

Thin films of polymers

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Polymers in thin films are exiting class of materials since they can exhibit different properties from the bulk due to limited amount of matter and surface interactions. Consequently, phenomenon like nanostructuration arising from self-organization of block polymers, phase separation, crystallization or swelling in solvent vapors can be greatly affected in thin films. In this presentation, we will highlight this specific behavior by selected recent examples of our group.

As a first example, we will deal with the self-organization of a poly(styrene)-block-poly(isoprene)-block-poly(lactide) copolymer (PS-*b*-PI-*b*-PLA) for which the strong incompatibility between the adjacent PI and PLA blocks places the copolymer in a situation of intense frustration.¹ For volume fractions that normally lead to lamellar structures ($f_{PS} = f_{PI} = f_{PLA}$) we have shown that this situation leads, in volume, to the formation of an unexpected cylindrical core/shell morphology, with a non-constant curvature PS/PI interface. The effect was exalted in the thin film situation, where the formation of exotic morphologies such as spheres on cylinders has been observed.

Phase separation between incompatible homopolymer can also shows singular behavior in thin films. That was demonstrated in films of blends of polystyrene (PS) and polylactide (PLA), with thicknesses ranging from 20 nm up to 400 nm.² We showed that depending on the dip coating deposition parameters, various morphologies such as layered film and laterally phase-separated domains were formed for a given blend/solvent pair. In selected conditions, laterally phase-separated domains with sub- μm size (as small as 20 nm in the optimal conditions) could be formed. In this later case, the selective extraction of one of the components in the blends provided useful platforms for the generation of nanomasks that were used as (i.) templates for the formation of inorganic nanostructures and (ii.) nanomasks for silicon plasma etching.

Dip coating process was also used to control the crystalline structure of thin films of poly(L-lactic acid) which can be of great importance for applications where mechanical or optical properties are involved.³ Thin films were studied by Atomic Force Microscopy and Grazing Incidence Angle X-ray Diffraction. Withdrawing the silicon substrate in the draining regime (at high speed) led to amorphous films with flat surface whatever the solvent and the molar mass. At low speeds (capillary regime), AFM demonstrated the presence of spherulites or hedrites in the films depending on the solvent and the molar mass. GIXRD showed that spherulites were less crystallized than hedrites.

In a last part of the presentation, we will deal with polymer-solvent interaction. Polymer-solvent affinity, estimated from the Hansen Solubility Parameters (HSP), was compared to experimental results of dissolution and swelling of polymer prepared in the specific form of thin film. This was carried out for 3 common polymers (PS, PLA, PMMA)⁴ and a new range of poly(glycidyl carbamate) obtained from the direct polymerization of glycidyl carbamates.⁵ The observed deviations were attributed to the inability of the HSP theory derived from data acquired in polymer solutions to be extrapolated to the particular case of swollen polymer films.

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