Gaussian Distributions of the Decay Times of the Singlet Excited State of Aromatic Amines Dispersed in Polymer Films

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ABSTRACT: The fluorescence maximum of amino-substituted 1,3,5-triphenylbenzenes dispersed in polystyrene and polycarbonate is shifted to longer wavelengths compared to isooctane, and this shift is larger in polycarbonate than in polystyrene. The shift is attributed to a partial relaxation of the matrix around the dispersed molecules during the excited-state lifetime. The nonexponential fluorescence decays obtained at different emission wavelengths can be analyzed globally assuming a Gaussian distribution of decay rates with a standard deviation that does not depend upon the emission wavelength. This Gaussian distribution of decay rates is attributed to a distribution of sites with different interaction with the polymer matrix. The sites giving the largest excited-state stabilization are characterized by the slowest average decay rate.

Introduction

Dispersions of amino-substituted 1,3,5-triphenylbenzenes[1,2] have been proposed as hole transport components in xerographic systems. Dimer or excimer-forming sites have been proved to yield efficient hole traps in organic photoconducting systems.[3-5] As the presence of such sites can be expected to influence the fluorescence spectrum,[6] the fluorescence of the amino-substituted 1,3,5-triphenylbenzenes dispersed in polycarbonate and polystyrene was studied at different loadings.

In solution a highly polar relaxed excited state was obtained upon the excitation of amino-substituted 1,3,5-triphenylbenzenes.[7] This was attributed to either a conjugated intramolecular charge transfer state (ICT)[8-11] or a twisted intramolecular charge transfer state (TICT).[12-14] In a polymer matrix dipolar relaxation of the matrix[15] or geometric relaxation of the excited state[15,16] is expected to take place to a limited extent during the excited-state decay time. Therefore one can expect the emission to occur from different sites characterized by a large distribution of polymer–chromophore interactions.[17-20] The formation of a broad distribution of ill-defined interchromophore aggregates[18,19] can enhance this phenomenon. Those distributions of energy levels of the excited state will lead to a distribution of decay rates. According to Ware, many nonexponential fluorescence[21-24] decays could be analyzed by a Gaussian distribution of decay times or a linear combination of two Gaussian distributions of decay times.[25,26] Such a distribution of decay times was also proposed[27] for tetraphenylbutadiene in PMMA.

In the present contribution the influence of the percentage of added chromophore and the chemical composition of the matrix on the singlet excited-state properties of amino-substituted 1,3,5-triphenylbenzenes will be investigated to obtain information on the nature of the interactions between the fluorophores and the polymer, the intermolecular aggregation of the fluorophores, and the extent of relaxation of the environment during the excited-state lifetimes.

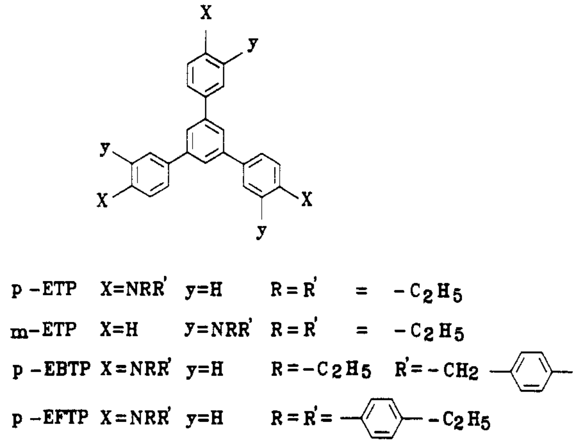

Figure 1. Structures of p-EBTP, p-ETP, m-ETP, and p-EFTP.

Experimental Section

The preparation and purification of 5′-[4-[bis(4-ethylphenyl)-amino]phenyl]-*N,N,N′,N′*-tetrakis(4-ethylphenyl)-[1,1′:3′,1″-terphenyl]-4,4″-diamine (p-EFTP), 5′-[3-(diethylamino)phenyl]-*N,N,N′,N′*-tetraethyl-[1,1′:3′,1″-terphenyl]-3,3″-diamine (m-ETP), 5′-[4-(diethylamino)phenyl]-*N,N,N′,N′*-tetraethyl-[1,1′:3′,1″-terphenyl]-4,4″-diamine (p-ETP), and 5′-[4-(benzylethylamino)phenyl]-*N,N′*-dibenzyl-*N,N′*-diethyl-[1,1′:3′,1″-terphenyl]-4,4″-diamine (p-EBTP) (Figure 1) have been reported earlier.[28]

The samples were prepared by coating a poly(ethylene terephthalate) substratum with a 10-μm thick layer of the amine molecularly dispersed in high molecular weight polycarbonate (Makrolon 5700) or polystyrene. Residual casting solvent (methylene chloride) was removed by heating the film in air to 50 °C for 16 h.

Absorption spectra were recorded with a Perkin-Elmer Lambda 6 UV–vis spectrometer. Corrected fluorescence and excitation spectra were obtained with a SPEX Fluorolog 212. Excitation always occurred at 320 nm. To avoid interference of scattered excitation light the fluorescence spectra were obtained with 0.25-mm slits. Due to the large Stokes shift and the use of a front-face geometry, no distortions of the fluorescence spectra due to reabsorption of fluorescence occurred.

