Molecular Disorder and Mesoscopic Order in Polydisperse Acrylic Block Copolymers Prepared by Controlled Radical Polymerization

Anne-Valérie Ruizette,* Sylvie Tencé-Girault, and Ludwik Leibler

Laboratoire Matière Molle et Chimie (UMR 7167 ESPCI-CNRS), ESPCI, 10 rue Vauquelin, 75005 Paris, France

Florence Chauvin and Denis Bertin

Laboratoire Chimie, Biologie et Radicaux Libres (UMR 6517), Université d’Aix-Marseille 1, 2 et 3-CNRS, Marseille, France

Olivier Guerret and Pierre Gérard

Groupement de Recherche de Lacq, ARKEMA, Lacq, France

Received March 10, 2006; Revised Manuscript Received June 9, 2006

ABSTRACT: Self-assembly of high molecular weight polydisperse acrylic block copolymers and their blends is presented under conditions as close as possible to thermodynamic equilibrium. Di- and triblock copolymers comprising a poly(butyl acrylate) (PBA) first or middle block, and poly(methyl methacrylate) (PMMA) second or outer blocks, denoted MBA and MBAM, respectively, are prepared by nitroxide-mediated polymerization (NMP). Their particularity is that the acrylic block is controlled while the methacrylate block is polymerized via an uncontrolled radical process under the synthesis conditions used. Overall composition and molecular weight polydispersities are large. Molecular disorder does not yield macrophase separation, and TEM on solvent cast films reveals lamellar and poorly ordered bicontinuous, cylindrical, or spherical morphologies. Except for the lamellar phase, clear multiple orders of diffraction are not visible in SAXS, and scattering profiles instead indicate a liquidlike order of microdomains. More importantly, morphology boundaries are strongly shifted compared to those commonly accepted for model monodisperse block copolymers. Hence, symmetric copolymers adopt morphologies with highly curved interfaces while lamellae are displaced to PMMA-rich compositions. These results suggest that unbalanced polydispersity between the two blocks can induce interfacial curvature toward to broadest molecular weight distribution, thereby releasing stretching energy of the whole chain. This effect is expected to be encountered in radical or hybrid block copolymer syntheses whenever control cannot be optimized for all blocks.

I. Introduction

Microphase-separated block copolymers comprising two or more incompatible polymer blocks present great interest since they combine at the nanometer scale the intrinsic properties of different homopolymers. Highly ordered periodic lamellar, bicontinuous, cylindrical, or spherical nanostructures are typically observed. Multiblock or graft architectures, as in ABA triblock copolymers, further bring unique rubber elasticity or toughness arising from molecular bridges between different microdomains. Some of these advantages can also be harnessed in blends with homopolymers, provided macroscopic phase separation between copolymer-rich and homopolymer-rich domains can be avoided or limited during melt processing.

For a model AB diblock with strong enough degree of segregation $\chi N$, where $\chi$ is the Flory–Huggins segmental interaction parameter and $N$ the total number of segments in the copolymer chain, a lamellar phase is expected when both blocks occupy equal volume fractions, $\phi_i$, and morphologies with curved interfaces—hexagonally packed cylinders and then closed-packed spheres—for increasingly asymmetric compositions. For slight asymmetries and over a certain temperature range, the bicontinuous double-gyroid phase can also be observed. Phase diagrams and morphology boundaries of AB diblocks are not necessarily symmetric around $\phi_A = 0.5$ because of conformational asymmetry, which is a measure of packing and chain flexibility differences between the two blocks. This effect has been investigated theoretically and quantified experimentally for the most studied diblock copolymers, for which complete phase diagrams have been determined. For multiblock and graft copolymers, architecture is an extra parameter that affects interfacial curvature and copolymer morphologies.

The vast majority of block copolymers used today is based on styrene, butadiene, isoprene, and their derivatives and prepared by living anionic polymerization. This method produces tailored block copolymers of controlled molecular weight and molecular weight distribution (MWD), chain-end functionalization, and architecture, through precise sequencing of two, three, or even more monomers. It has met great commercial success with SIS (polystyrene-$b$-polyisoprene-$b$-polystyrene) and SBS (polystyrene-$b$-polybutadiene-$b$-polystyrene) triblock copolymers, despite the stringent synthesis conditions required. More recently, anionic polymerization has been extended to other commercially important vinyl monomers, among which acrylates or methacrylates. Clever solutions overcoming technical obstacles such as very low reacting temperatures for these copolymers are starting to emerge.

A very attractive alternative for the direct synthesis of block copolymers which remain challenging for anionic polymerization is controlled radical polymerization (CRP). Considerable...