Investigation of polymer blend miscibility using excimer fluorescence

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The excimer fluorescence of a random copolymer, poly(ethylene terephthalate-*co*-caprolactone) (TCL) containing 89 wt% ethylene terephthalate units, was used to investigate its miscibility with chlorinated poly(vinyl chloride) (CPVC). The thermally induced phase separation of TCL/CPVC blends can be observed by measuring the excimer to monomer emission intensity ratio I_E/I_M since the intermolecular excimer forming-site concentration is controlled by the extent of the TCL chain aggregation. Temperatures of phase separation can be determined by this method. The measurements indicate lower critical solution temperature (LCST) values in miscible TCL/CPVC blends which are below the values measured by differential scanning calorimetry. This result emphasizes the differences between the two methods and the greater sensitivity of fluorescence spectroscopy towards the detection of the beginning of the phase separation phenomenon.

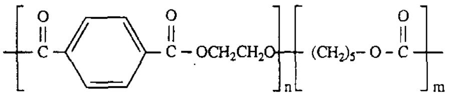
(Keywords: excimer fluorescence; miscibility; random copolymer; phase separation; differential scanning calorimetry)

INTRODUCTION

It is now established that a large number of polymer blends exhibit phase separation at high temperatures. Most often, this transition is detected by so-called cloud point measurements, i.e. the visual appearance of cloudiness upon an increase in temperature (it does not matter if the detector is an eye, or a photocell in a microscope, or a light scattering apparatus). This method is useless if the difference of refractive index between the two species is too small. It is also limited by the fact that a significant amount of scattering occurs only when structures of the order of the wavelength of the incident radiation have developed, which may require a long time to occur in the binodal region.

Therefore, there is a need to develop techniques which are able to probe the development of phases at a smaller level. Fluorescence spectroscopy is believed to be one of them. It has been shown[1] that, with a suitable choice of chromophores, the measurement of the non-radiative energy transfer (NRET) between fluorescent labels attached to the polymers characterizes the polymer miscibility at scale of about 3 nm. Among other useful fluorescence techniques, two examples can be mentioned: the quenching of the anthracene chromophore attached to polystyrene (PS) by the ether functions of poly(vinyl methyl ether) (PVME) was used to determine both the spinodal and binodal phase diagrams in PS/PVME blends[2]; also, the excimer fluorescence in polymers containing aromatic side groups, such as PS and poly(vinyl naphthalene), was used to investigate their miscibility with other polymers and to study quantitatively their kinetics of phase separation[3,4].

In this paper, the use of excimer fluorescence of a polymer containing aromatic groups in its main chain was examined. A random copolymer, poly(ethylene terephthalate-*co*-caprolactone) (TCL) containing 89 wt% ethylene terephthalate units was used:



Studies about the intrinsic fluorescence of poly(ethylene terephthalate) (PET) indicate that an excimer emission is observed at about 380 nm upon the excitation of monomeric units at 300 nm and below[5–9]. The fluorescent states of the excimer are populated by efficient energy migration from the excited monomeric units, which have their emission spectrum centred at about 330 nm, to the excimer-forming sites, each of which is formed by two aromatic rings having a coplanar sandwich geometry. It should be noted that the emission around 380 nm can also arise from the presence of a groundstate dimer which can be directly excited at about 340 nm, but which is not observed when the excitation occurs below 300 nm (ref. 9).

Since PET contains aromatic rings in its main chain, the formation of an intramolecular excimer between rings located in two adjacent repeat units is not possible. However, two other types of excimers, characteristic of the chain interactions, can be formed: excimers can be formed either intramolecularly between non-adjacent rings or intermolecularly between rings in different chains. Therefore, the intrinsic fluorescence of PET can be considered as being a molecular probe of its miscibility with other polymers. With an excitation of the monomeric units at the appropriate wavelength, due to the high efficiency of energy migration, it is reasonable to assume that the excimer fluorescence intensity of PET is

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controlled by the concentration of excimer-forming sites; this concentration increases in a blend with the PET chain aggregation resulting from phase separation, but decreases upon dilution with a second polymer in the miscible state.

In this study, solution-cast films of the PET copolymer mentioned above, TCL, and blends with chlorinated poly(vinyl chloride) (CPVC) have been prepared. It will be shown that, under suitable conditions, the excimer to monomer emission intensity ratio is indeed related to the blend miscibility and allows the determination of temperatures of phase separation.

