Macromolecules **1996,** *29,* 3161−3166

Light-Emitting Polymers with Pendant Chromophoric Groups. 2. Poly[styrene-*co*-(*p*-(stilbenylmethoxy)styrene)]

M. Aguiar,[†] B. Hu,[‡] F. E. Karasz,*[,‡] and L. Akcelrud[†]

Instituto de Quimica, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil, and Department of Polymer Science and Engineering, University of Massachusetts at Amherst, Amherst, Massachusetts 01003

Received October 19, 1995; Revised Manuscript Received February 15, 1996[⊗]

ABSTRACT: A new fluorescent polystyrene derivative is reported in which a stilbene-based chromophoric pendant group is attached on average to each third monomeric unit. Poly[styrene-*co*-(*p*-(stilbenylmethoxy)-styrene)] showed fluorescence emission from intra- and interchain interaction. The model compound *p*-((*p*-ethylphenoxy)methyl)stilbene is the first stilbene derivative to show aggregate emission in solution at room temperature reported to date. It is proposed that the emission originates from the association of chromophores in the ground state forming a fluorescent dimer or aggregate complex.

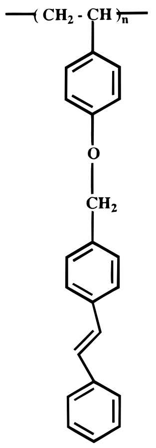
Introduction

Conjugated polymers are semiconducting materials that combine interesting electrical and nonlinear optical properties with good film-forming and chemical stability characteristics, making them especially suitable for the fabrication of various kinds of electronic and optoelectronic devices, such as transistors, diodes, and light-emitting diodes (LEDS).[1−17] In the last few years, we have reported on several novel electroluminescent polymers, emitting at various frequencies in the visible spectrum,[18−22] focusing mainly on well-defined structures with discrete emitting centers. In a recent contribution,[23] we reported an electroluminescent polymer in which stilbene-based chromophores were attached to each monomeric unit of a vinylic, nonconjugated backbone, namely, poly[*p*-(stilbenylmethoxy)-styrene] (structure A). Because photoluminescence is a necessary condition for electroluminescence, steady-state measurements of optical absorption and photoluminescence were performed to establish the correlation between the nature of the emission center and the related emitting properties. We demonstrated that electroluminescence was provided by a fluorescent dimer, formed through the interaction of adjacent pendant groups, and that no monomeric emission existed in the solid state.

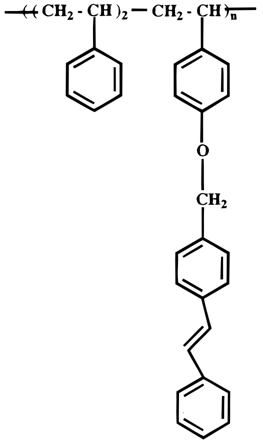
To gain further insight on the emission characteristics of this chromophore, we prepared a similar structure, placing spacers between the chromophores in such a way that each one is separated by an average of two styrene monomeric units. The photophysical behavior of this new structure, poly[styrene-*co*-(*p*-(stilbenylmethoxy)styrene)] (structure B), is the subject of the present contribution.

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 ACS) was stirred and heated to reflux. After this, potassium carbonate (Fisher ACS; 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.



structure A



structure B

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

Synthesis of the Precursor Copolymer. Styrene (Fisher ACS) was washed free of inhibitor with 5% aqueous NaOH, dried over $CaCl_2$, and distilled under vacuum using sulfur as inhibitor and copper wire in the column; 6 mL (0.0057 mol) of styrene and 4 mL (0.0025 mol) of *p*-acetoxystyrene (Polysciences) were added to 40 mL of benzene (Fisher ACS). After addition of 0.1 g of benzoyl peroxide (Aldrich), the mixture was allowed to polymerize at 80 °C for 6 h. After this it was poured into a 10× vol of methanol (Fisher ACS), and the precipitated polymer was collected after standing for 5 h. After drying at room temperature, a 80% conversion was obtained.

Synthesis of the Emitting Copolymer. A 1 g solution of the precursor copolymer in 40 mL of DMF (Fisher ACS) was stirred and heated to reflux. After this, a total of potassium carbonate (Fisher ACS) (1 g, 0.0072 mol) and a second solution composed of 1 g (0.0044 mol) of *p*-(chloromethyl)stilbene (Aldrich) were added to the first solution. Both additions were made alternately in small portions.

