Development of Layered Polymer Nanocomposites Using Supercritical Fluid Technology

Natalia Levit, Ozge Guney-Altay, Dmitry Pestov, and Gary Tepper*

Mechanical Engineering Department, Virginia Commonwealth University, Richmond, Virginia 23284

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ABSTRACT: Layered organic polymer nanocomposites were developed utilizing supercritical fluid technology and solid-state polymerization. Intimately mixed composite particles consisting of one amorphous and one crystalline component were precipitated by the method known as rapid expansion of supercritical solutions (RESS). The crystalline component was 2,5-distyrylpyrazine (DSP), a diolefinic monomer with solid-state reactivity. The amorphous component was a fluoroalkyl acrylate (FAA) polymer. The DSP monomer, though normally highly crystalline, was rapidly precipitated in a nonequilibrium state and recrystallized and polymerized in the solid state. The process of DSP monomer reorganization within the organic polymer matrix resulted in the formation of well-organized alternating nanoscale layers of DSP and FAA phases throughout the particle volume.

Introduction

Research in the area of polymer nanocomposites has recently attracted significant attention due to the potential to realize substantial improvements in thermal, mechanical, and optical properties in these materials.[1−4] Prospective applications for polymer nanocomposites include structural materials, pharmaceuticals, optics, quantum dots, photonic crystals or dielectric lattices, and chemical sensors.[1−5]

Various methods have been utilized to develop nanocomposites including sol−gels, self-assembly, incorporation of preformed nanostructures (clusters, particles, nanotubes) into a polymer matrix, and formation of hybrids using porous or layered inorganic materials by interpenetration.[6−8] Polymer layered 2D nanocomposites are of particular interest due to their predictably nonhomogeneous physical, optical, and chemical properties.[7] The conventional method utilized to prepare layered polymer nanocomposites is to make use of a naturally layered inorganic material (e.g., layered silicate) as a host lattice and to fill between the layers with a polymer using techniques such as intercalation.[7,8] However, this fabrication method is not applicable to many materials, and it is difficult to produce layered nanoparticles, which are in demand in such areas as controlled drug release, optics, and sensing.[9]

This paper introduces a different approach based on the direct reorganization and phase segregation of intimately mixed materials within composite nanoparticles precipitated from a supercritical ternary solution. Previously, we demonstrated that nanoparticles of diolefinic monomers with the property of solid-state polymerization can be developed from a rapidly expanding supercritical solvent.[10,11] The highly crystalline diolefinic monomers are produced in a nonequilibrium, disordered state as a result of the extremely fast, supersonic phase separation inherent to the supercritical precipitation process.[10] The nonequilibrium particles were found to undergo self-organization at room temperature, and this natural recrystallization process could be accelerated by exposure to a “plasticizing” vapor, such as methyl L-lactate or heptane, which helps molecular rearrangement.[11] In this paper we report our initial study on the reorganization of diolefinic monomers with solid-state polymerization within composite nanoparticles.

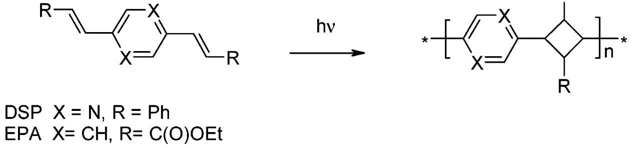
Experimental Section

The 2,5-distyrylpyrazine (DSP) diolefinic monomer was synthesized by the method of Hasegawa et al.[12] and recrystallized from toluene. The monomer purity was checked by TLC chromatography. The melting point of the DSP monomer was measured to be 223 ± 1 °C (toluene). A second diolefinic monomer, diethyl *p*-phenylenediacrylate (EPA), was synthesized using the general method described by Grinev et al.[13] with the following modifications. After the reaction was completed, water was added 3:1 by volume to the reaction solution. EPA (68%) was obtained as a white powder after precipitation for about 0.5 h and filtration. The melting point of the EPA monomer was 97 ± 1 °C (ethanol). The polymer was 2,2,2-trifluoroethyl methacrylate (FAA) with M_n of 300 000 from Daikin Industries, Ltd. FAA has a glass transition temperature of 80−90 °C according to the manufacturer. The FAA polymer was used as received without any additional purification. Chlorodifluoromethane was from DuPont and used as the supercritical solvent. The RESS apparatus and particle precipitation technique were described previously.[14] The RESS particles were examined by a high-resolution SEM (Hitachi 4700), AFM (Digital Instruments, NanoScope IIIa), and Phillips X’Pert MRD diffractometer.

