Fluorescence Measurements on Poly(ethylene terephthalate-*co*-ethylene-2,6-naphthalene dicarboxylate) Containing 1 mol % Ethylene Naphthoate

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ABSTRACT: The fluorescence behavior of poly(ethylene terephthalate-*co*-ethylene-2,6-naphthalene dicarboxylate) containing 1 mol % ethylene naphthoate is investigated. The low content of naphthoic units allows to neglect excimer formations between two naphthoic moieties. Thus, the fluorescence of monomeric naphthoic units embedded in a PET matrix is analyzed. The naphthoic units act as traps for the PET fluorescence. When exciting the terephthalic units, fluorescence of naphthoic units is observed. Time-resolved fluorescence and fluorescence depolarization experiments show that excitation energy transfer takes place from terephthalic units to naphthoic traps. This energy transfer leads to a distribution of decay times. In the case of direct excitation of naphthoic units above the absorption range of terephthalic units, also nonexponential fluorescence decay curves are observed, indicating interactions of naphthoic units with the PET matrix.

Introduction

Observation of fluorescence serves as a useful tool to study electronic excitation and energy migration in polymers containing aromatic rings in the main chain. Therefore, the fluorescence behavior of poly(ethylene terephthalate) (PET) has been extensively studied over the past years.[1−6] The terephthalic monomer unit can be excited up to about 310 nm, and in this case the corresponding fluorescence is characterized by a broad excimer emission band.[1,4] Time-resolved studies of the fluorescence caused by monomer unit excitation reveal multiexponential decay, indicating a complex emission behavior due to excitation energy transfer toward traps.[3] At excitation wavelengths above the regime of monomer excitation, structured fluorescence spectra[1−3] and decreasing decay times[2,3] are observed, which can be attributed to direct excitation of ground-state stable dimers.[1−3,5,6] Static depolarization measurements carried out at the fluorescence emitted after excitation of the monomer units result in a vanishing anisotropy r (i.e., $r = 0$), which indicates a depolarization due to energy transfer between excited and emitting sites.[1] In contrast, excitation of ground-state stable dimers of PET leads to emission anisotropy of $r = 0.35$,[1] which indicates that excitation and emission are localized at the same site; i.e., no energy transfer is involved. These dimers are only formed in the noncrystalline regions and allow to determine the orientation functions of oriented PET films by depolarization measurements.[2,5,6]

Excitation of monomer units of poly(ethylene-2,6-naphthalene dicarboxylate) (PEN) results in a broad excimer fluorescence spectrum, too.[7,8] The naphthoic monomer unit is excitable up to about 370 nm.[7] Time-resolved fluorescence measurements indicate a distribution of decay times when exciting the naphthoic unit.[9] Model calculations have demonstrated that such a distribution of decay times is observed when the excitation energy can migrate among the naphthoic units until an excimer trap is reached.[9] The energy transfer mechanism is assumed to be based on Förster type dipole−dipole interactions.[10]

In the present paper a copolyester of PET and PEN containing 1 mol % ethylene naphthoate is investigated. This allows to study the fluorescence of naphthoic units in a PET matrix.

Experimental Section

Sample Preparation. The copolyester of PET and PEN containing 1 mol % ethylene naphthoate was synthesized by copolycondensation of the dimethyl esters of terephthalic acid and 2,6-naphthalenedicarboic acid with ethylene glycol.[11] For purification the copolyester was dissolved in a mixture of dichloromethane:trifluoroacetic acid (4:1 vol %) and precipitated in methanol. After drying in vacuo amorphous films were prepared by melt-pressing for 120 s at 290 °C and subsequent quenching in iced water (sample thickness about 200 μm). A molecular weight $M_W = 18\,000$ was determined by viscosity measurements in the solvent 1,1,1,3,3,3-hexafluoro-2-propanol.[12]

The PET was synthesized by polycondensation of dimethyl terephthalate with ethylene glycol.[11] Amophous films were prepared as described above. The dimethyl 2,6-naphthalene dicarboxylate was purified by sublimation at 160 °C and 2 mbar and dissolved in chloroform.

