Synthesis and Optical Properties of Polystyrene Bearing Stilbenoid Side Chains

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ABSTRACT: Four series of random graft copolymers with stilbenoid side chains on a polystyrene (PS) backbone were synthesized, and their optical properties were compared with blends of a series of model compounds in PS. The graft loading (5, 15, and 25 mol %), the type of link to the polymer backbone ("ether" or "direct"), and the number of methoxy groups substituted on the stilbene moiety were systematically varied. Absorption, emission, and time-resolved photoluminescence (PL) properties are presented for the compounds in solution and as spin-coated films, and relative quantum yields have been determined. Mixed monomer/excimer emission was found to be the characteristic emission for all grafts, while the reversibility of the excimer formation seems to vary for the different grafts. In the blends the miscibility of the model compounds is quite different: the 4-methoxystilbene/PS system readily forms aggregates and crystallites, whereas the 3,4,5-trimethoxy-4′-methylstilbene/PS system forms uniform mixtures showing excimer-type emission. The PL efficiencies decreased with concentration in all cases where excimeric emission was found. For the blend containing 4-methoxystilbene, however, the PL efficiency increased with concentration.

1. Introduction

The rich photochemistry and photophysics of stilbenes have been investigated thoroughly during the past 40 years.[1−3] Still, new research is being triggered by the fact that the physicochemical behavior of stilbene strongly depends on the environment in which the molecule is excited. The observed properties include photoisomerization,[4−7] photodimerization,[8−10] light emission, and nonlinear optical effects.[11,12] It has been observed that the associated stilbene molecules, in either the ground (physical dimer) or excited state (excimer), play a key role in these processes. In the case of stilbene, dimers, larger aggregates, and excimers have been observed and studied in many systems including (frozen) solutions,[13] fatty acid surfactant assemblies,[14,15] oligonucleotides,[10,16,17] and proteins.[18] Covalently bound stilbene units can be found in assemblies such as bis(stilbenes),[19] stilbenophane,[19,20] and paracyclophane-cored distilbenes.[21,22] Polymers offer another environment in which the versatility of stilbene can be tailored toward various practical applications,[23−25] the one directly related to this work being the organic light-emitting diode (OLED). A lot of activity in this field has been triggered by the work of Tang and Vanslyke[26] and by Burroughes et al.,[27] who reported on the properties of poly(*N*-vinylcarbazole)-based (PVK) OLEDs and on the electroluminescence of poly(*p*-phenylenevinylene) (PPV), respectively. The oligomeric counterparts of PPV have attracted attention for this purpose as well,[26,28] since they are easier to synthesize and are expected to allow a better control of the optoelectronic properties of the final product. In the UV−vis spectral region, stilbene chromophores are a natural choice as the emitter. Another example of a polymer emitting in this wavelength range is PVK.[29] Much research is directed toward improving the PL quantum efficiency and the spectral purity. Among the key units determining these processes are, again, excimers, dimers, and larger aggregates and crystalline domains. If small molecules are involved, the long-term stability with respect to phase separation is improved in comparison with blends, when the oligomer is covalently bound to the polymer host.[30−32]

We report on the synthesis and optical properties of a series of systematically varied random graft copolymers composed of styrene and stilbene-substituted styrene monomer units. The primary goal is to obtain a polymer matrix with a high loading of stilbene chromophores, resulting in a high luminescence yield. Previous studies on this type of polymers confirm that small systematic variations of the structural properties of the stilbene chromophores cause large effects on the photophysical properties of these systems, thereby influencing the ability to form ground-state dimers and larger aggregates, as described by Aguiar et al.[33−37] Here, in contrast, we report on the ability of stilbene-based graft copolymers to form excimer states. A second important difference is the specific type of chromophores used in this work and their intrinsic photophysical properties. For instance, we will show that upon going from 4-methoxystilbene (MSt) to 3,4,5-trimethoxy-4′-methylstilbene (TMSt) the fluorescence lifetime in toluene is increased by a factor of 10. Also, the chain folding mechanism is expected to be strongly dependent on the concentration of the chromophore, the type of link to the polymer backbone, ether linked (EL) or direct linked (DL) graft polymers, and the specific stilbenoid used.[30,34−36] Similar graft copolymers have been used in the study of the photoinduced phase segregation in polymers.[38,39] The compounds are likely to be of interest in the field of extreme UV (x-UV, in this case typically around 60 nm) detection as well.[40] In addition, the properties of these new materials are compared with a series of blends containing the same chromophores in PS.

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2. Experimental Section

2.1. Syntheses. All starting materials were obtained from Acros or Aldrich and used as received. Diglyme and dimethylformamide (DMF) were dried over 4A and 3A molecular sieves, respectively. THF was distilled from sodium/benzophenone. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity-400 apparatus in $CDCl_3$ with tetramethylsilane (TMS) as the internal reference. Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments 2920 apparatus, operating under a N_2 flow of 50 mL min^{-1} using aluminum sample pans and an empty aluminum pan as reference. A sample mass of approximately 1−2 mg was used. The heating rate was 5 °C min^{-1}, and controlled cooling was achieved by means of the TA Instruments RCS cooling system.

*4-(tert-Butyldimethylsilyloxy)-3,5-dimethoxybenzaldehyde (**1**).* Syringaldehyde (3.6 g, 0.02 mol) and imidazole (2.0 g, 0.03 mol) were dissolved in dry DMF (50 mL) at 0 °C under a nitrogen atmosphere. *tert*-Butyldimethylsilyl chloride (3.0 g, 0.02 mol) was added, and the mixture was stirred for 2 h at 0 °C and overnight at room temperature. The resulting mixture was poured into ice water and washed three times with hexane (150 mL). The combined hexane fractions were washed with water and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The yield was 4.8 g (81%); mp 67−70 °C. ^{1}H NMR ($CDCl_3$): δ 0.16 (s, 6H, $SiCH_3$), 1.02 (s, 9H, Bu^t), 3.87 (s, 6H, OCH_3), 7.10 (s, 2H, H(3)/H(5)), 9.82 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$): δ −4.33 ($SiCH_3$), 18.99 (CSi), 25.88 (Bu^t), 56.02 (OCH_3), 107.03 C(3)/C(5), 129.64 C(4), 140.98 C(1)/C(6), 152.24 C(2), 191.09 (CHO).

*(4-Methylbenzyl)diethylphosphonate (**2**).* A mixture of α-chloro-*p*-xylene (21.0 g, 0.15 mol) and triethyl phosphite (48.1 g, 0.29 mol) was gently refluxed for 8 h. The mixture was then cooled to room temperature, the excess triethyl phosphite was evaporated, and the resulting liquid was used without any further purification.

