Charge-Transfer Fluorescent Probes Applied to the Characterization of Thermal and Mechanical Properties of Polymers

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Charge-transfer fluorescence probes show a strong response of the intensity and wavelength positions of their spectra to solvent polarity and mobility. Such properties have been applied in the past to follow polymerization kinetics and solvent-induced effects (e.g., swelling) in polymeric materials. An important advantage of charge-transfer fluorescence probes is that they can be measured at extremely low concentrations, hence interference with the polymeric system is limited. Furthermore they report from "within," since they are only sensitive to phenomena which occur in their immediate surroundings. In this paper it is shown that charge-transfer fluorescence probes can also be applied to study mechanical and thermal properties of polymers. The charge-transfer fluorescence probe Fluoroprobe (1-phenyl-4-[(4-cyano-1-naphthyl)methylene]piperidine) was doped into a polyether–polyester block copolymer, which was submitted to thermal and mechanical stress. The effect of strain applied to the polymers in various forms (fibers, sheets) and the effect of thermal processes (glass transition temperatures, phase transitions, melting points) are clearly reported by the changes in fluorescence intensity and wavelength of the Fluoroprobe molecule.

INTRODUCTION

Donor–bridge–acceptor systems, showing intramolecular charge transfer fluorescence (CTF) with a strong dependence on the polarity and polarizability of the medium, have been applied with success to the study of polymerization reactions and polymer properties [1–7]. The response of CTF probes to the significant change in viscosity occurring during the formation of a polymer is

obvious: a blue shift of the fluorescence spectrum is observed as a result of the reduction in mobility of the probe in the matrix. CTF probes have also been applied with success to monitor solvent-induced swelling of polymer particles (resulting in medium mobility and polarity changes) [5,6] and appearing to respond to phase transitions in solids [8].

The donor–bridge–acceptor system which will be applied in this study is 1-phenyl-4-[(4-cyano-1-naphthyl)methylene]piperidine, commonly referred to as Fluoroprobe. Fluoroprobe shows an extreme sensitivity to solvent polarity, with emission maxima at 400 nm in nonpolar solvents (n-hexane, cyclohexane) and at 700 nm or beyond in polar solvents (e.g., acetonitrile) [9].

In this study the application of Fluoroprobe to study the thermal and mechanical properties of polymers will be investigated. Polymers are versatile materials. Subtle

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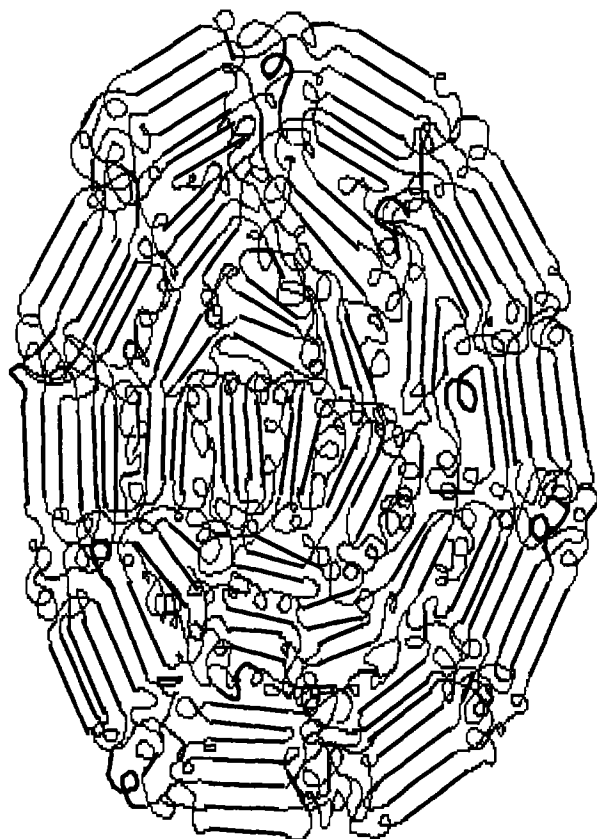
Fig. 1. Schematic representation of spherulitic morphology. The heavy lines represent the PBT blocks.

changes of the composition of polymeric materials and of the processing conditions, which are applied to manufacture polymer products, result in specific mechanical and thermal properties. Of particular interest are block copolymers, materials which are composed of interconnected blocks of homopolymers. An interesting question in such materials is whether the properties of the two homopolymers can still be observed in the copolymer. The CTF approach may provide a means to discriminate between the (properties of) the two types of polymers in such a copolymer.