Fluorescence Spectra and Time-Resolved Fluorescence Measurements. Fluorescence spectra were measured by means of an Aminco SPF-500 spectrofluorometer in transmission geometry. Time-resolved fluorescence measurements were performed at the beamline VISUV (VISible and UV) at the Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches Elektronensynchroton DESY. To use synchrotron radiation for these experiments allows for a continuous tuning of the excitation wavelength. The pulse width of the storage ring DORIS is about 150 ps (fwhm) with a repetition rate of 2 or 5 MHz depending on the operation mode. The excitation light was monochromatized by a grating monochromator (Jobin Ivon type H225, bandwidth 8 nm). The luminescence light passed through a second monochromator (Jobin Ivon type H320, bandwidth 4 nm). For single photon counting detection a microchannel plate photomultiplier type R3809U-50 from Hamamatsu was used. The instrument response function was observed by scattering at milk (fwhm about 300 ps). The polymer films were mounted in a quartz glass cell filled with glycerol and were measured in transmission geometry. All measurements were carried out at 298 K. Acquisition time was

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varied from a few minutes to hours to observe fluorescence curves with at least 30 000 counts in the maximum channel. The time interval between adjacent data points was 196 ps. All curves were fitted by a sum of exponential functions. The curve fitting procedure is described in another paper of the authors.[9]

Fluorescence Depolarization. To obtain vertically polarized excitation light, a Glan-Taylor prism purchased from Melles Griot was mounted after the primary monochromator. The primary intensity of the beam was measured by means of a photodiode. A quartz glass beam splitter was used to separate about 10% of the primary beam which was focused onto the photodiode. The photocurrent was amplified and via a voltage-to-frequency converter monitored by a counter. This counter value c was used to correct the measured intensity of the time-resolved fluorescence curves to the primary intensity. The counts accumulated along a measurement represent the average primary intensity present during the acquisition. This correction was made for each channel of the $I(t)$ curve, and the emission anisotropy $r(t)$ was calculated by the following equation:

$$r(t) = (I(t)_{vv}/c_{vv} - gI(t)_{vh}/c_{vh})/(I(t)_{vv}/c_{vv} + 2gI(t)_{vh}/c_{vh}) \quad (1)$$

The first index v indicates a vertically polarized primary beam. The second index v or h characterizes the polarization direction of the fluorescence light. It was measured by using a Glan-Thomson prism (Melles Griot) mounted in front of the entrance slit of the secondary monochromator. If the intensity of the fluorescence light was too weak, a band-pass filter was used instead of the second monochromator. To correct for the influence of the optics on the different polarization directions, a factor g was introduced. It was determined by exciting the sample with horizontally polarized light and measuring the fluorescence in two perpendicular directions, i.e., with the analyzer vertically or horizontally oriented. In this case both analyzer orientations are perpendicular to the polarization direction of the primary beam and should theoretically give the same intensity. To correct for differences in the observed intensities, the factor g was calculated by the equation

$$g = I_{hv}c_{hh}/I_{hh}c_{hv} \quad (2)$$

I is the integral intensity of the measured time-resolved fluorescence curve determined by summing up all data points. Additionally, all curves were initially background corrected by subtracting a constant value observed in the curve region of pure scattering.

Results and Discussion

The fluorescence behavior of poly(ethylene terephthalate-*co*-ethylene-2,6-naphthalene dicarboxylate) containing 1 mol % ethylene naphthoate is investigated. The sample represents a PET matrix with a few naphthoic units; therefore, it is useful to compare the fluorescence of pure PET with the fluorescence of the copolyester. Figure 1 shows the fluorescence spectra of an amorphous PET film and of the copolyester, both excited at 300 nm. This wavelength is in the excitation range of the terephthalic unit which is excitable up to about 310 nm.[1] The small shoulder in the PET spectrum located around 330 nm can be attributed to the emission of the terephthalic monomer unit.[4] The broad red-shifted emission band arises from PET excimer sites.[4] In contrast, the emission of the sample containing 99 mol % PET and only 1 mol % naphthoic units starts to emit at about 360 nm, and the spectrum is structured. The emission range and the structure can be assigned to the emission of naphthoic units. Additionally, the excitation spectrum of the copolyester (λ_{em} = 380 nm) is shown in Figure 1. A large overlap between the emission spectrum of PET and the excitation spectrum

