Experimental Characterization and Molecular Modeling of the Intramolecular Excimer in Poly(*p-tert*-butylstyrene)

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ABSTRACT: Steady-state fluorescence spectra have been obtained for isotactic poly(*p-tert*-butylstyrene) and for the atactic polymer prepared by two different methods. Excimer emission is observed in all samples of poly(*p-tert*-butylstyrene) in dilute solution in 1,2-dichloroethane. The monomer and excimer bands are more closely spaced in poly(*p-tert*-butylstyrene) than in polystyrene, and the values of I_D/I_M are smaller in the former polymer. Here I_D/I_M denotes the ratio of the intensities of excimer and monomer emission. The isotactic sample has a value of I_D/I_M that is slightly larger than that of the atactic samples. Molecular modeling identifies the tt conformation of the meso diad and the tg$^-$ and g$^-$t conformations of the racemic diad as the conformations most conducive to formation of an excimer by neighboring rings. The angle, ψ, between the normals to the best planes of the two rings in these compounds is ≈20°, which is substantially larger than the corresponding angles in the molecules without the pendant *tert*-butyl groups. This increase in ψ undoubtedly accounts for the diminished energetic separation of the monomer and excimer bands.

Introduction

Excimer emission is commonly observed in fluid solutions and in solid films of aryl vinyl polymers.[1] Both intra- and intermolecular excimers might exist in solid films, but only intramolecular excimers can be formed in dilute solution. Polystyrene is the prototype of an aryl vinyl polymer that is capable of the formation of intramolecular excimers.[2] The extent of excimer emission is affected by physical conditions, such as temperature,[3-5] the size of the chain, as reflected by its molecular weight,[5] and the local covalent structure, i.e., by stereochemical composition,[3,6,7] substitution at the α position,[5,8] and substitution on the aromatic ring.[3,6,7,9] With polystyrene, the emission bands for the monomer and excimer are located at about 285–290 and 335 nm, respectively. There is little change in the position of the emission band for the excimer when a methyl group is placed at the para position.[3] If the methyl group is replaced by the more bulky isopropyl group, however, the position of this band moves from 335 to 323 nm.[9]

The formation of a singlet excimer occurs when a pair of chemically identical chromophores adopts a coplanar sandwich geometry, with their centers separated by ≈3–4 Å,[10] and one of them is in the singlet excited state. Bulky substituents on the rings interfere with the formation of this excited-state complex, as is illustrated by the observation of less excimer emission in poly(*p*-isopropylstyrene) than in polystyrene.[9] Even greater bulk is present in the poly(*p-tert*-butylstyrene) chains that are the subject of the present work. Nevertheless, excimer emission is easily detected in poly(*p-tert*-butylstyrene). Comparison of samples of poly(*p-tert*-butylstyrene) with different stereochemical compositions shows that excimer emission is higher in samples with larger values of p_m, the probability for a meso diad, as is well-known to be the case in polystyrene.[11,12]

Molecular modeling shows how the excimers formed by nearest-neighbor rings in the meso and racemic diads accommodate themselves to the bulk of the pendant *tert*-butyl groups. The potential functions used for this purpose are designed to reproduce the conformational energies of molecules in their electronic ground states. The repulsive steric term is the one that is principally responsible for the difference in the modeling of polystyrene and poly(*p-tert*-butylstyrene), and this term is treated adequately in the potential functions for the electronic ground state. The ground-state potential functions will not always be appropriate for the interpretation of the influence of substituents on the extent of excimer emission, as shown, for example, by their inability to rationalize the effects of the various halogens in poly(*p*-halostyrenes), where changes in intersystem crossing rates and heavy-atom effects become important (unpublished work).

Methods

All solvents, of spectrophotometric grade, were purchased from Aldrich Chemical Co. and used without further purification. Polystyrene was purchased from Scientific Polymer Products, Inc. Thermally polymerized poly(*p-tert*-butylstyrene) was recovered from monomer that had been stored at room temperature. Atactic poly(*p-tert*-butylstyrene) was prepared by bulk polymerization at 60° using azobis(isobutyronitrile) (AIBN) as initiator. Isotactic poly(*p-tert*-butylstyrene) was prepared from a benzene solution of the monomer at 60°, using a catalyst prepared from triethyl aluminum and a suspension of $TiCl_3$–AA in heptane. The polymers were purified by several reprecipitations from benzene solution into methane followed by vacuum drying.