EXPERIMENTAL

The synthesis and characterization of the TCL copolymer have been described elsewhere[10]. This copolymer, containing 89 wt% ethylene terephthalate units (intrinsic viscosity = 0.68 dl g^{-1}), was blended with CPVC (M_w = 100 kg mol^{-1}, BF Goodrich, Breckville, OH, USA). Films having a thickness of about 20 μm were obtained by casting 2% isobutane solutions onto glass plates. They were dried under vacuum at room temperature over at least 2 weeks in order to remove any residual solvent. Using this procedure, no crystallization of the ethylene terephthalate units was observed.

Differential scanning calorimetry (d.s.c.) measurements were carried out with a Perkin–Elmer DSC-4 apparatus calibrated with indium, at a heating rate of 20°C min^{-1}. The investigation of phase separation was performed with the following annealing cycle: the samples were first cooled to −100°C for 5 min, and a first scan was then made at a heating rate of 200°C min^{-1} up to the chosen annealing temperature. The sample was maintained for 3 min at that temperature and quenched to −100°C. It was left again for 5 min at that temperature before a second scan at a heating rate of 20°C min^{-1} to an annealing temperature 10°C above the annealing temperature of the previous scan.

Fluorescence emission measurements were made using a Shimadzu RF-540 spectrofluorophotometer with a band pass of 5 nm. The samples were excited at 290 nm using front-face illumination with the sample surface oriented 60 and 30° relative to the incident exciting beam and the axis of observation, respectively. The emission spectra were not corrected for the wavelength-dependent efficiency of the photomultiplier tube.

RESULTS AND DISCUSSION

The fluorescence emission spectra of PET and TCL, in bulk and in trifluoroacetic acid solution (9 × 10^{-4} M), are given in *Figure 1*. It can be seen that the spectrum of the TCL film is very similar to that of PET, with a dominant excimer emission in the 380 nm region and a smaller monomer emission at about 330 nm. Similar spectra were recorded for other TCL copolymers containing more caprolactone units (up to 60%)[10]. This result indicates that the random incorporation of the caprolactone units in the PET chain does not alter its emission properties in the solid state; the efficient energy migration from excited monomeric units to excimer-forming sites leads to a dominant excimer emission. In contrast, as can be expected, both PET and TCL dilute solutions show only the monomer emission, with a maximum emission intensity at about 330 nm.

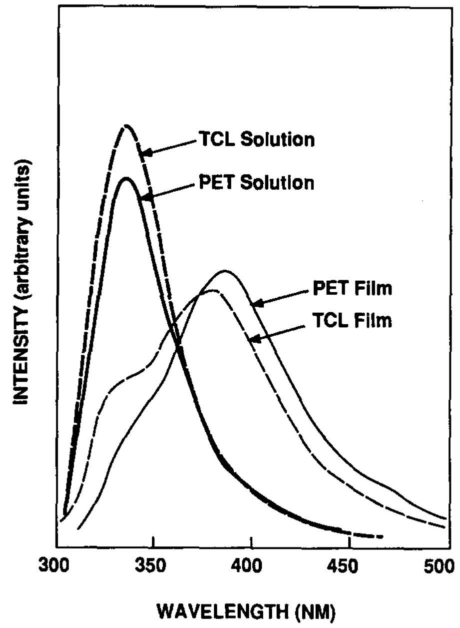

Figure 1 Emission spectra of PET and TCL in bulk and in trifluoroacetic acid solution (9 × 10^{-4} M)

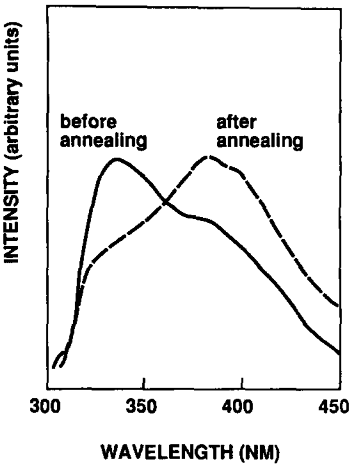

Figure 2 Emission spectra of the TCL/CPVC blend containing 30% TCL before (———) and after (---) annealing at 160°C

Figure 2 gives the emission spectra of a TCL/CPVC blend containing 30% TCL, before and after annealing at 160°C. It can be seen that the sample before annealing (this sample was kept all the time at room temperature after solution casting) exhibits a dominant monomer emission, although, unlike the spectrum taken in dilute solution, some excimer emission also takes place; in contrast, the emission spectrum of the annealed sample is similar to that of TCL in the bulk, showing a dominant excimer emission. These observations indicate that phase separation was induced in the miscible blend at 160°C. Differential scanning calorimetry measurements show a single value of the glass transition temperature (T_g) before annealing[10]. The TCL chains are then diluted by CPVC chains and the excimer-forming sites have a lower concentration. However, annealing leads to more aggregation of the TCL chains and, thereby, to an increased intensity of the excimer fluorescence.