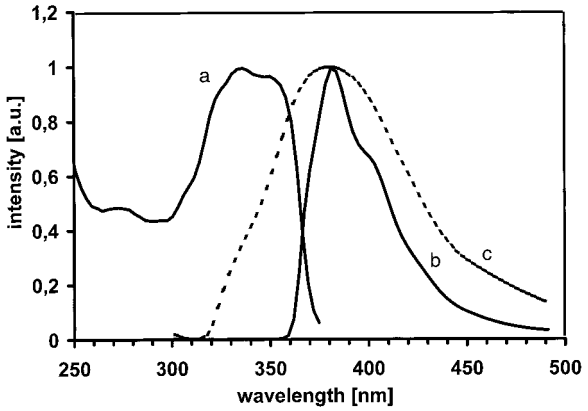

Figure 1. (a) Excitation spectrum of the copolyester (λ_{em} = 380 nm), (b) fluorescence spectrum of the copolyester (λ_{ex} = 300 nm), and (c) fluorescence spectrum of amorphous PET (λ_{ex} = 300 nm).

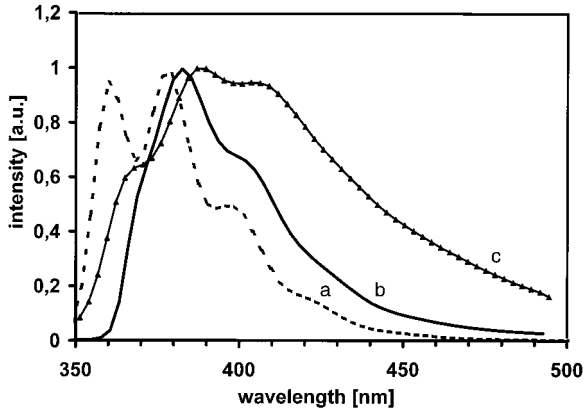

Figure 2. (a) Fluorescence spectrum of DMN in dilute chloroform solution ($c = 10^{-4}$ M, λ_{ex} = 340 nm), (b) fluorescence spectrum of the copolyester (λ_{ex} = 340 nm), and (c) fluorescence spectrum of amorphous PET (λ_{ex} = 340 nm).

of the copolyester can be seen. Thus, when exciting the terephthalic unit in the copolyester excitation energy transfer to naphthoic traps can take place.

Figure 2 shows the fluorescence spectrum of the copolyester excited at 340 nm. This wavelength is above the absorption regime of the terephthalic unit. The naphthoic unit is excitable up to about 370 nm.[7] The observed spectra of the copolyester being excited at 300 and 340 nm are identical. To prove that the observed fluorescence of the copolyester is caused by the naphthoic units, it is compared with a spectrum of dimethyl 2,6-naphthalene dicarboxylate (DMN). DMN was dissolved in chloroform at a concentration of 10^{-4} M. DMN serves as a structure unit model compound for the naphthoic units built into the PET matrix. In the solid state the fluorescence maxima are slightly broadened and red-shifted, but the observed structure is similar except for the first maximum. The absence of the first maximum in the copolyester spectrum can be attributed to reabsorption effects.