The number-average molecular weights of the polymers, as determined by gel permeation chromatography, were 3×10^6, 2.05×10^5, and 2.6×10^5 for the thermal-initiated, AIBN-initiated, and isotactic polymers, respectively. Although the isotactic polymer is surprisingly soluble in common solvents, it is highly crystalline and has a melting point of approximately 310 °C. NMR analysis indicates it to contain more than 95% meso diads.

Fluorescence measurements were performed with an SLM 8000C fluorometer equipped with a double-excitation monochromator in the excitation path. Slit widths for excitation and emission were 16 nm. Solvent blanks were measured, but they provided such a small signal, relative to those obtained with solutions of poly(*p-tert*-butylstyrene), that no subtraction was necessary from the fluorescence spectra for the samples. Polarizers in the excitation and emission paths were set for magic-angle conditions. Quinine sulfate in 1 N sulfuric acid was the standard for measurement of the fluorescence quantum yields. Absorption measurements were performed with an HP 8415A diode array spectrophotometer. Typical absorbances at 262 nm were 0.1.

The molecular modeling was performed with the Tripos force field contained a SYBYL, version 5.2, from Tripos Associates, Inc. The software was run on a Silicon Graphics 4D/70GT computer. Solvent was not included in the calculations.

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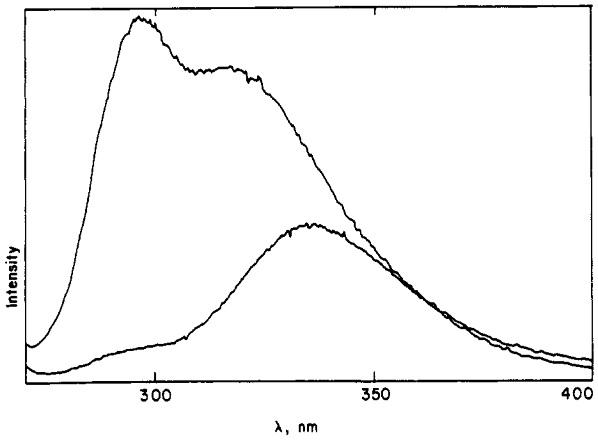

Figure 1. Fluorescence emission spectra in 1,2-dichloroethane at 25 °C for atactic polystyrene (bottom) and atactic poly(*p*-*tert*-butylstyrene) prepared by a polymerization initiated with free radicals (top). The samples have the same absorbance at the wavelength of excitation, 262 nm.

Experimental Results

Atactic Polymers. Figure 1 depicts the fluorescence emission spectra for dilute solutions of atactic polystyrene and atactic poly(*p*-*tert*-butylstyrene) in dichloroethane at 25 °C. The latter polymer was prepared by free-radical-initiated polymerization. The samples have the same absorbance at 262 nm, which is the wavelength of excitation in the fluorescence measurement. Both samples exhibit two emission bands. The emission band slightly below 300 nm is from the monomer. A broad structureless band is also seen above 300 nm. This band is at higher energy in poly(*p*-*tert*-butylstyrene) than in polystyrene, with the positions being at about 320 and 335 nm, respectively. The broad, structureless band at 335 nm is from the excimer formed by polystyrene.[2] Since the band at 320 nm in poly(*p*-*tert*-butylstyrene) is also broad, structureless, and red-shifted from the monomer band, it has the characteristics expected for a band that originates from an excimer. If the monomer emission is subtracted from the spectrum for poly(*p*-*tert*-butylstyrene), the excimer emission is found to be maximal at ≈323 nm. It is considerably blue-shifted from the location of the emission from the excimer in polystyrene, poly(*p*-methylstyrene), and poly(*p*-ethylstyrene).[3,7,9] However, it is only slightly blue-shifted from the position of the emission from the excimer in poly(*p*-isopropylstyrene).[9] Repulsive steric interaction of the *tert*-butyl groups has previously been shown to cause poly(2-*tert*-butyl-6-vinylnaphthalene) to have a smaller ratio of excimer to monomer emission than poly(2-vinylnaphthalene).[13]

Casual inspection shows that the relative contributions to the fluorescence by the monomer and excimer bands are much different in the two spectra depicted in Figure 1. The ratio of the intensity of excimer emission to the intensity of monomer emission, I_D/I_M, is much larger in atactic polystyrene than in atactic poly(*p*-*tert*-butylstyrene). On the other hand, the fluorescence quantum yield, Q, which is proportional to the area under the curve in Figure 1, is much larger for poly(*p*-*tert*-butylstyrene) than for polystyrene. These conclusions apply also to the samples of atactic poly(*p*-*tert*-butylstyrene) prepared by thermal polymerization, as shown in Table I. The sample of poly(*p*-*tert*-butylstyrene) that was prepared by thermal polymerization has a somewhat lower value of Q than the other sample, for reasons that remain elusive. Both samples of atactic poly(*p*-*tert*-butylstyrene) show a similar value for I_D/I_M.