As the undoped polycarbonate gives upon excitation at 320 nm a weak emission with a maximum at 370 nm, this emission could distort the emission spectrum of the triphenylbenzene derivative. As the emission at 350 nm will be mainly due to the

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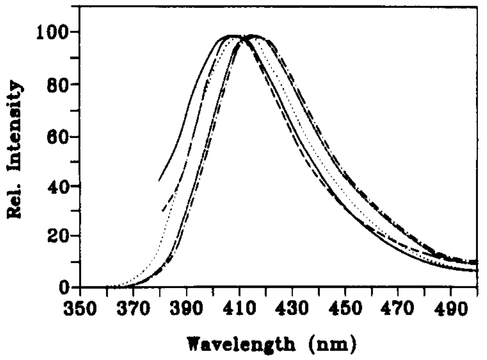

Figure 2. Influence of the loading on the normalized emission spectra of p-EFTP in polycarbonate (excitation occurred at 320 nm): (—) 0.1%; (– – –) 1%; (···) 5%; (- - -) 20%; (– · –) 50%.

matrix, the different emission spectra were corrected for the emission of the matrix by subtracting the emission spectrum of the matrix normalized at 350 nm. To the extent that part of the emission at 350 nm is also due to the amine, this procedure can lead to a small overcorrection. This correction of the emission spectra does not influence the position of the emission maximum.

The fluorescence decays were recorded by the single-photon-timing technique.[29] Excitation of the sample at 320 nm occurred by the frequency-doubled output of a synchronously pumped mode-locked dye laser with DCM (Spectra Physics 375). The dye laser was pumped by an argon laser (Spectra Physics Model 2020). The fluorescence decays were fitted to a double-exponential decay and to a Gaussian distribution[25,26] of decay times using single-curve and global analysis[30-32] with reference convolution. Global analysis involves the simultaneous analysis of fluorescence decays observed at different wavelengths, concentrations, or different time scales while one or more decay parameters (e.g., decay times or ratios of preexponential factors) are linked over the different experiments. As this procedure reduces the number of unknown decay parameters that have to be determined, it allows a more accurate determination of the decay parameters. This more accurate determination of the decay parameters will also lead to a better capacity to discriminate between different models. The goodness of fit was evaluated by visual inspection of the residuals and their autocorrelation function and by the calculation of the statistical parameters χ^2 and Z_{χ^2} (or χ_g^2, and $Z_{\chi_g^2}$), the Durbin–Watson parameter (DW), and the "ordinary runs test" (OR). Using single-curve analysis fluorescence decays characterized by values of χ^2 and Z_{χ^2} larger than 1.30 or 3.00, respectively, were considered as unacceptable. Using global analysis the same criteria were used for the individual decays. Furthermore, analyses where χ_g^2 or $Z_{\chi_g^2}$ exceeded 1.30 or 5.00, respectively, were considered as only marginally acceptable even when the statistical parameters of the analysis individual decays were acceptable. Xanthione, *p*-terphenyl (PTP), and dimethyl-popop, with a decay time (τ_r) of 0.45, 1.1, and 1.1 ns, respectively, were used as references.

Results and Discussion

Stationary Fluorescence Spectra of *p*-EFTP in Polycarbonate and Polystyrene. The fluorescence spectrum of p-EFTP in polycarbonate consists of a structureless band whose maximum shifts from 408 nm for a loading of 0.1% to 417 nm for a loading of 50% (Figure 2). The fluorescence spectra do not depend upon the excitation wavelength. Although it has similar features, the emission spectrum of p-EFTP in polystyrene is shifted to shorter wavelengths (Table I). At a loading of respectively 0.1 and 50% the emission maximum is situated at 390 and 412 nm. In polycarbonate the fwmh of the emission spectrum of p-EFTP does not depend upon the loading and amounts to 2815 ± 100 cm^{-1}. This value corresponds to the fwmh of the emission spectrum of p-EFTP in dibutyl ether. For p-EFTP in polystyrene the fwmh of the emission spectrum increases from 2770 ± 200 cm^{-1} at a loading of 0.1% to 3070 ± 100 cm^{-1} at a loading of 50% (Table I). Those values correspond to the fwmh of the emission spectrum of p-EFTP in dibutyl ether and diethyl ether, respectively.

Table I
Influence of the Concentration on the Spectral Properties of p-EFTP in Polystyrene

X^a (%)	emission max (nm)	fwmh^b (cm^{-1})
0.1	390	2770
1	397	2980
10	406	2940
30	411	3100
50	412	3070

^{a} Weight percentage of p-EFTP. ^{b} Frequency width at medium height.

In polycarbonate the emission of p-EFTP is situated at considerably longer wavelengths than in isooctane,[7] and for the dilute samples (1%) the value of the emission maximum is intermediate between that in diethyl ether and that in tetrahydrofuran. This indicates that emission occurs from an excited state in a medium with a relatively high polarity. As the compounds are apolar in the ground state, extensive solvation by the polymer must occur during the excited-state decay time. The solvation of a polar excited state by dipolar groups of the polycarbonate is also suggested by the fact that in polystyrene, a less polar polymer, the emission maximum of a sample with 1% p-EFTP is shifted over 740 cm^{-1} to higher energies compared to polycarbonate. The latter argument also suggests that the solvation is not due to residual casting solvent. This conclusion is supported by the absence of spectral changes when the cast films are dried at 353 or 373 K instead of at 323 K. Although a relaxation of the environment occurs before the excited singlet decays, it is by no means certain that this relaxation is complete. As a matter of fact, the hypsochromic shift (1130 cm^{-1}) observed for a dilute (0.1%) dispersion of p-EFTP is polystyrene compared to benzene suggests that the relaxation is incomplete.