*4-Hydroxy-3,5-dimethoxy-4′-methylstilbene (**3**).* A mixture of (4-methylbenzyl)diethylphosphonate (**2**) (7.1 g, 29 mmol) and sodium hydride (1.2 g, 29 mmol) in dry THF (80 mL) was stirred under a nitrogen atmosphere, and the solution was heated to 60 °C. Subsequently, 4-(*tert*-butyldimethylsilyloxy)-3,5-dimethoxybenzaldehyde (**1**) (4.3 g, 14.5 mmol) in dry THF (20 mL) was added dropwise, and the resulting mixture stirred at 60 °C under the nitrogen atmosphere for 20 h. After cooling to room temperature, concentrated HCl (10 mL) and water (100 mL) were added, and the new mixture was stirred for 48 h to deprotect the phenol moiety. The latter was extracted with dichloromethane, and the organic fractions were evaporated under reduced pressure. After the addition of methanol and water, a brown solid was collected by filtration. The yield was 2.8 g (65%); mp 109−112 °C. ^{1}H NMR ($CDCl_3$): δ 2.34 (s, 3H, CH_3), 3.91 (s, 6H, OCH_3), 6.72 (s, 2H, H(2)/H(6)), 6.94 (d, 2H, H(2′)/H(6′)) 7.14 (d, 2H, =CH), 7.37 (d, 2H, H(3′)/H(5′)). ^{13}C NMR ($CDCl_3$): δ 21.19 (CH_3), 56.38 (OCH_3), 103.55 C(2)/C(6), 126.23 C(β), 126.88 C(2′)/C(6′), 127.92 C(3′)/C(5′), 129.25 C(4), 129.40 C(α), 134.74 C(1′), 134.92 C(4′), 137.18 C(1), 147.33 C(5)/C(3).

*3,4,5-Trimethoxy-4′-methylstilbene (**4**) (TMSt).* A mixture of (4-methylbenzyl)diethylphosphonate (**2**) (12.1 g, 0.05 mol) and sodium hydride (2.0 g, 0.05 mol) in dry THF (150 mL) was stirred under a nitrogen atmosphere. 3,4,5-Trimethoxybenzaldehyde (10 g, 0.05 mol) was added, and the mixture was stirred for 4 h at 60 °C and overnight at room temperature. The resulting mixture was then poured into ice water and washed three times with ether (150 mL). The ether fractions were combined, the solvent was evaporated, and chloroform (10 mL) was added to the compound. To this resulting slurry 150 mL of ethanol was added, followed by the slow addition of 100 mL of water. A fine yellow powder precipitated. The yield was 10.4 g (72%); mp 112 °C. ^{1}H NMR ($CDCl_3$): δ 2.36 (s, 3H, CH_3), 3.87 (s, 3H, *p*-OCH_3), 3.91 (s, 6H, *m*-OCH_3), 6.73 (s, 2H, H(2)/H(4)), 6.98 (s, 2H, H(α)/H(β)), 7.17 (d, 2H, H(2′)/H(6′)), 7.40 (d, 2H, H(3′)/H(5′)). ^{13}C NMR ($CDCl_3$): δ 21.23 (CH_3), 56.22 (*m*-OCH_3), 61.3 (*p*-OCH_3), 103.78 C(2)/C(6), 126.39 C(β), 127.75 C(2′)/C(6′), 128.22 C(3′)/C(5′), 129.45 C(α), 133.34 C(4), 134.54 C(1), 137.52 C(4′), 138.13 C(1′), 153.50 C(3)/C(5).

EL-Type Graft Copolymers (EL-MSt-x and EL-TMSt-x). The precursor polymer, poly(styrene-*co*-vinylbenzyl chloride), was dissolved in DMF. A 10−20-fold excess (relative to the VBC content) of both the hydroxy-substituted stilbene and of K_2CO_3 was added. This mixture was refluxed overnight, after which it was poured into ethanol. The precipitate was filtered, redissolved in dichloromethane, and precipitated once more in ethanol.

*Poly[styrene-co-(diethyl(vinylbenzyl)phosphonate)] (**5**).* 1.0 g of the precursor polymer was dissolved in diglyme (80 mL). Triethyl phosphite (30 mL) was added to this solution, irrespective of the loading of VBC, which resulted in a phosphite excess of roughly 20−100. This mixture was refluxed overnight. The solvent and the excess triethyl phosphite were evaporated under reduced pressure. The resulting sticky polymer was used for the Wadsworth−Emmons reaction without further purification.

DL-Type Graft Copolymers (DL-St-x and DL-TMSt-x). Poly[styrene-*co*-(diethyl(vinylbenzyl)phosphonate)] (**5**) was dissolved in dry diglyme. A 20-fold excess of both the appropriate benzaldehyde and of NaH was added, and this mixture was stirred overnight at room temperature in a nitrogen atmosphere. The polymer was then precipitated in ethanol, redissolved in dichloromethane, and once more precipitated in ethanol.

2.2. Optical Spectroscopy. *Sample Preparation.* PS standard (M_w = 1000 000) was purchased from Aldrich and used as received for the preparation of the blends. The concentration of the model chromophores was determined as the molar ratio between the model compound and the styrene units. The films were spin-coated from CH_2Cl_2 (DCM) in all cases, unless it is explicitly stated that $CHCl_3$ was used. Solutions with concentrations of about 6.0 mg mL^{-1} were spin-coated on quartz substrates at a speed of 1000 rpm for 40 s and then at a speed of 7000 rpm for another 20 s. The film thickness was measured on a DEKTAK 3030 Auto 1 profilometer and were found to vary between 40 and 200 nm.

Optical Spectroscopy. Absorption spectra were recorded on a Cary 5 UV−vis spectrometer. Luminescence spectra were recorded on a Cary Eclipse fluorometer. The spectra were corrected for the wavelength dependence of the instrumental response, using a set of secondary emission standards, following the procedure proposed by Gardecki and Maroncelli.[41] The reflection of the excitation light from the sample was used for the precise positioning of the quartz substrates in order to make a meaningful comparison. PL efficiencies in the polymer thin film were obtained by dividing the integrated emission by the absorption at the excitation wavelength of 320 nm. For internal comparison, the efficiency of the blend TMSt-5/PS was arbitrarily taken to be 1.

Time-Resolved Spectroscopy. Time-resolved spectra were recorded using a streak camera (Hamamatsu streak-scope C4334) allowing simultaneous recording of wavelength and time dependence. A Chromex spectrograph with 150 lines mm^{-1} grating was used to obtain a 90 nm spectral range. When needed, multiple exposures for overlapping spectral regions were combined. The images were corrected for the variation in the pixel sensitivity (shading) but not for the spectral sensitivity of the instrument. Pulses from an optical parametric amplifier (OPA), which was pumped by a Ti:sapphire regenerative amplifier from Spectra Physics, were used (repetition rate 1.5 kHz, pulse width 2 ps) as excitation source. The average power was kept below 0.1 μW, corresponding to a density of approximately 50 mW cm^{-2} at an excitation wavelength of either 270 or 295 nm. Although no decrease in emission intensity was found within minutes of excitation, samples were frequently moved to allow for recovery during a 15 min recording.