Table I
Fluorescence of Several Poly(*p*-X-styrenes) in 1,2-Dichloroethane

		present work, 25 °C		Ishii et al.,[9] 20 °C	
X	tacticity	Q^a	$I_D/I_M{}^b$	Q	I_D/I_M
hydrogen	atactic	0.018[c]	5.0[c]	0.034[d]	2.3[d]
tert-butyl[e]	atactic	0.050	0.9		
tert-butyl[f]	atactic	0.030	0.8		
methyl	isotactic			0.047	4.0
ethyl	isotactic			0.052	2.0
isopropyl	isotactic			0.082	1.8
tert-butyl	isotactic	0.054	1.1		

[a] The uncertainty is 10%. [b] Uncertainty is a few percent for poly(*p*-*tert*-butylstyrene) but slightly higher for polystyrene. [c] Molecular weight 1.2 × 10^4. [d] Molecular weight 11.2 × 10^4. [e] Prepared by free-radical polymerization. [f] Prepared by thermal polymerization.

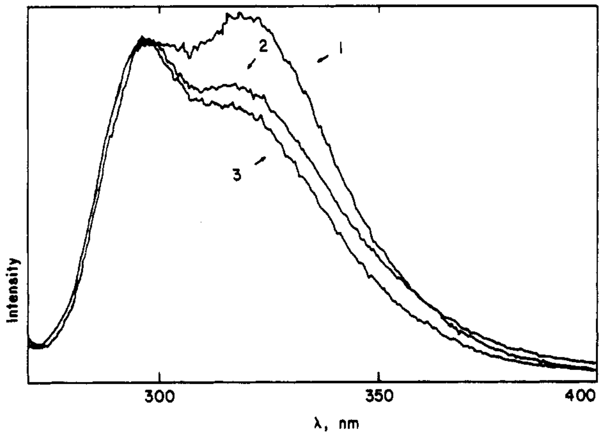

Figure 2. Fluorescence emission spectra in 1,2-dichloroethane at 25 °C, normalized at 298 nm, for three different samples of poly(*p*-*tert*-butylstyrene): (1) isotactic, (2) atactic, free radical, and (3) atactic, thermal.

Isotactic Poly(*p*-*tert*-butylstyrene). Figure 2 depicts the fluorescence emission spectra, normalized at 298 nm, for three samples of poly(*p*-*tert*-butylstyrene). The interest is in the relative intensities of the emission at 320 and 298 nm, which determines the value of I_D/I_M. (A value of I_D/I_M about 50% larger than the numbers reported in Table I for poly(*p*-*tert*-butylstyrene) would be obtained upon decomposition of the spectra into two component bands and taking the ratio of their areas. The curve-fitting procedure produces a larger I_D/I_M because the excimer band is broader than the monomer band.) Clearly I_D/I_M is larger for the isotactic sample than for either of the atactic samples. The two atactic samples have nearly identical values of I_D/I_M. As is the case in polystyrene,[9] the value of I_D/I_M increases when p_m increases. However, the magnitude of the change is smaller in poly(*p*-*tert*-butylstyrene) than in polystyrene. Ishii et al.[9] find I_D/I_M is 4 times larger for isotactic polystyrene than for atactic polystyrene, but Figure 2 shows that I_D/I_M is only about 25% larger for isotactic poly(*p*-*tert*-butylstyrene) than for atactic poly(*p*-*tert*-butylstyrene).