In a polystyrene matrix the shift of the emission maximum of p-EFTP upon increasing the loading is more than 2 times larger than in a polycarbonate matrix. This suggests that in polystyrene the interaction with other p-EFTP molecules replaces the weaker interactions with pending phenyl moieties.[33] Therefore it is not surprising that for the highest loading (50%) the emission spectra of p-EFTP in polycarbonate and polystyrene nearly coincide.

Stationary Fluorescence Spectra of p-EBTP, p-ETP, and m-ETP in Polycarbonate. Upon excitation at 320 nm the emission spectra of p-EBTP, p-ETP, and m-ETP in polycarbonate consist of a structureless band. The maximum and the fwmh of the emission spectrum of different concentrations of a dispersion of the three compounds in polycarbonate and polystyrene are given in Table II. According to what is observed for p-EFTP, increasing the concentration of the amine shifts the emission maximum to longer wavelengths. The values of the emission maxima of p-EBTP, p-ETP, and m-ETP in polycarbonate correspond to the values of the emission maxima of the same compounds in diethyl ether or tetrahydrofuran. At all concentrations the emission of p-ETP always occurred at slightly longer wavelengths than that of p-EBTP. This correlates with the emission maximum (427 nm) of p-ETP in acetonitrile occurring at longer wavelengths than that of p-EBTP (415 nm). This difference can be attributed to the larger volume of the p-EBTP molecule. Although the electronic structure of the singlet excited state of m-ETP differs in polar solvents

Table II
Influence of the Concentration on the Spectral Properties of 1,3,5-Triphenylbenzene Derivatives in Polycarbonate

Emission Maxima (nm)

X[a] (%)	p-EBTP	p-ETP	m-ETP
0.1		387	390
1	388	391	392
5	390		
10	394	399	398
30	399		
50	400	409	406

fwmh[b] (cm^{-1})

X[a] (%)	p-EBTP	p-ETP	m-ETP
0.1		3190 ± 100	3550 ± 100
1	3530 ± 100	3310 ± 100	3520 ± 100
5	3550 ± 100		
10	3370 ± 100	3450 ± 100	3500 ± 100
30	3160 ± 100		
50	3170 ± 100	3660 ± 100	3400 ± 100

[a] Weight percentage of the 1,3,5-triphenylbenzene derivative. [b] Frequency width at medium height.

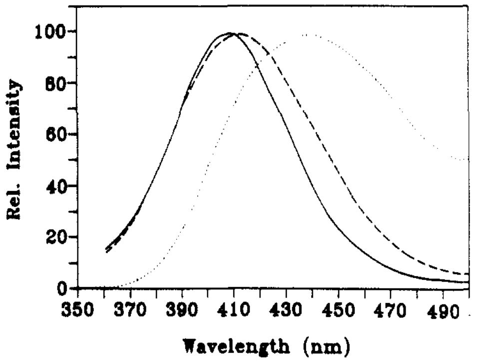

Figure 3. Time-resolved emission spectra of 5% p-EFTP in polycarbonate (excitation occurred at 320 nm: (—) between 0 and 100 ps after excitation: (···) between 10 and 11 ns after excitation; (- - -) between 0 and 11 ns after excitation.

from that of the singlet excited state of p-ETP or p-EFTP,[7] the emission maximum or m-ETP in polycarbonate suggests an environment of the singlet excited state that has at least the same polarity as that probed by p-ETP or p-EFTP.

For m-ETP in polycarbonate the fwmh of the emission spectrum is at all concentrations intermediate between the values obtained in diethyl ether and tetrahydrofuran. On the other hand, the fwmh of the emission spectrum of p-ETP in polycarbonate increases from the value obtained in butyl acetate at a loading of 1% to the value obtained in tetrahydrofuran at a loading of 50%.

Time-Resolved Emission Spectroscopy of p-EFTP Dispersed in Polycarbonate. When the time-resolved fluorescence spectrum of a polycarbonate film containing 5% p-EFTP (Figure 3) obtained between 0 and 100 ps after excitation is compared to that obtained between 10 and 11 ns, a bathochromic shift of the emission maximum from 408 to 440 nm is observed in the latter. This bathochromic shift is accompanied by an increase of the fwmh from 3240 ± 200 to 4870 ± 200 cm^{-1}. At a lower loading (0.5%) the emission maximum shifts from 406 nm immediately after excitation to 426 nm at longer times, and meanwhile the fwmh increases from 3340 ± 200 to 4900 cm^{-1} (Figure 4). For both loadings the maximum of the emission spectra obtained within a time window from 0 to 11 ns after excitation corresponds within experimental error to that of the stationary emission spectra.

Fluorescence Decay of the Emission of p-EFTP in Polycarbonate and Polystyrene. Contrary to what was observed in fluid solution the fluorescence decay of p-EFTP in polycarbonate and polystyrene could not be analyzed as a single exponential for wavelengths between 400 and 460 nm. This can be due either to a slow relaxation of the matrix or to the presence of different sites in the matrix which interact to a different extent with the excited molecule.

