On the fluorescence properties of poly(ethylene terephthalate co-*p*-oxybenzoate) copolymers

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Polarized fluorescence properties of the series of PET/xPHB copolymers are studied in solution and in solid state. The fluorescence results give evidence to a fluorophor, which is formed by a molecular association of PHB segments. A residual fluorescence contribution of pure PET is found. In accordance with the results of other experimental methods, the PET/80PHB sample shows a completely different behaviour in comparison to the copolymers with lower PHB content. The polarized fluorescence of the PET/30PHB sample was used to determine orientation coefficients in uniaxially stretched films.

INTRODUCTION

The series of copolyesters of poly(ethylene terephthalate) (PET) modified with *p*-hydroxybenzoic acid (PHB) has gained considerable interest since their synthesis by Jackson and Kuhfuss in 1976[1]. These copolymers, referred to as PET/xPHB (x = mole% PHB), have been shown to exhibit thermotropic liquid crystalline behaviour at or above 35 mole% PHB[1]. They belong to the group of the main chain liquid crystalline polymers (LCPs), in which the mesogenic units are part of the polymer chain. The alternation between more rigid (PHB) and more flexible (PET) sequences, which gives rise to outstanding mechanical properties, has led to the terms molecular composites or self-reinforcing polymers for these materials[2].

Several experimental methods have been used to study the formation of the thermotropic nematic phase[3], for example, thermal and rheological techniques, polarized optical microscopy and diffraction methods. Macroscopically oriented films of the copolymers have been investigated by X-ray diffraction[3] and n.m.r. methods[4].

By means of polarized fluorescence spectroscopy additional information on a molecular level in unoriented and oriented polymer films can be obtained. In particular where the fluorophore is formed by a molecular association, e.g. excimers or groundstate-stable dimers, the fluorescence properties reflect the local interaction of neighbouring aromatic groups. The intrinsic fluorescence of an aromatic polymer has been used in the case of PET to obtain further information on the local packing and anisotropy in randomly oriented and uniaxially stretched films[5,6]. The PET/xPHB copolymers, whose fluorescence properties have not been reported so far, are studied by (polarized) fluorescence measurements in order to gain further insight into the structure on a molecular level.

MATERIAL AND METHODS

PET/xPHB copolymers with x = 30, 60, 70 and 80 mole% PHB (Eastman Kodak, Kingsport, USA) were investigated. Specimens with x = 30 mole% PHB were measured in dilute $CHCl_3$ solution and in the form of melt-crystallized, isotropic, clear films of 90 μm thickness. The glass transition temperature T_g of the film was 363 K at 1 Hz as determined by d.m.t.a. The melting point was found to be at 486 K with a small enthalpy of fusion $\Delta H \approx 12$ J/g (DSC 7 Perkin Elmer), indicating the low crystallinity of the sample. This was also evidenced by X-ray diffraction patterns. The birefringence in the plane of the film was below 4×10^{-4} and indicates the approximate isotropy of the film.

Specimens with x = 60, 70 and 80 mole% PHB were only available as melt-crystallized, turbid films of 120 μm thickness. In these films, glass transition temperatures and melting points could not be observed by d.s.c. measurements. The nematic liquid crystalline phase was detected by optical polarized microscopy at temperatures above 538 K for PET/60PHB.

Corrected fluorescence and excitation spectra were run on a Perkin–Elmer MPF 44 spectrofluorimeter specially equipped for polarized measurements of solid samples. The emission anisotropy

$$r(I_{VV} - I_{VH})/(I_{VV} + 2I_{VH}) \qquad (1)$$

was corrected for the apparatus effect.

Solution spectra were obtained with a triangular cuvette of outer quadratic cross-section, which diminishes reabsorption even in the case of concentrated solutions (10^{-1} mole/l) to a negligible value.

Fluorescence decay laws were determined by an apparatus based on the single photon-counting method.
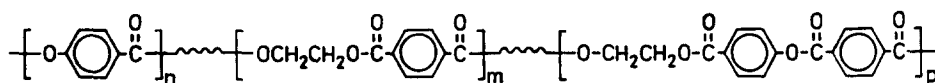
Figure 1 Structure of poly(ethylene terephthalate-co-*p*-oxybenzoate) with possible segment types *n*, *m* and *p*

Stretching experiments were performed in a thermostatable tension machine which is part of a fluorescence polarization apparatus.