3. Results and Discussion

3.1. Syntheses. To make a meaningful comparison between blends and the corresponding graft polymers,

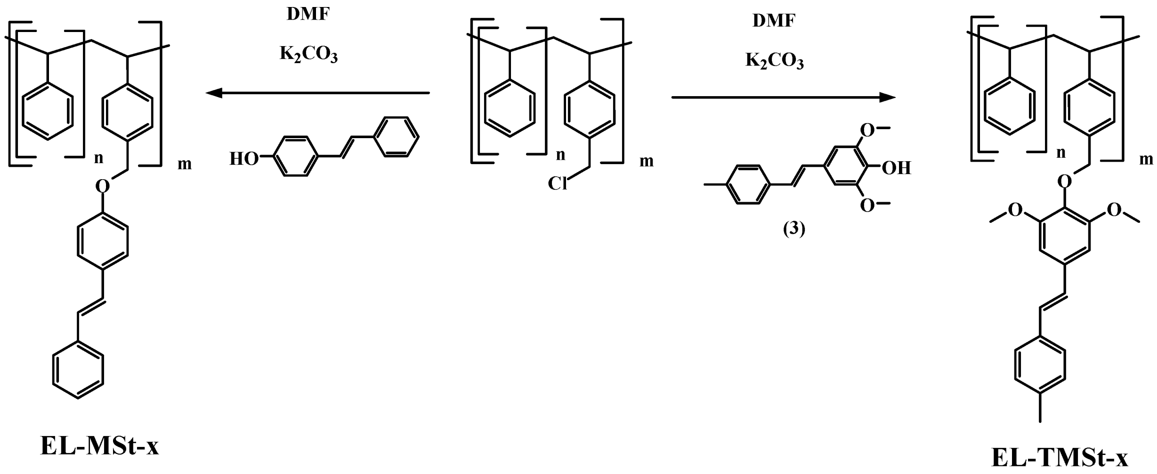

Figure 1. Synthetic pathways to the EL-MSt and EL-TMSt series of graft copolymers.

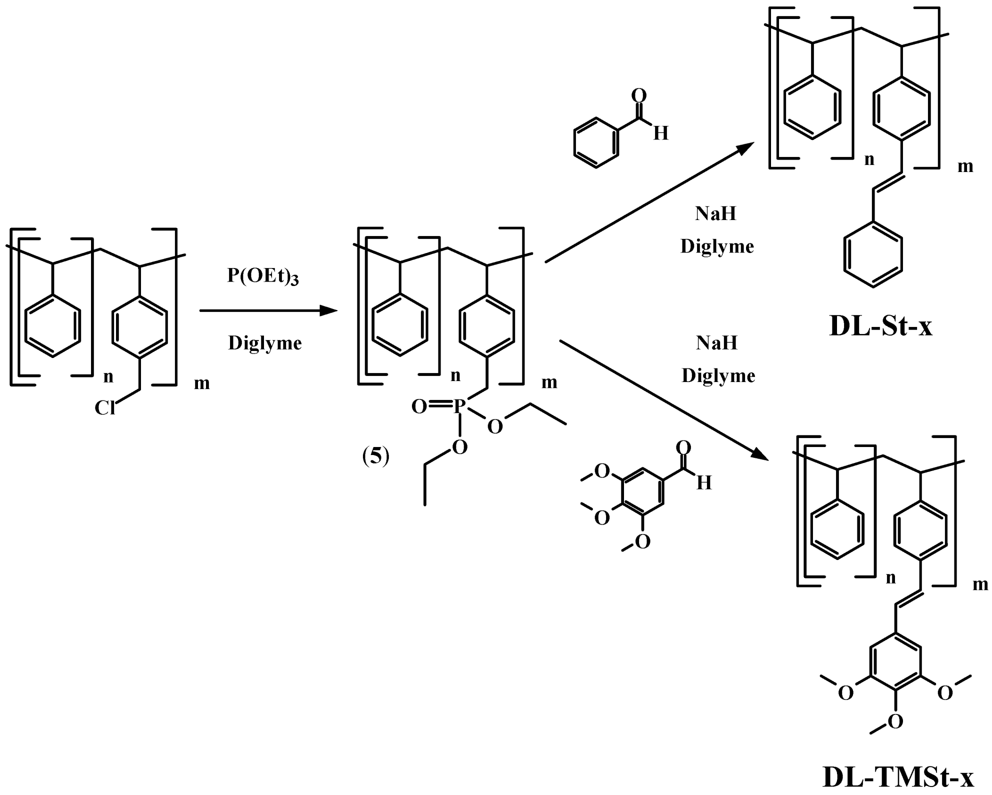

Figure 2. Synthetic pathways to the DL-St and DL-TMSt series of graft copolymers.

we have chosen a polymer system in which the chromophores are distributed randomly throughout the polymer chain. A versatile precursor polymer for the synthesis of this kind of graft copolymers is poly(styrene-*co*-vinylbenzyl chloride). In this polymer the reactive chloromethyl groups are distributed randomly along the polymer backbone, ensuring a random distribution of the chromophores in the final graft copolymer. This randomness can be easily deduced from the relative reactivity ratios r of the monomers: 0.99 for 4-vinylbenzyl chloride and 1.06 for styrene. Poly(styrene-*co*-vinylbenzyl chloride) was prepared according to the procedure described by Belfield and Wang.[42]

In two of the series of graft copolymers studied, the stilbene moiety was attached to the backbone via a flexible ether linkage. The synthesis consisted of a Williamson ether condensation of the appropriate hydroxy-functionalized stilbene with the precursor polymer in refluxing DMF using potassium carbonate as base (Figure 1). To make sure that all chloromethyl groups were converted, an excess of the stilbene compound was used. 4-Hydroxystilbene is commercially available, and 4-hydroxy-3,5-dimethoxy-4′-methylstilbene was synthesized under standard Wadsworth–Emmons conditions. After the reaction was completed, the polymer was precipitated in ethanol. ^{1}H NMR confirmed that the reaction had proceeded quantitatively. The absorption spectrum in solution of this type of graft copolymer corresponds well to that of a matching concentration of the free stilbene (Figures 3 and 4), confirming that the amount of chromophores incorporated in the polymer system corresponds to a quantitative conversion of the chloromethyl groups. The thus-obtained graft copolymers are called EL-MSt-x (ether-linked methoxystilbene x mol %) and EL-TMSt-x (ether-linked trimethoxystilbene x mol %), where x represents the molar concentration of the chromophore.

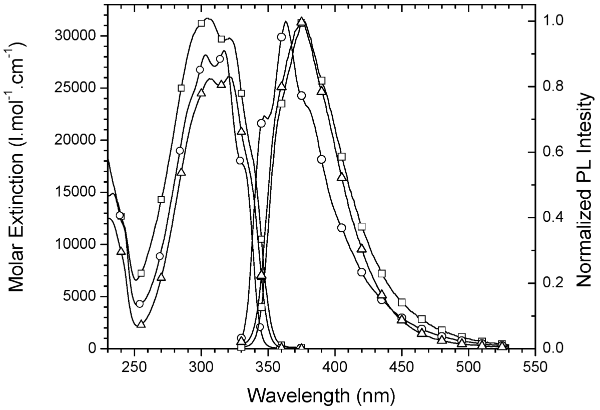

Figure 3. Absorption and emission spectra of the model compound MSt (△) and the graft copolymers EL-MSt-25 (□) and DL-St-25 (○) as 10^{-5} M solutions in CH$_2$Cl$_2$.

