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SCIENCE DIRECT

Polymer 46 (2005) 6605–6613

polymer
www.elsevier.com/locate/polymer

Structures and rheological properties of reactive solutions of block copolymers. Part I. Diblock copolymers in a liquid epoxy monomer

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Abstract

P(S-*b*-MMA) and P(B-*b*-MMA) diblock copolymers (BCP) have been solubilized in a liquid epoxy. The obtained solutions have been characterized by rheology and small angle X-ray scattering (SAXS). As in the solid state, BCP can self-organize in solution to form well-ordered micellar structures. The two blocks respective roles have been clearly identified: at room temperature the PS or the PB block microsegregates while the PMMA block for which epoxy constitutes a good solvent, acts as a stabilizer of the microphase separation. The geometries and thermal stabilities of the ordered structures depend strongly on the molar masses and the chemical nature of the BCP blocks. For instance, the total molar mass of the BCP has to be high enough to obtain a periodic structure. On the contrary, if this molar mass is too high, too long relaxation times prevent the system from reaching its equilibrium. For the P(S-*b*-MMA) copolymer solution, a transition temperature from an order to a disorder state (T_{ODT}) is observed. The origin of this transition has been attributed to a solubilization of the PS domains around T_{ODT}. Macroscopically, this transition can be defined as a solid-like to a liquid-like transition. In the case of the P(B-*b*-MMA) copolymer solution, no order–disorder transition has been observed: it can be explained by the fact that the PB blocks are not soluble in epoxy at any temperature, up to $T = 200$ °C.

Keywords: Block copolymers; Reactive solvent; SAXS

1. Introduction

The self assembling ability of block copolymers (BCP) has received considerable attention over the last decades [1–4]. When cooled down from the melt, BCP undergo an order–disorder transition (ODT) for a well-defined temperature and form spatially periodic microdomains structures induced by microphase separation. The connectivity between the BCP blocks is responsible for this behaviour by preventing the usual macroscopic phase separation observed in homopolymer blends. In the weak segregation regime, above the T_{ODT}, Leibler [5] presented a scattering theory for the phase behaviour of diblock copolymers in the framework of a random phase approximation. Within mean-field theory, two parameters which are the chain composition f and the product χN of Flory–Huggins interaction parameter χ with the total degree of polymerization N dictate BCP phase behaviour. The knowledge of the T_{ODT} can be very useful in many applications.

Elastic scattering techniques (SAXS, SANS) have been used extensively to study the structural changes occurring in BCP samples since, they provide an in situ characterization during the phase transitions. Secondary peaks, showing long range order, disappear as T_{ODT} is approached, and the first peak intensity drops to a weak intensity level relevant to the broad scattering maximum from disordered melts. It is also well established that a microphase separation affects the rheological behaviours [6–9]. The long relaxation modes, as observed in the dynamic moduli at low frequencies, drop significantly when heating through the T_{ODT}. Another indication of the ODT is the frequency dependence of the moduli which changes from non-terminal solid-like behaviour in the ordered state ($G' \sim G'' \sim \omega^{0.5}$) to terminal,

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doi:10.1016/j.polymer.2005.05.014

liquid-like behaviour in the disordered state ($G' \sim \omega^2$ and $G'' \sim \omega^1$).

Because the variation of χ with temperature is very small, this transition can only be observed on BCP having a very low molar mass. As in the solid state, the BCP can self-associate in solution [10] but the segregation power is significantly decreased and gives rise to easily observable ODTs [11]. In most cases, BCP are in a selective solvent that means that only one block is swelled while the insoluble one is microsegregated. An extensive literature, both theoretical and experimental, exists on the unusual rheological properties exhibited by BCP in selective solvents [4,12–19]. At low temperatures and high BCP concentrations, the solution exhibits solid-like behaviour while at temperatures higher than T_{ODT}, it exhibits a liquid-like behaviour.