RESULTS AND DISCUSSION

PET/30PHB copolymer in solution

Figure 2 shows the unpolarized excitation spectra of PET/30PHB in diluted (10^{-4} mole (repeating unit, r.u.)/l) and concentrated (10^{-1} mole (r.u.)/l) $CHCl_3$ solution. The excitation in dilute solution as well as the corresponding fluorescence spectrum (cf. *Figure 3*) cannot be assigned either to individual PET segments (structural formula cf. *Figure 1, m*) or to individual PHB segments (cf. *Figure 1, n*). This was verified by measurements with the corresponding monomer compounds in solution, i.e. dimethylterephthalate for (*m*) and *p*-hydroxybenzoic acid for (*n*).

From the spectra, clear identification of the chemical nature of the fluorophore is impossible, since they are common to very different compounds. For instance, the spectra of the 10^{-4} mole(r.u.)/l solution are very similar to the solution spectra of 2,6-dimethylnaphthalate or, if somewhat redshifted, of *N*-methylcarbazole. Therefore, we take the spectra of the dilute solution as an indication of the existence of traps with a different chemical structure in the copolymers.

In the narrow concentration range between 10^{-4} and 10^{-3} mole(r.u.)/l, the fluorescence spectra change completely (cf. *Figure 3*). No further variation of spectra occurs at higher concentrations, which was proved up to 1 mole(r.u.)/l.

At a concentration 10^{-3} mole(r.u.)/l and above, the fluorescence spectra become partially polarized, with a value of $r \approx 0.15$ (cf. equation 1) in the low-wavelength region, and $r \approx 0.08$ at wavelengths beyond 400 nm. Temperature dependent polarization measurements indicate that the increased polarization is caused by restricted rotational mobility of the fluorophores, e.g. a solution of 10^{-2} mole(r.u.)/l shows values of $r \approx 0.12$ at 265 K and $r \approx 0.06$ at 330 K for the long-wavelength fluorophore at 430 nm.

As can be seen from *Figure 3* there is no isoemissive point in the concentration range mentioned above. This behaviour, the well-structured shape of the fluorescence spectrum, and its high polarization exclude the attribution of the fluorescence to a simple excimer. The fluorescence is tentatively attributed to a molecular association including (*p*)- or (*n*)-sequences. This view is further supported by the fluorescence properties in solid state.

PET/30PHB copolymer in solid state

The solid state fluorescence spectrum of PET/30PHB is similar to the spectrum in concentrated $CHCl_3$ solution, but the degree of polarization is substantially higher, i.e. $r \approx 0.35$ in the low-wavelength region and $r \approx 0.27$ in the long-wavelength region. From the high value of *r* compared to the value in solution, we learn immediately
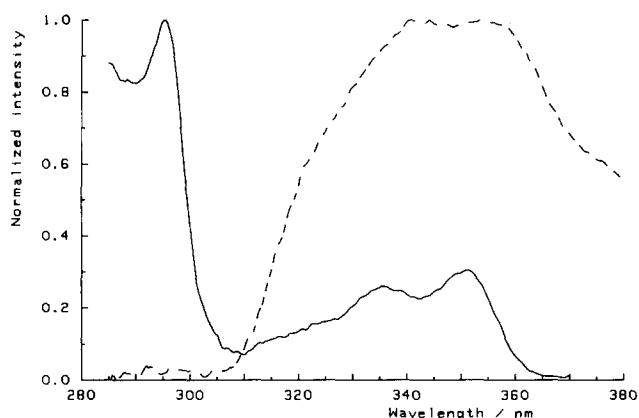

Figure 2 Excitation spectra of PET/30PHB in $CHCl_3$ solution. Wavelength of fluorescence $\lambda_{flu} = 390$ nm, slit width 3 nm, room temperature. ———, 10^{-4} mole(repeating unit (r.u.)/l; -----, 10^{-1} mole(r.u.)/l
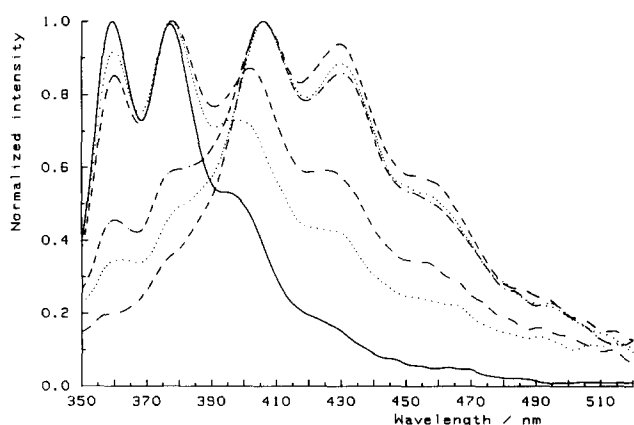

