymeric structure (poly(stilbenyl-*p*-methoxystyrene)) in which the conjugation is confined to pendant groups attached to a nonconjugated backbone. The only analogous structure reported so far is poly(*N*-vinylcarbazole), which emits violet-blue light when an electron transport layer is inserted between the polymer and the metal cathode.[30]

Analogous pendant functional structures based on poly(methyl methacrylate)[31-33] or poly(vinyl ether)[34] containing azo-chromophoric groups have been prepared for NLO studies. Such PMMA copolymers were synthesized by copolymerizing methyl methacrylate with the appropriate chromophoric vinyl derivative, and for the grafted poly(vinyl ether) synthesis, the azo dye molecules were attached by a Williamson condensation route. In the present case, the latter strategy was selected because the former could lead to the possibility of concurrent homopolymer formation, which could be difficult to detect and separate; additionally, the anticipated molecular weights are liable to be reduced due to the steric hindrance imposed by the side group during radical copolymerization.

The model compound, *p*-((*p*-ethylphenoxy)methyl)-stilbene, was prepared through the Williamson condensation of *p*-(chloromethyl)stilbene and *p*-(hydroxyethyl)-benzene (Scheme 1).

The attachment of the chromophoric groups into the polystyrene backbone was accomplished through the reaction of *p*-(chloromethyl)-*trans*-stilbenene with poly-(*p*-acetoxystyrene) (Scheme 2).

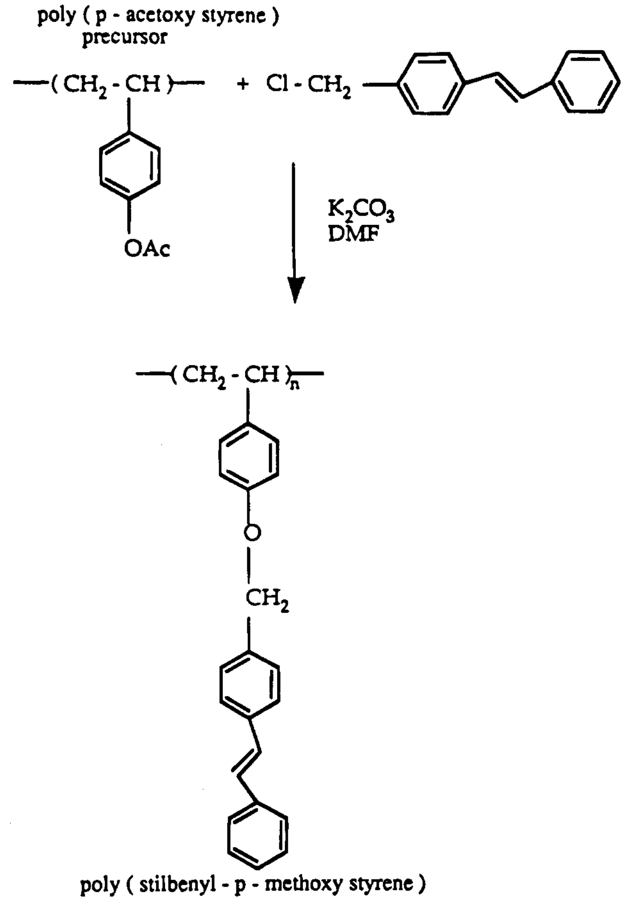
Experimental Section

Synthesis of *p*-((*p*-Ethylphenoxy)methyl)stilbene. A 1 g (0.0082 mol) solution of *p*-ethylphenol (Aldrich 99%) in 40 mL of DMF (Fisher A.C.S.) was stirred and heated to reflux. After this, potassium carbonate (Fisher A.C.S.) (1 g, 0.0072 mol) and a second solution composed of 1 g (0.004 mol) of *p*-(chloromethyl)stilbene (Aldrich 95%) in 10 mL of DMF were added.