The solution was stirred and refluxed overnight after the addition. The resulting mixture was filtered and poured into 500 mL of methanol. The precipitate was collected on the following day and dried under vacuum overnight.

Characterization of the Precursor. The ^{1}H NMR spectrum (Figure 1A) was obtained on a Varian XL-200 spectrometer. The sample was dissolved in $CDCl_3$; chemical shifts shown are referred to TMS. Anal. Calcd: C, 84.3; H, 7.0 (for the expected 2:1 styrene/acetoxystyrene copolymer). Found: C, 84.1; H, 7.1.

[†] Instituto de Quimica.

[‡] University of Massachusetts.

[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1996.

0024-9297/96/2229-3161$12.00/0

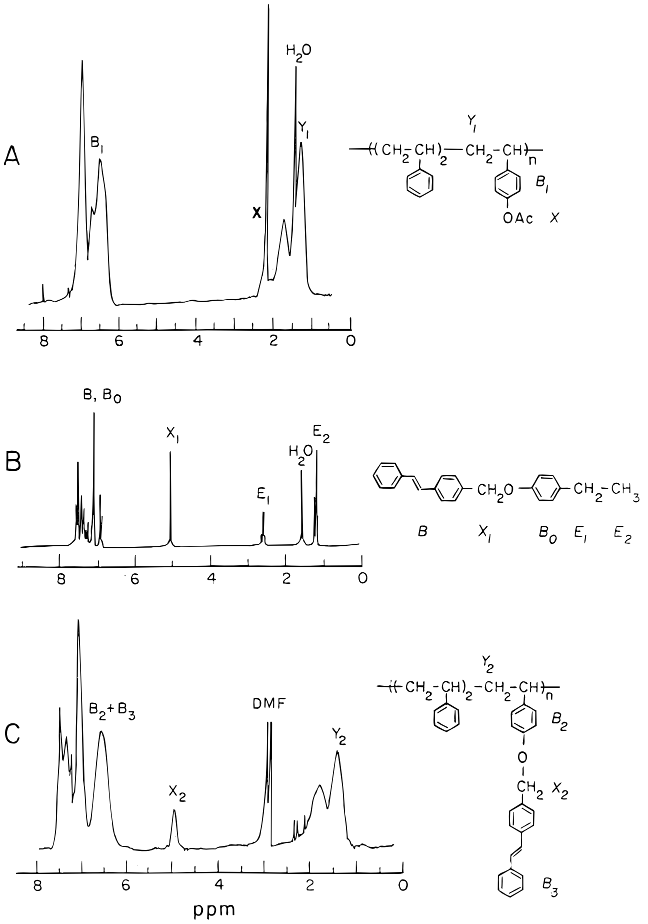


Figure 1. ^{1}H NMR spectra of (A) the precursor poly[styrene-*co*-(*p*-acetoxystyrene)], (B) the model compound *p*-((*p*-ethylphenoxy)methyl)stilbene, and (C) poly[styrene-*co*-(*p*-(stilbenylmethoxy)styrene)].

The copolymer composition was confirmed by the FTIR spectrum of a 0.02 M solution of the polymer in chloroform, by means of a calibration plot for the carbonyl band of the acetoxy group (1755 cm^{-1}), which was made from spectra of the monomer *p*-acetoxystyrene in predetermined concentrations in chloroform (Figure 2A,B,D).

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 Emitting Copolymer. The FTIR spectrum is shown in Figure 2C, and the assigned ^{1}H NMR spectrum is shown in Figure 1C. Anal. Calcd: C, 90.0; H, 6.9. Found: C, 89.3; H, 7.1.

Elemental analyses were carried out by the Microanalysis Laboratory of the University of Massachusetts, Amherst, MA. 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 instrument, using N_2 as gas carrier (60 mL/min), heating rate 10 °C/min. Runs were carried out with heating and quenching with a mixture of 2-propanol/dry ice from −5 °C. The DSC traces used correspond to the third run, which reproduced the second one, for each sample.

GPC chromatograms were obtained on Waters equipment, coupled to a Waters R403 differential refractometer, using THF as solvent, and polystyrene standards were used for calibration.

Absorption spectra were obtained in chloroform solutions on an IBM 9420 UV−visible spectrophotometer, and fluorescence spectra were obtained in chloroform solutions on a Perkin Elmer MPF 66 fluorescence spectrophotometer. Photoluminescence spectra were recorded on a system assembled in our laboratory and calibrated against a Perkin Elmer MPF 66 fluorescence spectrophotometer previously standardized with photoluminescence measurements of compounds of known fluorescence properties.

