



Morphology development in photopolymerization-induced phase separated mixtures of UV-curable thiol-ene adhesive and low molecular weight solvents

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ABSTRACT

The influence of photopolymerization rate, solvent quality, and processing parameters on the photopolymerization-induced phase separated morphology of mixtures of thiol-ene based optical adhesive with mixed solvents of diglyme and water or acetone and isopropanol is described. Upon exposure to UV radiation ($\sim 50 \text{ mW/cm}^2$, 365 nm) for periods of 10–90 s, homogeneous solutions of 5–10 wt% NOA65 and NOA81 adhesive formed phase separated structures with characteristic sizes ranging from 400 nm to 10 μm , with increased photopolymerization rates leading to smaller feature sizes. In the systems containing diglyme and water, morphologies formed by phase separation at a lower degree of photopolymerization were characteristic of spinodal decomposition, while morphologies formed by phase separation at a higher degree of photopolymerization exhibited characteristics of viscoelastic phase separation. In the systems containing acetone and isopropanol, interactions between evaporation and photopolymerization-induced phase separation led to the development of more complicated morphologies, including three-dimensional sparse networks. These morphologies provide a combination of connectivity and low overall volume fraction that can significantly enhance the performance of many multi-functional structures.

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1. Introduction

Controlled phase separation in polymer solutions has long been used as an effective means of creating useful polymer products based on well-defined morphological features. Examples include scaffolds for biological tissues [1], absorbent fibers [2], liquid crystal displays [3], foams [4], and microporous carbon [5]. Both thermally induced phase separation [6] and reaction-induced phase separation [7,8] have been used in the applications cited above. For large-scale production, reaction-induced phase separation based on UV photochemistry (photopolymerization-induced phase separation, or PIPS) is often attractive because (1) it is conveniently scaled to large size; (2) structure formation can be accomplished in a short time, thus it is readily incorporated into continuous production processes; and (3) the incorporation of macro-scale patterning is achieved with simple and reliable masking techniques.

An additional advantage of thermosetting PIPS processes is that they readily form structures with a sub-micron feature size [9]. As the increase in polymer molecular weight drives the system towards increasing instability with respect to composition over time, rapid polymerization can result in virtual immobility of the

polymer chains before coarsening processes have time to take effect. Structures formed by PIPS thus can retain many of the characteristics of patterns formed in the early stages of spinodal decomposition, such as a uniform feature size and a high degree of connectivity [10]. As an additional benefit, the cross-linked nature of the polymers formed during thermosetting PIPS typically imparts sufficient durability for the structures to survive subsequent handling and processing without being damaged.

In recent years, many of the effects observed in PIPS have been systematically explained using viscoelastic phase separation theory, which takes into account the drastic differences in the mobility of the separating phases [11–14]. As a result, the range of polymer morphologies that may be produced “on demand” (via scientific investigation followed by selection of the appropriate production process) has been extended to include, for example, very small droplets and sparse networks (interconnected morphologies formed by a component at low volume fractions). To date, though, the exploitation of viscoelastic phase separation to form such morphologies [15] has been limited.

If viscoelastic phase separation can be exploited to form polymer structures such as micro-droplets or sparse networks via a thermosetting PIPS processes, then the advantages for large-scale production inherent in PIPS will become available for affordably creating a wider range of useful morphologies. In fact, the formation of sparse network morphologies using thermosetting PIPS has

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already been noted on occasion in the context of forming polymer dispersed liquid crystals, even though in those cases it was not studied extensively since it was not the primary focus of the work [16–18]. However, for larger scale industrial applications, materials that are less expensive than liquid crystals need to be investigated. Potential applications for these controlled polymer microstructures include separation media, super-absorbents, and temperature-insensitive electrically conductive structures employing a sparse network of conductive polymer.

In what follows we describe how we utilized the principles of viscoelastic phase separation to create well-defined polymer microspheres and three-dimensional interconnected networks through a PIPS process using solutions of photopolymerizable thiol-ene adhesives. We investigated the effect of process variables such as polymerization rate, adhesive/solvent interaction energy, and solvent boiling point on the final morphology obtained by UV cure-induced phase separation. We found a number of simple and easily scalable techniques for controlling the size, interconnectedness, and three-dimensionality of the structures formed. The results may be readily extended to other material systems, demonstrating the potential of PIPS as an effective process for generating well-defined polymer microstructures in a wide variety of applications.

2. Experimental

Our general experimental procedure consisted of undertaking UV photopolymerization-induced phase separation under ambient conditions ($22 \pm 1^\circ\text{C}$, $30 \pm 5\%$ relative humidity) on solutions of commercially available thiol-ene optical adhesive formulations. The photopolymerization kinetics of thiol-enes has been previously studied [19–22] and the adhesives have been frequently employed in PIPS experiments [16,17,23]. The effect of polymerization rate was examined by employing two different commercial grades of the optical adhesive. The effect of adhesive/solvent interaction was studied by systematically varying co-solvent ratios. Lastly, comparisons were made between PIPS experiments carried out using high and low boiling solvent mixtures.