In order to further check this interpretation, i.e. the evolution from a one- to a two-phase system, the same miscible TCL/CPVC blend was annealed at different

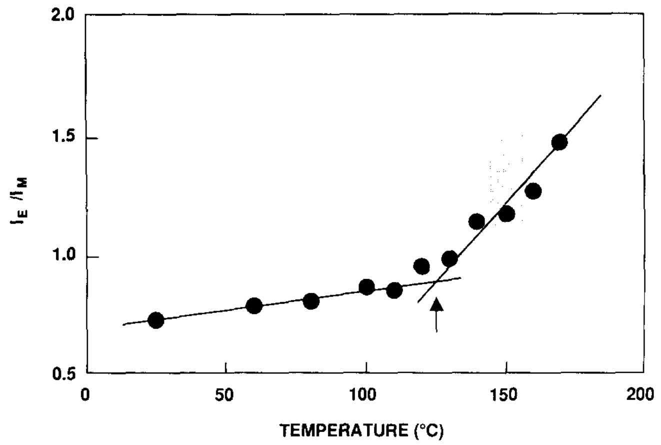

Figure 3 I_E/I_M ratio *versus* annealing temperature for the TCL/CPVC blend containing 30% TCL. The d.s.c. range of the glass transition is the shaded area

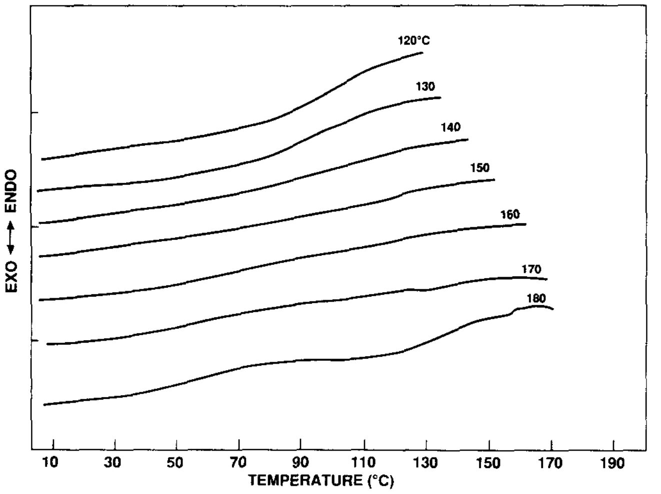

Figure 4 Differential scanning calorimetry thermograms of the TCL/CPVC blend containing 30% TCL annealed at different temperatures

temperatures for 3 min, and the fluorescence emission measurements were carried out, after quenching the film to room temperature. Even if the process of phase separation is in principle thermodynamically reversible, quenching at room temperature, i.e. in the one-phase region, will not permit the homogenization to occur, since room temperature is below the T_g of the system and, under these conditions, the diffusion of the molecules is almost stopped.

In *Figure 3*, the emission intensity ratio of excimer to monomer, I_E/I_M, measured at 380 and 330 nm, respectively, is plotted as a function of the annealing temperature. It shows that the I_E/I_M value increases very slightly up to about 110°C and then there is a sharp increase above 120°C. The intersection of these two straight lines at about 125°C, marked by an arrow, which corresponds to the beginning of a significant increase in the aggregation of the TCL chains, can be taken as the temperature of phase separation (T_d). The temperature of phase separation obtained by d.s.c., as shown in *Figure 4*, is also indicated.

Figure 4 gives the d.s.c. curves for this blend under the annealing cycle described above. These thermograms show a single T_g up to 130°C, then a broadening of the glass transition zone at 140°C, and, finally, two T_gs can be distinguished at 150°C and above. The temperature of phase separation was hence considered to be around 150°C, which is higher than that determined from *Figure 3* (125°C).