Discussion

Poly[styrene-*co*-(*p*-(stilbenylmethoxy)styrene)] was prepared through the Williamson condensation of the precursor poly[styrene-*co*-(*p*-acetoxystyrene)] and *p*-(chloromethyl)stilbene. This precursor was chosen because styrene (**1**) and *p*-acetoxystyrene (**2**) have suitable reactivity ratios ($r_1 = 0.85$, $r_2 = 1.3$);[24] also acetoxy is a good leaving group for the Williamson condensation, and the latter can be easily quantified by infrared spectroscopy.

A monomer feed of 5.7/2.5 styrene/*p*-acetoxystyrene molar ratio yielded a copolymer composition with an average of two styrene units for each *p*-acetoxystyrene unit. To confirm this structure, a FTIR calibration curve was made using the carbonyl stretching vibration at 1755 cm^{-1} of the *p*-acetoxystyrene monomer as shown in Figure 2. The infrared spectrum (Figure 2B) together with elemental analysis and NMR spectroscopy (Figure 1) confirmed a 2/1 styrene/*p*-acetoxystyrene composition. The attachment of the chromophoric groups into the polystyrene backbone was accomplished through the reaction of *p*-(chloromethyl)stilbene with the precursor copolymer (Scheme 1).

The absence of carbonyl absorption in the infrared spectrum (Figure 2C) indicated that complete substitution was achieved. Further evidence was given by elemental analyses and ^{1}H NMR spectroscopy (Figure 1C and Table 1). GPC measurements showed a difference of 12% between the calculated value for total substitution ($M_n = 25\,000$) and the observed ($M_n = 22\,000$, Table 1) for the emitting copolymer. This can be explained in terms of different hydrodynamic volumes of the substituted chains relative to the unsubstituted ones. We cannot exclude the possibility of some degradation that might have occurred during the condensation.

DSC analysis showed that the copolymer backbone glass transition had the same value as that of the polystyrene homopolymer (102−106 °C), but the attachment of the pendant chromophoric groups decreased the glass transition temperature of the copolymer to 71 °C (Table 1). No other transitions were observed in the DSC.

The model compound *p*-((*p*-ethylphenoxy)methyl)stilbene was prepared through the Williamson condensation of *p*-(chloromethyl)stilbene and *p*-(hydroxyethyl)benzene (Scheme 2). Figure 3 shows that the absorption spectra of the polymer (a) is coincident with that of the model compound (b) except for the absorption at the 350−400 nm region, where the model compound practically does not absorb.

The fluorescence behavior of the model compound in relation to concentration and excitation wavelength is shown in Figure 4. When excited at 320 nm, a peak centered at 360 nm is the main emission for low concentrations (10^{-4}−10^{-5} M, curves 4Aa,b). For higher concentrations (>10^{-4} M, curves 4Ac−e), a red-shifted emission begins to appear, while the first peak intensity decreases. This behavior, characteristic of excimers or aggregate emission, has not been observed previously in stilbene nor in any of its derivatives in solution at room temperature.

Excimer emission was detected for crystalline 2,4-dichloro-*trans*-stilbene at −186 °C but not at room