Earlier works [20,21] on block copolymers dissolved in reactive solvents like styrene have been revalorised recently using thermoset (TS) precursors like epoxy systems [22–34]. With an appropriate design of the BCP architecture, these block copolymers self-assemble to form ordered or disordered morphologies before reaction in the solution of the thermoset precursors. The role of the thermoset curing is to lock in the morphology that is initially present or formed in the earlier stages of the reaction. Finally after reaction, BCP are self-associated into spherical micelles, wormlike micelles or vesicles and these nanostructures can increase the fracture resistance of epoxy networks [29–34]. Most of the studied networks are based on diglycidyl ether of bisphenol A, DGEBA cured with different hardeners. Several types of BCP have been used, reactive and non-reactive AB, ABA and ABC. To prevent macroscopic phase separation of the BCP during reaction, the common characteristic is to have one block that is miscible in the growing thermoset at any stage of the reaction or just expulsed in a local scale. This is the case for example of poly(methyl methacrylate), PMMA [29] or poly(ethylene oxide), PEO [22] in some DGEBA-diamine systems.

Knowing the selectivity of the liquid DGEBA for the PMMA [35] compared to the polystyrene [36] and the polybutadiene [37] homopolymers, an addition of diblock copolymers like poly(styrene-*b*-methyl methacrylate), SM or poly(butadiene-*b*-methyl methacrylate), BM is expected to lead at low temperature to, respectively, PS and PB microsegregated domains. These systems are supposed to be ordered at some a concentration and to present an ODT. Our aim is to study these two latter aspects. Based on a PMMA block, (i) the length of the PMMA block, (ii) the total molar mass of the BCP and (iii) the state of the microsegregated domains (liquid when the PB is microsegregated, vitreous in the case of PS) will be varied. Small angle X-ray scattering (SAXS) and rheology will be used to characterize the ODT. Only moderate concentrated solutions containing 30 wt% of diblocks will be studied.

This study on diblock copolymers in liquid DGEBA will be useful to understand the behaviour of triblock copolymers, SBM in the same reactive and selective solvent. This latter study will constitute the second part of this work. This is why our aim is not to discuss exhaustively the complex behaviour of diblock copolymers in a selective solvent (for example, possibilities of order–order transitions have not been investigated), but rather to describe the several microstructural events occurring in the solutions as a function of the temperature.

2. Experimental

2.1. Materials

The thermoset precursor is a liquid epoxy acting as a selective solvent: diglycidyl ether of bisphenol A (DGEBA $n = 0.15$) supplied by Huntsman as Araldite LY 556.

The block copolymers are a diblock poly(styrene-*b*-methyl methacrylate), SM and a diblock poly(butadiene-*b*-methyl methacrylate), BM whose characteristics are given in Table 1. The adopted nomenclature is similar to the one used in our previous publications [29–31], S or $\mathrm{B}_t^x\mathrm{M}_v$ with t and v corresponding to the mass percent of blocks and x to the PS or PB block number average molar mass in kg/mol. All the blends contain 30 wt% of block copolymers. The antioxydant Irganox was provided by Ciba. Chloroform (99.9%, supplied by SDS) was used as received without any purification.

2.2. Sample preparation

The samples were prepared by dissolving DGEBA and the block copolymers in chloroform. The chloroform was evaporated during 1 week at ambient pressure and temperature, then one night in a vacuum oven at 50 °C. An additional thermal ageing at 150–160 °C is performed in order to remove the residual solvent. When the block copolymers contain a PB block, a stabilizing agent (Irganox) is added (2 wt% of the total mass of the block copolymer). When it is indicated, the samples have been annealed at high temperature for 24 h and cooled down at room temperature at 0.2 °C/min. For solutions containing SM or BM diblock, the annealing temperature was set to 120 °C which is always higher than the upper T_g to facilitate molecular mobility and nanostructural development.

2.3. Experimental techniques

Rheological analyses were conducted on a TA stress-controlled rheometer (AR1000) equipped with 40 mm diameter parallel plates. The sample thickness was set to 0.8 mm. The linear viscoelastic domain has been determined at the highest frequency and the lowest temperature. When frequency sweep experiments are conducted, the temperature is raised from 20 to 180 °C by step of 10 °C. Measurements are started after a 30 min stabilization step.