

Graphene Oxide: a novel support for Transmission Electron Microscopy of Polymers

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The design and synthesis of self-assembled block amphiphilic copolymers are of interest for the preparation of multifunctional polymeric nanostructures. By tuning the hydrophilic/hydrophobic balance of these polymers a range of morphologies can be accessed, including spherical micelles, cylinders and vesicles. These materials are of potential interest in applications such as nanoreactors or delivery vehicles [1,2]. However, accurate nanometre scale measurement of morphology is essential in order to give control and optimize these systems. Although transmission electron microscopy (TEM) and associated analytical techniques can supply information about morphology and chemical composition at sub-nanometre levels, scattering from light elements is weak. This leads to very low contrast when this type of specimen is examined upon a conventional support film such as amorphous carbon or formvar. The most common approach to overcome this problem is to stain the specimen with a heavy element (e.g. using OsO₄, or Phosphotungstic Acid PTA) to increase contrast, allowing morphology and the polymer phases in the system to be visualized. Nevertheless, staining is an invasive technique which may affect the morphology, can lead to significant and misleading artifacts, and make compositional analysis difficult or impossible. Analysis of polymer systems without staining would represent a major step forward.

Graphene is a highly electron-transparent material, as it consists of a single sheet of carbon atoms. It has found applications in recent years as a support film for nanoparticle analysis [3], but has the disadvantage that manufacture of graphene coated grids is both time-consuming and expensive and that graphene itself is hydrophobic. Graphene oxide (GO), however, is hydrophilic and water soluble, and large areas of single-sheet GO for use as TEM support films are extremely easy to prepare by drop casting methods. Furthermore, the chemical manufacture of GO is also simple and is a very low-cost process in comparison with graphene. GO retains the hexagonal symmetry of the unmodified graphene without any ordering in the functional groups [4]. It has been also demonstrated by TEM that GO is highly electron transparent and stable under the electron beam. The electron transparency of GO is close to that of graphene itself, and its hydrophilicity makes it easy to deposit samples directly from solution, and consequently it is an ideal support film for self-assembled diblock copolymer nanostructures. Furthermore, the chemistry of the GO surface can be tailored by further functionalisation, opening up the possibility of new fields of experimentation.

In this work, we show how diblock copolymer systems can be imaged on GO allowing morphological and compositional analysis to be carried out without staining. GO support films were prepared by drop casting from a 0.25 mg ml⁻¹ GO aqueous suspension onto a lacy carbon TEM grid. The diblock co aggregates, consisting of Polylactide (aka Polylactic acid, PLA) (Hydrophobic) and Poly acrylic acid (PAA) (hydrophilic), were deposited directly onto this support and examined in a JEOL 2100 LaB₆ TEM operating at 200 kV. A typical image is shown in Fig. 1. The contrast in this TEM image arises from both mass-thickness and phase contrast mechanisms. To enhance the phase contrast, the image was recorded in under-focus conditions, i.e. inducing a phase shift of the scattered electrons. It is evident from the structural characterization of the unstained diblock copolymer on GO is that there is a wall

thickness of ~ 2 nm which could not be observed in the stained specimen Fig. 2. Additionally, the stained specimen does not reveal the presence of both open and closed cylinder nanostructures as can be observed in the specimen prepared directly on the GO support. The mottled background is contamination arising from the diblock copolymer deposition, its removal will enable further advances in resolution and detailed analysis of these self-assembled nanostructures.

References

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Figures

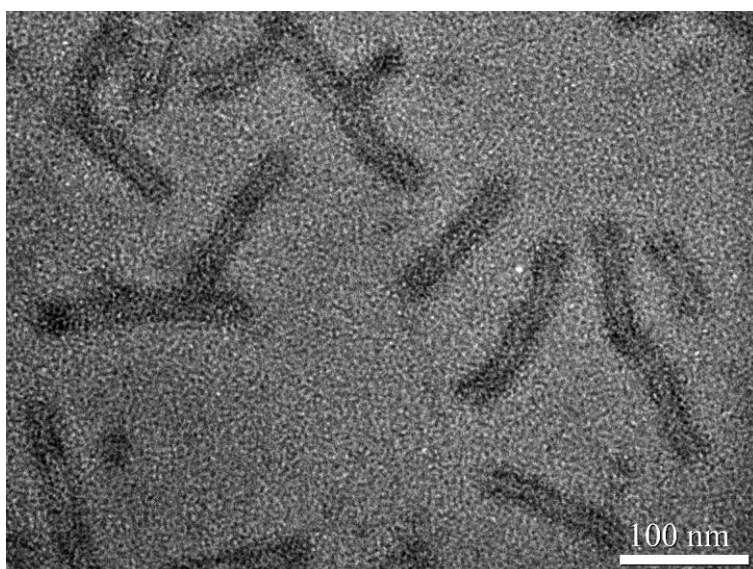


Figure 1. TEM image of the copolymer deposited directly on the GO support film.

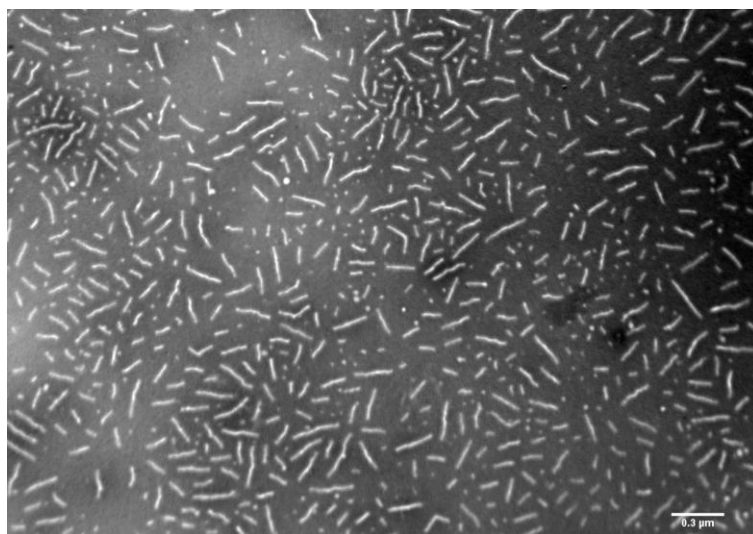


Figure 2. TEM image of the PTA-stained copolymer on a carbon support film.