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By Juan Sebastian Montana, Sébastien Roland, Guillaume Miquelard Garnier, Emmanuel Richaud

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EFFECT OF THERMAL OXIDATION ON THE SELF-ASSEMBLY OF TRIBLOCK TERPOLYMERS

By Juan Sebastian MONTANA, Sébastien ROLAND, Guillaume MIQUELARD GARNIER, Emmanuel RICHAUD*

Arts et Métiers ParisTech, CNRS, CNAM, PIMM UMR 8006, 151 bd de l'Hôpital, Paris, France

* corresponding author : emmanuel.richaud@ensam.eu

ABSTRACT

This paper reports an investigation of the thermal degradation of a poly(styrene-*b*-butadiene-*b*-methyl methacrylate) triblock terpolymer compared with those of butadiene rubbers and poly(styrene-*b*-methyl methacrylate). According to sol-gel properties changes, it was proposed that polybutadiene blocks undergo mainly crosslinking. However, these latter coexist with chain scissions occurring in polybutadiene blocks, which generates poly(butadiene-*b*-methyl methacrylate) and poly(butadiene-*b*-styrene) diblock chains, and possibly chain scissions occurring in polystyrene and poly(methyl methacylate) blocks. The consequences of the degradation on the self-assembly of triblock terpolymer were studied through the annealing kinetics monitored by Atomic Force Microscopy. It appears that at low conversion degrees, chain scissions induce a faster self-assembly kinetics. At higher oxidation degrees, crosslinking of butadiene phase combined with scissions induces a "frozen" state at high annealing times characterized by a macrophase separation.

KEYWORDS

Block terpolymers, thermal oxidation, crosslinking, chain scissions, self-assembly

INTRODUCTION

Triblock terpolymers are made of immiscible segments linked by covalent bonds. Their self-assembly has aroused a considerable amount of literature in the last decade, since those materials can spontaneously arrange in several nanoscopic structures depending on tunable physicochemical characteristics such as the nature and the relative proportion of each monomer and the polymerization degree of each block [1,2].

In the simple case of diblock copolymers, the equilibrium morphology (e.g. lamellar, cylindrical, gyroidal…) is predicted from a phase diagram « volume fraction vs χ.N » (χ being the Flory interaction parameter and N the polymerization degree) expressing the effect of the enthalpy/entropy balance on self-assembly. To summarize, low values of χ.N correspond to a disordered state where all components are miscible, whereas "high" χ.N values correspond to