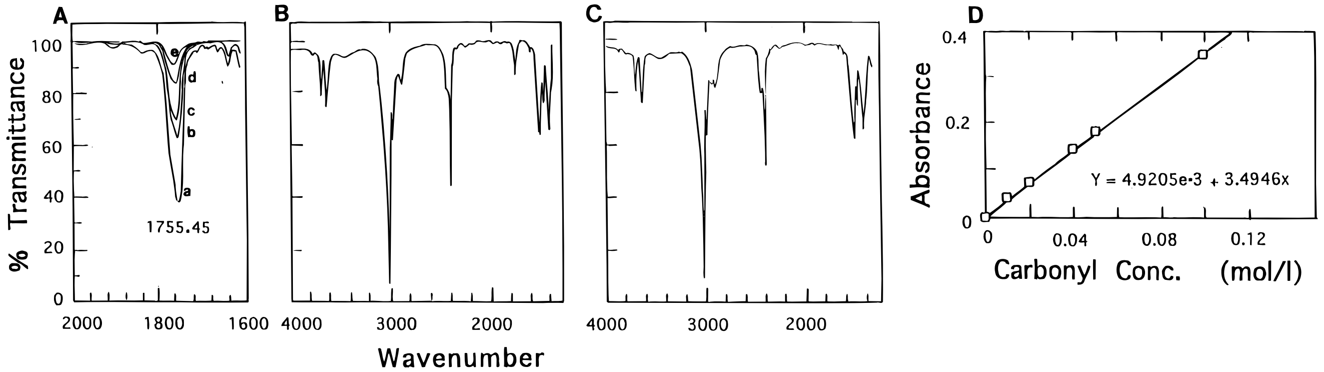


Figure 2. (A) FTIR spectra of *p*-acetoxystyrene monomer in the region 1755 cm^{-1} (a = 0.1 M, b = 0.05 M, c = 0.04 M, d = 0.02 M, and e = 0.01 M), (B) IR spectrum of poly[styrene-*co*-(*p*-acetoxystyrene)] (concentration = 0.02 M), (C) IR spectrum of poly[styrene-*co*-(*p*-(stilbenylmethoxy)styrene)] (same concentration as part B), showing the absence of carbonyl absorption (chloroform solutions), and (D) calibration curve.

Scheme 1

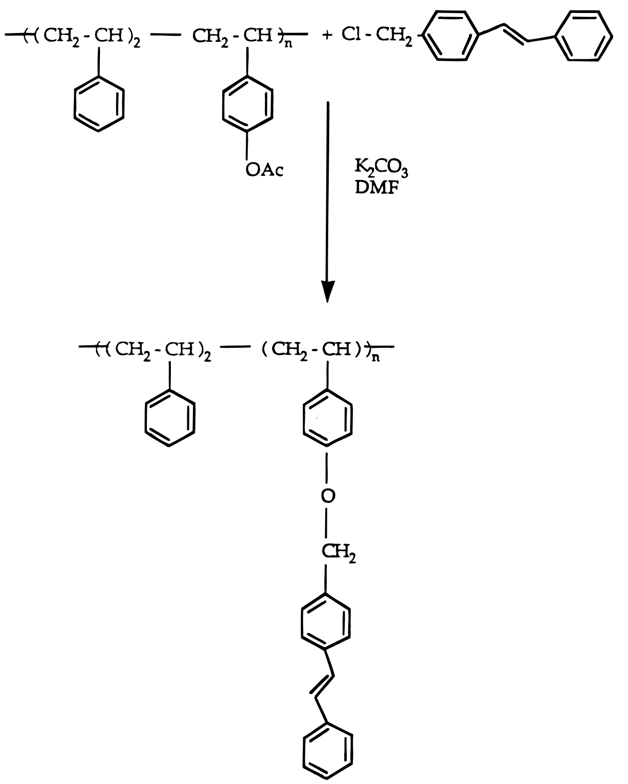


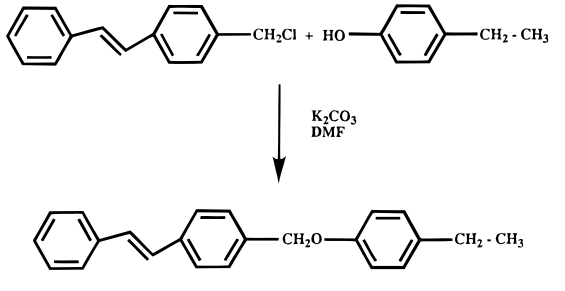
Table 1. Characterization Data for the Precursor Poly[styrene-*co*-(*p*-acetoxystyrene)] and the Emitting Polymer Poly[styrene-*co*-(*p*-(stilbenylmethoxy)styrene)]

polymer	M_w[a]	M_n[a]	M_w/M_n[a]	T_g, °C[b]
precursor	40 300	17 800	2.2	106
emitting	47 300	22 000	2.1	71

[a] From GPC. [b] From DSC.

temperature or in a methylcyclohexane glass.[25] The explanation for the absence of *trans*-stilbene excimer emission is the high limiting quantum yield for photodimerization (0.77), that is, the molecule reacts much faster than it fluoresces, indicating a very short singlet lifetime (<100 ps).[26] On the other hand, *trans*-stilbene excimer fluorescence has been reported to occur upon warming squalene solutions after γ-irradiation at 77 K.[27] The solid-state photodimerization of stilbenes and other alkenes is subject to topochemical control: The two reactive double bonds must be parallel and separated by <4.2 Å.[28,29] More recently, in a picosecond study of the 2 + 2 photodimerization of stilbene, a new intermediate was reported that was assigned to the *trans*-stilbene excimer or a biradical species.[30]

Scheme 2



p - (*p*-ethylphenoxy methyl) stilbene

When *p*-((*p*-ethylphenoxy)methyl)stilbene is irradiated at 360 nm, where its absorption is practically zero (Figure 3b), only the emission at the lower frequencies is seen, even at concentrations as low as 10^{-5} M (Figure 4Ba). The emission at the higher frequencies was assigned to the stilbene moiety in the chromophore by comparing with the emission of this molecule (curve 4Bc). This apparent anomalous behavior will be discussed later. The ratio between the intensities of the monomeric (I_m) and aggregate (I_d) emission increases linearly with concentration as shown in Figure 5 when the excitation wavelength is 320 nm.