Results and Discussion

The solid-state polymerization of diolefinic compounds is known as a four-center polymerization reaction and is depicted in Scheme 1.[12,15] The reaction proceeds upon irradiation by UV and visible light, does not require the

Scheme 1. Solid-State “2 + 2” Photopolymerization of Diolefinic Monomers



DSP X = N, R = Ph
EPA X= CH, R= C(O)OEt

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[*] Corresponding author: Ph (804)-827-4079, fax (804)-827-7030, e-mail gtepper@vcu.edu.

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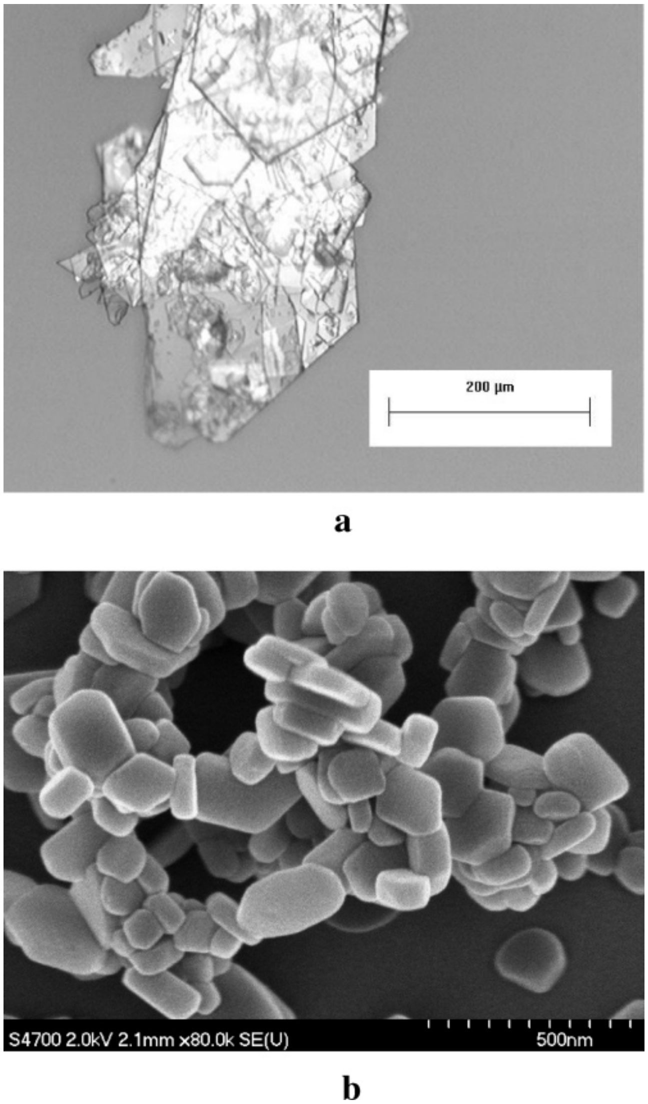

Figure 1. (a) Optical image of the original DSP crystal. (b) SEM image of the DSP particles precipitated by RESS.

use of a photoinitiator, and yields a high molecular weight linear polymer. During polymerization, macroscopic DSP crystals disintegrate into smaller fragments as a result of internal stress formation within the crystal.[15] However, we previously demonstrated that crystal-to-crystal polymerization of diolefinic monomers can proceed without disintegration if the crystal size is below a critical value. The critical diameter for DSP particles was found to be ~500 nm.[10,11,16] Figure 1a is an optical image of a macroscopic DSP crystal, and Figure 1b is an SEM image of the micronized DSP particles produced by RESS. The micronized precipitates exhibit the same general shape of the macroscopic material, but without any indication of internal fragmentation.

