

Ruthenium tetroxide staining of polybutylene terephthalate (PBT) and polyisobutylene-*b*-PBT segmented block copolymers

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A ruthenium tetroxide (RuO_4) staining method has been evaluated for segmented polyisobutylene-*b*-polybutylene terephthalate (PIB-*b*-PBT). Solution cast films and melt pressed samples have been studied. For comparison PBT has also been studied. PBT and PIB-*b*-PBT could be stained with RuO_4 at room temperature. The observed structures on the PBT and PIB-*b*-PBT films were spherulitic with lamellae. In some regions in the PIB-*b*-PBT films large scale phase separation was observed. In the melt pressed PIB-*b*-PBT samples the spherulitic and lamellar structures were less well developed. The PBT segments appeared to have crystallized out in bundles and the PIB phase was present as microspheres with diameters of 3–6 nm.

(Keywords: polyisobutylene; polybutylene terephthalate; segmented block copolymer; staining; ruthenium tetroxide; structure)

Introduction

Segmented telechelic polyisobutylene-*b*-polybutylene terephthalate (PIB-*b*-PBT) is a thermoplastic elastomer. Segmented block copolymers are built from soft and hard segments and have a lamellar structure¹.

Segmented block copolymers, like polyether-polyesters, are two-phase materials with one amorphous and one crystalline phase. The structure is like that in semicrystalline homopolymers, namely spherulitic with lamellae¹.

The block copolymer PIB-*b*-PBT (30/70) has two glass transitions and a melting temperature and is thus a three-phase system^{2,3}. The lowest glass transition at -65°C is from the PIB phase, the glass transition at 35°C is from the amorphous PBT-rich phase and the melting temperature at 210°C is from the crystalline PBT phase. The crystallinity of the PBT phase is in the order of 30%. The volume ratios are: PBT crystalline 20%, PBT amorphous 40% and PIB 40%.

To study the relationship between the structure and properties of these materials the polymer morphology was studied using transmission electron microscopy (TEM). Osmium tetroxide (OsO_4) is the most commonly used chemical for staining polymers with some degree of unsaturation^{4–6}. PIB and its isomers are difficult to stain with OsO_4 due to their high degree of saturation. Ruthenium tetroxide (RuO_4) is a comparatively new staining agent and is known^{7–10} to be a stronger oxidizing and a more versatile agent than OsO_4 . RuO_4 staining has successfully been used for segmented copolyesters¹¹, polyesterurethanes^{12,13} and polyetherurethanes¹⁴. One method of staining with RuO_4 starts from ruthenium trichloride and sodium hypochlorite¹⁵. It was found that *in situ* RuO_4 obtained in this way appears to be at least as effective as commercial RuO_4 .

The aim of this study is to evaluate the staining of PBT and segmented PIB-PBT and to study the structure of PIB-*b*-PBT segmented block copolymers using RuO_4 as the staining agent.

Experimental

Materials. PBT and telechelic PIB-*b*-PBT were synthesized in the melt^{16,17}. The PIB-*b*-PBT contained 30 wt% PIB with a block length of 1500 g mol^{-1} . The PIB contained an unsaturated group at its chain end. The inherent viscosity¹⁶ of a 1% solution of the polymer in phenol/1,1,2,2-tetrachloroethane (50/50) at 25°C is 1.69 dl g^{-1} .

Sample preparation for TEM. NaIO_4 (supplied by Merck) was dissolved in deionized water (25°C) 1 day before staining and kept in a refrigerator overnight. $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ (supplied by Janssen) was added to the chilled NaIO_4 solution 5 min prior to use. As $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ began to dissolve, an olive green solution was formed. It was found that the quicker the container was filled and closed the longer the solution stayed green. It was established that if these precautions were taken the liquid stayed green at room temperature for up to 72 h and at 75°C for up to 4–5 h.

The polymer samples were dissolved in a mixture of 1,1,2,2-tetrachloroethane and phenol (1:1 mol/mol) to obtain a 0.5 wt% solution. Glass slides were dipped in the solution. The solvent was evaporated at 160°C to leave thin films which were first floated off onto the water surface and then transferred to microscope grids. Some thin films on glass slides and other films on microscope grids were exposed to RuO_4 vapour. The samples were stained in glass-covered dishes at room temperature for 15 min (ref. 18), 1, 3 and 5 h and at 75°C (above the glass transition of PBT) for 3 h.