Furthermore, it is known that at 340 nm ground-state stable dimers of PET are excitable.[1,2,5,6] Thus, the emission spectrum of PET ground-state stable dimers is represented in Figure 2. This spectrum is likewise structured, and from the figure an overlap of the DMN spectrum with the ground-state stable dimer spectrum cannot be excluded when explaining the copolyester spectrum. But, as already mentioned, the spectra of the copolyester excited at 300 and 340 nm are identical, and

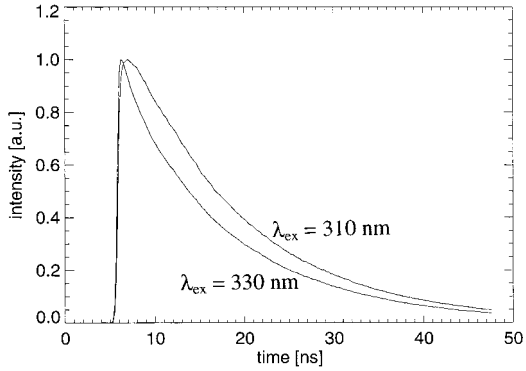

Figure 3. Fluorescence decay curves of the copolyester normalized to maximum intensity (λ_{em} = 380 nm, λ_{ex} = 310 and 330 nm).

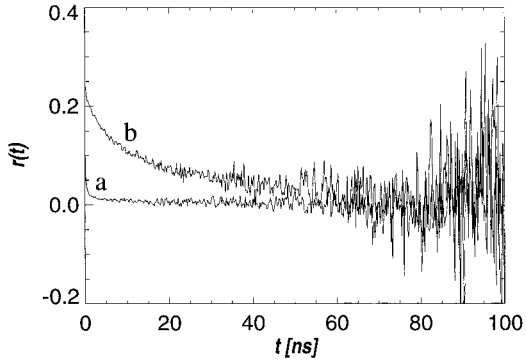

Figure 4. Emission anisotropy $r(t)$ of the copolyester: (a) λ_{ex} = 290 nm, λ_{em} = 400 nm, g = 1.05; (b) λ_{ex} = 340 nm, λ_{em} = 380 nm, g = 1.01.

ground-state stable dimer excitation is negligible at 300 nm in pure PET films.[1] Thus, the observed copolyester spectrum after excitation at 340 nm arises from naphthoic units. This shows that the fluorescence arising from 1 mol % naphthoic units is much stronger than the fluorescence of ground-state stable dimers in the PET matrix.

Figure 3 shows time-resolved fluorescence curves of the copolyester. The decay curve observed after excitation at 310 nm, i.e., within the excitation range of terephthalic units, exhibits a delayed maximum. On the other hand, excitation at 330 nm gives a sharp maximum, which indicates direct excitation of naphthoic units. The emission was measured at 380 nm. The delayed maximum shows that naphthoic units are excited by a delayed mechanism. We assume that terephthalic units are excited by the incoming light pulse, and then excitation energy transfer takes place from terephthalic units to naphthoic traps. The observed intensity is emitted only from the naphthoic units.

Time-resolved fluorescence curves were measured over an extended excitation range. The sample was excited from 270 to 350 nm in 20 nm steps (λ_{em} = 380 nm). Two sets of curves can be distinguished: curves with a delayed maximum in the range from 270 to 310 nm and curves with a sharp maximum at 330 and 350 nm. Thus, only two representative curves are shown in Figure 3. In addition, the sample was excited at 340 nm, and the emission was measured from 370 to 470 nm in 10 nm steps. All curves look like the curve with the sharp maximum represented in Figure 3. Thus, excimer formation is negligible in this copolyester. Otherwise, a broadening of the decay curves at increasing emission wavelengths should have been observed.[9] A negligible content of naphthoic excimers in poly(ethylene terephthalate-*co*-ethylene-2,6-naphthalene dicarboxylate) containing 1 mol % ethylene naphthoate was also found by Jones et al.[13]