The copolymer chosen for the investigation is a block copolyether–polyester, composed of alternating blocks of polybutylene terephthalate (PBT) and polyethylene glycol (PEG) [10]. The composition of the polymer is determined by the amount and molecular weight of the PEG used in the polymerization reaction, which determine to a large extent the final properties of the copolymer (e.g., its hydrophilicity). The individual PBT and PEG blocks possess opposing features, giving the block copolymer a set of very useful properties. At am-

bient temperature PBT is rigid, semicrystalline, and hydrophobic, which gives the copolymer its morphology and processability, whereas PEG is flexible and hydrophylic, leading to a more elastomeric character of the copolymer. The supramolecular structure of the polymer is mainly determined by the applied processing method, in particular, the mode of crystallization of the PBT. In sheets, fabricated by flat die melt-extrusion of the copolymer (thickness, about 10 μm), PBT is present in long, chain-folded lamellar crystallites ($\pm 1000 \times 100$ Å) forming a more or less continuous network in an amorphous phase. As a result of the extrusion conditions under which the sheets are formed, the lamellae grow out into spherulites (Fig. 1) [11–13]. In the interfaces between the "continuous" PBT blocks, the PBT and PEG phases are believed to form an amorphous, interpenetrating submatrix. The copolymer used in the present investigation is composed of 70 wt% PBT (M_w 9000) and 30 wt% PEG (M_w 4000). To evaluate the effect of the processing conditions, the block copolymeric system has also been examined in the form of a thread (diameter, ~ 1 mm), directly quenched from the (homogeneous) melt.

EXPERIMENTAL

Materials

The synthesis of Fluoroprobe and its spectral characteristics are extensively described in Ref. 9.

The PEG/PBT copolymer is prepared by a conventional ester interchange reaction from the dimethyl ester of terephthalic acid with a molar excess of short-chain diol, butane diol, and a long-chain diol, polyethylene oxide glycol, in the presence of tetra-n-butoxytitanate (an ester interchange catalyst) [10]. As ester interchange reactions are reversible, a randomization of both diols over the polymer chain occurs, resulting in a polybutylene terephthalate chain randomly interrupted by blocks of polyethylene oxide. The final polymer can be considered as an alternating block copolymer. The final block copolymer has a weight-average molecular weight of the order of 30,000 to 60,000 and is thus composed of several alternating blocks. The thread (diameter ~ 1 mm) is not processed in any way and directly cooled down from the (homogeneous) melt. The sheets (thickness, 10 μm) are produced by flat die extrusion (also from the melt) and are obtained as large sheets that are 1.70 m in width.

Reference experiments were done in the pure homopolymers. PBT (M_w $\sim 25,000$) was synthesized from terephthalic acid and butanediol in a reaction analogous

Table I. Fluorescence Maxima (λ_{max}) of Fluoroprobe (nm) in the Polymers Under Investigation

Sample	λ_{max} (nm)
PBT 25000	540
PEG 4000	515
PBT/PEG	
Sheet	520
Thread	560

to that used in the first step of the synthesis of the copolymer. PEG 4000 (Hüls) was used as received.

Fluoroprobe was introduced into the copolymer by swelling polymeric sheets or threads in solutions (concentration, <1 μM) of Fluoroprobe. After preliminary experiments, it was decided to use a Fluoroprobe/dichloromethane solution as the swelling medium. The same procedure, using dichloromethane as the swelling medium, was used to introduce Fluoroprobe into the PBT sample. The PEG samples were prepared by dissolving the polymers in a solution of Fluoroprobe in dichloromethane (concentration, <1 μM) and applying the solution thus obtained on a thin glass plate. After evaporation of the solvent the samples were obtained as opaque solid solutions.

Fluorescence Measurements

Steady-state fluorescence spectra (λ_{ex} = 310 nm) were measured on a Spex Fluorolog 2 spectrofluorimeter in front-face geometry. During the stretching experiments an optical fiber was used, whose head can be positioned just above the sample, with the the fiber carrying the excitation as well as the emission light. The spectra were corrected for the wavelength dependence of the detector response. Since CT fluorescence spectra generally are strongly asymmetric, the weighted fluorescence maximum was determined by taking the weighted average across the spectrum, after transformation from the wavelength axis to the wavenumber axis.