Figure 3 Fluorescence spectra of PET/30PHB in $CHCl_3$ solution. Wavelength of excitation $\lambda_{exc} = 338$ nm, slit width 3 nm, room temperature. Concentrations: (1, 2.5, 5, 6, 8, 10) 10^{-4} mole(r.u.)/l. The corresponding spectra go from top to bottom at 360 nm, and from bottom to top at 430 nm, respectively

that rotational mobility of the fluorophore is much more restricted. Furthermore, the density of the fluorophores must be low enough to prevent migration of excitation energy among them, which would also lead to depolarization.

By comparison with the spectrum of a PET film, a small contribution of the pure PET spectrum (around 15–20% of total intensity) is suggested. This contribution of the PET-like fluorescence is comparatively small, in spite of 70 mole% PET content in the nearly random[7] copolymer. Because in solid state the PET fluorophore itself is a molecular associate (i.e. a ground-state-stable dimer[5]), we may conclude that the additional PHB-segments prevent its formation and reduce the concentration of the PET fluorophore. But it is also possible that the large contribution of the PHB fluorophore to the PET/30PHB spectrum is determined by, for example, its higher quantum yield with respect to
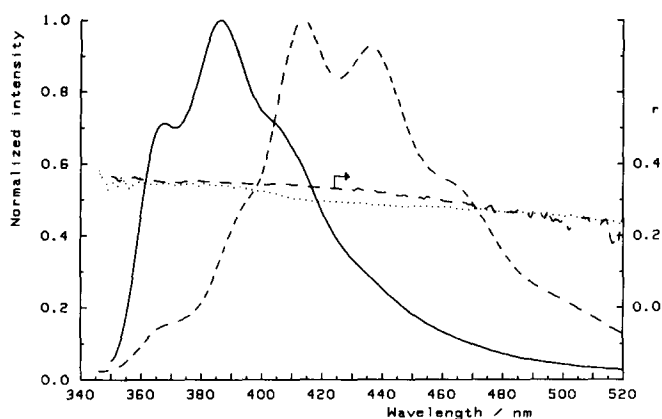
Figure 4 Polarized fluorescence spectra of PET/30PHB and PET films. Wavelength of excitation $\lambda_{exc} = 338$ nm, slit width 3 nm, room temperature. Normalized unpolarized fluorescence intensity $(I_{VV} + 2I_{VH})$: -----, PET/30PHB; ———, PET. Emission anisotropy r (right ordinate): ·····, PET/30PHB; -----, PET
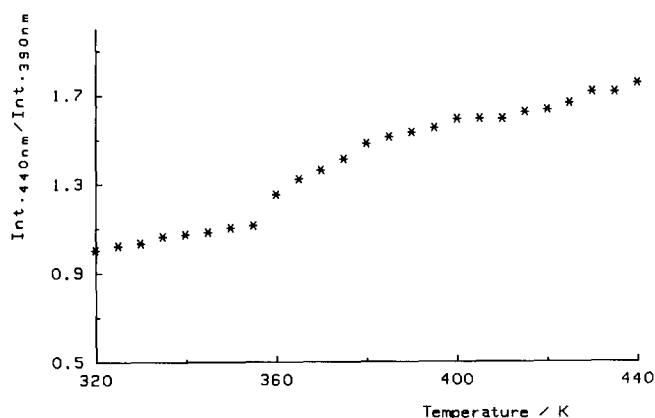

Figure 5 Temperature dependence of the fluorescence spectrum of PET/30PHB film as indicated by the ratio of fluorescence intensities at 440 nm and 390 nm. Ratio normalized to 1 at 320 K. Wavelength of excitation $\lambda_{exc} = 338$ nm.

the PET fluorophore. Because the concentration of fluorophores is unknown, the relative quantum yield cannot be determined. A transfer of excitation energy from the PET to the PHB fluorophore is excluded by the high value of r.