The solution was stirred and refluxed overnight and the resulting mixture poured into distilled water. The precipitate was collected after standing 4 h, dried in air at ambient temperature, washed with acetone, dried under vacuum overnight, and recrystallized from chloroform (Fisher A.C.S.).

Synthesis of Poly(*p*-acetoxystyrene). Freshly distilled *p*-acetoxystyrene (10 mL; Polysciences) was added to 50 mL of purified benzene (Fisher A.C.S.). After the addition of 0.05 g of benzoyl peroxide, the mixture was allowed to polymerize at reflux temperature for 12 h and then added to 10 times the volume of methanol (Fisher A.C.S.). The precipitated polymer was collected after standing 5 h and dried at room temperature; 60% conversion was obtained. The ^{1}H NMR spectrum, with assignments, is shown in Figure 1a.

Scheme 2



Synthesis of the Poly(stilbenyl-*p*-methoxystyrene). A 3 g solution of the precursor in 40 mL of DMF was stirred and heated to reflux. After this, potassium carbonate (2.5 g) and a second solution composed of 6.0 g (0.0263 mol) of *p*-(chloromethyl)stilbene in 40 mL of DMF were added.

The solution was stirred and refluxed overnight; the resulting mixture was filtered and poured into 1000 mL of methanol. The precipitate was collected after 24 h and dried under vacuum overnight. A small amount of lower molecular material was separated through fractional precipitation (DMF/methanol).

Characterization of the Model Compound *p*-((*p*-ethylphenoxy)methyl)stilbene. The assigned NMR spectrum is shown in Figure 1b. Anal. Calcd: C, 87.8; H, 7.0. Found: C, 87.7; H, 7.0.

Characterization of the Precursor Poly(*p*-acetoxystyrene). The assigned NMR spectrum is shown in Figure 1a and the FTIR spectrum in Figure 2a. Anal. Calcd: C, 74.0; H, 6.2. Found: C, 73.6; H, 6.2.

Characterization of the Emitting Polymer. The IR spectrum is shown in Figure 2b, and the assigned ^{1}H NMR spectrum is shown in Figure 1c. Anal. Calcd: C, 88.5; H, 6.4. Found: C, 87.9; H, 6.2.

NMR spectra were recorded on a Varian XL-200 spectrometer. All the samples were dissolved in $CDCl_3$, and chemical shifts are referred to TMS. The elemental analyses were carried out by the Microanalysis Laboratory of the University of Massachusetts.

FTIR spectra were taken in chloroform solutions on an IBM system IR/3X Type 913 FTIR spectrometer equipped with Nicolet PC/IR Operation software. DSC analyses were performed on a Perkin-Elmer TAC7, using N_2 as carrier gas (60 mL/min) and a heating rate of 10 °C/min. The DSC traces presented correspond to a third run, which reproduced the