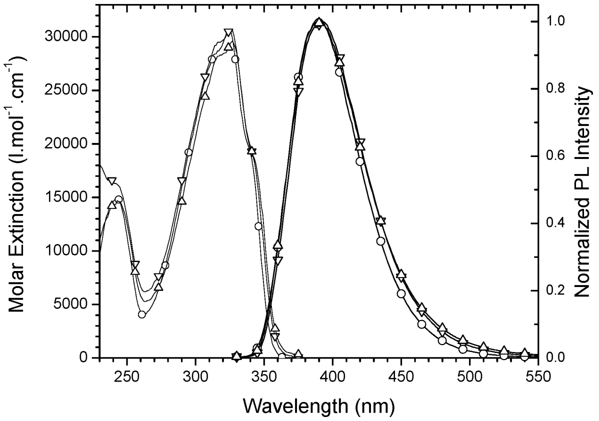

Figure 4. Absorption and emission spectra of the model compound TMSt (○) and the graft copolymers EL-TMSt-25 (△) and DL-TMSt-25 (▽) as 10^{-5} M solutions in CH$_2$Cl$_2$.

Two other series of graft copolymers, based on the same type of substituted stilbenes as in the EL series, were synthesized. In these graft copolymers, the chromophores were attached to the polymer backbone in a rigid way, so that one phenyl ring of the stilbene is part of the polystyrene backbone (Figure 2). This synthesis was first described by Belfield and Wang[42] and was used here without any major changes. In the first step, the precursor polymer is converted into the polymer-bound phosphonate, poly[styrene-*co*-(diethyl(vinylbenzyl)phosphonate)] (**5**), in a classical Michaelis−Arbuzov reaction. ^{1}H NMR confirmed that the phosphonate formation was quantitative. This phosphonate was then reacted with the appropriate benzaldehyde under Wadsworth−Emmons conditions to yield the desired compound. The absence of any benzylic signal between 3 and 5 ppm in the ^{1}H NMR spectrum confirmed that the conversion was quantitative. FTIR measurements showed no sign of the P=O vibration, usually found around 1255 cm^{-1}, which also confirmed the absence of unreacted phosphonate groups in the final polymer. The thus-obtained graft copolymers are called DL-St-*x* (direct linked stilbene *x* mol %) and DL-TMSt-*x* (direct linked trimethoxystilbene *x* mol %), where *x* represents the molar concentration of the chromophore. The glass transition temperatures are summarized in Table 1. It can be concluded from the data in Table 1 that the direct linked (DL) series have, in general, higher glass transition temperatures than the ether-linked (EL) series due to the lower flexibility of the chromophores in the former.

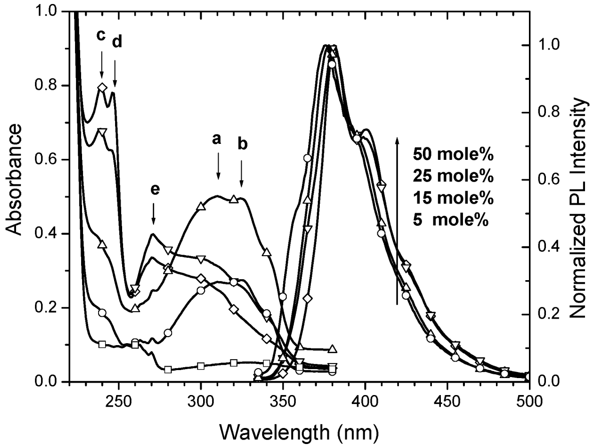

Figure 5. Absorption and emission spectra of MSt-*x* blended in PS for *x* = 0 (□), 5 (○), 15 (△), 25 (▽), and 50 (◇). See text for an explanation of a, b, c, d, and e.

Table 1. Glass Transition Temperatures (°C) of the Different Graft Copolymers

	loading			
	5%	15%	25%	40%
precursor	103	101	98	98
DL-St	101	123	122	
DL-TMSt	112	126	134	
EL-M St	109	113	114	116
EL-TMSt	100	103	104	

The comparison of aggregation behavior in grafts vs blends also required a set of model compounds, analogous to the ones grafted to the copolymer, which were blended in PS. 3,4,5-Trimethoxy-4′-methylstilbene (**4**) (abbreviated TMSt and TMSt-*x* when blended) was chosen as the model for the DL-TMSt-*x* and EL-TMSt-*x* series, where *x* represents the molar concentration of the chromophore, and was synthesized under standard Wadsworth−Emmons conditions. 4-Methoxystilbene (abbreviated MSt, or MSt-*x* when blended) was used as a model for the EL-MSt-*x* series; it was purchased from Acros and used as received. By the same token, stilbene is the proper model compound to describe DL-St-*x*, yet no blends were made with this compound, as much information regarding its behavior can be found in the literature.

3.2. Optical Properties in Solution. Justification for directly associating MSt and TMSt with the chromophoric parts of the graft copolymers can be found in the optical absorption and emission spectra recorded in dilute dichloromethane solution, as depicted in Figures 3 and 4. They show that the spectra of the model compounds and the graft copolymers (with 25 mol % loading) are nearly identical for the two series, indicating that the model compounds retain their optical (absorption and fluorescence) properties to a large extent, when they are incorporated in the polymer. Only a small increase on the red side of the spectra is observed (see also the inset in Figure 9 concerning DL-St-*x* in dichloromethane solution), which indicates that no large quantities of intra- or intermolecular aggregates or excimers are formed in 25 mol % loaded grafts in dilute solution, neither between two different stilbenes nor between a stilbene and a styrene moiety.[21] Excitation spectra from these solutions (not shown) were found to be independent of the emission wavelength and showed no trace of ground-state aggregates. Second, the ether link present in EL-TMSt and EL-MSt is found to

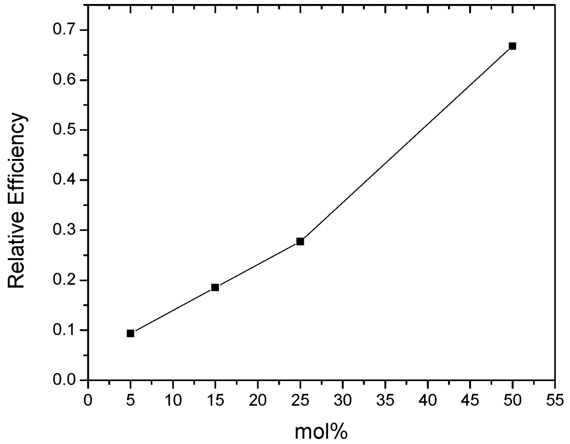

Figure 6. Evolution of PL efficiency (relative to TMSt-5) in thin film for the aggregate-forming MSt-*x*. The accuracy was estimated to be 20%.