The copolymerization technique affords a new type of dilution superimposed on ordinary concentration effects: i.e., the separation of the chromophores along the polymer chain. This approach has been used for the study of the fluorescence behavior of several vinyl aromatic polymers including polystyrene, poly(1-vinylnaphthalene) and its copolymers with styrene and methyl methacrylate, poly(2-vinylnaphthalene),[31] alternating copolymers of styrene with methyl methacrylate or 2-naphthyl methacrylate, alternating copolymers of 2-vinylnaphthalene with methyl methacrylate,[32] and random copolymers of styrene with methyl methacrylate.[33−38] Excimers in these systems were observed under a variety of conditions. In each of the polymers, the shorter wavelength band in the fluorescence spectrum, which is often structured, was attributed to monomeric emission, whereas the longer wavelength band was assigned to the fluorescence of intra- or interchain excimers. These conclusions were substantiated by results from spectra of one- and two-chromophore model compounds.[31−38]

In Figure 6 the emission of poly[styrene-*co*-(*p*-(stilbenylmethoxy)styrene)] (structure B) is shown. It can

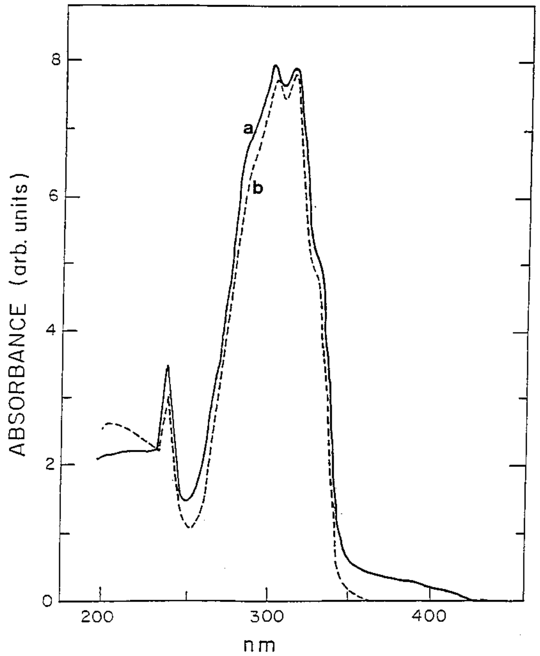


Figure 3. Absorption spectra of (a) poly[styrene-*co*-(*p*-(stilbenylmethoxy)styrene)], 10^{-4} M (chromophore concentration), and (b) *p*-((*p*-ethylphenoxy)methyl)stilbene, 10^{-5} M.

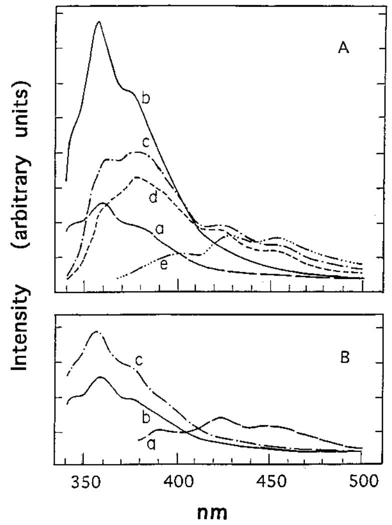


Figure 4. Fluorescence spectra of (A) the model compound at (a) 1×10^{-5}, (b) 1×10^{-4}, (c) 5×10^{-4}, (d) 1×10^{-3}, and (e) 1×10^{-2} M and (B) (a) model compound, excitation wavelength 360 nm, 1×10^{-5} M, (b) model compound, excitation wavelength 320 nm, 1×10^{-5} M, and (c) *trans*-stilbene, excitation wavelength 260 nm, 1×10^{-4} M.