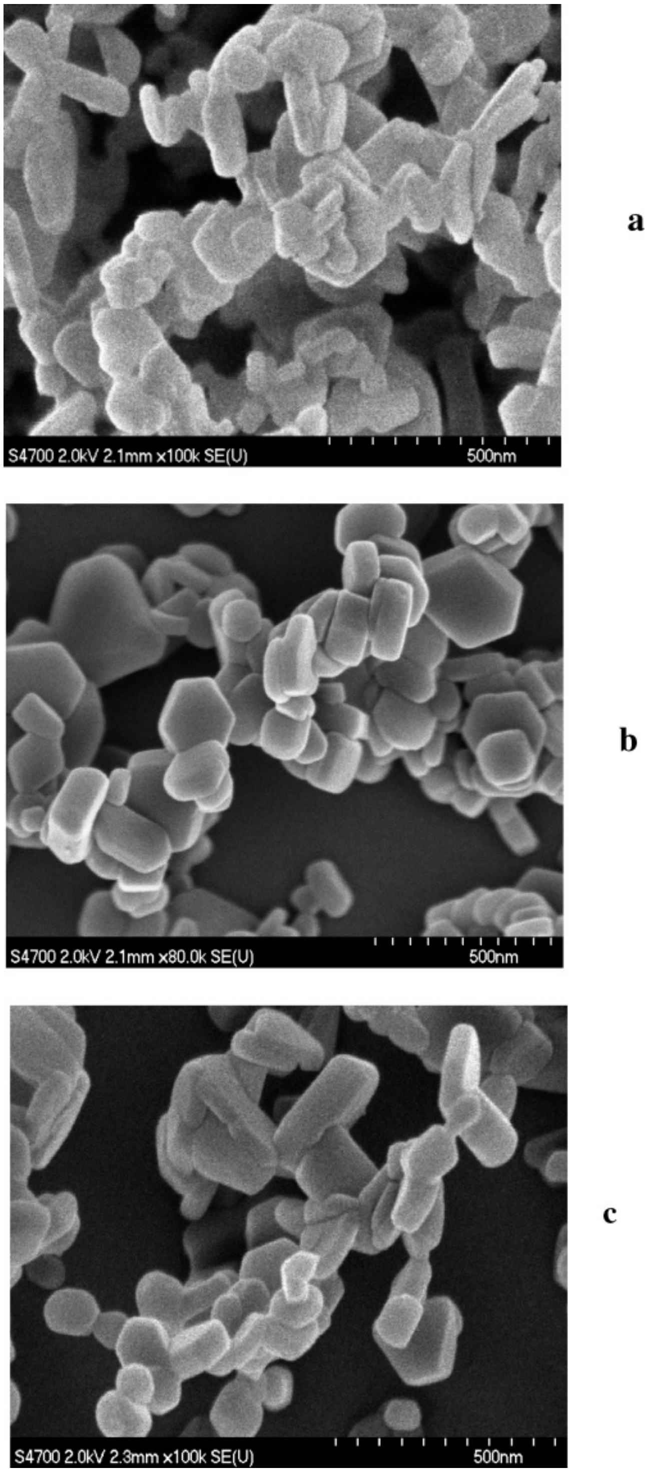

Figure 2. Changes in DSP particles produced by RESS. Polymerized (a) immediately after RESS, (b) 1 month after RESS, and (c) after vapor (heptane) treatment. All particles presented here were polymerized for 10 min by UV light to "lock" the morphology.

The rapid expansion of supercritical solution (RESS) process is based on the sudden change in solute solubility and solvent density upon the rapid decompression of supercritical solution through an expansion device, such as an orifice or a capillary nozzle. The solvent becomes a gas after the expansion and separates from the solute, leaving behind dry solute particles. In general, the RESS precipitates have a narrow and tunable size distribution with a mean diameter ranging from nanometers to micrometers depending on the expansion conditions. The phase separation and particle precipitation take place at a time scale determined by the local speed of sound and the geometry of the expansion device.[17] Therefore, it is possible to develop particles with nonequilibrium thermodynamic properties.

Because of the extremely rapid precipitation kinetics inherent to the RESS process and fast solvent separation from the solute, the normally crystalline DPS monomer particles are produced in a metastable, dis-