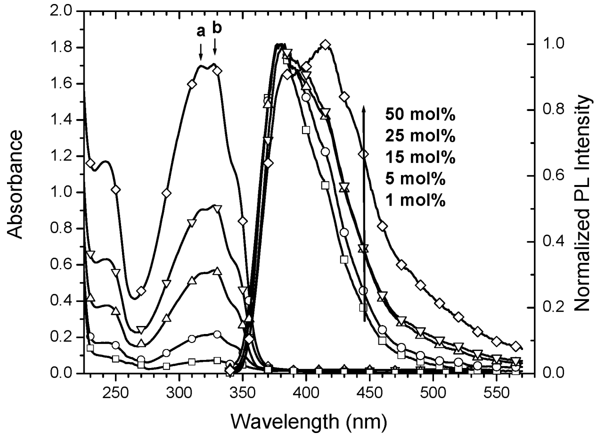

Figure 7. Absorption and emission spectra of TMSt-*x* blended in PS for *x* = 1 (□), 5 (○), 15 (△), 25 (▽), and 50 (◇). See text for an explanation of a and b.

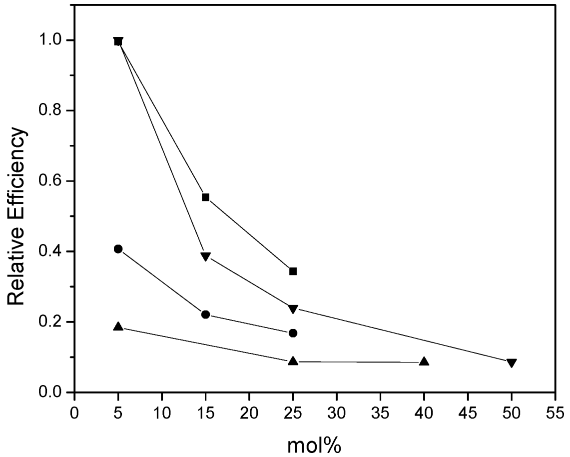

Figure 8. PL efficiencies of TMSt-*x* (▼), DL-TMSt-*x* (■), EL-TMSt-*x* (●), and EL-MSt-*x* (▲) measured relative to a 5 mol % TMSt/PS blend for which the efficiency was arbitrarily taken to be 1.

efficiently disrupt the conjugation of the stilbene with the styrene unit, as no red shift is observed for these compounds relative to the model chromophores. Finally, the nearly equal extinction values of the isolated chromophores and the grafts, obtained from the absorption measurements, confirm the quantitative loadings of the copolymers.

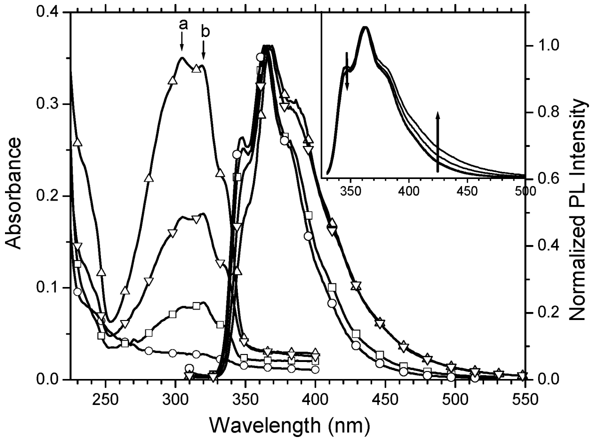

Figure 9. Absorption and emission spectra of thin films of the DL-St-*x* series for *x* = 1 (○), 5 (□), 15 (▽), and 25 (△). See text for an explanation of a and b. The inset shows the emission spectra of the same grafts recorded in 10^{-5} M solution in CH_2Cl_2 upon increasing graft loading as indicated by the arrows.

3.3. Optical Properties of Blends in PS. *4-Methoxystilbene (MSt).* In the absorption spectra of MSt-*x*, shown in Figure 5, one observes for *x* = 5 and 15 the expected chromophore band with substructure (peaks marked a and b), very similar to the chromophore spectrum measured in solution (Figure 3). However, this drastically changes at higher concentrations: the optical density in the 300−350 nm region decreases, and new features, denoted by c, d, and e, appear in the spectrum at 239, 247, and 270 nm, respectively. Additionally, a polarized optical microscopical analysis of the blends indicates that microcrystals are formed for MSt (and not for TMSt, as will be explained below), starting from a loading of 15 mol %; this seems to correspond to a threshold for phase segregation. These microcrystals increase in size for 25 mol % loading; for 50 mol % loading the field view is almost completely filled with relatively large crystallites. It can be concluded that the new features in the spectra for loadings higher than 15 mol % originate from the absorption by the crystalline regions in the film.

The emission spectra of MSt-*x* are also given in Figure 5. The main peak, centered at 376 nm, gradually red shifts over 5 nm with increasing loading, while the intensity of the vibronic structure in the emission band decreases at the high-energy side and increases at the low-energy side of the spectrum. Considering the increasing number of crystalline domains with loading, it is surprising that the PL spectrum hardly changes with increasing loading. The small red shift of the emission wavelength and the fact that the spectrum resembles the emission spectrum of the free stilbene are in good agreement with the results of theoretical calculations on stilbene dimers and trimers: INDO/SCI calculations performed by Cornil et al.[43] demonstrated that, when stacked in a cofacial conformation, a significant coupling exists between the excited and the ground state, but the transition dipole moment is expected to decrease with a decreasing distance between the stacked molecules. Moreover, they found by performing AM1/CI calculations that the main geometrical deformations in the lowest excited state occur in the central unit, in such a way that the relaxed electron−hole pair could be assumed to extend over at most three units in the aggregate. The predicted red shift in emission was only 80 meV on going from larger distances to 4 Å (as derived

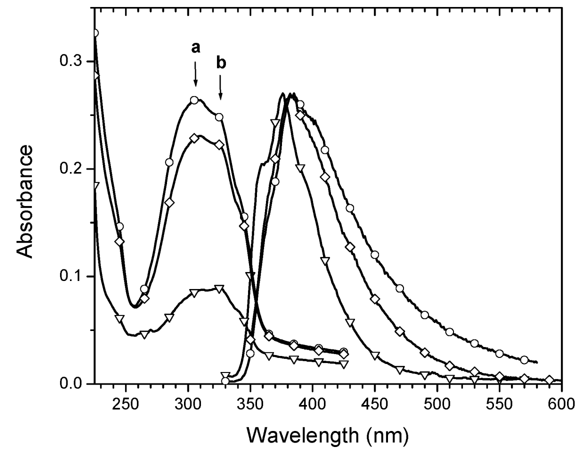

Figure 10. Absorption and emission spectra of thin films of the EL-MSt-*x* series for $x = 5$ (▽), 25 (◇), and 40 (○). See text for an explanation of a and b.