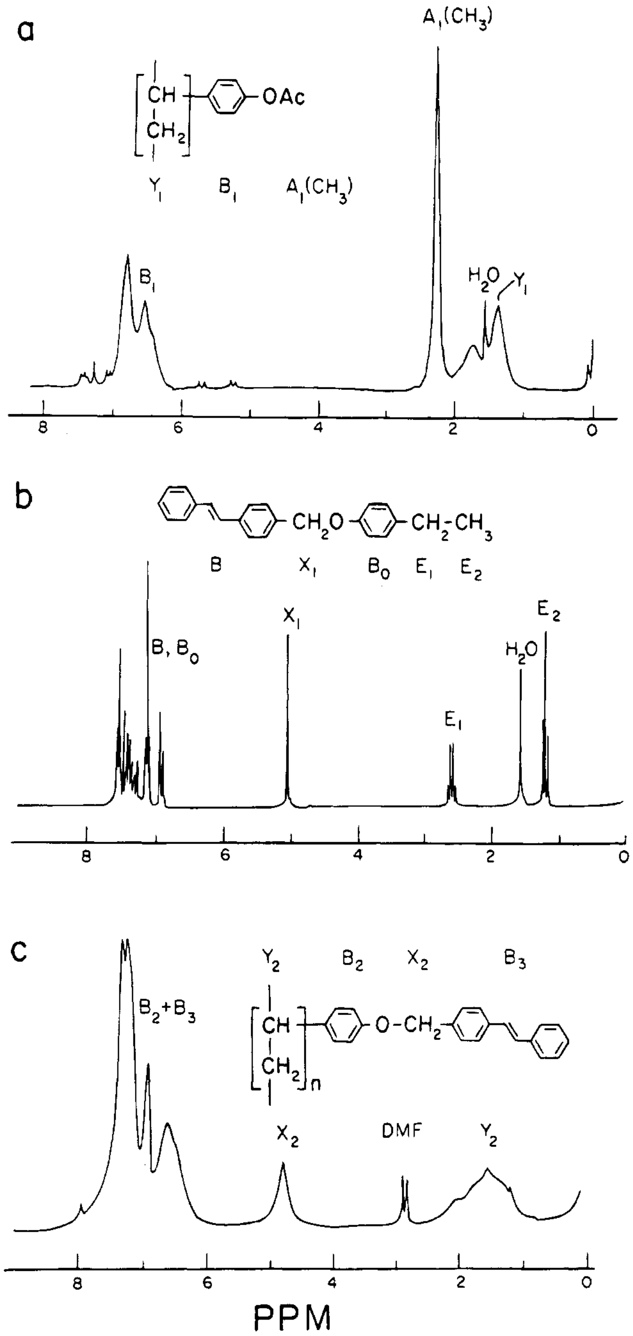


Figure 1. (a) ^{1}H NMR spectrum of the precursor poly(*p*-acetoxystyrene); (b) ^{1}H NMR spectrum of the model compound *p*-((*p*-ethylphenoxy)methyl)stilbene; (c) ^{1}H NMR spectrum of poly(stilbenyl-*p*-methoxystyrene).

second one, for each sample. GPC chromatograms were obtained on a Waters instrument coupled to a Waters R403 differential refractometer, using THF as solvent and polystyrene standards. Absorption spectra were obtained in chloroform solutions on an IBM 9420 UV–visible spectrophotometer. The concentration for the model compound was 1 × 10^{-5} M and the concentration of the polymer was 0.0031 g/L, which corresponds to 1 × 10^{-5} M in chromophoric groups. Fluorescence spectra were obtained in chloroform solutions on a Perkin-Elmer MPF44 fluorescence spectrophotometer.

Photoluminescence (PL) and electroluminescence (EL) spectra were recorded on a system assembled in our laboratory and calibrated against a Perkin-Elmer MPF-66 fluorescence spectrophotometer previously standardized with PL measurements of compounds of known fluorescence properties.

Fabrication of the LED Device. A solution of the EL-active polymer in $CHCl_3$ was filtered and spin-coated on a precleaned glass substrate covered with an ITO conducting layer. Typical thicknesses of the polymer films were 30–80 nm. The film was covered by a butyl PBD [2-(4-biphenylyl)-5-(*p*-*tert*-butylphenyl)-1,3,4-oxadiazole] transport layer and dried under vacuum, and calcium electrodes were evaporated in a vacuum of ca. 10^{-5}–10^{-6} Torr. Wires were attached to the respective electrodes with a conductive epoxy adhesive.