Bulk Polymer Analysis

Differential scanning calorimetry (DSC) was carried out with a Perkin Elmer DSC-7, using the following temperature program: $-100°C$ (3 min isoth.) at 10°C/min $\rightarrow$ 240°C (3 min isoth.) at 10°C/min $\rightarrow$ $-100°C$ (3 min isoth.) and at 10°C/min $\rightarrow$ 240°C (3 min isoth.).

Thermal mechanical analysis (TMA) was carried out using a Mettler TMA-40. Sheets were measured (in a helium atmosphere) in the sheet module, using a sample with dimensions of 10 × 6 mm. The sheets were immobilized and loaded with 8.5 Mpa. Measurements were carried out using the following temperature program: $-$ 30°C at 10°C/min $\rightarrow$ 100°C.

Stretching experiments were carried out using a Minimat miniature materials tester from Polymer Laboratories. The apparatus was equipped with a homemade climate chamber and a remote microprocessor controlled electronics control unit. Load beams were interchangeable.

RESULTS AND DISCUSSION

Room-Temperature Measurements

Fluorescence spectra were first measured for Fluoroprobe in the homopolymers of which both types of copolymer are composed and in the block copolymer at room temperature. For the PBT/PEG copolymer PBT (M_w ~25,000) and PEG (M_w 4000) homopolymers were applied. The fluorescence maxima of Fluoroprobe (at room temperature) in the various polymers are compiled in Table I: spectra are shown in Fig. 2.

All wavelengths and wavelength differences can be explained satisfactorily when the polarity and morphology of the various matrices are taken into account. The wavelength position (540 nm) in PBT, although higher in molecular weight than the PEG sample, is significantly red-shifted with respect to the polyether since its polar groups and its amorphous regions provide the probe molecules with a more polar and still mobile environment.

The fluorescence spectra in the two types of copolymeric materials (a more or less isotropic homogeneous, thread and a—slightly—oriented sheet) are also compiled in Table I (see experimental for sample preparation). From comparison of data obtained for the homopolymers and those of the copolymeric materials, an interesting feature emerges. The fluorescence wavelength of Fluoroprobe in the PBT/PEG thread is 560 nm, whereas in the (crystalline) homopolymers the fluorescence maxima are 515 and 540 nm for PEG and PBT, respectively. Thus, a more mobile environment seems to be present in the PBT/PEG copolymer than in the two homopolymers. This is probably a result of the inhibition of crystal formation in the rapidly quenched copolymer, resulting in a structure relatively rich in amorphous regions. As expected when this is the case, DSC meas-
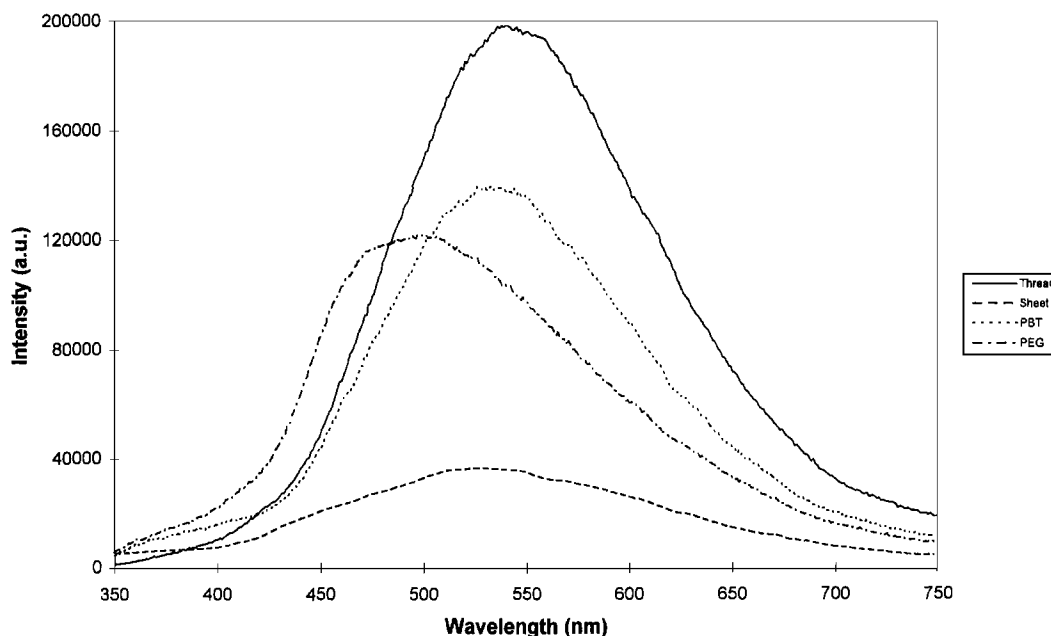
Fig. 2. Fluorescence spectra of Fluoroprobe embedded in PBT 25000 homopolymer, PEG 4000 homopolymer, PBT/ PEG block copolymeric sheet, and PBT/PEG block copolymeric thread.