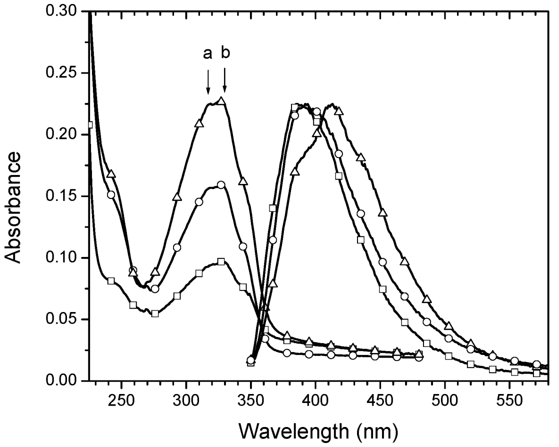

Figure 11. Absorption and emission spectra of thin films of the EL-TMSt-*x* series for $x = 5$ (□), 15 (○), and 25 (△). See text for an explanation of a and b.

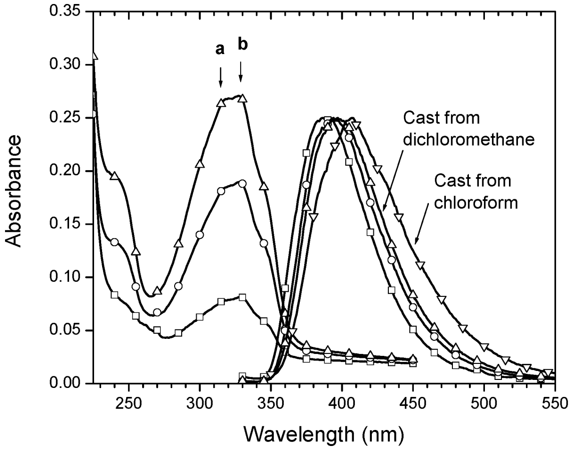

Figure 12. Absorption and emission spectra of thin films of the DL-TMSt-*x* series for $x = 5$ (□), 15 (○), and 25 (△), spin-coated from CH_2Cl_2 solution. The emission spectrum of DL-TMSt-25 (▽) was recorded after spin-coating from $CHCl_3$ solution. See text for an explanation of a and b.

from Figure 6 in ref 43). In the case of both MSt-*x* and DL-St-*x*, on going from 1 to 25 mol %, we found 52.8 ± 0.5 meV, and in the case of EL-MSt-*x* a value of 65.0 ± 0.5 meV was observed. These red shifts were calculated from the spectra in Figures 5, 9, and 10, respectively.

The evolution of the PL efficiency as a function of concentration for the blends of MSt/PS is shown in Figure 6. The approximately linear increase is rather remarkable. Recently, similar results have been reported on the increasing efficiencies of more crystalline regions in a PPV derivative.[44] Yet, as a counterexample, aggregates of coumarin in PVK were found to quench the luminescence.[45] In our case we explain this phenomenon in terms of the decay pathway present in isolated molecules of 4-methoxystilbene, which is governed by a 90° rotation in the excited singlet over the vinylene C=C bond.[46] This process opens a nonradiative decay channel in the 10−300 ps time domain, depending on the substituents and solvent,[2,47] for molecules in solution, and on the vibrational energy that is available,[6] for molecules in the gas phase. In the crystalline environment, this torsion must be sterically hindered, even compared to the free molecules in a PS matrix, and as a result, a higher emission efficiency is found for increasing concentrations of MSt-*x*. The increasing fraction of crystalline phase in the films and the larger quantum efficiency of this phase, compared to diluted molecules in PS, are the origin of the steady increase of PL efficiency shown in Figure 6.

Specifically for MSt, we note that comparison of the spectral properties with those of the corresponding graft copolymers should be made carefully due to the immiscibility of the compound in PS. Only the spectra recorded for lower concentrations, below 15 mol %, can be used as reference material in the study of the graft copolymers. The spectral features observed in the emission spectra at higher concentrations are likely to be attributed to a cofacial-type stacking in the crystallites.

3,4,5-Trimethoxy-4′-methylstilbene (TMSt). The miscibility of TMSt and PS is very different from that of MSt and PS. In polarized microscopy no indication for crystallites is found up to the highest loading. The difference with MSt is also evident from the absorption spectra of TMSt, shown in Figure 7. It is clear from these spectra that TMSt does not form ground-state aggregates: the vibronic bands in the absorption spectrum labeled a and b show no significant change in relative intensity, indicating very good mixing in this blend. The additional methoxy substituents at positions 3 and 5 in TMSt, compared to MSt, are thus found to enhance the solubility of the stilbene derivative in the polystyrene matrix, an effect which is well-known in solution. In turn, the emission spectra of these blends show a relatively broad band at 420 nm with a shoulder at 435 nm and a substantial tail at increasing concentration. This emission is attributed to excimer formation. The total emission efficiency drops in this case with increasing concentration as depicted in Figure 8 because of the lower quantum efficiency of the long-lived excimer state.

3.4. Optical Properties of the Graft Copolymers. As it is known that excimer emission is not observed as a fluorescence quenching process in stilbene solutions at room temperature, even at high concentrations,[8] an excimer between two stilbene units was not observed until 1993, in that case in bis(stilbenes) and stilbenophane.[19] Previously, excimers between hydroxystilbenes were observed in copolymers with (−)-menthyl acrylate in 1983.[23] Later, they were observed in stilbene−carboxamides linked between oligonucleotides.[16] From these studies one is left with the impression that close contact between stilbenes in a cofacial arrangement is required in order to form excimer states. At this point it should be mentioned that in such a configuration excimers are expected to be the intermediate state

