Kinetics of the water swelling of amphiphilic diblock copolymers with adhesive properties

Centre de recherche Paul-Pascal, CNRS and Bordeaux-1 Univ. Frédéric NALLET [1]

1 Introduction

Asymmetric diblock AB copolymers, in the case where the longer block A is both hydrophobic and "soft", whereas the shorter block B is hydrophilic and "hard" are the subject of this study. Materials with such a particular combination of physico-chemical and mechanical properties have distinctive advantages, in particular for designing water-compatible adhesive materials. Here, we report about the kinetics of the swelling with water of such materials, as monitored through gravimetry and–in some sense–"time-resolved" small-angle x-ray scattering (SAXS). Disordered, as well as 3D-, 2D- or 1D-ordered structures are all found to absorb significant amounts of water.

2 Gravimetry

A climatic test chamber is used for the kinetic study at short and intermediate times. Samples, deposited as films of thickness 100 μm onto metallic substrates, are weighed at regular time intervals for about one day. This experiment gives direct access to the kinetics at intermediate times, *i.e.* in the range 10^2–10^4 s, with a satisfactory description in terms of a Fickian behaviour and indirect evidences for plasticisation at short times. It also reveals the occurrence of non-Fickian processes in the long-time limit, better investigated with SAXS–see below.

As far as gravimetry is concerned, the structured amphiphilic copolymers, although featuring a mostly hydrophobic matrix, are found to essentially behave as homogeneous, effective media. The materials exhibit a high hydrophilic character linearly increasing with the amphiphilic content, whereas water diffusivity simultaneously decreases.

3 Small-angle x-ray scattering

The structural characteristics of the slow relaxation phenomena evidenced by gravimetry have been studied by SAXS. Though a conventional x-ray source has been used (with spectra recorded in typically 4×10^3 s), the study is nearly "time-resolved", thanks to the large value of the associated characteristic times, in the range of 10^5 s. Depending on the composition of the (initially

[1]E-mail: nallet@crpp-bordeaux.cnrs.fr

dry) block copolymers, the uptake of water leads to either simple swelling–the initial microstructure is preserved during the swelling process–or to structural transitions. In the latter case, the transition is most often directly revealed by a qualitative analysis of the spectra. Evidence for a "hidden", swelling-induced body-centred-to-face-centred cubic structural transition will be discussed in terms of a detailed analysis of the SAXS spectra, as given by the example displayed in Fig. 1.

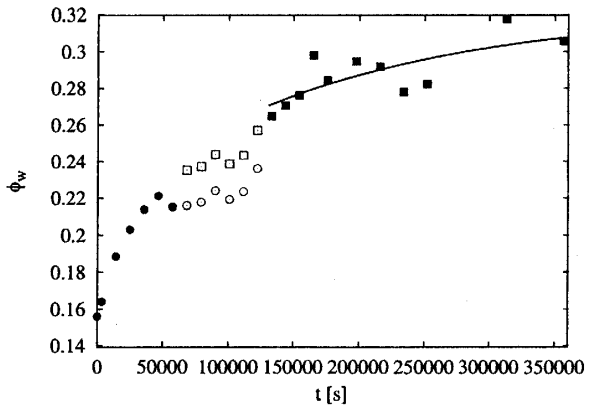

Figure 1: Time dependence of the amphiphilic domain volume fraction ϕ_w, assuming a bcc structure at shorter times (○ or ●), and a fcc one at longer times (□ or ■). The structural transition takes place in the range where open symbols are used

Simple swelling, as well as swelling-induced structural transitions imply that the large amounts of water accommodated within the amphiphilic materials require local and slow copolymer chain rearrangements.

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A more complete account of this work can be found in Ref. [2].

References

[1] K. Schierholz *et al.*, Macromolecules **36** (2003) 5995

[2] S. Poivet *et al.*, Eur. Phys. J. E, to appear (2006)