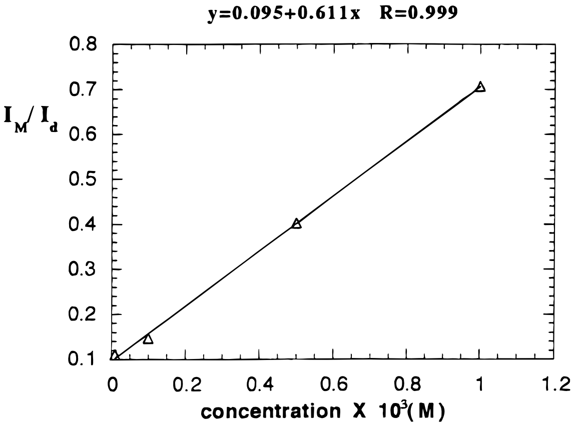


Figure 5. Variation of the ratio I_m/I_d (intensity of monomer emission/intensity of aggregate emission) with concentration.

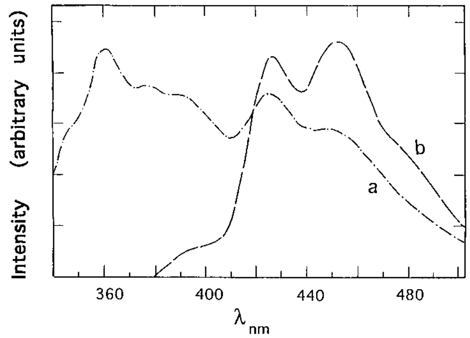


Figure 6. Fluorescence spectra of poly[styrene-*co*-(*p*-(stilbenylmethoxy)styrene)]: (a) excitation wavelength 320 nm and (b) excitation wavelength 360 nm, 1×10^{-4} M (chromophore concentration).

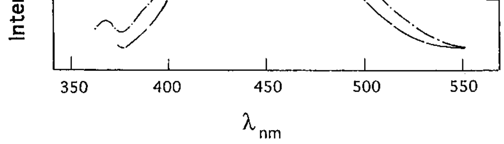


Figure 7. Photoluminescence spectra in solid state of poly[styrene-*co*-(*p*-(stilbenylmethoxy)styrene)]: (a) excitation wavelength 320 nm and (b) excitation wavelength 360 nm.

be seen that a dramatic change takes place when the wavelength of the exciting light is changed from 320 to 360 nm, for the polymer in solution. At 320 nm (Figure 6a), the emission is consistent with that of the model compound (Figure 4), but at 360 nm (Figure 6b), only the emission attributed to the associated form is seen. The same effect was observed for solid films, which emitted only in the lower frequency region for both excitation wavelengths, as shown in Figure 7.

The fact that only the copolymer absorbs at 360 nm leads us to propose that this band originates in fluorescent ground-state dimers or aggregates which are responsible for the emission at the lower wavelengths. When attached to a polymer backbone, the localized concentration of the chromophores will be much higher than in the nonbound state, due to conformational restrictions imposed on the polymer chain, making the number of associated sites in the polymer much greater than for the "free" chromophore. However, the presence of aggregates from the model compound in solution is evident from the data of Figure 4, where the variation of the solution concentration brings about both monomeric and aggregate emission when excited at 320 nm.

Observation of excimer fluorescence in confined media has been reported for systems such as stilbene containing fatty acids or surfactants in self-assembling layers[39,40] or in complementary nucleotide sequences having a stilbene spacer in each strand.[41] A similar bathochromic shift has also been observed for fluorescence emission from pendant stilbene groups attached to polyglutamic acid[42] and to copolymers of 4-hydroxystilbenyl acrylate−methyl acrylate[43] and ladder-structured poly(*p*-phenylene)s.[44,45]

It should be made clear that the classical definition of an excimer assumes that these are formed from an *excited* singlet-state chromophore interacting with another in the ground state. In this work the experimental evidence indicates that the association between chromophores occurs in the ground state generating a fluorescent ground-state complex, and therefore we purposely avoided the term "excimer" for the lower frequency emission observed for both emitting polymer and model compound.