urements reveal melting peaks that are broadened and shifted to lower temperatures for the copolymer with respect to the homopolymers (Fig. 3). The PBT in the copolymer is about equally present in amorphous and in crystalline form; however, the effect is especially strong for PEG, which is predominantly present in amorphous form in the copolymer.

The fluorescence maximum of Fluoroprobe, when measured in the copolymeric sheet, is strongly hypso-chromically shifted compared to that in the thread (see Table I). This indicates that, upon processing of the copolymers into sheets, parts of the amorphous material have been oriented (the polymer chains have been either lined up or forced to form small crystals), thus diminishing their stabilizing ability toward the probe molecules as a result of the reduced mobility of the probe molecules.

Stretching Experiments

After the reference experiments described in the previous section, two types of experiments were conducted, in which the copolymers were submitted to physical and thermal changes, respectively. First, the PBT/PEG threads and sheets have been stretched (in a controlled manner) up to their breaking point, and the concomitant changes in the Fluoroprobe fluorescence spectrum recorded. Thus induced changes in the micro-

structure of the polymer should reveal themselves by a shift in the fluorescence wavelength. The results of these experiments are represented graphically in Fig. 4.[4] The percentage stretch is calculated by comparison of the length of the sheets before and after stretching, i.e., if a 1-cm sheet is stretched to 2 cm, stretch = 100%. The elongation at break is at about 550% stretch.

The isotropic thread shows a monotonous blue shift upon stretching. This is attributed to the increasing orientation of the polymer chains, which results in a decrease in their stabilizing ability toward the probe molecules due to a concomitant reduction of mobility, thus causing a hypsochromic shift of the fluorescence wavelength. The fluorescence behavior in the sheet, however, is markedly different. Upon stretching initially a bathochromic shift of the fluorescence maximum occurs (up to ~50% stretch); the "expected" (hypso-

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[4] It should be noted that it was checked whether there was a measurable difference in fluorescence wavelengths upon stretching of the samples parallel or perpendicular to the direction in which they were stretched during the flat die extrusion. Within experimental accuracy, no such effects could be measured. However, to make absolutely certain that the stretching experiments would not be influenced by such effects, all samples were stretched parallel to the direction in which they were stretched during extrusion. Also, it was verified that no spurious effects were detected due to nonrandom polarization of the exciting or the emitted radiation; the fiber-optic bundle which was applied to guide the radiation resulted in complete depolarization of the transmitted light.
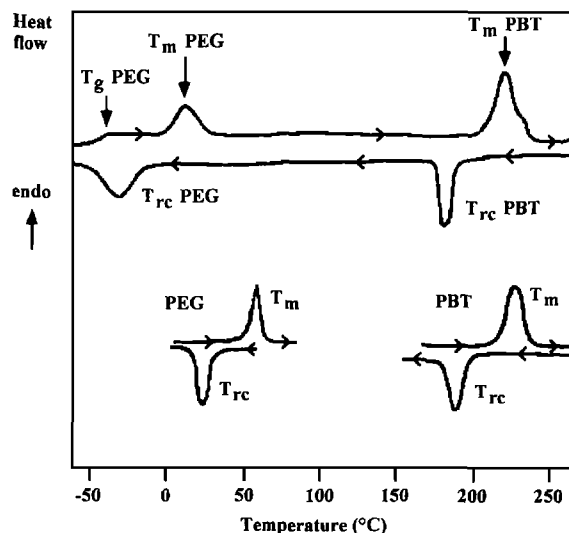
Fig. 3. DSC traces of PBT/PEG copolymer (top trace) and the corresponding homopolymers (bottom traces).