Comparison of the present results for poly(*p*-*tert*-butylstyrene) with the trends reported by Ishii et al.[9] for increasing substituent size in the series composed of poly(*p*-methylstyrene), poly(*p*-ethylstyrene), and poly(*p*-isopropylstyrene) is made in Table I. The method used by Ishii et al.[9] to prepare their three para-substituted polystyrenes should yield isotactic polymers. The results reported by Ishii et al.[9] show that I_D/I_M decreases and Q increases, with the bulk of the substituent in the para position for isotactic polymers where the substituent is methyl, ethyl, or isopropyl. The values of I_D/I_M reported

Table II
Conformations of Optimized Structures for Meso and Racemic 2,4-Bis(*p-tert*-butylphenyl)pentane[a]

conformn	ϕ_2, deg	ϕ_3, deg	ψ, deg	d, Å	d_{xy}, Å
		Meso			
tt**	−165 (−174)	−179 (174)	22 (6)	3.5 (3.0)	1.3 (0.2)
tg$^+$ (≡g$^-$t)	−176 (−175)	−84 (−82)	4 (1)	5.2 (5.3)	4.4 (4.6)
tg$^-$ (≡g$^+$t)	176 (175)	62 (61)	49 (49)	6.5 (6.5)	5.8 (5.9)
g$^+$g$^+$ (≡g$^-$g$^-$)	−59 (−58)	−61 (−60)	47 (48)	6.9 (6.9)	6.4 (6.4)
g$^+$g$^-$	−61 (−60)	94 (94)	86 (88)	7.2 (7.2)	5.8 (5.8)
g$^-$g^{+*}	64 (65)	−91 (−91)	19 (5)	3.5 (3.2)	1.5 (1.2)
		Racemic			
tt*	161 (172)	161 (172)	1 (5)	3.7 (4.7)	2.3 (3.7)
tg$^+$ (≡g$^+$t)	−173 (−172)	−69 (−69)	48 (45)	6.9 (7.0)	6.4 (6.5)
tg^{-**} (≡g$^-$t)	177 (179)	61 (65)	21 (6)	3.5 (3.1)	1.4 (0.8)
g$^+$g$^+$	−58 (−58)	−58 (−58)	86 (87)	7.3 (7.3)	6.0 (5.9)
g$^+$g$^-$ (≡g$^-$g$^+$)	−64 (−63)	90 (91)	52 (51)	6.5 (6.5)	5.8 (5.9)
g$^-$g$^-$	78 (78)	79 (78)	5 (2)	5.4 (5.5)	4.6 (4.8)

[a] Results for meso and racemic 2,4-diphenylpentane are in parentheses.

here for isotactic poly(*p-tert*-butylstyrene) follow the trend, but the value of Q does not. Taken together, the results from the two laboratories yield I_D/I_M values of 4.0, 2.0, 1.8, and 1.1 as the para substituent progresses through the series methyl, ethyl, isopropyl, and *tert*-butyl. In contrast, the value of Q reported here for isotactic poly(*p-tert*-butylstyrene) is comparable to the one reported by Ishii et al. for poly(*p*-ethylstyrene). Our values of Q were obtained by using quinine sulfate as a standard, and Ishii et al. used *p*-terphenyl as their standard. In our hands, use of *p*-terphenyl as a standard produces the same values of Q as does use of quinine sulfate, and hence the differences cannot be attributed to the adoption of different standards. Since our interest here is in I_D/I_M, the origin of the behavior of Q will not be pursued further.

Modeling of the Excimers

The structures of the excimers that might be formed by nearest-neighbor chromophores were determined by investigation of the conformational characteristics of model compounds for meso and racemic diads. These model compounds are the meso and racemic isomers of 2,4-bis(*p-tert*-butylphenyl)pentane. A parallel investigation was performed of the models for these diads in polystyrene. Nine conformations, corresponding to the selection of t, g$^+$, and g$^-$ states for each of the two C–C bonds to the sole methylene group, were examined for each molecule. Every conformation was subjected to a minimization in the conformational energy in which dihedral angles, bond angles, and bond lengths were subject to variation, as in the recent study of conformations conducive to excimer formation in polyacenaphthalene.[14] The structures described here are those achieved after this minimization in the conformational energy.

The pertinent characteristics of the optimized structures are summarized in Table II. Here ϕ_2 and ϕ_3 are the dihedral angles at the two C–C bonds to the methylene group. A single entry is used for pairs of conformations, such as tg$^+$ and g$^+$t for the racemic compound, that have identical values of ψ, d, and d_{xy}. The angle between the normals to the best planes through the two rings is denoted by ψ, and d is the length of the vector from the centroid of one ring to the centroid of the other. The final parameter in Table II, d_{xy}, is a measure of the overlap of two rings that have a small value of ψ. It is calculated as $d_{xy}^2 = d^2 - d_z^2$, where d_z is the projection of $\mathbf{d}$ onto the normal to the best plane through one of the rings. The values of ϕ_2 and ϕ_3 in the table refer to the first member of each such pair.