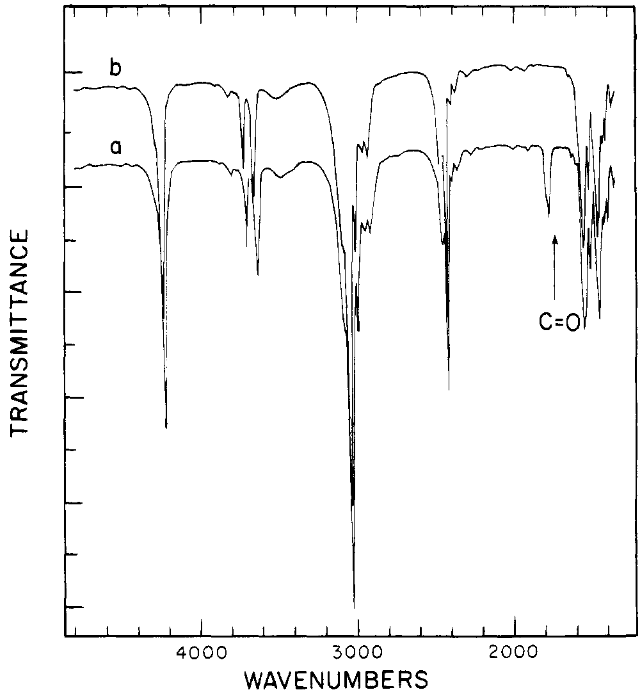


Figure 2. FTIR spectra of (a) poly(*p*-acetoxystyrene) and (b) poly(stilbenyl-*p*-methoxystyrene), showing the absence of carbonyl absorption in the latter; chloroform solutions.

Results and Discussion

The ^{1}H NMR spectrum of poly(stilbenyl-*p*-methoxystyrene) shown in Figure 1c is consistent with that corresponding to the model compound (Figure 1b), and the absence of carbonyl absorption in the infrared spectrum (Figure 2b) indicates that complete substitution was achieved. Further evidence was given by elemental analysis and GPC measurements. The increase in molecular weight of this polymer corresponded to the calculated amount for complete replacement of the acetoxy groups in the precursor.

DSC analyses showed that the glass transition of the precursor had the same value as the polystyrene homopolymer (101–102 °C),[35] but the pendant chromophoric groups had a stiffening effect in the backbone chain, raising the glass transition temperature of the polymer to 116 °C. No other thermal transitions were observed.

The polymer was soluble in chloroform and formed yellow transparent solutions at 5 wt % concentration. Free-standing films could be cast and spin-coated from the same solution, producing substantially pinhole-free thin films of the substrate.

Photo- and Electroluminescence. Figure 3 shows the absorption spectrum of the polymer (a) and of the model compound (b). It should be noted that the molar concentration of the chromophoric groups in the polymer solution was the same as that in the model compound solution. The polymer spectrum is still related to that of *trans*-stilbene, but new features are apparent. Besides the broadening of the main absorption centered at 300–320 nm, a new broad band peaking at 370 nm can be observed.

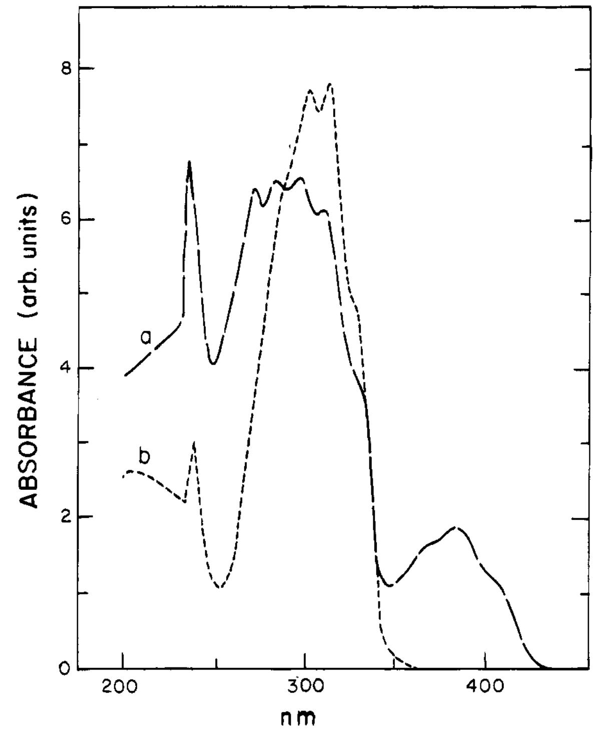


Figure 3. Absorption spectra of (a) poly(stilbenyl-*p*-methoxystyrene) and (b) *p*-((*p*-ethylphenoxy)methyl)stilbene.

