

Block copolymer nanostructures in commodity plastics: why and how it works

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In this era of portability and rapid technological advances, polymers are more than ever under pressure to be cheap and offer tailored property profiles. Often, the key lies in designing blends and alloys of existing polymers carefully structured at the submicrometer or nanometer scale. Block copolymers — two or more different polymer chains linked together — offer a technologically attractive and versatile solution to fabricate such nano-structured heterogeneous plastics. Local segregation of mutually incompatible polymer blocks yields self-assembly and molecular scale aggregates of tunable size.

When blended with homopolymers presenting selective affinity for one block type, block copolymers act as macromolecular surfactants and can stabilize a wide range of dispersions at the nano-scale with combinations of mechanical, optical, electrical or barrier properties difficult to achieve otherwise¹. These copolymer dispersions include micelles (spherical or cylindrical), vesicles and other bi-layer aggregates, disordered co-continuous phases or lyotropic lamellar, hexagonal or cubic ordered phases, depending on concentration (Fig.1)^{2,3,4}.

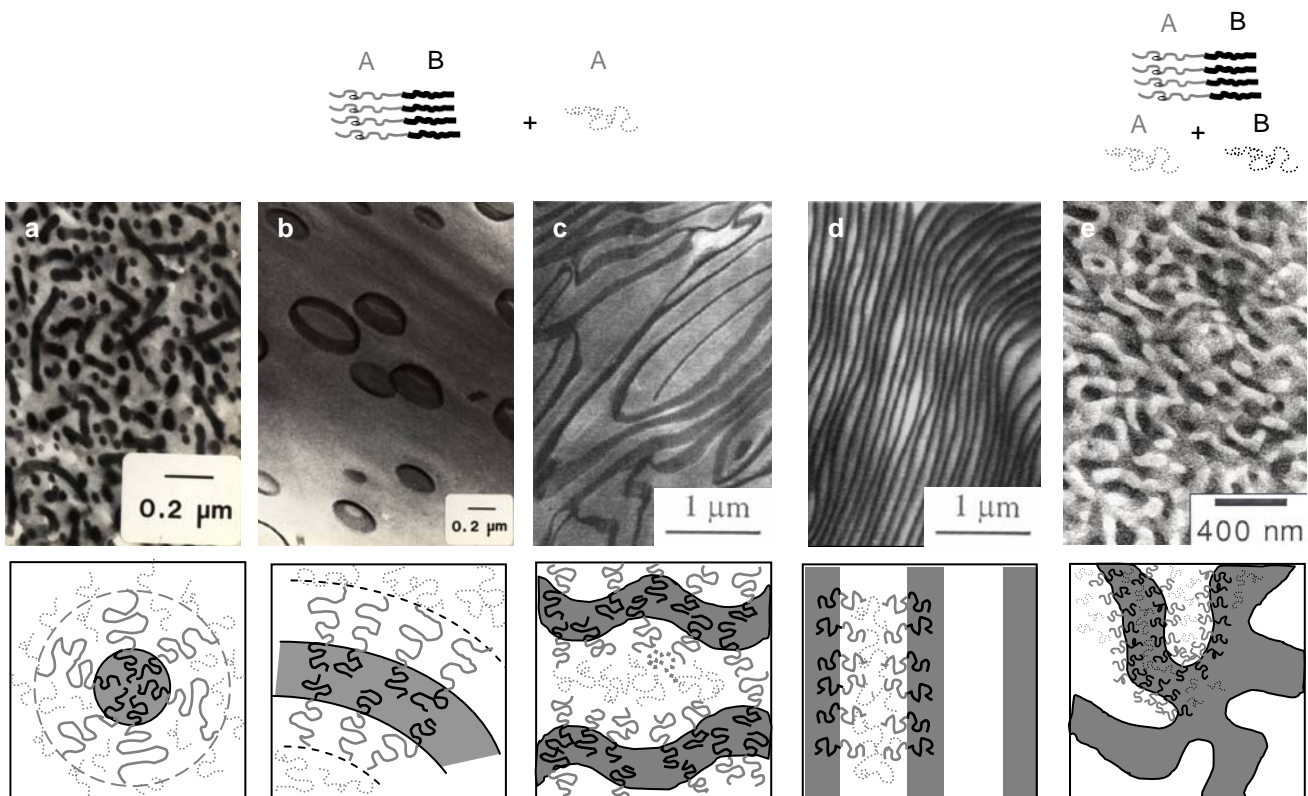


Figure 1. Block copolymer dispersions in homopolymers.

In binary AB+A blends (a-d), block copolymers self-assemble into micelles (a), vesicles (b), fluctuating bi-layers (c), or regular lyotropic phases such as swollen lamellae at higher copolymer fractions (d). In presence of a second homopolymer, as in ternary A/AB/B blends, co-continuous microphases analogous to micro-emulsions can also be obtained (e). TEM micrographs are reproduced from ref. 2, 3 and 4 and display dispersions of a soft polymer B stained in black in a rigid unstained A matrix.

Over the past decade, progress in synthetic chemistry has unveiled unprecedented opportunities to prepare tailored block copolymers at reasonable cost and fully explore the benefits of these nanostructures in commodity or engineering plastics. In designing such blends, however, a technologically important challenge remains which is related to the tendency of block copolymer and homopolymer chains to phase separate. It is indeed relatively easy to disperse nano-scale copolymer aggregates such as micelles in a polymer matrix composed of short chains. In contrast, macroscopic phase separation in copolymer-rich and homopolymer-rich areas is often the rule for matrixes composed of long polymer chains presenting a real technological interest.

Paradoxically, molecular disorder or imperfections, whether inherent to the synthesis method or artificially introduced during blend fabrication, are highly beneficial to avoid macrophase separation and achieve desirable nanostructures in short processing times⁵. The introduction of exothermic interactions between homopolymer chains and copolymer blocks should be another powerful lever that, together with thermal history of the blends, controls the level and stability of copolymer nanostructures in polymer matrices⁶. We illustrate these aspects for the toughening of polystyrene and polymethyl methacrylate, two transparent but highly brittle rigid plastics. Self-assembly of block copolymers comprising rubbery and rigid blocks in these matrices yields nanostructured plastics displaying unique combinations of ductility and transparency. The relationship between block copolymer architecture, processing conditions, and mechanical properties in these systems will be presented.

Keywords: blends, polymers, block copolymers, free-radical polymerization, anionic polymerization, nanostructures, self-assembly, mechanical properties, optical properties, processing.

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