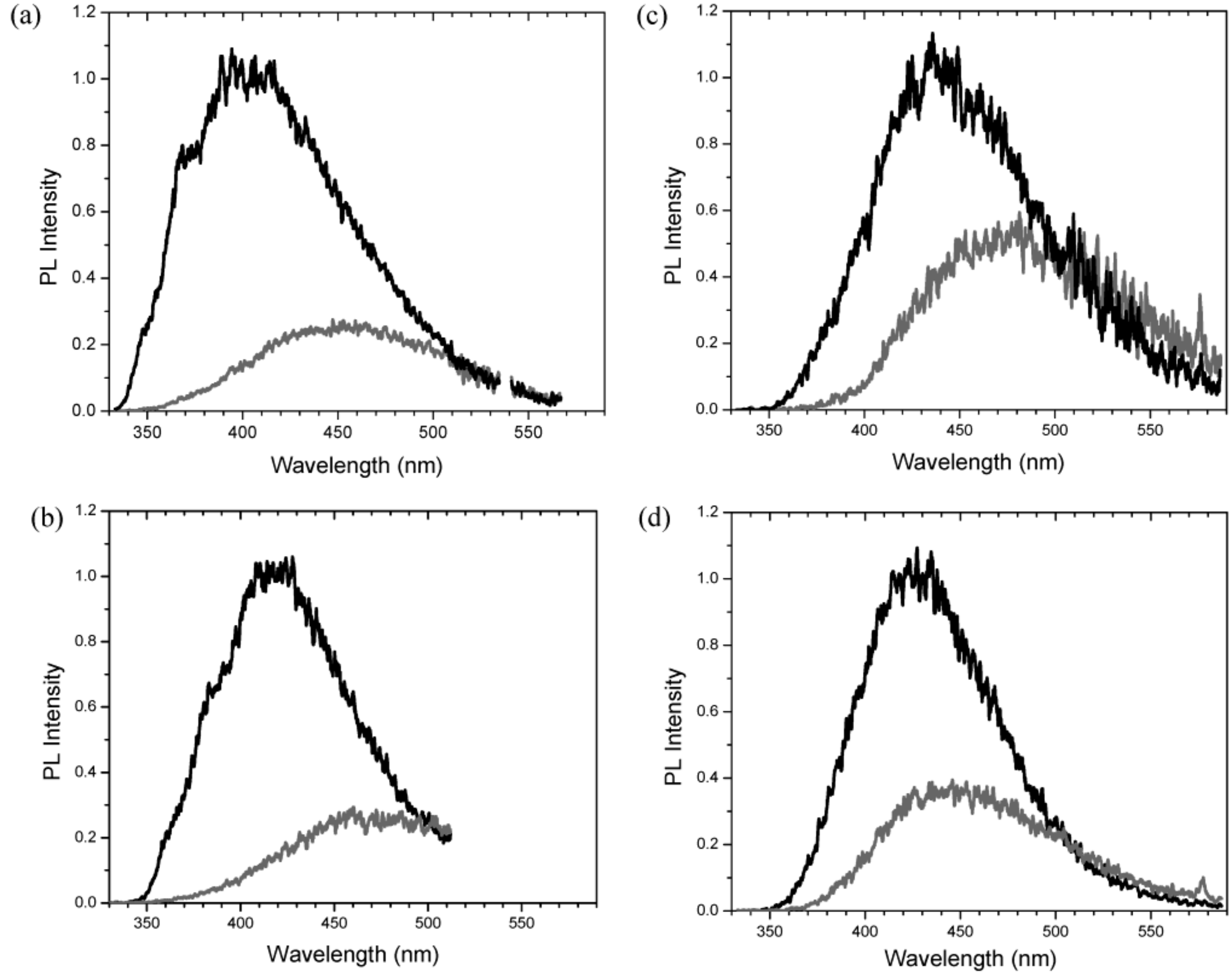

Figure 13. Emission spectra of DL-St-25 (a), EL-MSt-25 (b), EL-TMSt-25 (c), and DL-TMSt-25 (d), integrated over the interval 0−500 ps (upper black curve) and over the interval 1.5−4 ns (lower gray curve). The excitation wavelength was 270 nm for (a) and (b) and 295 nm for (c) and (d).

in possible photodimerization processes.[8−10,48,49] On the other hand, ground-state aggregates, consisting of 3−7 stilbene chromophores arranged in a pinwheel fashion, have been found in closely packed stilbenes such as stilbenes in phospholipid layers and vesicles.[14] In graft copolymers with styrene, a different type, one with red-shifted absorption, has been observed as well.[35] Similar aggregates have been observed in solution for stilbenes substituted with polar substituents which are not conjugated to the stilbene backbone.[37] On the contrary, when the substituents are conjugated to the stilbene backbone, excimers and, in some cases, subsequent photodimerization are observed both for isolated molecules[48,49] and graft coploymers.[23] Therefore, it is expected that in the graft polymers we describe here there will be excimer formation, but this will not happen in large quantities, as the process is limited by the availability of the required pair conformations in the disordered polymer films, which are very rare and are not likely to be formed after excitation. In these films, the few excimer states that are formed can be populated by energy transfer, and thus act as a trap, resulting in a reduced PL efficiency at higher concentration, as shown in Figure 8. Indirect evidence for the fact that the graft copolymers described in this work do form excimers is provided by the observation that solutions, after evaporation under tube light, show signs of gelation when redissolved due to partial cross-linking. Care was taken therefore to use fresh solutions for further characterization in the solid state. These processes are strongly suppressed in the films (solid state)—blends or grafts—in which no significant irreversible effects could be detected during the spectral as well as time-resolved optical measurements.

The absorption and normalized emission spectra of the graft copolymers in thin solid film are presented in Figures 9−12 for DL-St-*x* ($x = 1$, 5, 15, and 25), EL-MSt-*x* ($x = 5$, 25, and 40), EL-TMSt-*x* ($x = 5$, 15, and 25), and DL-TMSt-*x* ($x = 5$, 15, and 25), respectively. The spectra resulting from the time-resolved measurements are shown in Figure 13, where the spectra have been split into an “oligomeric” and an “excimeric” part, over the time domains from 0 to 500 ps and from 1.5 to 4 ns, respectively. From the absorption and emission spectra, given in Figures 9−12, it is clear that strong effects of phase segregation, as observed at higher concentrations in blends of MSt-*x* in PS, are absent in all graft series, as expected. On the other hand, a subtle effect in absorption, relating to the relative intensity of the two bands labeled a and b at 305 and 325 nm as shown in Figures 9 and 10, is observed for the (M)St grafts DL-St-*x* and EL-MSt-*x*. A similar effect was observed for stilbene associates with strong excimer emission.[10]

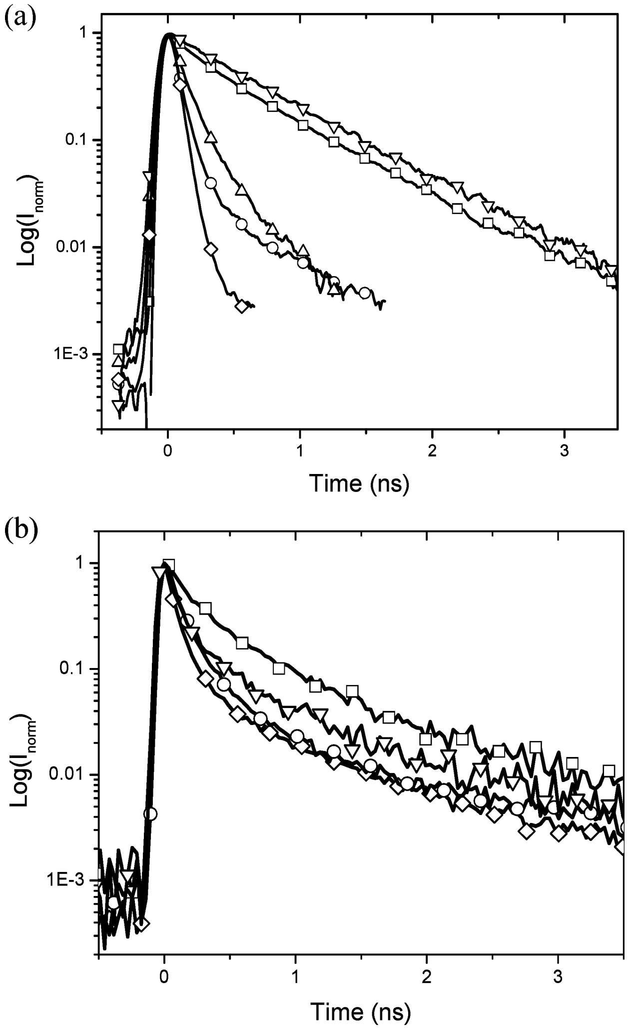

Figure 14. (a) PL decay curves recorded in toluene solution ($c < 10^{-4}$ M) for MST (△), TMSt (▽), DL-TMSt-25 (□), EL-MSt-25 (○), and DL-St-25 (◇). (b) PL decay curves recorded from the spin-coated thin film and integrated over the interval from 350 to 400 nm, after excitation at 300 nm, for DL-TMSt-25 (□), EL-TMSt-25 (▽), EL-MSt-25 (○), and DL-St-25 (◇).