Melt pressed bars were obtained by heating dry PIB-*b*-PBT in a press to 250°C and cooling under

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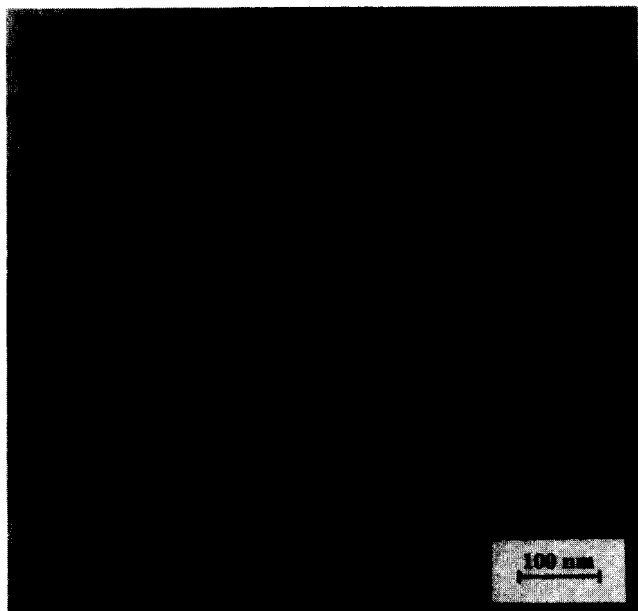


Figure 1 Electron micrograph of PBT film stained with RuO₄ for 1 h at room temperature

pressure at $\sim 20^\circ\text{C min}^{-1}$. For structure analysis the middle sections of the melt pressed bars were trimmed with a razor blade to form a trapezoidal top with a cutting surface of $100\ \mu\text{m}^2$. A LKB Nova ultramicrotome fitted with a diamond knife was used for sectioning. The cutting speeds were in the range of $5\text{--}20\ \text{mm s}^{-1}$.

Cryogenic sectioning was conducted with the specimen cooled down to -100 to -110°C and the knife cooled to -50 to -70°C . Unfortunately the sections obtained were statically charged and difficult to handle. The sections were removed from the knife edge with an eyelash and then transferred to a 2 mm wide wire loop filled with a concentrated aqueous sucrose solution. The sections with the sucrose drop were placed on the grids and the sucrose washed away. The slices were stained in RuO₄ vapour for 16 h at room temperature.

Staining the trimmed sample first and then sectioning at room temperature was also used. With this method the sections were much easier to handle and sections with the right contrast could be chosen for analysis. Staining of the trimmed samples was carried out by suspending the bar in aqueous RuO₄ solution for 24 h at room temperature or 16 h at 75°C (twice refreshed).

Transmission electron microscopy. The micrographs of the films were taken with a Jeol JEM-200CX transmission electron microscope operated at an accelerating voltage of 200 kV. The image wobbler was used for focusing at calibrated magnifications of $\times 50\,000$ or below.

Results and discussion

PBT. (1) Film. On the unstained solution cast PBT films only a vague structure could be observed. If stained for 1 h at room temperature a spherulitic structure becomes visible (Figure 1) and the lamellae are 11–13 nm thick. Staining for longer times or at higher temperature (75°C) gave similar results.

(2) Melt pressed. With cryogenic sectioning of melt pressed samples it was very difficult to obtain smooth slices. A lamellar structure could be observed but the

overall quality of the images was not so good as for the films. Neat sections could be obtained by cutting stained bars at room temperature. If the bars are stained for 15 h at 75°C the depth of staining is $1.5\text{--}2.5\ \mu\text{m}$. Good quality images could be obtained from a depth of $1.4\ \mu\text{m}$. The edges of the slices were usually damaged by the oxidizing effect of RuO₄. The lamellae of the melt pressed samples are 9–10 nm thick.

PIB-b-PBT (30/70). (1) Film. PIB-b-PBT-cast film could be stained at room temperature in 15 min (Figure 2). Staining for longer times or at higher temperature (75°C) gave similar results. The structure of the block copolymer is spherulitic with 9–10 nm thick lamellae. The observed structure is the same as for polyetherester^{19,20} and polyetheramide^{21,22} block copolymers. At lower magnifications dispersed droplets ($0.6\text{--}7\ \mu\text{m}$) with a weaker contrast were observed. This means that in these films next to a lamellae structure of the block copolymer a macro dispersed phase is also present.

(2) Melt pressed. The melt pressed samples could best be sectioned at room temperature after staining at room temperature. Staining at 75°C is also possible.

The structure in the melt pressed samples is also lamellar (Figure 3a). The lamellae are the least stained areas and they are most probably the crystalline PBT phase. With d.s.c. it was found that the heat of melting did not change with staining, suggesting that the crystalline phase was not stained. The lamellae are stacked in prespherulite/sheaf-like structures which seem to be twisted. The lamellar spacing is either very small (2–3 nm) or relatively large (8–14 nm). The very small spacing was seen as an 'edge on' view and the larger spacing as a 'tilted' view of a lamella. At other places bundle-like structures were visible (Figure 3b). The bundles are 100–600 nm and are positioned at different angles to the cut view plane. These bundles seem to consist of a matrix with rod-like unstained phases with thicknesses of 3–6 nm and heavily stained regions (spheres 3–6 nm). At the boundaries between the bundles