As mentioned before, the copolymer composition ratio is 2/1 styrene (sty)/chromophore (chr) monomeric units. The calculated distribution[46] of monomeric units along the chain is sty−sty = 44.5%, sty−chr = 44.4%, and chr−chr = 11.1%. These results show that a nonnegligible amount of dimers can be formed between adjacent chromophores as reported for polystyrene[31] and for poly(vinylnaphthalene).[32] Nevertheless, the possibility must be considered that interactions can occur between chromophores on adjacent turns of the polymer coil because in the solid film only aggregate emission is detected. In fact, interchain excimer emission is predominant over monomeric emission in bulk polymers and, in several cases, was the only emission observed.[47] Excimers formed from nonnearest neighbors were reported for poly(1-naphthyl methacrylate)[48] and poly(acenaphthalene).[31−38]

The comparison of the fluorescence behavior of polymers with model compounds is not straightforward because of the participation of singlet or triplet energy migration in the polymer emission mechanism. It is generally accepted that singlet energy migrates from the absorption center either to preformed excimer sites or to locations where a conformational change would give rise to such a site within the lifetime of the exciton.[49] From the copolymer emission spectra irradiated at 320 nm (Figure 6a), we know that in solution the associated species coexist with the nonassociated. This indicates that singlet energy migration is a possibility to be considered, since the associated species is already in a geometry suitable for pair formation, and it is generally accepted that excimers can act as traps for energy migration due to their lower energy level.[49,32] The fact that only aggregate emission is detected in the solid state favors this hypothesis, since the majority of the chromophores are isolated along the chain (sty−chr units concentration is 44.4%).

The linearity of I_m/I_d versus chromophore concentration for the model compound (which corresponds to the "free" chromophore, Figure 5) in dilute solution shows that, other than emission and association, no additional photophysical mechanisms such as energy migration are involved. Under these conditions, an increase in solution concentration leads to an increase in monomeric emission rather than in aggregate emission. It has been reported that, when the naphthyl chromophore is bound to a polymer backbone as in poly[styrene-*co*-(1-vinylnaphthalene)], increases in the chromophore concentration along the chain lead to decreases in the I_m/I_d ratio, although not in a linear fashion.[31] In other cases where chromophores are present in the pendant groups of a polymer chain, it has not been possible to establish any simple relationship involving only I_m/I_d and chromophore concentration. The present results therefore show that for the free molecule in dilute solution secondary processes are avoided, whereas when it is bound to a polymer chain, a much more complex situation is involved.[50]

It is noteworthy that a similar polystyrene stilbene derivative (polystyrene with phenylenevinylene segments in side chains) showed no evidence of excimer or aggregate emission.[51] This suggests that the polarity of *p*-(phenoxymethyl)stilbene might play a role in the ground-state association of this group.

To summarize, we report on the formation of a fluorescent dimer of a stilbene derivative in nonrestricted medium, at room temperature, for the first time. This species originates from a ground-state complex, and when attached to a polymeric backbone, the complex can be formed either intra- or intermolecularly.

