



Feature Article

Self-assembly of nanoparticles employing polymerization-induced phase separation



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ABSTRACT

Nanoparticles (NPs) may be homogeneously dispersed in the precursors of a polymer (reactive solvent) by an adequate selection of their stabilizing ligands. However, the dispersion can become metastable or unstable in the course of polymerization. If this happens, NP-rich domains can be segregated by a process called polymerization-induced phase separation (PIPS). This occurs mainly due to the decrease in the entropic contribution of the reactive solvent to the free energy of mixing (increase in its average size) and, for a reactive solvent generating a cross-linked polymer, the additional contribution of the elastic energy in the post-gel stage. The extent of PIPS will depend on the competition between phase separation and polymerization rates. It can be completely avoided, limited to a local scale or conveyed to generate different types of NPs' aggregates such as crystalline platelets, self-assembled structures with a hierarchical order and partitioning at the interface, and bidimensional patterns of NPs at the film surface. The use of a third component in the initial formulation such as a linear polymer or a block copolymer, provides the possibility of generating an internal template for the preferential location and self-assembly of phase-separated NPs. Some illustrative examples of morphologies generated by PIPS in solutions of NPs in reactive solvents, are analyzed in this feature article.

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1. Introduction

The concept of a polymerization-induced phase separation (PIPS) may be easily introduced by considering a solution of a linear polymer. The Gibbs free energy of the solution may be described by the Flory–Huggins model:

$$\Delta G/RT = (\phi_p/V_p) \ln \phi_p + (\phi_s/V_s) \ln \phi_s + (\chi/V_R)\phi_p\phi_s \quad (1)$$

In this equation ϕ and V represent, respectively, volume fractions and molar volumes of polymer (P) and solvent (S), V_R is a reference volume, χ is the interaction parameter between both components, T is the absolute temperature and R is the universal gas constant. In most cases, the interaction parameter is represented by a function of temperature and composition that takes positive values and therefore acts against the dissolution of the polymer. The first two terms are entropic contributions to the Gibbs free energy and take negative values (volume fractions are less than 1), favoring the dissolution of the polymer. However, as $V_p \gg V_s$ the entropic contribution provided by the small solvent molecule is what permits to dissolve the polymer in the selected solvent. Besides, the chemical structure of the selected solvent must be compatible with the chemical structure of the polymer in order that the interaction parameter takes low values to make the solution possible.

In the case of a reactive solvent composed of a monomer, a hardener and catalyst or initiators, its polymerization produces a continuous increase in the average molar volume, V_s . At a certain conversion in the polymerization reaction the solution loses stability by the decrease in the absolute value of the entropic contribution to the free energy and phase separation takes place. Additionally, if a cross-linked polymer is generated, an elastic energy term must be added to the description of the Gibbs free energy in the post-gel stage [1]. This term does also contribute to the phase separation process of the linear polymer from the cross-linked polymer. But in most cases phase separation takes place before gelation driven by the increase in the average molar volume of the reactive solvent. Typical rubber-modified thermosets are obtained by this process.

PIPS also takes place when the linear polymer is replaced by other modifiers such as small organic molecules than can form a liquid crystalline phase upon phase separation. The generated dispersions of liquid crystal-rich domains in a cross-linked polymer, called polymer-dispersed liquid crystals (PDLC), are used in electro-optical devices such as reflective displays, optical switches and variable transmittance windows.

Nanoparticles (NPs) can be homogeneously dispersed in reactive solvents when the structure of chemical groups present at their surfaces is affine with the chemical structure of the solvent. The thermodynamics of these colloidal solutions can be also described by a modified Flory–Huggins equation [2]. And again, the increase in the average molar volume of the reactive solvent in the course of polymerization destabilizes the solution and might produce the phase separation and self-assembly of NPs, producing different kinds of hierarchical structures and generating specific properties in the final material (e.g., electrical conductivity generated by percolated structures of carbon nanotubes or metallic NPs). But PIPS can be avoided or limited to a local scale by covalently bonding the stabilizing ligands to the polymer matrix or by adjusting experimental conditions to generate a polymerization rate much faster than the phase separation rate.

PIPS can also take place in ternary systems including a linear or a block copolymer (BCP) in the solution of NPs in the reactive solvent. In this case, phase separated domains of the linear polymer or the BCP can act as templates for the self-assembly of NPs in the ternary blend. This can generate a variety of morphologies and structures useful for practical applications.

The aim of this feature article was to analyze a few selected examples of PIPS occurring in both binary NPs/reactive solvent formulations and ternary NPs/modifier (either a linear polymer or a BCP)/reactive solvent systems. Selected examples will illustrate the variety of organized structures that can be self-generated by NPs upon their phase separation from the solution. The article does not aim at reviewing the literature in the field but to illustrate the variety of structures and associated properties that may be generated by PIPS in solutions of NPs in reactive solvents.

2. PIPS in binary NPs/reactive solvent formulations

2.1. NPs forming conventional crystals upon phase separation

Polyhedral oligomeric silsesquioxanes (POSS) of structural formula $(\text{RSiO}_{1.5})_n$, where R is an organic group and $n = 8, 10$ or 12 , are perfectly defined NPs with overall sizes in the range of 1 nm (depending on the size of the organic group). Typical POSS are cubes with the structure shown in Fig. 1. Due to its regular structure some POSS are crystalline with characteristic X-ray diffraction (XRD) spectra.

The solubility of POSS in reactive solvents can be achieved by an appropriate selection of the chemical structure of the organic groups. For example, a POSS cube with 7 isobutyl groups and 1 glycidyloxypropyl group at its corners could be dissolved at high temperatures in epoxy precursors based on stoichiometric amounts of diglycidylether of bisphenol A (DGEBA) and 4,4' methylenebis(2,6-diethylaniline) (MDEA) [3]. Fig. 2 shows the initial experimental phase diagram and the predicted phase diagrams at two advanced conversions, $p = 0.1$ and 0.2 . Curves show a discontinuity at the transition from a liquid–liquid (L–L) phase separation at high temperatures to a crystal–liquid (C–L) phase separation at low temperatures. The L–L curve is continued with a dashed line in the region where the C and L are the thermodynamic stable phases. Homogeneous solutions are located at the left of the curves.

The morphologies arising from PIPS will depend on the composition of the blend and the polymerization temperature. For example, a solution with 10% by volume of POSS polymerized at 135°C will undergo an L–L phase separation when the conversion increases above 0.1. The final morphology is a dispersion of spherical POSS-rich domains produced by a typical nucleation-growth process (Fig. 3). Cooling from the polymerization temperature generates crystallization of POSS inside the spherical domains as revealed from XRD spectra and differential scanning calorimetry (DSC) thermograms [3].

The situation changes completely if the polymerization is carried out at lower temperatures and POSS concentrations. For example, a solution with 5% by volume of POSS polymerized at 115°C undergoes a C–L phase separation at conversions close to 0.1. Direct crystallization generates a distribution of POSS platelets (Fig. 4). At advanced conversions the system enters the metastable L–L region and spherical domains coexisting with the crystalline platelets are also produced [3].

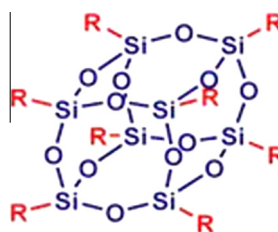


Fig. 1. Chemical structure of a POSS with $n = 8$.

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