Fig. 5. Stress–strain curves for the copolymeric sheet, for PBT, and for a rubber.
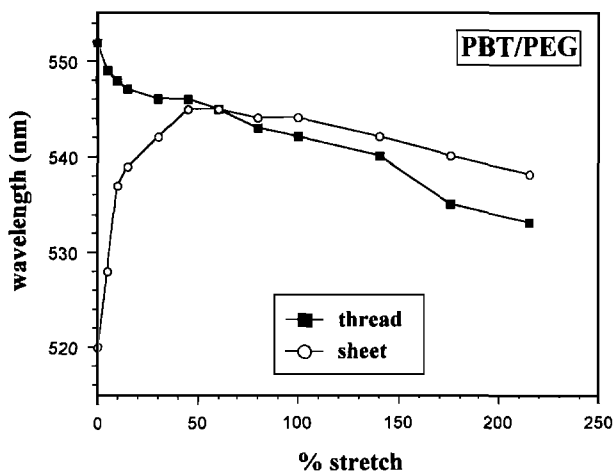

Fig. 4. Response of the Fluoroprobe fluorescence maximum to stretching of the PBT/PEG copolymeric thread and sheet.

chromic) shift occurs only beyond this point (~50% stretch until break). The remarkable bathochromic shift must be a result of increasing mobility (by a decrease in ordering) in the regions in which the probe molecules are dissolved. In view of previous studies on the changes in morphology of the PBT/PEG sheets [10–13], it seems likely that the loss in spherulitic structure of the PBT-rich regions is responsible for the increase in mobility. Since the Fluoroprobe molecules will occupy predominantly amorphous regions, the change in morphology is also reflected in the intercrystalline regions. The absence
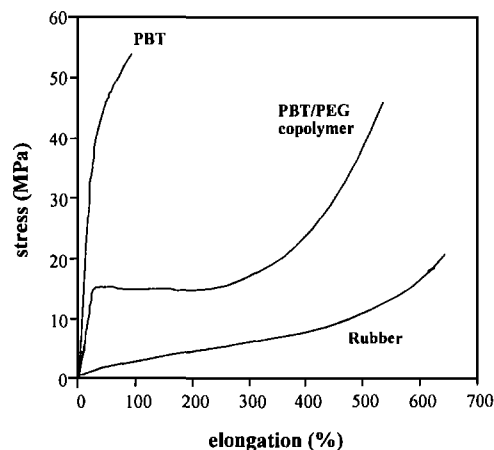
of a red shift of the fluorescence in the (isotropic) threads as a result of stretching supports the above interpretation.