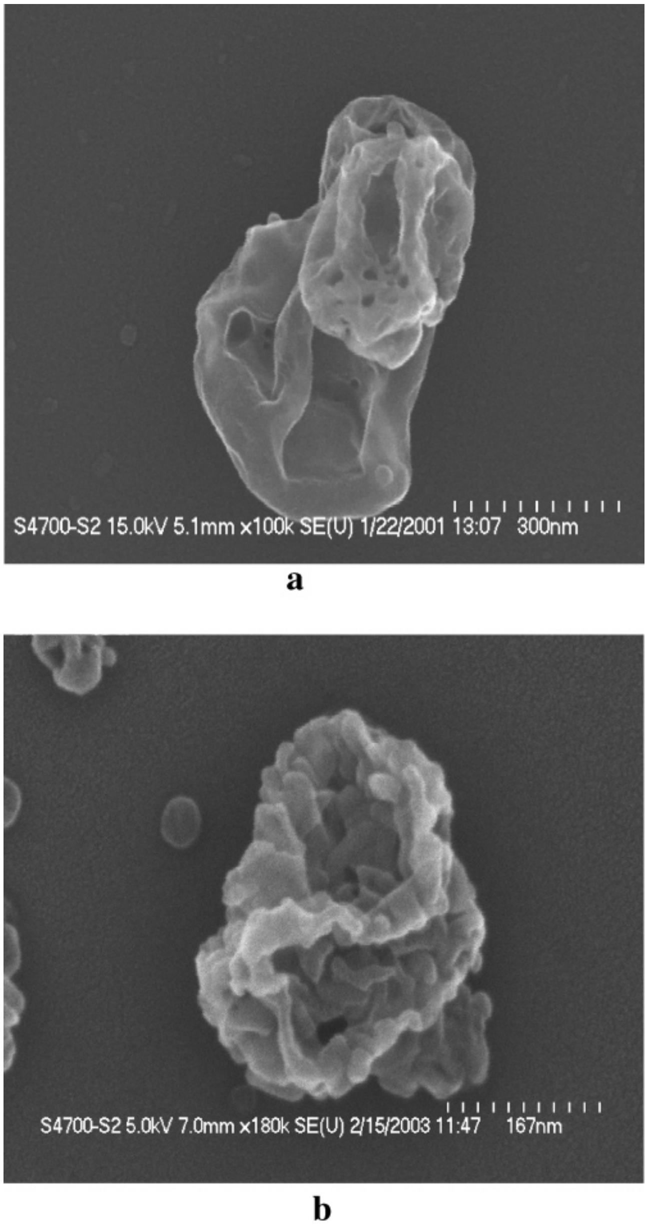

Figure 3. Particles developed by RESS: (a) pure FAA polymer particle; (b) FAA−DSP composite particle without vapor treatment.

ordered state and undergo natural recrystallization at room temperature.[10] We reported that the natural recrystallization kinetics for the DSP particles produced by RESS is on the order of 2 weeks at room temperature but can be greatly accelerated by exposure to an organic "plasticizing" vapor.[10,11] This process is illustrated in Figure 2. Immediately after RESS (Figure 2a), the DSP particles appear somewhat rounded, and the boundaries between the individual particles are not well-defined. XRD measurements of these particles showed a lack of significant crystallinity.[10] After equilibration for 1 month (Figure 2b), the particles changed substantially and appear more crystal-like with well-defined boundaries between individual particles. This change in the observed morphology corresponds to the emergence of peaks in the XRD spectrum.[10] We have found that the recrystallization in the diolefinic monomer can be accelerated by exposure to organic vapor. Vapor treatment, heptane in this case (Figure 2c), stimulates the molecular rearrangements and changes the particle appearance and structure in a manner similar to that caused by the natural recrystallization, but on a time scale of minutes rather than weeks.[11] This phenomenon of self-organization of the RESS-produced diolefinic monomers is utilized in the present work to develop layered organic nanocomposites. Particles consisting of an intimate mixture of a diolefinic DSP monomer and a glassy FAA polymer were produced by RESS. The DSP monomer component was recrystallized using methyl L-lactate vapor treatment producing unique composite particles exhibiting well-organized, phase segregated layers.

The DSP monomer was coprecipitated with an amorphous fluoroalkyl acrylate polymer from a single supercritical chlorodifluoromethane solution. The RESS experimental conditions were selected to obtain submicron particles less than 500 nm in diameter and to achieve complete blending of the two solutes within the particles. The relationship between the RESS processing parameters and the particle morphologies was studied and will be reported elsewhere.

The FAA polymer−DSP monomer composite particles were precipitated at a preexpansion pressure of 276 bar and a preexpansion temperature of 120 °C. The total solute concentration of the FAA−DSP mixture was 0.15 wt %, 10 wt % of which was DSP. The average diameter of the composite particles was about 200 nm. One set of particles was polymerized by exposure to UV light