Figure 4 shows the emission spectra of the model compound taken with excitation wavelengths of 320 (A), 260 (B), and 360 nm (C) at concentrations of 1×10^{-5} (a) and 1×10^{-2} M (b). When the excitation wavelength was 320 nm (Figure 4A), which corresponds to the absorption maximum (as shown in Figure 3), it was observed that in the "dilute" spectrum (a), an emission centered at 360 nm predominates, whereas in the "concentrated" spectrum (b), the main peaks appear at 430 and 460 nm. The same trend was observed when the excitation wavelength was 260 nm (Figure 4B). It also can be seen from Figure 4B(c) that the "dilute" emission spectrum of the model compound is consistent with that of pure *trans*-stilbene. Besides this shift in the emission spectra with concentration, it was also observed that higher emission intensities were obtained from the dilute solutions (4A(a) and 4B(a)).

On the other hand, with an excitation wavelength of 360 nm (Figure 4C), where the model compound practically does not absorb (Figure 3), the more intense emission originated from the concentrated solution (b), i.e., opposite to that observed with excitation wavelengths of 320 and 260 nm. These results indicate that the emitting center in dilute solution is the *trans*-stilbene unit, whereas in concentrated solution the emission may originate from a fluorescent excimer. This assumption is substantiated by the differences found in the absorption behavior of *p*-((*p*-ethylphenoxy)methyl)-*trans*-stilbene (Figure 3). When covalently linked to a polymer backbone as a pendant group, it shows an absorption at 360 nm, whereas the free molecule at the same concentration shows no absorption at this wavelength. In this case, we compared "free" with "bound" molecules in the same global concentration but with different local concentrations, and the observed effect can be attributed to conformational restrictions imposed on the polymer structure.

Therefore we assign the absorption at 360 nm in the polymer absorption spectrum (Figure 3a) to an associated species, which is believed to be a ground state π complex. This would explain the strong emission from the concentrated solution of the model compound when irradiated with 360 nm wavelength. The observed shift to lower frequencies of the concentrated solutions in relation to dilute solutions is characteristic of excimer emission, and the higher emission intensities observed in Figures 4A(a) and 4B(b) are ascribed to a higher number of nonassociated molecules in dilute solutions, which fluoresce as the pure *trans*-stilbene (Figure 4B(c)). Observation of excimer fluorescence of low-molar-mass species in confined media has been reported for glasses[36] and for other polymer systems including copolymers of *trans*-4-hydroxystilbenyl acrylate–menthyl acrylate[37] and ladder-structured poly(*p*-phenylene)s. In the latter a yellow emission (λ_{max}: ca. 600 nm) was observed in addition to blue electroluminescence (λ_{max}: 450 nm). This was attributed to excimer emission resulting from parallel arrangements of the chains. When the coplanarity was disturbed by the introduction of torsion-inducing spacers, only the blue emission was detected.[38–42]