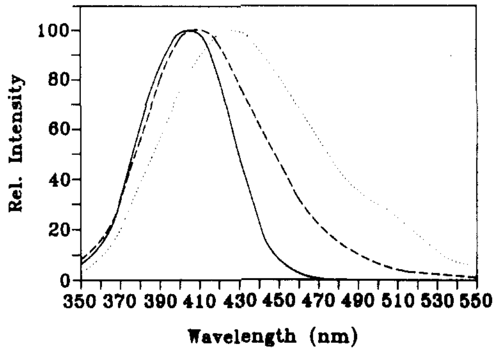

Figure 4. Time-resolved emission spectra of 0.5% p-EFTP in polycarbonate (excitation occurred at 320 nm): (—) between 0 and 100 ps after excitation; (···) between 10 and 11 ns after excitation; (- - -) between 0 and 11 ns after excitation.

According to the first hypothesis,[34-36] the average solvation of the excited molecules will increase as a function of time, and this will induce a time-dependent spectral shift. This corresponds to the observations of the time-resolved emission spectra. However, to the extent that the molecules, which probe a more polar environment and emit therefore at longer wavelengths, are characterized by a longer fluorescence decay time, the second hypothesis is also compatible with the time-resolved emission spectra. As the photophysical properties of p-EFTP in liquid solution suggest that the latter condition is met,[7] it is impossible to discriminate between the hypotheses on the basis of the time-resolved emission spectra.

According to the first hypothesis, the relaxation of the matrix surrounding the excited molecules occurs on the same time scale as the fluorescence decay. It is therefore expected that, if analyzed within the framework of a sum of exponentials, the analysis of decays obtained at the long-wavelength side of the emission should yield a negative amplitude for at least one of the components. For, e.g., *p*-(9-anthryl)-*N*,*N*-dimethylaniline such a growing in was already observed at wavelengths where the emission was still largely due to the locally excited state.[21]

Analysis as a Double-Exponential Decay. Global analysis as a double-exponential decay linking both decay times of the decay of the emission of p-EFTP in polycarbonate obtained at different emission wavelengths between 400 and 460 nm always leads to values of χ_g^2 below 1.20. $Z_{\chi_g^2}$, however, generally exceeds 3.00, and for most loading values even larger than 5.00 are obtained for $Z_{\chi_g^2}$. This suggests that this analysis is marginally acceptable. Although the contribution of the slowly decaying component increases at longer emission wavelengths (Table III), even the analysis of the emission at 460 nm in the tail of the emission spectrum (Figure 2) does not yield a component with a negative preexponential factor.

Global analysis as a double-exponential decay linking both decay times of the decay of p-EFTP in polystyrene obtained at different wavelengths between 400 and 460 nm yielded acceptable values of χ_g^2 and $Z_{\chi_g^2}$ at low p-EFTP concentrations (Table IV). At high p-EFTP concentrations χ_g^2 and $Z_{\chi_g^2}$ exceeded 1.30 and 3.00, respectively. This suggests that the fluorescence decay of p-EFTP in polystyrene can be analyzed as a linear combination of

Table III
Decay Parameters of p-EFTP in Polycarbonate[a]

sample[b]	λ_{em}	α_1	λ_1 (ns^{-1})	α_2	λ_2 (ns^{-1})
no. 1[c] (35%)	400	0.835	0.956	0.165	0.465
	420	0.667	0.956	0.331	0.465
	440	0.561	0.956	0.439	0.465
	460	0.398	0.956	0.602	0.465
no. 2[d] (35%)	400	0.860	0.910	0.140	0.434
	420	0.770	0.910	0.230	0.434
	440	0.710	0.910	0.290	0.434
	460	0.584	0.910	0.416	0.434
no. 1[e] (20%)	400	0.756	0.887	0.244	0.457
	420	0.526	0.887	0.474	0.457
	440	0.376	0.887	0.624	0.457
	460	0.256	0.887	0.744	0.457
no. 2[f] (20%)	400	0.810	0.847	0.190	0.424
	420	0.727	0.847	0.273	0.424
	440	0.616	0.847	0.384	0.424
	460	0.480	0.847	0.520	0.424
no. 1[g] (5%)	400	0.800	0.788	0.200	0.460
	420	0.582	0.788	0.418	0.460
	440	0.423	0.788	0.587	0.460
	460	0.244	0.788	0.756	0.460
no. 2[h] (5%)	400	0.802	0.816	0.198	0.439
	420	0.678	0.816	0.322	0.439
	400	0.534	0.816	0.462	0.439
	460	0.402	0.816	0.598	0.439

[a] The fluorescence decay was analyzed as a sum of two exponentials: $\alpha_1 \exp(-\lambda_1 t) + \alpha_2 \exp(-\lambda_2 t)$. For each concentration, λ_1 and λ_2 were linked over the different analysis wavelengths. [b] Weight fraction (X) of p-EFTP is given in parentheses for each sample. [c] Sample 1, $\chi_g^2 = 1.18$, global $Z_{\chi_g^2} = 5.27$. [d] Sample 2, $\chi_g^2 = 1.19$, global $Z_{\chi_g^2} = 6.28$. [e] Sample 1, $\chi_g^2 = 1.02$, global $Z_{\chi_g^2} = 0.653$. [f] Sample 2, $\chi_g^2 = 1.18$, global $Z_{\chi_g^2} = 5.95$. [g] Sample 1, $\chi_g^2 = 1.11$, global $Z_{\chi_g^2} = 3.25$. [h] Sample 2, $\chi_g^2 = 1.14$, global $Z_{\chi_g^2} = 4.67$.

two exponentials only at low concentrations. Increasing the emission wavelength increased the amplitude of the component with a long decay time, but even at 460 nm it was 3 times smaller than that of the component with the small decay time.