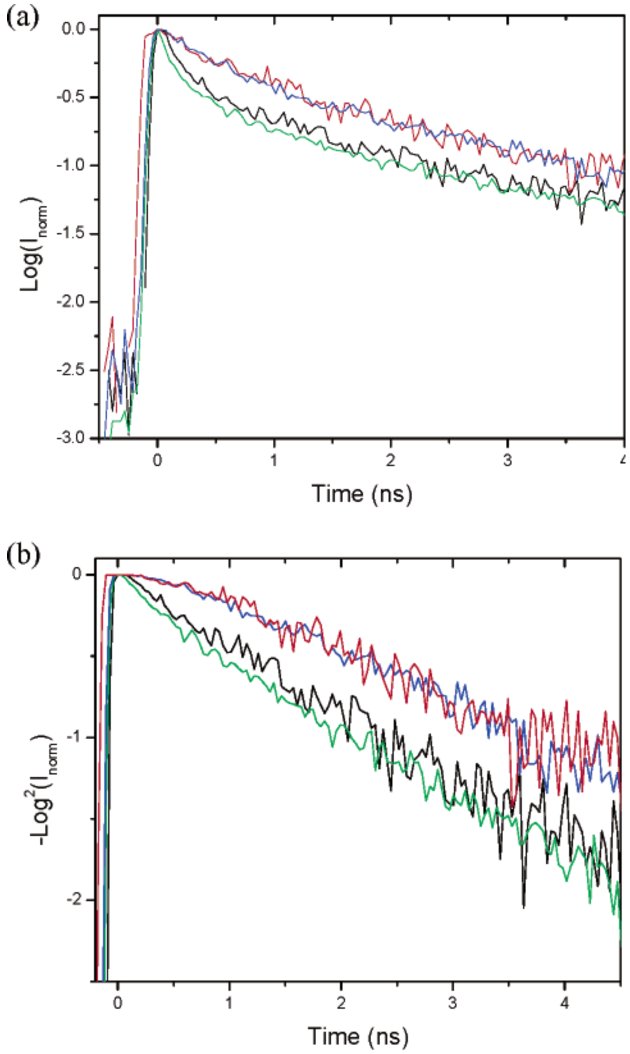

Figure 15. PL decay curves of DL-TMSt-25 (red), EL-TMSt-25 (blue), EL-MSt-25 (green), and DL-St-25 (black) as films for the interval 500−570 nm, excited at 300 nm. In (a) the logarithm and in (b) the negative of the squared logarithm of the intensity are plotted against time.

In good agreement with this, both steady-state and time-resolved emission spectra show a red-shifted emission, observed as a tail in the steady-state PL spectra (Figures 9 and 10), which was already visible in the solution spectra as shown for increasing loading of DL-St-*x* in the inset of Figure 9. This excimer emission also appears as a red-shifted band in the delayed spectra shown in Figure 13a,b. The difference between the ether-linked and direct linked stilbene in this twosome is small, with a slightly larger red shift for the ether-linked (92 nm) than for the direct linked (87 nm) stilbene. These red shifts have been determined as the difference between the maximum in the steady-state emission spectra and the maximum in the delayed spectra shown in Figure 13. As shown in Figure 15, the decay of the photoluminescence at these long wavelengths is independent of the linkage as well. In either case the decay traces obey a stretched exponential behavior.

The TMSt grafts have the fact that their PL yield is higher, in common, and this is due to the intrinsic properties of the attached chromophore. The emission spectra of EL-TMSt-*x* (Figure 11) are very similar to those observed in the blend; in the case of DL-TMSt-*x* the precise shape depends on the solvent used for spin-coating as shown in Figure 12. This might be an indication that the specific chain-folding mechanism is important for the excimer emission to occur. The delayed luminescence was found to be only weakly red-shifted, with an asymmetric shape (Figure 13c,d). Again, the ether-linked derivative has a larger red shift (80 nm) compared to the direct linked compound (49 nm). The decay traces of both compounds, recorded at the long emission wavelength, were similar: they can be seen as a combination of an exponential and a stretched exponential behavior, in accordance with the kinetics shown by reversible excimer-forming systems.[50] Further indications for the possible reversibility of this process in our case are found in the observed decay traces for the monomeric part of the grafts in thin film (Figure 14b) as compared to dilute toluene solution (Figure 14a). In solution, most compounds exhibit a nearly exponential decay, with the TMSt series having a higher fluorescence lifetime (640 ps) as compared to the MSt derivatives (<100 ps), as shown in Figure 14a. In thin film, the decay is nonexponential, with a fast initial decay resembling the solution decay, and a slow non-exponential tail. This delayed luminescence could be attributed to excimer emission extending to this high-energy spectral region, but alternatively, reconversion to monomer emission cannot yet be excluded, taking into account the small red shift between monomer and excimer spectra. This possibility of monomer emission upon excimer dissociation deserves further investigation. The faster initial decay of EL-TMSt-25 is unexpected, as it is in contrast with the observed slow initial decay seen for both TMSt and DL-TMSt-25 in solution and film.

4. Conclusions

We have successfully synthesized four series of random graft copolymers based on polystyrene in which the attached stilbene groups keep their chromophoric properties in solution. The properties of these new materials are compared with blends containing a set of model compounds in PS. Films prepared from these materials show a variety of optical characteristics which allow an understanding of their aggregate and excimer forming properties. In blends containing 4-methoxystilbene (MSt), the formation of crystallites is observed starting from 15 mol %, which dominates the absorption spectra at higher concentrations, while 3,4,5-trimethoxy-4′-methylstilbene (TMSt) forms uniform blends up to the highest loading. The grafts derived from this compound (EL-MSt-*x*) and from stilbene (DL-St-*x*) show the ground-state interaction to a lesser extent, and their emission drops with concentration as excimers are formed upon excitation. Grafts and blends derived from 3,4,5-trimethoxy-4′-methylstilbene (TMSt) generally have a higher PL quantum yield at low concentration. The direct linked graft based on the latter compound was found to be superior to the ether-linked one, as the excimer emission could be strongly reduced, depending on the solvent used for spin-coating. These materials, all based on stilbene, span a wide range with respect to their aggregate- and excimer-forming capabilities, and they offer new possibilities for the fabrication of near-UV organic light-emitting diodes as such or as a host for blue light-emitting oligomer-based devices.

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