2.1. Materials

Norland[®] optical adhesives (products NOA81, which cures rapidly, and NOA65, which cures more slowly) were obtained from Norland Products (Cranbury, NJ) and used as-received. NOA65 has been reported as containing a mixture of trimethylpropane diallyl ether, trimethylpropane trithiol, and isophorone diisocyanate ester, with a benzophenone photoinitiator [23–25]. Polyethylene glycol (PEG) (average molecular weight ~ 4000), isopropanol, 2-methoxyethyl ether (diglyme, m.w. = 134), and acetone were purchased from Aldrich (histological grade, 99.5% pure) and used as-received. De-ionized water ($\sim 4.0 \text{ M}\Omega$) was provided from an in-house source.

2.2. Fabrication with high-boiling point solvents

A total of 100 mg of either thiol-ene mixture were weighed out in 20 mL glass sample vials at room temperature. The adhesive dissolved quickly with the addition of 1.3–1.6 g diglyme. De-ionized water was then slowly added to the solution over approximately 2 min to make a final composition of 5.5 wt% adhesive with diglyme/water ratios of 3:1, 4:1, 5:1, and 8:1 by weight. Rapid addition of water was avoided in order to prevent precipitation of the adhesive. The stability and homogeneity of these solutions were further verified by cooling small samples of each until precipitation was observed, then returning them to room temperature. In all cases, the precipitate re-dissolved

completely and no signs of inhomogeneity were seen on standing for several days. In addition, cloud points for various solution compositions were obtained with the aid of a Cincinnati Sub-Zero Micro-Climate chamber using heating and cooling rates of $0.1^\circ\text{C}/\text{min}$.

Solutions freshly prepared and maintained at room temperature were blade cast onto clean glass microscope slides to form $\sim 180 \mu\text{m}$ thick films. After coating, samples were exposed to $\sim 50 \text{ mW}/\text{cm}^2$ 365 nm UV light from a Norland Opticure 4 UV Curing Unit with the emitter fixed in place 1 cm above the sample for 60 s for NOA81 and 300 s for NOA65. In all cases, a translucent white precipitate formed and the formation times were noted. The films were then allowed to dry at ambient conditions.

2.3. Fabrication with low boiling solvents

A 2.5 wt% polyethylene glycol in acetone solution was formed through sonication. A total of 100 mg of NOA81 were then dissolved using 150–400 mg of isopropanol, followed by the addition of 500–750 mg of PEG/acetone solution over approximately 2 min so as not to induce product precipitation. The final concentration of NOA81 was 10.0 wt%.

As with the high-boiling solvents, the solutions were blade cast onto glass microscope slides to form $\sim 180 \mu\text{m}$ thick films and exposed to $\sim 50 \text{ mW}/\text{cm}^2$ 365 nm UV light for 60 s, with the times required for the onset of phase separation noted. The samples were then heated on a digitally monitored hot plate at 100°C in ambient air for 1.25 min, and allowed to cool gradually. Once cooled to room temperature the samples were submerged in a de-ionized water (ambient temperature) bath for 5 min to selectively dissolve the PEG while maintaining the structure formed by the NOA81.

2.4. Characterization

Atomic force microscopy (AFM) was performed on a Veeco Digital Instruments 3100 with a Nanoscope 3A controller. Fourier Transform-Infrared Spectroscopy (FT-IR) was performed on a Nexus 870 series FT-IR spectrometer in ATR mode. A Spectratech Foundation Series Thunderdome ATR adapter was used in conjunction with the Nexus operating system. Scanning electron microscopy (SEM) was performed with a Zeiss EVO-50 30 kV maximum accelerating voltage scanning electron microscope. Samples were observed at a maximum of 20 kV accelerating voltage under high vacuum with a variable pressure detector.

3. Results and discussion

3.1. PIPS in mixtures of thiol-ene and high-boiling solvents

In addition to the phase behavior, key variables that can influence morphology development during PIPS include the chemical composition, temperature, and UV radiation intensity. A check of the evaporation rates of diglyme and water in our laboratory found that within the time frame and geometrical parameters of the experiments, the change in composition due to evaporation was negligible. The high clarity and low thickness of the wet films used in our investigation helped to ensure that a significant gradient in intensity did not exist through the film thickness. Because of the slow rates of evaporation, temperature gradients caused by evaporative cooling were also judged negligible. Therefore, under the conditions used for our investigation, the photopolymerization rate and the initial system composition in relation to the phase diagram were expected to be the main factors controlling the development of morphology.

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