The contribution of the PET fluorophore in the wavelength region below 400 nm is further indicated by the increase of the emission anisotropy towards the value of PET at these wavelengths.

The excitation with wavelengths below 300 nm yields structureless, unpolarized fluorescence spectra, similar to those observed with pure PET films and attributed to PET excimers[5]. Time-resolved fluorescence measurements of the PET/30PHB film specimen show a PET-like decay law at 390 nm (requiring a biexponential fit: $\alpha_1 = 98\%$, $\tau_1 = 1.1$ n.s.; $\alpha_2 \approx 2\%$, $\tau_2 \approx 7$ ns) and an almost single exponential decay ($\tau = 1$ ns) at 432 nm.

Additional evidence for the attribution of the main fluorophore in the PET/30PHB copolymers to a molecular associate comes from the temperature dependence of the fluorescence spectrum. In *Figure 5*, the ratio between the intensities at 440 nm and 390 nm is plotted *versus* temperature. The graph exhibits a break near the glass transition temperature. Heating the sample to temperatures above T_g facilitates the formation of the

associates which fluoresce at longer wavelengths. The intensity measured at 390 nm behaves just as in pure PET films, i.e. it decreases over the whole temperature range[5].

PET/xPHB copolymers with $x > 30$

The fluorescence spectra of specimens with $x = 60$ and 70 mole % PHB are similar to those with $x = 30$ mole % (cf. *Figure 3*), except for the polarization. The fluorescence of samples with $x > 30\%$ PHB is unpolarized because of light scattering. This is already suggested by the turbidity of the films. The liquid crystalline superstructure of these copolymers is frozen in and prohibits the use of polarized fluorescence methods.

The spectrum of the film with $x = 80$ mol % PHB deviates completely. A different behaviour of the 80% sample with respect to the samples of lower x was reported also by Nicely et al.[7] from n.m.r. measurements and Blackwell et al.[8] from X-ray and electron diffraction patterns. Blackwell et al. found the structure of the $x = 80$ sample to be very similar to a single crystal of PHB homopolymer, in which PET sequences are distributed as defects. It seems possible that the observed change in the fluorescence spectrum is due to the fact that the fluorescent associates cannot be formed in the ordered regions of PHB (as PET dimer fluorescence is not found in PET crystals[5]). Therefore, the fluorescence of the PET/80PHB results mainly from PET dimers at defect positions in the PHB lattice.

Uniaxial stretching of PET/30PHB films

The polarized excitation and fluorescence spectra of a uniaxially stretched PET/30PHB film show that the polarization, but not the spectra, are altered by stretching. Hence, orientation of fluorophores occurs but there is no detectable change in the energetic situation of the fluorophores. The value of the emission anisotropy r in the nearly isotropic state is high enough to provide a preferential direction of transition moments within the fluorophore.

In comparison with pure PET films, the orientational behaviour is obviously more complicated. The usual procedure[6] to evaluate the orientation coefficients $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ of the direction of the transition moment during uniaxial stretching failed because physically unreasonable values, especially of $\langle P_{400} \rangle$, of
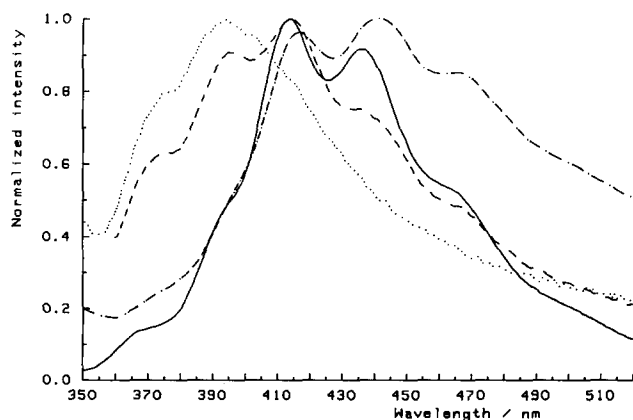