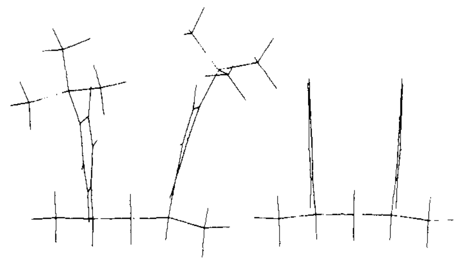

Figure 3. Optimized stick structures of the tt conformation of meso 2,4-bis(*p-tert*-butylphenyl)pentane (left) and meso 2,4-diphenylpentane (right) showing the distortion in bond angles.

Inspection of Table II shows that optimization causes ϕ_2 and ϕ_3 to change by as much as 34° from the initial values of 180°, −60°, and 60°. The largest changes are in the conformations (g$^+$g$^-$ and g$^-$g$^+$) that generate the strongly repulsive second-order interaction in polyethylene. These changes do not involve the *tert*-butyl group, because they can be seen in 2,4-diphenylpentane. Of greater interest are those conformations in which the dihedral angles of the optimized conformations change by more than 4° upon attachment of the *tert*-butyl groups. There are two such conformations. The differences of up to 9° in ϕ_2 and ϕ_3 for the tt conformation of the meso isomer come from the necessity to relieve the strong repulsion of the *tert*-butyl substituent when $\phi_2 = \phi_3 = 180°$. Here the molecule is responding to the repulsive part of the nonbonded interaction. In the tt conformation of the racemic isomer, however, it is the attractive part of the nonbonded interaction that is responsible for changes of 11°, the changes being in the direction that brings the phenyl groups closer together.

The ideal conformation for an excimer would have $\psi = 0$, $d \approx 3.5$ Å, and $d_{xy}^2 = 0$.[10] Asterisks in Table II denote the five conformations that have d in the range 3–4 Å. All other conformations have $d > 5$ Å. Four of the five conformations of 2,4-bis(*p-tert*-butylphenyl)pentane denoted by asterisks have values of d_{xy} that are in the range 1.3–1.5 Å, and the fifth conformation, tt for the racemic 2,4-disubstituted pentane, has $d_{xy} = 2.3$ Å. The latter value of d_{xy} signifies that there is very little overlap of the two aromatic rings in the tt conformation of the racemic molecule. For this reason the tt conformation of the racemic diad will not receive further consideration as an important source of the excimer emission in poly(*p-tert*-butylstyrene). The conformational energy for the tt conformation of meso 2,4-bis(*p-tert*-butylphenyl)pentane is 5.5 kcal/mol lower than the conformational energy of the g$^-$g$^+$ conformation. Consequently, tt is taken to be the dominant excimer-forming conformation in the meso diad. Hence, the consideration of d, d_{xy}, and the optimized conformational energy leads to the three conformations denoted by double asterisks as being those most conducive to formation of an excimer. The values of ψ are 21–22°.

The rotational isomers that are identified here as being most conducive to formation of an excimer in the 2,4-bis(*p-tert*-butylphenyl)pentanes are the same ones as those identified previously[12] for 2,4-diphenylpentanes. However, the details of the structures of these rotational isomers differ in important ways. These details can be gleaned from the numbers in Table II and from the structures depicted in Figures 3–6. All molecules in Figures 3–6 are viewed from the same perspective, which is along the line that bisects the CH–CH$_2$–CH angle. Comparison of the two structures in Figure 3 and in Figure 4 shows that the repulsion of the *tert*-butyl groups in the tt conformation of the meso diad increases the angle between the nor-

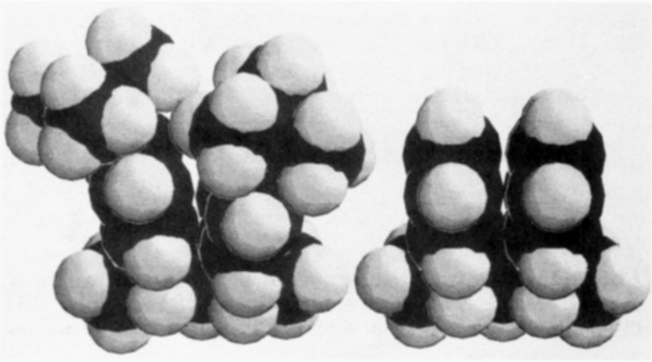

Figure 4. Optimized space filling structures of the tt conformation of meso 2,4-bis(*p*-*tert*-butylphenyl)pentane (left) and meso 2,4-diphenylpentane (right).