To obtain more information about the excitation energy transfer, time-resolved fluorescence depolarization experiments were performed. The observed emission anisotropy $r(t)$ is shown in Figure 4. It was calculated from the fluorescence decay curves obtained by illuminating the sample with linearly polarized light. The emission was recorded through a polarization analyzer as described in the Experimental Section. The representation of $r(t)$ in Figure 4 starts after the rise time of the excitation pulse. When the sample is excited in the excitation range of the terephthalic units, an emission anisotropy of zero is observed. As an example for this situation the anisotropy curve observed at λ_{ex} = 290 nm and λ_{em} = 400 ± 20 nm (band-pass filter, g = 1.05) is shown. An emission anisotropy of zero indicates that the excitation energy does not remain localized at the initially excited units. The excitation energy transfer leads to a loss of the initial anisotropy. One possible excitation energy transfer could be caused by the interaction of the initially excited terephthalic units with the nearest naphthoic unit. In this case only one transfer step would be involved between excited terephthalate and naphthoate. Assuming parallel absorption and emission moments of both molecular sites and a random orientation distribution, the emission anisotropy in this case would decrease from 0.4 to 0.02.[14] As in our case, an emission anisotropy $r(0)$ close to zero is observed; this is in agreement with the assumption made above. However, transfer steps among the terephthalic units before a naphthoic unit is reached cannot be excluded. In addition, also interactions between naphthoic sites are possible which will be discussed later.

In the case of direct excitation of naphthoic units at λ_{ex} = 340 nm an initial emission anisotropy of $r(0)$ = 0.25 is observed, as shown in Figure 4. The emission was measured at 380 nm (monochromator, g = 1.01). Considering parallel absorption and emission moments with random orientation, one would observe $r(0)$ = 0.4. When the excitation energy is localized, this value stays constant during the fluorescence decay. But as can be seen in Figure 4, the emission anisotropy vanishes within the time interval of observation. A process that leads to a loss of anisotropy is the reabsorption of emitted photons. As can be seen from Figure 2, this process takes place in the investigated copolyester. In addition, we assume that excitation energy transfer takes place among the naphthoic units. The transfer rate k_T of Förster excitation energy transfer is given by

$$k_T = (3/2)\kappa^2 k_M (R_0/R)^6 \text{ (ref 14)} \qquad (3)$$

R is the distance of interacting molecules, R_0 the Förster radius, and k_M the fluorescence decay rate of the molecule including radiative and nonradiative decay. κ^2 is an orientation factor. For isotropically distributed static emission and absorption moments $\langle\kappa^2\rangle = 0.476$.[14] Usually the Förster radius amounts to a few tens of angstroms.[15,16] One can estimate the mean distance of naphthoic moieties by assuming all molecules in the centers of cubes. Taking the density of amorphous PET to be ρ = 1.338 g/cm^3, and a molar mass of 192 g/mol, a mean distance of 29 Å is calculated between every

Table 1. Calculated Decay Times and Amplitudes Observed by Fitting the Decay Curves of the Copolyester with Sums of Exponential Functions; Emission Has Been Monitored at 380 nm and the Excitation Wavelength Is Given in the Table

λ_{ex}/nm	τ_1/ns	A_1/%	τ_2/ns	A_2/%	τ_3/ns	A_3/%	χ^2	counts at max
270	0.67 ± 0.05	−28 ± 2	12.78 ± 0.01	128 ± 1			1.54	36 000
290	0.72 ± 0.01	−21 ± 1	12.78 ± 0.01	121 ±1			2.72	73 000
310	0.94 ± 0.03	−26 ± 1	13.00 ± 0.01	126 ± 1			2.30	91 000
330	0.85 ± 0.06	12 ± 1	6.21 ± 0.14	19 ± 1	13.55 ± 0.02	69 ± 1	1.06	163 000
350	0.81 ± 0.05	10 ± 1	6.20 ± 0.09	19 ± 1	13.50 ± 0.01	71 ± 1	1.74	352 000

hundredth molecule that represents a naphthoic site in the copolyester. If R_0 is about 30 Å, the mean k_T is on the order of k_M. This explains the vanishing of anisotropy during the range of observation. Taking the distribution of distances into account, a distribution of k_T is realized. Our comparatively small value of $r(0) = 0.25$ can be explained by transfer steps being fast compared to the minimum observation time.