When the reversibility of the stretching process is examined, it is found that the shift of the fluorescence maximum is completely reversible over the entire stretching range, with one important exception: when the copolymeric sheet is stretched, for the first time, in the 0 to 30% stretching range, the wavelength shift is found not to be reversible! If, for instance, a PBT/PEG sheet is stretched from 0 to 20% (λ_{max} shifts from 520 to 540 nm), and then released (upon which it will return to its original length since it is still in its elastic trajectory), the fluorescence maximum will only shift back to ~536 nm! After this initial change, the wavelength shift *is* reversible on this trajectory, i.e., when the sheet is repeatedly stretched and released between 0 and 20%, the fluorescence wavelength will shift from 536 to 540 nm and back. The initial irreversibility and subsequent reversibility of the wavelength shift corroborates that a certain degree of ordering is (irreversibly) lost in the early (0–50%) stretching region of the sheets. This observation is confirmed when the tensile behavior of both copolymeric sheets is investigated (Fig. 5); at ~30% stretch a distinct "yield point" (the point at which there is a sharp change in stress, required to elongate the sample) is found [14]. Thus, in the stretching region below the yield point the copolymers resemble a "hard" polymer like PBT; once past this point their behavior resembles that of a pure elastomer like rubber. Interestingly, although the sheets become mechanically irreversibly deformed in the 30% break stretching region, the wavelength shift is reversible in this stretching region.
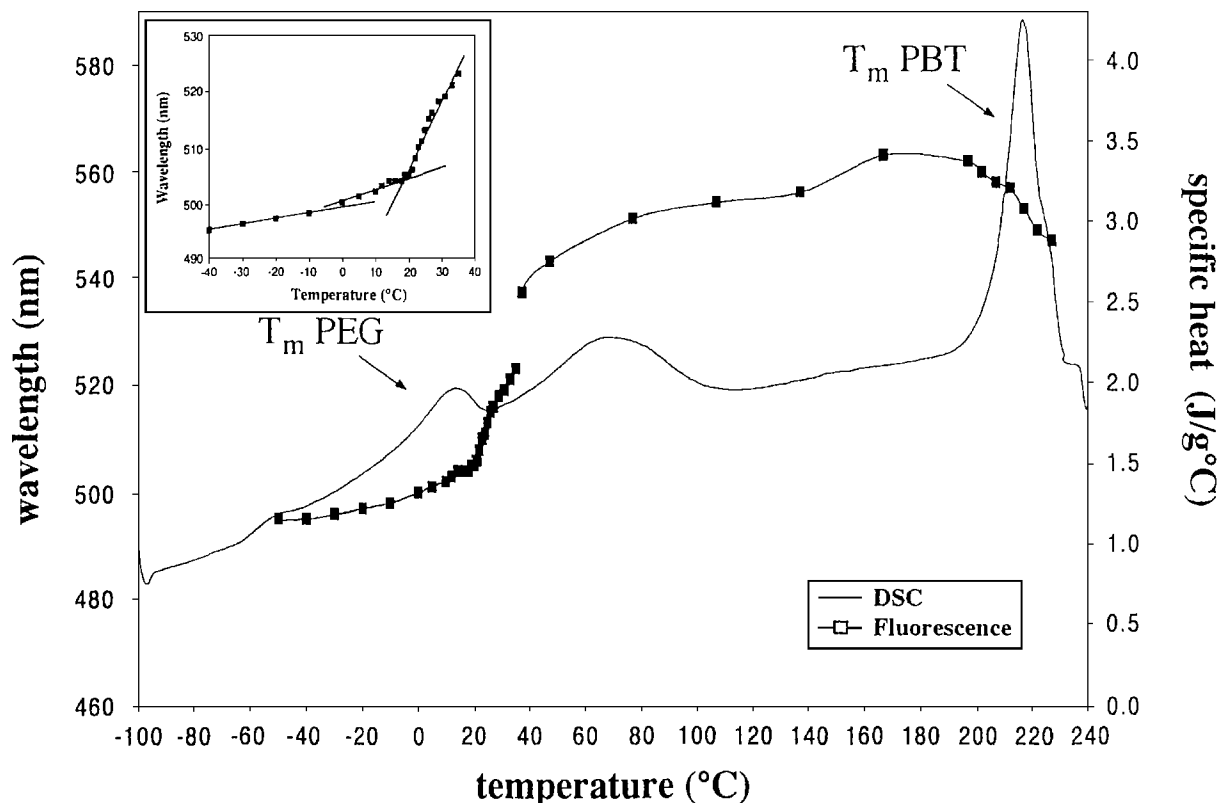
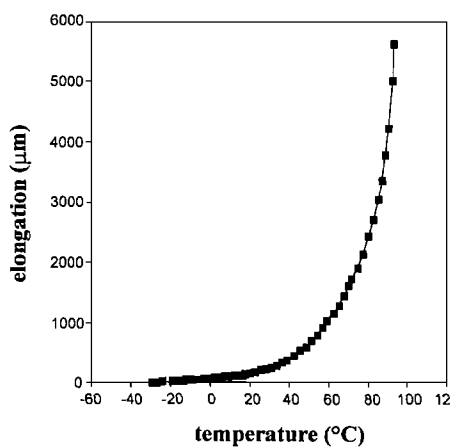Fig. 6. DSC trace and temperature dependence of fluorescence maxima of Fluoroprobe in PBT/PEG copolymer.

Fig. 7. TMA scan of the PBT/PEG copolymeric sheet.

Temperature-Dependent Fluorescence Measurements

In the second series of experiments the influence of temperature on the fluorescence of the incorporated probe molecules was investigated. Fluorescence spectra

were measured at different temperatures for Fluoroprobe in the PBT/PEG copolymeric sheets; for reference, DSC and TMA scans were recorded for the same samples. In Fig. 6 the change in the fluorescence maximum of Fluroprobe in the PBT/PEG sheet during a temperature scan is compared to a DSC scan of the same material.

The fluorescence maximum displays a continuous red shift between -50 and $0°C$ as a result of the slowly increasing mobility of the matrix. This red shift accelerates at $\sim 0°C$ (inset, Fig. 6), which seems to be a result of the melting of the PEG blocks (DSC trace in Fig. 6); this assumption was confirmed by thermal mechanical analysis (TMA; see Experimental) of the copolymer (Fig. 7). At $\sim 0°C$, the TMA signal starts to deviate from the baseline, revealing the start of the PEG melting process. In previous studies on homopolymers the fluorescence wavelength of probe molecules appeared to shift *hypsochromically* upon melting of the matrix (probably above the melting point solvation of the charge separated state becomes impaired as a result of the thermal motion of the matrix molecules [15,16]. The bathochromic shift encountered in this experiment upon melting of the PEG molecules must therefore be a result of the copolymeric

structure of the matrix: although the PEG molecules are molten, their covalent attachment to the PBT blocks limits their thermal motion to such an extent that more stabilization is experienced by the probe molecules!