Figure 5 gives the temperature of phase separation of several TCL/CPVC blends, determined from both the fluorescence method and the d.s.c. measurements. The error bars indicate the estimated uncertainty of the measurements. It can be seen that the values obtained by excimer fluorescence are generally below those obtained by d.s.c. This result indicates a higher sensitivity of the fluorescence technique as compared with d.s.c. for the determination of the temperature of phase separation. This can be ascribed to the fact that the increase in the intensity of excimer fluorescence results from an increase in the extent of chain aggregation, irrespective of the phase size; it can occur even at the beginning of the phase separation. In contrast, the d.s.c. measurements probe the phase separation through the appearance of two T_gs, which can be detected only when the phase domains of one component are larger than 10 nm (ref. 11). However, in blends where TCL is the major component, like that containing 70% TCL (*Figure 5*), the excimer fluorescence method becomes less sensitive than it is at smaller TCL concentrations, since a large amount of chain aggregation is already present before the phase separation, such that a significant increase in the intensity of excimer fluorescence is observed at relatively late stages of the phase separation.

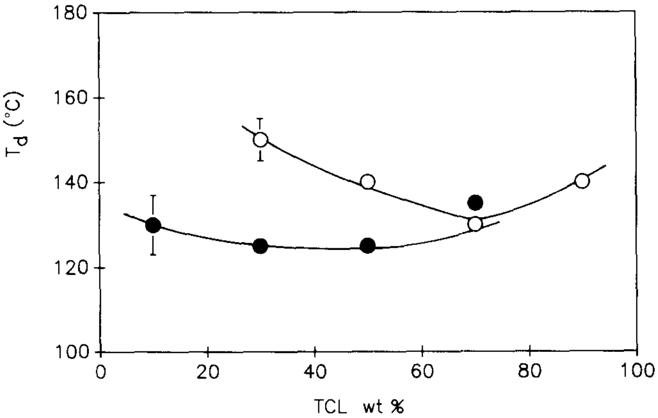

Figure 5 Phase separation temperatures in TCL/CPVC blends determined by d.s.c. (○) and excimer fluorescence (●) measurements

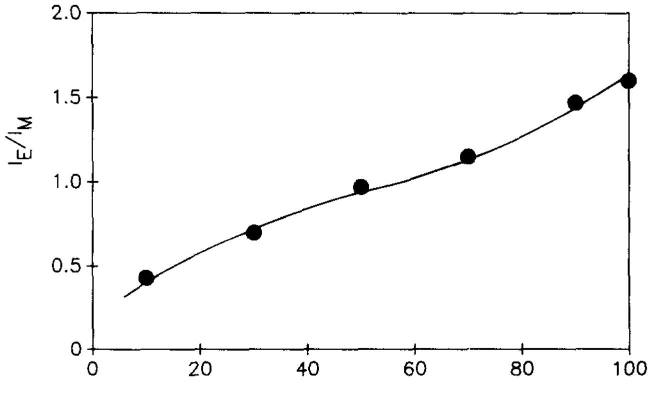

Figure 6 I_E/I_M ratio as a function of the TCL concentration in miscible TCL/CPVC blends

The concentration-dependent I_E/I_M ratio of miscible TCL/CPVC blends is shown in *Figure 6*, where the I_E/I_M value is plotted as a function of the TCL concentration. It is seen that this ratio increases significantly with the TCL content, in spite of the fact that each of these blends is miscible. The I_E/I_M value for bulk TCL, 1.6, can be taken as a reference value for the phase-separated blends containing two phases of pure TCL and CPVC since CPVC does not contribute to the fluorescence emission. Hence, it can be noted that the difference in the I_E/I_M ratio between miscible and immiscible blends decreases rapidly with increasing the TCL concentration, with I_E/I_M values of 0.7 for the blend containing 30% TCL but 1.15 for the blend containing 70% TCL.

The change of the emission intensity ratio of excimer to monomer with blend miscibility can also be used to investigate the kinetics of phase separation, as has been done by Frank *et al.* for polymers containing aromatic side groups[3,4]. As shown in *Figure 7*, where the evolution at 160°C of I_E/I_M of a TCL/CPVC blend containing 30% TCL is plotted as a function of time, there is a rapid increase of this ratio in a period of about 5 min, indicating phase separation, but the I_E/I_M ratio becomes constant after 10 min. A quantitative analysis of this curve would require the knowledge of the ratio of the intrinsic quantum yields of excimer and monomer fluorescence, which has not yet been determined for TCL.