For p-EFTP in polycarbonate the long decay time is within the experimental error independent of the p-EFTP concentration, but the short decay time decreases significantly when the p-EFTP concentration is increased. The contribution of the slowly decaying component shows a small decrease at lower p-EFTP concentrations. Contrary to what was observed for p-EFTP in polycarbonate, both decay times decreased significantly upon increasing the p-EFTP concentration in polystyrene. When polystyrene was used as a matrix, the contribution of the slowly decaying component was within the experimental error independent of the p-EFTP concentration. The decrease of the short decay time when the p-EFTP concentration is increased suggests in the present model that the relaxation becomes faster when the p-EFTP concentration is increased. This should suggest a larger free volume at high p-EFTP concentrations. The decrease of the long decay time at high p-EFTP concentration in polystyrene could be due to the formation of intermolecular aggregates characterized by a smaller decay time.

Analysis Using a Gaussian Distribution of Decay Rates. In the framework of the second hypothesis one assumes that the molecules are present in different sites between which no interconversion occurs during the excited-state decay time and that in each site the relaxation of the solvation by the matrix is faster than the time resolution of the setup. In this case the nonexponential decay reflects a distribution of decay times. Already Siemiarzuk et al.[21] proposed a fluorescence decay determined by a distribution of decay times at low temperature (115 K) for molecules such as *p*-(9-anthryl)-*N*,*N*-dimethylaniline and *p*-(9-anthryl)-*N*,*N*,3,5-tetradimethylaniline that are assumed to form TICT states. The sites could differ by, e.g., a different degree of interaction between the matrix and the molecule or by the intramolecular torsion angle. In the first case this interaction must require a much larger movement of the polymer than the first step of the solvation. If one assumes that the distribution is linked to intramolecular torsion angles, it is probable that no important reorientation occurs during the excited-state decay time. In this respect it should be mentioned that[15] for *p*-(dimethylamino)benzonitrile dissolved in PMMA, poly(vinyl alcohol), or poly(vinyl chloride), where the rotating group is much smaller, formation of a charge-separated state occurs only to a very limited extent.

Table IV
Decay Parameters of p-EFTP in Polystyrene (Sample 3)[a]

λ_{em}	α_1	λ_1 (ns^{-1})	α_2	λ_2 (ns^{-1})
		$X^b = 50\%$[c]		
400	0.984	1.234	0.016	0.369
420	0.957	1.234	0.043	0.369
440	0.898	1.234	0.102	0.369
460	0.782	1.234	0.218	0.369
		$X^b = 30\%$[d]		
400	0.978	1.028	0.022	0.360
420	0.940	1.028	0.060	0.360
440	0.865	1.028	0.135	0.360
460	0.742	1.028	0.258	0.360
		$X^b = 10\%$[e]		
400	0.979	0.882	0.021	0.361
420	0.940	0.882	0.060	0.361
440	0.868	0.882	0.132	0.361
460	0.749	0.882	0.251	0.361
		$X^b = 1\%$[f]		
400	0.987	0.805	0.0127	0.284
420	0.963	0.805	0.0368	0.284
440	0.931	0.805	0.0694	0.284
460	0.868	0.805	0.1320	0.284
		$X^b = 0.1\%$[g]		
400	0.973	0.829	0.0267	0.222
420	0.952	0.829	0.0477	0.222
440	0.913	0.829	0.0867	0.222
460	0.831	0.829	0.1695	0.222

[a] The fluorescence decay was analyzed as a sum of two exponentials: $\alpha_1 \exp(-\lambda_1 t) + \alpha_2 \exp(-\lambda_2 t)$. Over each concentration λ_1 and λ_2 were linked over the different analysis wavelengths. [b] Weight fraction of p-EFTP. [c] $\chi_g^2 = 1.50$, global $Z_{\chi_g^2} = 14.78$. [d] $\chi_g^2 = 1.35$, global $Z_{\chi_g^2} = 10.42$. [e] $\chi_g^2 = 1.21$, global $Z_{\chi_g^2} = 6.18$. [f] $\chi_g^2 = 1.08$ global $Z_{\chi_g^2} = 2.21$. [g] $\chi_g^2 = 1.07$, global $Z_{\chi_g^2} = 1.94$.

When it is assumed that the fluorescence decay rate constant $k(X)$ depends on a parameter X, the fluorescence decay of the ensemble of molecules will be given by

$$f(t) = f(0)e^{-k_0 t}\int_{k(X)=0}^{k(X)=\infty} e^{-k(X)t}Y[k(X)]\,\mathrm{d}k(X) \qquad (1)$$

In eq 1 $Y(X)$ and k_0 are the probability that the variable X amounts to X and to the rate constant of the decay of the excited state when $k(X)$ equals zero, respectively. As the fluorescence rate constant, k_f, for p-EFTP depends only to a minor extent on the environment of the chromophore, k_0 should be at least equal to k_f. Making a first-order MacLaurin expansion of $k(X)$, $k(X)$ can be approximated by

$$k(X) \approx \alpha X = Z \qquad (2)$$

Expressing eq 1 as a function of Z yields

$$f(t) = f(0)e^{-k_0 t}\int_{Z=0}^{Z=\infty} e^{-Zt}Y'(Z)\,\mathrm{d}Z \qquad (3)$$