Figure 6 Unpolarized fluorescence spectra $(I_{VV} + 2I_{VH})$ of PET/xPHB films. Wavelength of excitation $\lambda_{exc} = 338$ nm, slit width 3 nm. ———, 30 mole %; -----, 60 mole %; -·-·-, 70 mole %; ·····, 80 mole % PHB
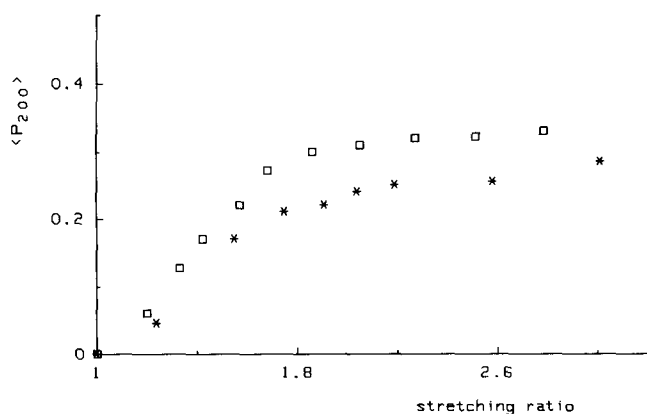
Figure 7 Orientation coefficient $\langle P_{200} \rangle$ of the direction of the transition moment of the fluorophores, evaluated at the wavelengths of fluorescence $\lambda_{flu} = 390$ nm and 432 nm. Measurement during stretching, at the wavelength of excitation $\lambda_{exc} = 338$ nm. Stretching temperature 383 K, stretching speed 0.15%/s. □, $\lambda_{flu} = 432$ nm (PHB); ★, $\lambda_{flu} = 390$ nm (PET)

these coefficients were obtained. On the other hand, no unusual behaviour of the stress–strain curve and the birefringence was found. We conclude, that at least one of the assumptions in the evaluation procedure of $\langle P_{200} \rangle$ and $\langle P_{400} \rangle$ from the polarized fluorescence intensities is violated. Among these assumptions, the most sensitive, particularly on $\langle P_{400} \rangle$, is the uniaxial rotational symmetry of both the sample and the geometry of the fluorophore. Furthermore, the uniaxial symmetry conditions are required for the molecular spectroscopic properties, i.e. the fluorophore must be fully characterized by an intrinsic value of r_0. Any deviation from these severe conditions during deformation of the sample can lead to orientation coefficients out of range. The molecular fluorescence properties are deformation invariant in the case of the usual well described fluorescent probe molecules, but with fluorescent associates, we have to admit a deviation of both the sample as well as the molecular properties.

To allow for such behaviour, the measured polarized fluorescence intensities were evaluated at each stretching ratio λ with various values of r in the range from 0.1 to 0.4. The variation of r is expected to work as a first-order correction to the above mentioned effects. The calculation yields different $\langle P_{400} \rangle$, $\langle P_{200} \rangle$ pairs (for each value of r), some of them outside the allowed limits of $\langle P_{400} \rangle$. To select between the physically allowed r– $\langle P_{200} \rangle$–$\langle P_{400} \rangle$ data, we need additional information.

This is available by assuming the most probable orientation distribution function[9], which predicts a certain $\langle P_{400} \rangle$–$\langle P_{200} \rangle$ relationship. By this procedure, values of $\langle P_{200} \rangle$ are obtained with an apparent r which deviates from the intrinsic value r_0 (as determined in the isotropic state of the sample). This deviation depends on stretching ratio λ. In the PET/30PHB sample a similar pattern of r versus λ was found for the data of the different fluorophores at 390 nm and at 432 nm. This suggests that the peculiar behaviour of polarized fluorescence during orientation originates from the given PET/30PHB sample and not from an intrinsic property of the fluorophores. The deviation r_0–r was found to be largest at stretching ratios below 1.5 where it amounts to r_0– $r \approx 0.2$ (cf. *Figure 4* for the values of r_0). At stretching ratios $\lambda > 2$, the most probable pairs of $\langle P_{400} \rangle$ and $\langle P_{200} \rangle$ exist only at negative values of $r_0 - r$.

The orientation coefficients $\langle P_{200} \rangle$ obtained are presented in *Figure 7* as a function of the stretching ratio. In the limits of the evaluation method, it is evident that the fluorescent species observed at 432 nm shows higher values of $\langle P_{200} \rangle$ than the species observed at 390 nm. Consequently, the molecular associates including PHB sequences are oriented higher than the PET sequences.

ACKNOWLEDGEMENTS

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