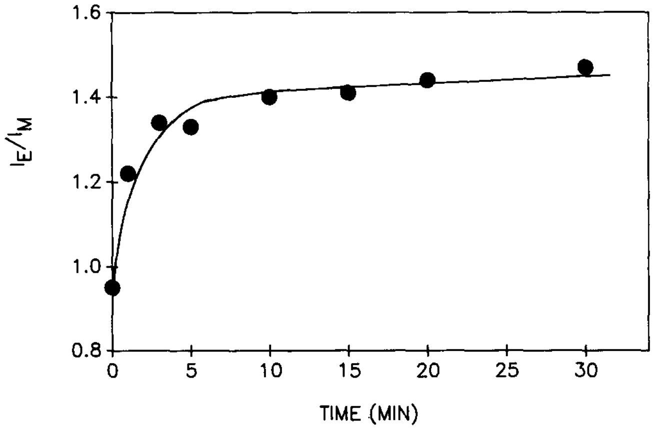

Figure 7 I_E/I_M ratio *versus* annealing time for the TCL/CPVC blend containing 30% TCL at 160°C

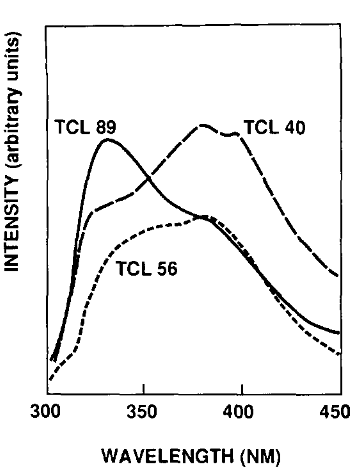

Figure 8 Emission spectra of miscible TCL/CPVC blends containing the same ethylene terephthalate unit concentration (27%) but made by using TCL copolymers having different ethylene terephthalate contents: 89% (TCL 89); 56% (TCL 56); 40% (TCL 40)

It is also interesting to look at the emission spectra (*Figure 8*) of three TCL/CPVC blends made by using TCL copolymers containing 89, 56 and 40 wt% ethylene terephthalate units, which are referred to as TCL 89, TCL 56 and TCL 40, respectively; for these spectra, blend compositions were chosen such that the ethylene terephthalate unit concentration in each blend was 27%. In spite of the miscibility of these three samples indicated by the d.s.c. measurements[10] and their concentration of fluorescent units which is the same, the excimer to monomer emission intensity ratios are very different, with the larger values shown by the blend having 70% TCL 40, corresponding to a large number of the TCL chain interactions. Conversely, the lower excimer emission values are found for the blend containing 30% TCL 89, in which the TCL chains are more diluted by the CPVC chains. This result reveals the intermolecular rather than intramolecular nature of the excimer in these copolymers.

Measurements have also been made in TCL blends with poly(vinyl chloride) (PVC). In agreement with a d.s.c. study[10], the results indicate in general the immiscibility of those blends, with higher emission intensity ratios of excimer to monomer as compared with blends prepared with CPVC. However, these I_E/I_M values are still smaller than the value found for bulk TCL, 1.6. There is also an increase of the emission intensity ratio with the TCL concentration, although much smaller than that observed in TCL/CPVC blends. These observations indicate the absence of pure PVC and TCL phases in these phase-separated blends.

CONCLUSIONS

Using a random copolymer of TCL containing 89 wt% ethylene terephthalate units, it is shown that I_E/I_M is related to the blend miscibility. This behaviour is related to the fact that the intermolecular excimer-forming site concentration is controlled by the extent of chain aggregation. In the immiscible state, there is a large number of chain interactions, resulting in a higher concentration of the excimer-forming sites, while in the miscible state, the chains are diluted by the CPVC chains, leading to a smaller concentration of excimer-forming sites. It is demonstrated that I_E/I_M can be used to determine the temperature of phase separation. In blends with a fluorescent polymer as the minor component, the fluorescence method exhibits a higher sensitivity than d.s.c. In other words, it 'sees' the very beginning of phase separation at temperatures where the T_g measurements still indicate miscibility.

The use of a polymer intrinsic fluorescence to investigate the blend miscibility is attractive since there is no need to attach fluorescent labels to the polymers. Hence, the sample is not perturbed by the presence of a large size chromophore. This method can certainly be extended to other PET-type polymers, such as, for example, poly(butylene terephthalate) which exhibits similar emission properties[7]. Polymers containing aromatic groups in the main chain and exhibiting an intermolecular excimer emission are suitable candidates for this sort of investigation since the intermolecular excimer fluorescence intensity is related to the chain interactions for different types of excimer.

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