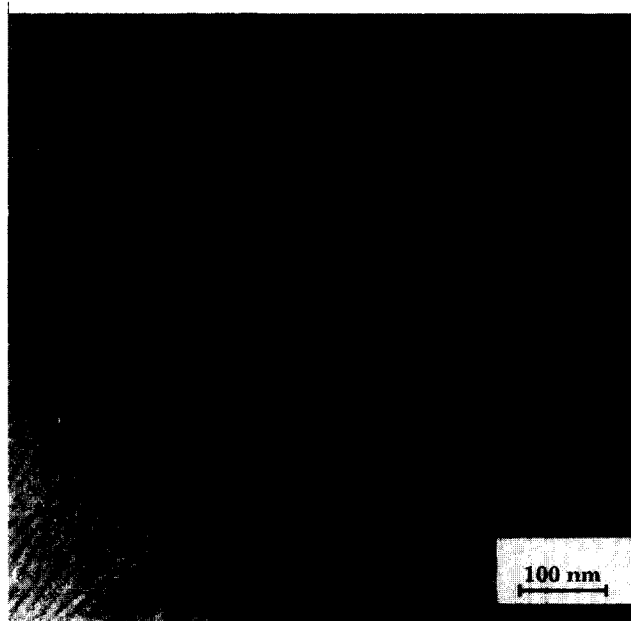


Figure 2 Electron micrograph of PIB-b-PBT film stained with RuO₄ for 15 min at room temperature

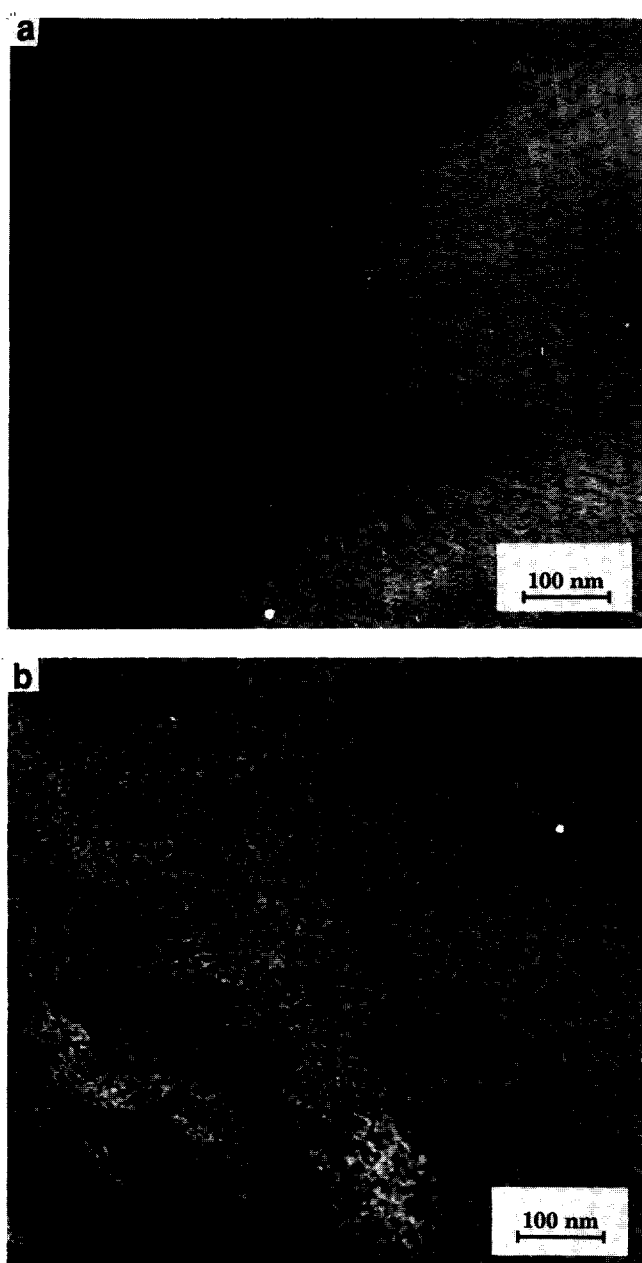


Figure 3 Electron micrographs of different regions in a PIB-b-PBT melt pressed sample first stained with RuO₄ for 24 h at room temperature and then microtomed: (a) lamellae visible; (b) bundle-like structures visible

the concentration and size of the heavily stained material is higher. The unstained material is thought to be crystalline PBT and the heavily stained regions PIB.

Conclusions

The RuO₄ staining technique was applied to PBT and PIB-b-PBT for morphological studies by TEM. Effective staining at room temperature is possible. For bulk samples it is preferable to stain the sample before microtoming at room temperature.

The structure of PIB-b-PBT (30/70) solution cast films is spherulitic with 9–10 nm thick lamellae. In some areas large scale phase separation takes place.

The melt pressed sample had a less well developed spherulitic structure and the lamellae seem to be twisted. In some places a bundle-like structure was observed with domain sizes of 100–600 nm where the PIB phase was present as 3–6 nm diameter microspheres.

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