Figure 5. Optimized stick structures of the tg$^-$ conformation of racemic 2,4-bis(*p*-*tert*-butylphenyl)pentane (left) and racemic 2,4-diphenylpentane (right) showing the distortion in bond angles.

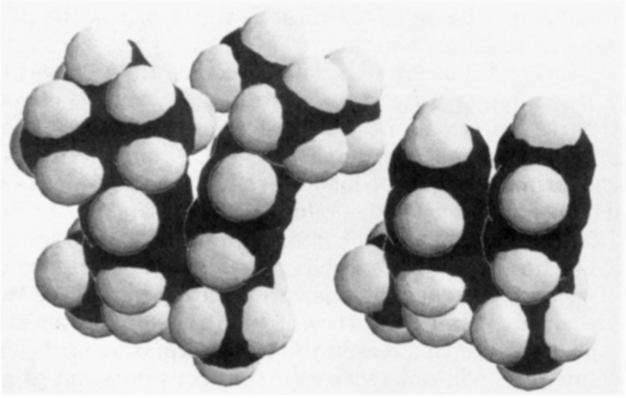

Figure 6. Optimized space filling structures of the tg$^-$ conformations of racemic 2,4-bis(*p*-*tert*-butylphenyl)pentane (left) and racemic 2,4-diphenylpentane (right).

mals to the two rings (as is also apparent from the values of ψ cited for the tt isomer of the meso compound in Table II). The increase in ψ is achieved in part by changes in ϕ_2 and ϕ_3, changes in the dihedral angles at the CH–C^{ar} bonds, and distortions of the aromatic rings themselves. The values of ϕ_2 and ϕ_3 are listed in the first line of Table II. The conformations most conducive to formation of an excimer in the racemic diad are depicted in Figures 5 and 6. Here also it is apparent that the *tert*-butyl groups produce an increase in the angle between the normals of the two rings, the rings are distorted, and the values of the dihedral angles at the CH–C^{ar} bonds are changed. Introduction of the *tert*-butyl groups also decreases the overlap (increases the value of d_{xy}) in the tt conformation of the meso compound and the tg$^-$ conformation of the racemic compound.

There are interesting comparisons between the behavior of poly(*p*-*tert*-butylstyrene) and the recently reported study of poly(9-vinylcarbazole) with pendant *tert*-butyl groups on the rings.[15] Both polymers show excimer emission, but the intensity of the excimer emission is reduced in the presence of the *tert*-butyl groups, and it is located closer to the monomer band. In both systems, molecular modeling shows that introduction of the *tert*-butyl groups decreases the overlap of the two ring systems in the excimer. The two systems differ in that both the meso and racemic diads of poly(*p*-*tert*-butylstyrene) can form an excimer, as shown in Table II, but only the racemic diad of poly(3,6-di-*tert*-9-vinylcarbazole) can form the excited-state dimer. The nature of the molecular modeling does not permit any comparison of the values of ψ in the excimers formed by these two polymers. Bond lengths and bond angles were held constant in the modeling of the substituted poly(vinylcarbazole), and the conformational space explored changed the overlap of the two rings but retained ψ at values very close to zero.

The result that values of ψ as large as 20° are compatible with the observation of excimer emission in poly(*p*-*tert*-butylstyrene) is in harmony with a recent analysis of the origin of the intramolecular excimer emission in polyacenaphthalene.[14] It is well-known that partial overlap of nearest-neighbor rings is sufficient to produce excimer emission in several aryl vinyl polymers.[15,16]

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Registry No. Poly(*p*-*tert*-butylstyrene) (homopolymer), 26009-55-2; isotactic poly(*p*-*tert*-butylstyrene) (homopolymer), 30998-04-0; *meso*-2,4-bis(*p*-*tert*-butylphenyl)pentane, 130525-35-8; *rac*-2,4-bis(*p*-*tert*-butylphenyl)pentane, 130525-36-9.