When it is assumed that X and therefore also Z depend on a large number of random variables,[37] $Y(X)$ or $Y'(Z)$

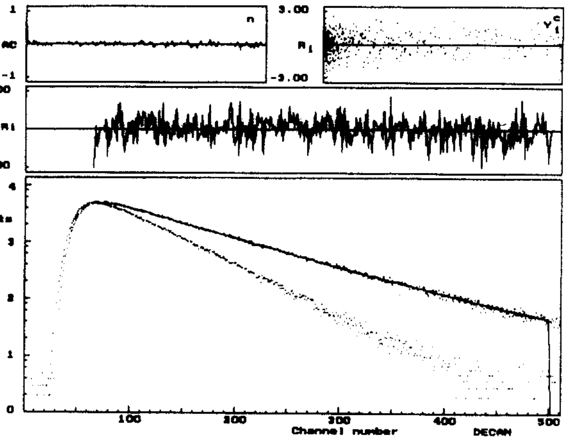

Figure 5. Fluorescence decay at 293 K of 20% p-EFTP (sample 2) in polycarbonate analyzed according to eq 5. $\lambda_{exc} = 320$ nm, $\lambda_{em} = 448$ nm, 23.9 ps per channel, $k_0 = 0.34$ ns^{-1}, $\mu = 0.143$ ns^{-1}, $\sigma = 0.25$ ns^{-1}, $\chi^2 = 0.92$, $Z_{\chi^2} = -1.23$, DW = 1.73, OR = −2.24; AC, R_i, and Y_i^C correspond to the autocorrelation function, the weighted residuals, and the calculated decay, respectively.

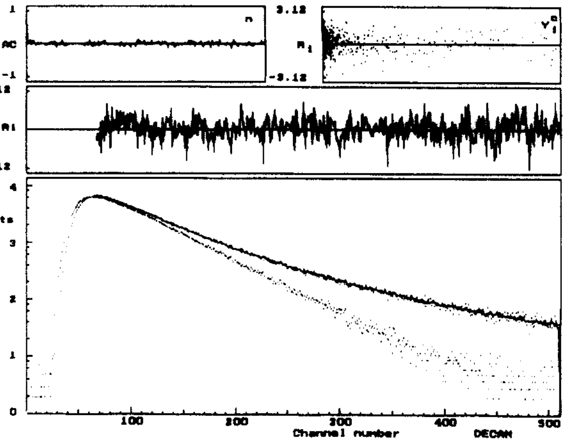

Figure 6. Fluorescence decay at 293 K of 30% p-EFTP in polystyrene (sample 4) analyzed according to eq 5. $\lambda_{exc} = 320$ nm, $\lambda_{em} = 448$ nm, 23.9 ps per channel, $k_0 = 0.078$ ns^{-1}, $\mu = 0.85$ ns^{-1}, $\sigma = 0.31$ ns^{-1}, $\chi^2 = 0.99$, $Z_{\chi^2} = -0.17$, DW = 1.84, OR = −1.74; AC, R_i, and Y_i^C correspond to the autocorrelation function, the weighted residuals, and the calculated decay, respectively.

will be given by a normal distribution:

$$Y'(Z) = \frac{1}{\sigma(2\pi)^{1/2}} exp\left[-\frac{1}{2}\left(\frac{Z-\mu}{\sigma}\right)^2\right] \qquad (4)$$

In eq 4, μ and σ correspond to the average value of Z and the standard deviation on the distribution of Z, respectively. Equation 4 is also a plausible distribution function when one assumes that when the free energy content of the different sites is developed in a Taylor series around $X(\mu)$, the value of X for which it is minimal, a Boltzman expression for the probability of the different sites will be proportional to $\exp\{-\beta[X - X(\mu)]^2/kT\}$ or $\exp[-{}^1/_2(Z - \mu)^2/\sigma^2 kT]$ with β equal to $\alpha/2\sigma^2 kT$.

Combination of eqs 3 and 4 leads to

$$f(t) = f(0)\exp(-k_0 t) \times \exp\left[\frac{t^2\sigma^2 - 2\mu t}{2}\right] \operatorname{erfc}\left[\frac{-\mu}{(2\sigma)^{1/2}} - \frac{\sigma t}{2^{1/2}}\right] \qquad (5)$$

Equation 5 differs from the expressions proposed by Ware[25,26] since it is based on a continuous distribution of decay rates instead of a discontinuous distribution of decay times and since the cutoff rate constant k_0 has been introduced. This avoids that a finite number of molecules has a physically unacceptable decay rate equal to zero. The fluorescence decays of p-EFTP in polycarbonate (Figure 5) and polystyrene (Figure 6) could be analyzed using eq 5. When fluorescence decays obtained at different emission wavelengths were analyzed simultaneously, acceptable statistical parameters for the fit could be obtained when k_0 and σ were linked (Tables V and VI). For all samples μ becomes smaller at longer wavelengths. However, as μ and k_0 are strongly correlated, a large relative error can be expected for k_0 for those samples where k_0 is small compared to μ. Therefore the values of k_0 and μ obtained at low loadings have to be considered with caution. However, also the average decay rate ($\mu + k_0$) decreases when the emission wavelength becomes larger. As the molecules emitting at longer wavelengths interact with a more polar environment, this trend could be correlated with the decrease of the rate of constant for the nonradiative decay of p-EFTP when the solvent polarity is increased.[7] The latter effect is also reflected by the smaller values of ($\mu + k_0$) in polycarbonate compared to polystyrene. For p-EFTP dispersed in polycarbonate values between 3.0×10^8 and 3.6×10^8 s^{-1} are obtained for k_0. For p-EFTP dispersed in polystyrene considerably smaller values of k_0 situated between 4.0×10^7 and 1.1×10^8 s^{-1} are obtained.