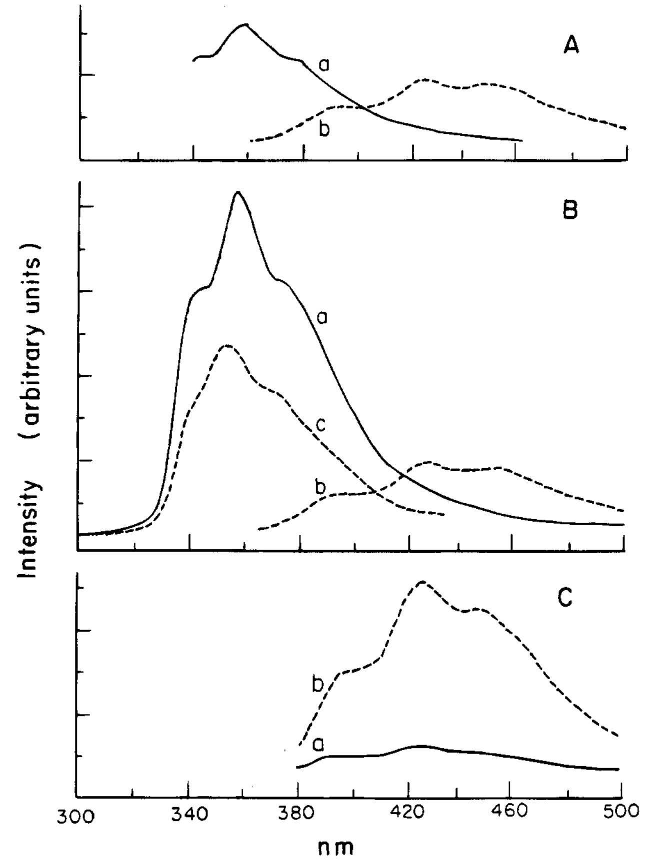


Figure 4. (A) Fluorescence spectra of the model compound: (a) 1×10^{-5} M; (b) 1×10^{-2} M. Excitation wavelength: 320 nm. (B) Fluorescence spectra of the model compound [(a) 1×10^{-5} M; (b) 1×10^{-2} M] and (c) fluorescence spectrum of *trans*-stilbene (1×10^{-5} M). Excitation wavelength: 260 nm. (C) Fluorescence spectra of the model compound: (a) 1×10^{-5} M; (b) 1×10^{-2} M. Excitation wavelength: 360 nm. In all cases $CHCl_3$ solutions were used.

The solution and solid-state fluorescence spectra of the polymer are shown in parts a and b of Figure 5, respectively. The same features as seen in concentrated solutions of the model compound are apparent for an excitation wavelength of 360 nm. The electroluminescence spectrum (Figure 5c) is consistent with these, and therefore we assign the photoluminescence and the electroluminescence to an excimer formed between adjacent pendant groups. The electroluminescence

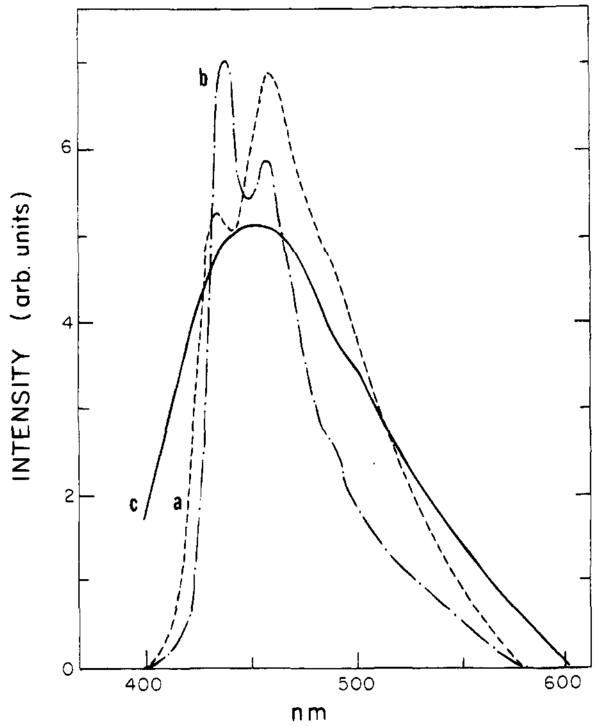


Figure 5. Poly(stilbenyl-*p*-methoxystyrene): (a) solution photoluminescence; (b) solid-state photoluminescence (excitation wavelength: 360 nm); (c) electroluminescence.

spectrum of the polymer peaked at 450 nm, when a blue-violet emission in the described device could be observed at room temperature with the imposition of a 35 V forward bias voltage.

Conclusion

A new photo- and electroluminescent polymer (poly(stilbenyl-*p*-methoxystyrene) was prepared in which conjugation is confined to pendant chromophoric groups. The polymer is soluble with good film-forming ability and emits a blue light when used as the active layer of an LED. The emitting center is assigned to an excimer formed between adjacent groups.

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