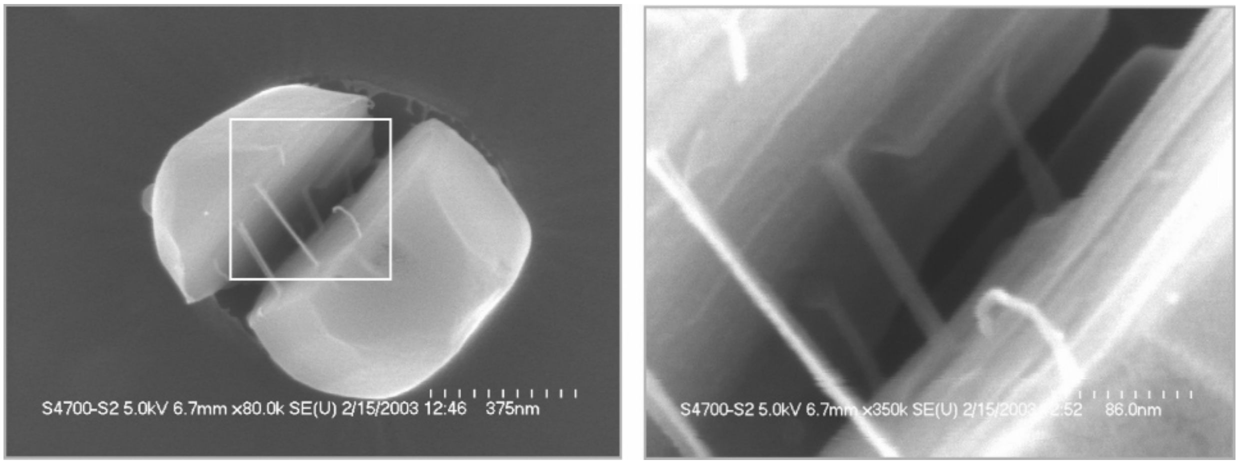

Figure 4. Composite DSP−FAA particles after vapor treatment. The particles were cracked open showing their cross-sectional structure.