Table V

Decay Parameters of p-EFTP in Polycarbonate[a]

sample[b]	λ_{em}	k_0 (ns^{-1})	μ (ns^{-1})	σ (ns^{-1})	$k_0 + \mu$ (ns^{-1})
no. 1[c] (35%)	400	0.34	0.58	0.35	0.92
	420	0.34	0.36	0.35	0.70
	440	0.34	0.24	0.35	0.58
	460	0.34	0.05	0.35	0.39
no. 2[d] (35%)	400	0.29	0.61	0.30	0.90
	420	0.29	0.53	0.30	0.83
	440	0.29	0.44	0.30	0.74
	460	0.29	0.33	0.30	0.63
no. 1[e] (20%)	400	0.34	0.44	0.25	0.78
	420	0.34	0.25	0.25	0.58
	440	0.34	0.14	0.25	0.48
	460	0.34	0.04	0.25	0.38
no. 2[f] (20%)	400	0.31	0.48	0.30	0.79
	420	0.31	0.39	0.30	0.70
	460	0.31	0.28	0.30	0.60
	480	0.31	0.16	0.30	0.47
no. 1[g] (5%)	400	0.36	0.37	0.20	0.73
	420	0.36	0.23	0.20	0.60
	440	0.36	0.14	0.20	0.50
	460	0.36	0.04	0.20	0.40
no. 2[h] (5%)	400	0.35	0.41	0.27	0.75
	420	0.35	0.29	0.27	0.63
	440	0.35	0.16	0.27	0.50
	460	0.35	0.04	0.27	0.39

[a] Analysis occurred according to eq 5. Over each concentration k_0 and σ were linked for the different analysis wavelengths. [b] Weight fraction (X) of p-EFTP is given in parentheses for each sample. [c] $\chi_g^2 = 1.03$, global $Z_{\chi_g^2} = 0.868$. [d] $\chi_g^2 = 1.09$, global $Z_{\chi_g^2} = 2.85$. [e] $\chi_g^2 = 1.01$, $Z_{\chi_g^2} = 0.149$. [f] $\chi_g^2 = 1.09$, global $Z_{\chi_g^2} = 2.97$. [g] $\chi_g^2 = 1.08$, global $Z_{\chi_g^2} = 2.40$. [h] $\chi_g^2 = 1.04$, global $Z_{\chi_g^2} = 1.34$.

The large fluctuations of the recovered values of k_0 for p-EFTP in polystyrene are due to the fact that the abundance of the molecules whose decay time equals k_0^{-1} is much smaller than that of the molecules whose decay time equals μ. The relative abundance of the molecules with a decay time k_0^{-1} compared to those with decay time μ^{-1} is given by

$$Y'_{rel}(k_0) = \exp\left[-\frac{1}{2}\left(\frac{\mu}{\sigma}\right)^2\right] \qquad (6)$$

For p-EFTP in polystyrene this relative abundance varies from 0.23 for the emission at 460 nm of a sample with a loading of 50% to 2.8×10^{-4} for the emission at 400 nm of a sample with a loading of 1%. The relative abundance increases in a systematic way when the emission

Table VI
Decay Parameters of p-EFTP in Polystyrene (Sample 3)[a]

λ_{em}	k_0 (ns^{-1})	μ (ns^{-1})	σ (ns^{-1})	$k_0 + \mu$ (ns^{-1})
		$X^b = 50\%^c$		
400	0.085	1.39	0.40	1.47
420	0.085	1.24	0.40	1.32
440	0.085	1.06	0.40	1.15
460	0.085	0.87	0.40	0.96
		$X^b = 30\%^d$		
400	0.078	1.10	0.31	1.18
420	0.078	0.98	0.31	1.06
440	0.078	0.85	0.31	0.93
460	0.078	0.73	0.31	0.80
		$X^b = 10\%^e$		
400	0.041	0.94	0.23	0.98
420	0.041	0.86	0.23	0.90
440	0.041	0.77	0.23	0.81
460	0.041	0.68	0.23	0.72
		$X^b = 1\%^f$		
400	0.041	0.89	0.22	0.93
420	0.041	0.84	0.22	0.88
440	0.041	0.76	0.22	0.80
460	0.041	0.67	0.22	0.71

[a] Analysis occurred according to eq 5. For each concentration k_0 and σ were linked for the different analysis wavelengths. [b] Weight fraction of p-EFTP. [c] $\chi_g^2 = 1.03$, global $Z_{\chi_g^2} = 0.950$. [d] $\chi_g^2 = 0.994$, global $Z_{\chi_g^2} = -0.169$. [e] $\chi_g^2 = 1.04$, global $Z_{\chi_g^2} = 1.22$. [f] $\chi_g^2 = 1.20$, global $Z_{\chi_g^2} = 3.47$.

wavelength becomes longer and when the loading becomes larger. However, as k_0 remains always considerably smaller than μ, most excited states decay with rates that are distributed symmetrically around μ.

