



Free-radical polymerization induced macrophase separation in poly(methyl methacrylate)/dimethacrylate blends: Experiment and modeling

Walter F. Schroeder*, Mirta I. Aranguren, Guillermo E. Elicabe, Julio Borrajo

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata – National Research Council (CONICET), Av. Juan B. Justo 4302, 7600 Mar del Plata, Argentina

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ABSTRACT

This work presents the analysis of a polymerization-induced macrophase separation taking place during free-radical copolymerization of styrene and dimethacrylate in the presence of poly(methyl methacrylate) (PMMA) as a modifier. The PMMA does not participate in the polymerization but induces phase separation in the course of the reaction. An experimental study based on real-time static light scattering measurements with the aim of monitoring the phase behavior during the isothermal copolymerization is firstly presented. Then, an original and innovative contribution is made by modeling the evolution of the unstable region of the phase diagram as a function of conversion and by predicting phase separation in spinodal condition. The analysis is performed using an expression for the free energy of a reactive network-forming mixture based on the Flory–Rehner lattice model for swollen gels. The accuracy of the proposed model is verified by the good agreement found between its predictions and the experimental results.

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1. Introduction

Polymerization-induced phase separation (PIPS) finds application in the synthesis of a set of useful materials such as high-impact polystyrene (HIPS) [1], thermoplastic-thermoset blends [2], polymer-dispersed liquid crystals [3], thermally reversible light scattering films [4], nanoporous polymer materials [5,6], nanostructured thermosets [7], and macroporous materials [8] which have been extensively applied for separation (beads, membranes, monoliths), analysis (various kinds of chromatography) and in many branches of technology including medicine [9] (tissue engineering, drug delivery).

The PIPS method consists of polymerizing the precursor monomers in the presence of an additional component (e.g. modifier), such as an oligomer, a polymer, or a small

molecule. During polymerization, a phase separation process takes place leading to different types of morphologies that depend on the initial composition and reaction conditions [10–13]. The ultimate properties of these materials depend on the morphologies generated in the course of the reaction [14]. Linear polystyrene was one of the first additives used to cause phase separation and to give place to macroporous materials based in styrene–divinylbenzene resins. In this case, it was shown that phase instability was very sensitive to the molecular weight of polystyrene [15]. Thus, understanding the thermodynamic principles that lead to phase separation becomes very useful in designing new materials. In addition, the ability of predicting phase behavior can help to avoid the trial-and-error procedures that are used in most cases. In this report, we present a thermodynamic model that allows to simulate the phase-separation process induced by free-radical polymerization of styrene (St) and bisphenol A glycidyl methacrylate (BisGMA) in the presence of poly(methyl methacrylate) (PMMA) as a modifier.

* Corresponding author. Tel.: +54 (223) 481 66 00; fax: +54 (223) 481 00 46.

E-mail address: wshroeder@fi.mdp.edu.ar (W.F. Schroeder).

A thermodynamic description of PIPS shows that the main driving force for phase separation is the decrease of the absolute value of the entropic contribution to the Gibbs free energy of mixing [16]. Other factors can also contribute to the demixing process such as a change in the interaction parameter due to changes in the chemical structure produced by polymerization or the development of elastic energy after gelation (in the case of a thermosetting polymer) [17]. Models that allow a good description of the PIPS process in systems that polymerize by a stepwise mechanism have been recently reported [18–20]. For this type of polymerization, statistical models that successfully describe the evolution of the species distributions as a function of conversion have been developed. If the presence of the modifier does not significantly affect such distributions, it is possible to combine the polymerization statistic model with a thermodynamic model, such as the lattice theory of Flory–Huggins [21], to successfully describe the PIPS process.

For chainwise polymerizations, the simplest case is illustrated by the polymerization of a vinyl monomer (styrene, (meth)acrylic monomer, etc.) in the presence of a modifier, leading to a linear polymer. Several recent papers have analyzed PIPS in this type of systems [12,22–24]. However, for thermosetting systems polymerizing by a chainwise mechanism the situation is much more complex. In these cases, the development of a polymerization statistic model is very difficult, due to the formation of highly crosslinked domains containing numerous intramolecular rings that do not contribute to the elastic properties of the network. Thus, in the few models that have been proposed, it has been necessary to introduce strong hypothesis on these aspects, and so predictions are of qualitative nature [25,26].