References and Notes

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
(2) Burns, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H. *J. Chem. Soc., Chem. Commun.* **1992**, 32.
(3) Burns, P. L.; Holmes, A. B.; Kraft, A.; Brown, A. R.; Bradley, D. D. C.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47.
(4) Doi, S.; Kuwabara, M.; Noguchi, T.; Ohnishi, T. *Synth. Methods* **1993**, *55−57*, 4174.
(5) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982.
(6) Braun, D.; Heeger, A. J.; Kroemer, H. J. *J. Electron. Mater.* **1991**, *20*, 945.
(7) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1991**, *30*, L1938.
(8) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Solid State Commun.* **1991**, *80*, 605.
(9) Braun, D.; Gustafsson, G.; McBranch, D.; Heeger, A. J. *J. Appl. Phys.* **1992**, *72* (2), 564.
(10) Greenham, N. C.; Brown, A. R.; Bradley, D. D. C.; Friend, R. H. *Synth. Methods* **1993**, *55−57*, 4134.
(11) Uchida, M.; Ohmori, Y.; Morishima, C.; Yoshino, K. *Synth. Methods* **1993**, *55−57*, 4168.
(12) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628.
(13) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1991**, *30*, L1941.
(14) Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36.
(15) Brown, A. R.; Greenham, N. C.; Burroughes, J. H.; Bradley, D. D. C.; Friend, R. H.; Burns, P. L.; Kraft, A.; Holmes, A. B. *Chem. Phys. Lett.* **1992**, *200*, 46.
(16) Musfeldt, J. L.; Reynolds, J. R.; Tanner, D. B.; Ruiz, J. P.; Wang, J.; Pomerantz, M. *J. Polym. Sci. B, Polym. Phys.* **1994**, *32*, 2395.
(17) Leising, G.; Grem, G.; Scherf, U. 2nd Congresso Brasileiro de Polimeros, Sao Paulo, SP, 1993; p 569.
(18) Hu, B.; Karasz, F. E.; Morton, D. C.; Sokolik, I.; Yang, Z. *J. Lumin.* **1994**, *60−61*, 919.
(19) Yang, Z.; Sokolik, I.; Hu, B.; Karasz, F. E. *Polym. Mater. Sci. Eng.* **1993**, *69*, 155.
(20) Yang, Z.; Hu, B.; Sokolik, I.; Karasz, F. E. *Macromolecules*, in press.
(21) Yang, Z.; Sokolik, I.; Karasz, F. E. *Macromolecules* **1993**, *26*, 1188.
(22) Sokolik, I.; Yang, Z.; Karasz, F. E. *J. Appl. Phys.* **1993**, *74*, 3584.
(23) Aguiar, M.; Karasz, F. E.; Akcelrud, L. *Macromolecules* **1995**, *28*, 4598.
(24) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; John Wiley and Sons: New York, 1989.
(25) Cohen, M. D.; Green, B. S.; Ludmer, Z.; Schmidt, G. M. J. *Chem. Phys. Lett.* **1970**, *7*, 486.
(26) Lewis, F. D. *Adv. Photochem.* **1986**, *13*, 166.
(27) Brocklehurst, B.; Bull, D. C.; Evans, M.; Scott, P. M.; Stanney, G. *J. Am. Chem. Soc.* **1975**, *97*, 2977.
(28) Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647.
(29) Cohen, M. D. *Angew. Chem., Int. Ed. Engl.* **1976**, *14*, 386.
(30) Peters, K. S.; Freilich, S. C.; Lee, J. *J. Phys. Chem.* **1993**, *97*, 5482.
(31) Fox, R. B.; Price, T. R.; Cozzens, R. F.; McDonald, J. R. *J. Chem. Phys.* **1972**, *57*, 534.
(32) Fox, R. B.; Price, T. R.; Cozzens, R. F.; Echols, W. H. *Macromolecules* **1974**, *7*, 937.

(33) David, C.; Lempereur, M.; Geuskens, G. *Eur. Polym. J.* **1973**, *9*, 1315.
(34) Abuin, E.; Lissi, E.; Gargallo, L.; Radic, D. *Eur. Polym. J.* **1984**, *20*, 105.
(35) Boudevska, H.; Brutchkov, C.; Astroug, H. *Eur. Polym. J.* **1983**, *19*, 737.
(36) Abuin, E.; Lissi, E.; Gargallo, L.; Radic, D. *Eur. Polym. J.* **1982**, *18*, 319.
(37) Ito, O.; Terazima, M.; Azumi, T.; Matsumoto, N.; Takeda, K.; Fujino, M. *Macromolecules* **1989**, *22*, 1718.
(38) Sienicki, K.; Bojarski, C. *Macromolecules* **1985**, *18*, 2714.
(39) Whitten, D. G. *Acc. Chem. Res.* **1993**, *26*, 502.
(40) Spooner, S. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1994**, *116*, 1240.
(41) Letsinger, R. L.; Wu, T. *J. Am. Chem. Soc.* **1994**, *116*, 811.
(42) Fissi, A.; Houben, J. L.; Rosato, N.; Lopes, S.; Pieroni, O. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 29.
(43) Altomare, A.; Carlini, C.; Ciardelli, F.; Solaro, R.; Houben, J. L.; Rosato, N. *Polymer* **1983**, *24*, 95.
(44) Grüner, J. F.; Hamer, P. J.; Friend, R. H.; Hüber, J.; Scherf, U.; Holmes, A. B. *Adv. Mater.* **1994**, *6*, 748.
(45) Graupner, W.; Mauri, M.; Stampfl, J.; Leising, G.; Scherf, U.; Mullen, K. *Solid State Commun.* **1994**, *91*, 7.
(46) Harwood, H. J. *Angew. Chem.* **1965**, *4*, 394.
(47) Zlatkevich, L. *Luminescence Techniques in Solid State Polymer Research*; Marcel Dekker, Inc.: New York, 1989.
(48) Somersall, A. C.; Guillet, J. B. *Macromolecules* **1973**, *6*, 218.
(49) Guillet, J. B. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, U.K., 1985.
(50) Aguiar, M.; Karasz, F. E.; Akcelrud, L. Unpublished results.
(51) Hesemann, P.; Vestweber, H.; Pommerehne, J.; Mahrt, R. F.; Greiner, A. *Adv. Mater.* **1995**, *7*, 388.

MA951561R