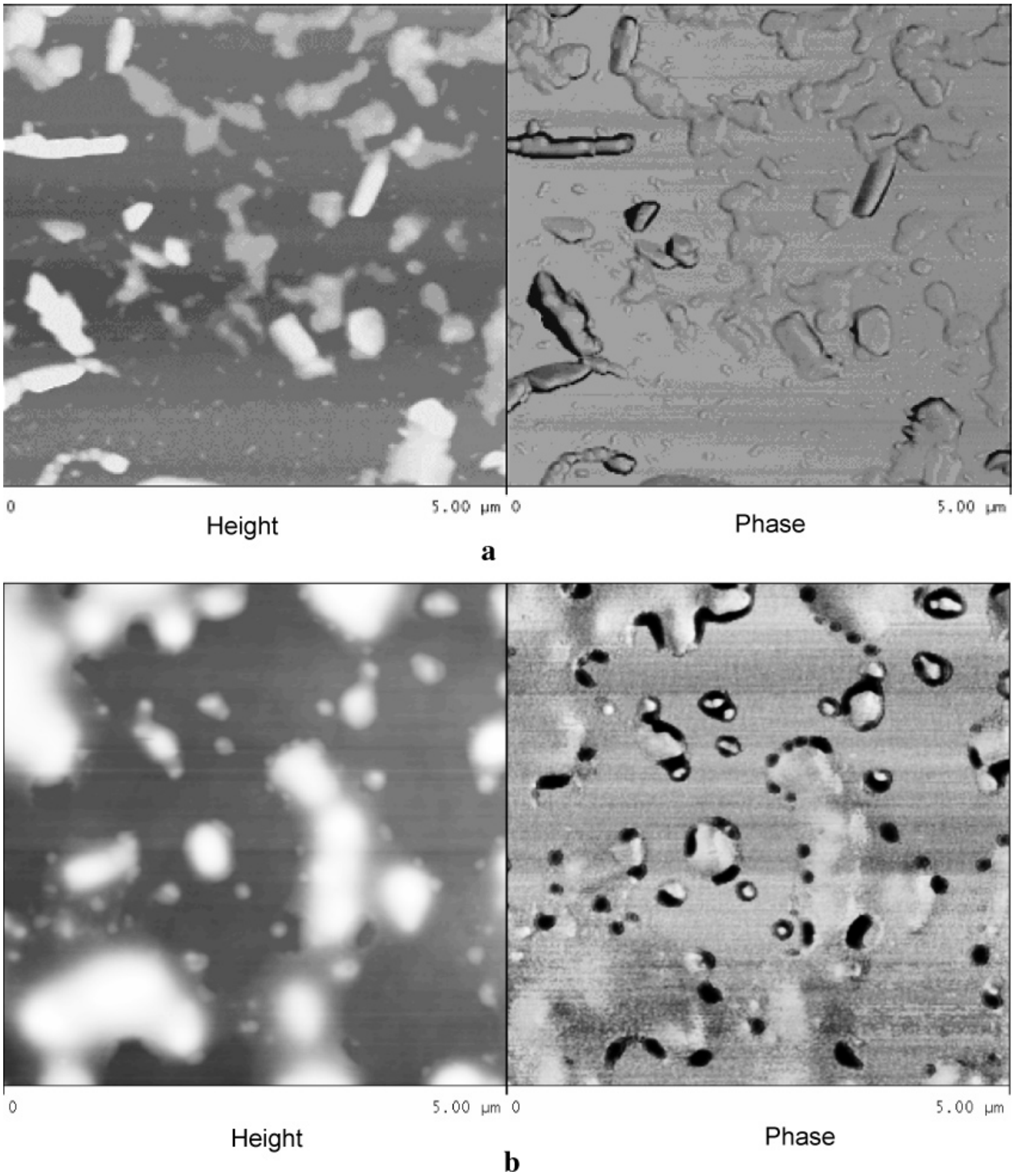

Figure 5. AFM height and phase images of EPA–DSP composite particles precipitated by RESS: (a) polymerized immediately after RESS and (b) polymerized after recrystallization by heptane vapor treatment.

for 10 min immediately after production, and no FAA–DSP phase separation was observed in AFM phase images even after 2 years of storage at room temperature. The overall shape of the FAA–DSP composite particles was very similar to the shape of pure FAA particles (Figure 3). Another set of particles was immediately exposed to saturated methyl L-lactate vapor at 20 °C for 40 min. The particles were then exposed to UV light for 10 min while still in the presence of the organic vapor to polymerize the DSP component. Figure 4 shows high-resolution SEM images of the resulting composite particles. First, one can see a striking transformation in the particle morphology as compared to Figure 3b. The open, granular structure of the original RESS composite particles transformed to a smooth, solid, well-organized structure. The electron beam caused the particles to rupture and revealed a layered sandwich-like morphology throughout the interior volume of the particles. The DSP monomer phase segregated and recrystallized into continuous layers separated by amorphous FAA layers. FAA fibers can be seen bridging the exposed crack in the particle shown in Figure 4. We estimate from the SEM images that the thickness of the individual layers is on the order of 10 nm. The fact that a small (10 wt %) amount of the DSP monomer surrounded by the FAA polymer can undergo phase segregation and self-organization into continuous layers was somewhat unexpected as it was believed that, for the topochemical reaction to proceed to form a continuous phase, the DSP double bonds must be in close proximity and proper orientation.[15] These results suggest that, in nanoscale structures, DSP molecules have sufficient molecular freedom to reorganize into the preferred equilibrium structure. Our findings demonstrate a novel approach for the creation of fully organic polymer nanocomposites using the ability of a nanodispersed monomer, driven by thermodynamics, to self-organize into continuous layers.

To explore a provision when both components in a composite particle can potentially undergo recrystallization and self-organization, two diolefinic monomers DSP and EPA were coprecipitated from supercritical chlorodifluoromethane by RESS. The total concentration was 0.07 wt %, in which 10 wt % was DSP. Figure 5 shows typical images of the EPA−DSP composite particles developed by RESS at a preexpansion pressure of 345 bar and a preexpansion temperature of 145 °C. The composite particles have an average diameter of about 900 nm, and the general shape is closer to pure EPA particles. An intimate mixture of DSP and EPA was achieved, and no phase separation was observed according to the AFM phase image (Figure 5a). However, pronounced phase separation was observed upon vapor exposure to either methyl L-lactate or heptane vapor (Figure 5b). The DSP monomer reorganized into separate islands within the EPA matrix. Unlike the DSP−FAA composite particles, a layered structure was not produced, possibly due to the simultaneous mobilization and self-organization of the DSP and EPA components. These preliminary results suggest that for the successful formation of layered composites using this approach one of the components, abundant in quantity, should be flexible enough to conform to the template produced by the rigid monomer reorganization.

Conclusions

Intimately mixed composite nanoparticles from two conventionally immiscible compounds were produced by coprecipitation from a common supercritical fluid. One of the components was a diolefinic monomer capable of solid-state photopolymerization, and the second component was a fluorinated polymer. The self-organization of the diolefinic monomer in the presence of the polymer was induced by vapor treatment, resulting in nanoparticles exhibiting a sandwich-like lamellar structure consisting of alternating nanolayers of 2,5-distyrylpyrazine and the fluoropolymer.

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