For p-EFTP in polycarbonate slightly different results are obtained. The relative abundance of the molecules whose excited singlet state decays with a rate k_0 varies from 0.99 for the emission at 460 nm of a sample with a loading of 35% to 0.12 for the emission at 400 nm of a sample with a loading of 5%. The relative abundance increases in a systematic way when the emission wavelength becomes longer. This means that at 460 nm most of the excited singlet states decay with a rate close to k_0 and that there are for the emission at 460 nm more molecules with a decay rate larger than $k_0 + \mu$ than molecules with a decay rate smaller than $k_0 + \mu$. On the other hand, at 400 nm the number of molecules whose excited state decays with a rate $k_0 + \mu$ is much larger than the number whose excited state decays with a rate equal to k_0.

Influence of the p-EFTP Concentration. While at 400 nm μ increases for both polycarbonate and polystyrene, when the loading becomes higher, μ does not depend upon the loading for the emission at 460 nm in polystyrene. However, as μ and k_0 are strongly correlated, a large relative error can be expected for k_0 for those samples where k_0 is small compared to μ. Therefore the values of k_0 obtained at low loadings have to be considered with caution. However, although both k_0 and μ can be subject to a relatively large error, the results demonstrate in an unambiguous way that the increase of the average decay rate ($\mu + k_0$) at short wavelengths becomes more important at high loadings. This could suggest that high loadings energy transfer to molecules in a site with a larger excited-state stabilization and a slower decay rate occurs.[38,39] Considering the large Stokes shift observed for p-EFTP, it is, however, not likely that R_0, the critical distance for Förster-type energy transfer,[40,41] is large enough to allow efficient energy transfer at a loading of 1% where the average molecular distance will approach 60–70 Å. This excludes that the nonexponential fluorescence decay is due only to energy transfer to molecules in a site with a large excited-state stabilization.

It is not likely that the increase of the average decay rate ($k_0 + \mu$) of the emission at shorter wavelengths which is observed upon increasing the loading is due to self-quenching or to a faster decay rate of intermolecular aggregates of the fluorophores. One could expect those aggregates to emit preferentially at the long-wavelength side of the emission spectrum; however, the average decay rate of the emission at 460 nm increases only slightly when the loading of the polymer is increased. Therefore as far as the solvation of p-EFTP by other p-EFTP molecules at high loadings leads to the formation of molecular aggregates the intermolecular interaction in the aggregates is too weak to change the absorption spectrum or the decay rate of the excited singlet state. The distribution of the sites can, on the other hand, not be reduced to a distribution between different types of aggregates because this distribution should shift to "monomers" at low loadings, leading to a more exponential decay characterized by the decay rate of the excited singlet state of the "monomers" at low loadings. The experimental results suggest, however, that the distribution of decay rates becomes broader at low loadings.

Contrary to what was observed for p-EFTP in polycarbonate, μ increases also for the emission at 460 nm when the loading is increased. However, as μ and k_0 are strongly correlated, a large relative error can be expected for μ for those samples where μ is small compared to k_0. Therefore the values of μ obtained at the long emission wavelengths have to be considered with caution. The increase of μ at short wavelengths when the loading is increased can be explained by energy transfer to molecules in sites with a more favorable solvation or conformation of the excited state. This excitation transfer could also explain the larger contribution at higher loadings of the molecules with a decay rate equal to k_0 to the emission at 460 nm. The increase of μ at long wavelengths could be related to the formation of aggregates, emitting at longer wavelengths and characterized by larger decay rates. This would, however, contradict the results obtained for p-EFTP in polystyrene. As already argued for p-EFTP in polystyrene, this energy transfer cannot explain the nonexponential decay at low loadings. In polycarbonate this is furthermore confirmed by the time-resolved emission spectra. While the larger shift observed at 5% loading can be due in part to excitation transfer, this process becomes improbable at 0.5% loading, where the average intermolecular distance approaches 75–85 Å.

Conclusions

The position of the maxima and the fwmh of the emission spectra of amino-substituted 1,3,5-triphenylbenzenes dispersed in polycarbonate correspond to a solvation intermediate between that occurring in diethyl ether and that occurring in tetrahydrofuran. This is only possible if an appreciable relaxation of the matrix occurs after the excitation of the apolar ground state. As at low loadings the emission occurs at longer wavelengths in polycarbonate compared to polystyrene, dipolar interactions must play an important role in the solvation of the excited state.

As the emission spectra show that during the excited-state decay time (always less than 10 ns) considerable relaxation of the environment can take place around the dipolar excited species, one can expect that on the same time scale a reorganization of the polymer matrix can occur around an oxidized p-EFTP molecule. As the average hopping time of the hole between two neighboring p-EFTP molecules in a polycarbonate matrix[1] containing 17% p-EFTP is always larger than 500 ns, the environment will relax to a large extent to an equilibrium distribution between two successive hops. Therefore one can expect that under those conditions the hole transport will be influenced not only by a distribution of sites[43-45] but also by polaronic effects.[46]

The bathochromic shift of the emission spectra when the loading of the polystyrene matrix is increased suggests that intermolecular interactions between the fluorophores also lead to a bathochromic shift. The latter interactions should not be considered as the formation of well-defined dimers (cf. the pyrene excimer[42,43]).

The nonexponential decay of the fluorescence is interpreted in the framework of a distribution of the fluorescing molecules over different sites characterized by a different molecular conformation or different interactions with the matrix.

The influence of the loading on the time-resolved fluorescence spectra and on the fluorescence decays suggests that a higher loadings energy transfer to molecules occupying a site with a larger stabilization of the excited state can occur.

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