Now we will discuss the shape of the time-resolved fluorescence curves in more detail. When the sample is excited in the range from 270 to 310 nm, identical curves with a delayed maximum are observed, as can be seen in Figure 3. The delayed maximum can be explained by assuming that naphthoic units are populated via excitation energy transfer from the terephthalic units. For simplification only one single transfer rate k_T from terephthalic units to naphthoic traps is taken into account. Considering the fluorescence of the naphthoic monomer, a biexponential decay

$$N_{naph}(t) = A(\exp(-k_{naph}t) - \exp(-(k_{tereph} + k_T)t)) \quad (4)$$

is calculated. In Table 1 the values observed by fitting the measured curves with two exponential functions are shown. The short decay time τ_1 arises from $(k_{tereph} + k_T)^{-1}$. Taking a distribution of transfer steps into account, a distribution of short decay times is observed.[16] A distribution is predicted because various different distances exist between terephthalic units and naphthoic traps. In addition, the excitation energy might be transported along various numbers of PET before a naphthoic trap is reached. Thus, our calculated decay time τ_1 only represents a mean value. The underlying distribution of decay times explains that one does not observe good fits with two exponential functions. Next we will discuss why the magnitude of the negative amplitude A_1 is small compared with A_2. From eq 4 the same magnitude of both amplitudes is expected in the case of no direct excitation of naphthoic units. As already mentioned, a distribution of k_T is present; thus, decay times on a picosecond time scale resulting from large transfer rates cannot be observed in our experiment. This would lower A_1 compared to the calculated value. In addition, the existence of directly excited naphthoic units in the excitation range from 270 to 310 nm would increase the value of A_2. Both effects are assumed to take place. Concerning eq 4, the calculated decay time τ_2 of about 13 ns represents the lifetime of the naphthoic units in a PET matrix. Also, in this case the assumption of a single decay time is too simple. If only a single decay time exists, one should observe single-exponential decays after direct excitation of naphthoic units, i.e., at 330 and 350 nm excitation wavelength. In this case at least three exponential functions are needed to fit the measured curves, and even then for excitation at 350 nm a poor χ^2 is found for the best fit. Thus, the calculated values only represent the mean values of a distribution of decay times. The short decay time τ_1 can be attributed to an overlaid emission from ground-state stable dimers of the PET matrix. Hemker et al. calculated an average decay time of 1.3 ns for the ground-state stable dimer emission.[3] Its contribution with about 10% is too low to be recognized in the spectrum of the copolyester, especially because the two spectra are very similar.

Next we want to discuss the intermediate decay time τ_2. We suggest that a part of the fluorescence of excited naphthoic units is quenched by interactions with the PET matrix. One possibility is excitation energy transfer from naphthoic units to ground-state stable PET dimers. On the other hand, one can also think of strong environmental interactions between naphthoic units and special formations of the PET matrix. The decay time τ_3 arises from unquenched naphthoic units. There might be a continuous transition between quenched and unquenched naphthoic units. This would also result in a distribution of decay times.

Conclusions

In poly(ethylene terephthalate-*co*-ethylene-2,6-naphthalene dicarboxylate) the naphthoic units act as traps for the excitation energy of the terephthalic units. Thus, only the fluorescence of naphthoic units is observed. When the terephthalic unit is excited, time-resolved fluorescence curves show a delayed maximum which shows that naphthoic units are excited via excitation energy transfer from terephthalic units. This is in agreement with the fluorescence depolarization experiments. We assume that also transfer steps among the terephthalic units take place. As different distances between interacting sites occur, a distribution of decay times is observed. In the long excitation wavelength range, i.e., above the excitation threshold of terephthalic units, naphthoic units are excited directly. The emission anisotropy decreases within the time of observation. The decrease is explained by reabsorption effects and excitation energy transfer among the naphthoic units. From the time-resolved fluorescence measurements we conclude in the case of direct excitation of naphthoic units, i.e., above the absorption range of terephthalic units, a small amount of ground-state stable dimer emission of PET is overlaid. According to the nonexponential behavior, we conclude that the naphthoic unit interacts with the PET matrix.

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