Our aim is to provide a thermodynamic description of PIPS in a reactive network-forming system polymerizing by a chainwise mechanism. The selected system is a dimethacrylate(BisGMA)/St resin containing PMMA as a thermoplastic modifier. The PMMA does not participate in the co-polymerization but induces phase separation in the course of the reaction. In general terms, the phase diagram of the St–BisGMA–PMMA ternary blend represents the initial thermodynamic state of the reactive system at zero conversion. This phase diagram has been studied and discussed in previous works [11,27]. Here, we are concerned with the phase behavior during reaction, when the system consists of four components, St, BisGMA, copolymer (St-co-BisGMA), and PMMA. The phase state of such a system should be represented by means of a quaternary phase diagram that describes the phase evolution by effect of conversion, an issue that to our knowledge has not been previously analyzed in the literature.

Phase separation can occur either by the nucleation and growth (NG) mechanism in the metastable region of the phase diagram, or by spinodal decomposition (SD) if the system becomes unstable. Depending on the relative rates of phase separation and polymerization, the compositional trajectory may be fully located in the metastable region, in which case phase separation would take place exclusively by an NG mechanism, or it may enter the unstable region, implying that SD has to be considered to account for the

morphology generated. Since the homogeneous nucleation is a slow process in comparison to SD [28], frequently the mixture quickly passes through the metastable region and then enters the unstable region where the spinodal decomposition process is initiated by small concentration fluctuations throughout the sample [29]. In the early stages of SD the amplitude of the concentration fluctuations increases while the characteristic distance between fluctuations remains constant. This event gives place to the appearance of a correlation peak located at a nonzero constant scattering vector (q), when the phase separation process is followed by light scattering experiments [30,31].

In this article we first present an experimental study based on real-time static light scattering measurements with the aim of monitoring the phase behavior during the isothermal copolymerization of St and BisGMA in the presence or not of a thermoplastic modifier. Then, a thermodynamic model of PIPS is introduced and its predictions are compared with the experimental results. In our thermodynamic analysis, we apply an expression for the free energy of a reactive network-forming mixture based on the Flory–Rehner lattice model for swollen gels [32] later modified by Dušek et al. [33]. This expression allows us to compute the evolution of the unstable region limited by the spinodal curve as a function of conversion. In this approach, it is assumed that the speed at which the trajectory crosses the metastable region on the phase diagram is sufficiently fast, such that no nuclei can be created during this time interval. Consequently, the isothermal phase separation process is strictly spinodal decomposition. We will present experimental evidence that supports such an assumption.

2. Theoretical background

Phase separation in reactive network-forming systems can be analyzed using the Flory–Rehner lattice model for swollen gels [32], later modified by Dušek et al. [33]. For a mixture of i components, the dimensionless mixing Gibbs free energy per mole of lattice sites is expressed as

$$\frac{\Delta G^{\text{mix}}}{MRT} = \sum_i \frac{\phi_i}{x_i} \ln \phi_i + \sum_{ij} \chi_{ij} \phi_i \phi_j + v_e \varepsilon \phi_g \left[\frac{3}{2} \left(\phi_g^{-\frac{2}{3}} - 1 \right) + \frac{2}{f} \ln \phi_g \right] \quad (1)$$

where R is the gas constant, T is the absolute temperature, and M is given by $M = \sum_i n_i x_i$ and represents the number of moles of cells in the system; n_i is the number of moles of the i -component, and x_i the number of cells occupied by i -component. The cell volume was taken as $116.85 \text{ cm}^3/\text{mol}$, which corresponds to the molar volume of St monomer. ϕ_i and ϕ_j are the volume fractions of components i and j respectively.

The first two terms on the right side of Eq. (1) represent the entropic and enthalpic contributions to the free energy expressed in terms of the binary interaction parameters, χ_{ij} ($\chi = a + b/T$, where a and b are constants); while the last term represents the elastic contribution to the free energy, which appears in the postgel stage of the reaction. ϕ_g is the

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