At 20°C, the wavelength shift accelerates markedly. Upon closer examination of the fluorescence behavior in this temperature region (inset, Fig. 6), it is obvious that this acceleration takes places in a very small temperature region and is much steeper than the one encountered at 0°C. The TMA plot (Fig. 7) reveals that, around this temperature, the glass transition of the PBT blocks probably occurs (increasing acceleration of the elongation). Because this copolymer consists of 70 wt% PBT, one would indeed, as a result of increasing mobility, expect a large effect of the PBT glass transition on the fluorescence wavelength.

This rapid acceleration of the red shift sets in at ~20°C and levels off at ~40°C, after which the fluorescence wavelength continues to shift at a more or less constant rate. The large transition found in the DSC trace between 40 and 100°C is a result of the evaporation of adsorbed water from the sample;[5] this transition cannot be found in the fluorescence data. Apparently the loss of water does not effect the mobility and/or polarity of the probe's environment. Between 170 and 230°C the fluorescence maximum starts to shift hypsochromically, first slowly but, from 200°C on, at a more rapid rate. As observed before, above the melting point of a polymer, solvation of the charge-separated state becomes impaired as a result of the thermal motion of the matrix molecules [15,16]. From the observation that the shift is hypsochromic, and the transition encountered in the DSC trace, it can be concluded that it is a result of the melting of the PBT. Although the DSC trace clearly shows melting does not set in until ~200°C, the (small) blue shift encountered between 170 and 200°C can be explained satisfactorily by invoking the occurrence of premelting of small PBT crystals in this temperature region. The three transitions occurring in the copolymer in this temperature range can thus also be monitored by examining the fluorescence data of the incorporated probe molecules.

Finally, it was found that in the copolymer the fluorescence behavior is not reversible after the PBT has melted; when a sample was first heated to 230°C and subsequently cooled, the fluorescence wavelength was found to be blue-shifted compared to that before the melting of the PBT. Whether this is a result of changes

in the structure of the copolymer upon recrystallization or a redistribution of the probe molecules after subsequent melting and recrystallization has yet to be investigated.

CONCLUSION

The fluorescence approach presented here presents a very promising technique for the monitoring of physical changes that take place in copolymeric materials, as has been demonstrated by exposing a copolyether–polyester to thermal and mechanical treatment. It is surprising that a CT fluorescent molecular probe, which responds to changes in its direct environment, on a molecular level, shows such a strong response to physical modifications applied to the copolymer. The changes in the CTF spectrum correspond to the observations made with bulk material characterization methods, such as DSC, TMA, and stress–strain measurements. During the stretching experiments the initial loss of structure induced in copolymeric sheets fabricated by flat die melt-extrusion, and the subsequent orientation of polymeric chains can be followed. The fluorescence behavior follows directly and reversibly the stress–strain curve once the initial orientation has been lost and the curve exhibits rubber-like behavior. Upon variation of the temperature, not only various (phase) transitions, but also crystallization processes can be monitored, which can be attributed to the two components of the copolymeric material separately. Of these events, some are very hard to detect using conventional, bulk, characterization methods or require the application of additional techniques.

Obviously, the observation of the changes in the CTF spectrum is not sufficient to interpret the various processes which take place. The interpretation can be done only with reference to other measurements, which provide insight into the changes in the bulk morphology of the system and modifications induced in the structure on a molecular level. However, once the relation between the CTF and the structural changes has been established, the CTF, easily measured with fiber optic-based instrumentation, can be used for simple, on-line monitoring of material properties, which may be applied even to control processing parameters. Since only a very small amount of fluorescent probe needs to be applied due to the inherent sensitivity of the measurement (typically an amount below 1 μM suffices), the influence of the presence of the probe on the material properties is negligible.

[5] The absence of the PBT glass transition in the DSC scan was also confirmed by recording a DSC trace for a sample from which the water was first removed.

ACKNOWLEDGMENTS

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