

Interpenetrating Networks from Photopolymerization in Lyotropic Liquid Crystal Templates

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Introduction

Monomer blending is a technique that has historically been used in industrial and laboratory settings alike to obtain new polymeric materials with unique properties. Blends of two crosslinking monomers have the ability to form separate interpenetrating networks (IPNs) that will often demonstrate a synergistic combination of each monomer constituent exhibiting properties unattainable from the homopolymerization of either monomer.^[1,2] One of the major complications in blending is that many multi-component monomer systems exhibit low compatibility between constituents resulting in phase separation, poor interfacial adhesion, and a low quality material.^[3] Furthermore, blends of two crosslinking monomers are typically highly incompatible due to the rapid increase in molecular weight and phase separation early in the polymerization.^[4]

Compatibilization of immiscible monomers has been studied extensively as a means to limit phase separation and increase the compatibility in multi-component systems. To date, compatibility in these systems has primarily been achieved through the use of surface active block copolymers or surfactants that are able to localize at the interfacial regions of immiscible blends.^[5-8] Surfactant molecules effectively decrease the size of the phase separated domains by reducing interfacial tension. Additionally, surfactant molecules will locate within each immiscible phase simultaneously to anchor the regions together and improve interfacial adhesion upon photopolymerization. Recent research in compatibilizing surfactants has demonstrated significant increases in the compatibility of immiscible monomers by reducing the phase separated domains to the micro scale through the use of emulsification and micro emulsion techniques.^[3]

The purpose of this work is to investigate the use of lyotropic liquid crystalline (LLC) mesophases as phase containing nanostructures for the compatibilization and polymerization of typically incompatible hydrophilic and hydrophobic monomers, towards the creation of IPN type materials. Possessing highly ordered structures with nanoscale dimensions, LLCs are formed by the self assembly of surfactant molecules in aqueous solutions. Previous research in this area has primarily focused on the use of LLCs as templates for polymerization reactions towards the formation of polymer networks with nanoscale structure that is derived from the LLC template.^[9-12] LLC mesophases, such as hexagonal or lamellar formations (Fig. 2) could also be utilized as a blend compatibilizing agent as these structures possess a well defined array of hydrophobic and hydrophilic domains on the nanometer size scale. Essentially, LLC mesophases could segregate immiscible hydrophilic and hydrophobic monomers in a highly ordered fashion into domains on a size scale that would approach molecular homogeneity.

The work described herein explores the use of LLCs as compatibilizing agents for a blend of incompatible, crosslinking monomers. Specifically, a self assembled hexagonal LLC mesophase is used as a monomer template to segregate hydrophobic and hydrophilic monomers into the highly ordered structural domains of the liquid crystal in the blend, as well as to limit the degree of phase separation during the polymerization process. The increase in compatibility achieved using the LLC method was analyzed by probing the type of network (IPN or phase separated) generated from the copolymerization of the immiscible crosslinking monomers within the LLC. Network swelling, mechanical, and glass transition temperature measurements were carried out to determine the physical properties of the compatibilized networks, as well as to assess the contributions of each monomer component on the final material.

Materials and Methods

Materials

Poly(ethylene glycol) diacrylate (PEGDA, Aldrich) was selected as the hydrophilic crosslinking monomer. The homopolymer of PEGDA is a rubbery, low modulus material at room temperature that exhibits considerable swelling in aqueous solutions. Hexanediol diacrylate (HDDA, Aldrich) was selected as the hydrophobic crosslinking monomer for this study. In contrast to PEGDA, HDDA is a glassy, high modulus material that exhibits little to no swelling in aqueous solutions. Poly(ethylene oxide) cetyl ether (Brij 56, Aldrich) is a low molecular weight surfactant that has been shown to self assemble into a number of LLC mesophases at specific concentrations in aqueous solutions.^[13] 2-hydroxy-1-[4-(92-hydroxyethoxy)phenyl]-2-methyl-propanone (HEPK, Irgacure 2959, CIBA Specialty Chemicals) was used as the photoinitiator in all reactions. Chemical structures of the monomers and surfactant used in this study are shown in Figure 1.

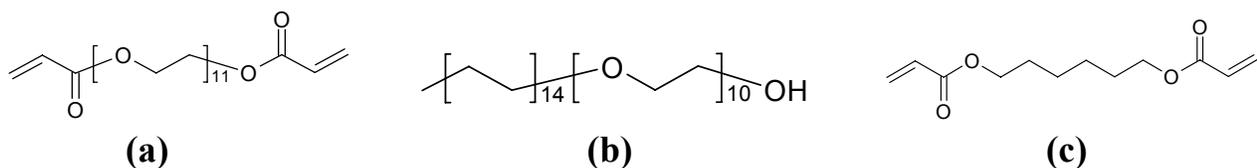


Figure 1. Chemical structures of (a) Poly(ethylene glycol) diacrylate (PEGDA), (b) Poly(ethylene oxide) cetyl ether (Brij 56), and (c) Hexanediol diacrylate (HDDA)

LLC/monomer preparation

Lyotropic liquid crystalline solutions were formed by mixing 40 wt% of a HDDA/PEGDA monomer blend, 0.5 wt% photoinitiator, and 59.5 wt% of a water/surfactant blend. The composition of the surfactant was varied to yield both isotropic and hexagonal solutions as shown in the phase diagram in Figure 3. Samples were mixed thoroughly and then pipetted into Teflon molds in a purged nitrogen glove box. Samples were cured for 10 minutes with a 365nm UV light source (1.8 mW/cm²). Post-polymerization, samples were solvent exchanged with ethanol to remove water and surfactant, and then dried in a vacuum oven. The formulation scheme for the compatibilization of immiscible monomers using LLC networks is shown in Figure 2.

Polarized Light Microscopy

A polarized light microscope (Nikon Eclipse E600W Pol, equipped with a hot stage from Instec, Boulder, CO) was used to observe the phase behavior of the monomer/LLC formulations as the surfactant/water composition in the blends was varied. LLC/monomer formulations were placed on a cover slip and brought to 25°C. The sample was then polymerized using a hand held 365nm UV light source (1.8 mW/cm²) for 10 minutes. Images from the PLM microscope were analyzed for characteristic birefringent patterns specific to certain LLC phases. Images from before and after polymerization were used to determine the degree of LLC disruption that occurred as the monomers were polymerized into crosslinked networks.

Network Swelling, Mechanical, and Glass Transition Temperature

Polymer network swelling was measured gravimetrically as dehydrated polymer disks were placed in 37°C deionized water. The degree of swelling was measured by removing the sample from the water solution, patting the surface dry, and then recording the weight of the polymer network. The weight percent water was calculated using previously established methods.^[12] This procedure was repeated until the mass of the hydrated samples did not change significantly as a function of the overall swell time. In all tests (swelling, mechanical, and glass transition temperature) three repeat samples were performed to determine the statistical error for each data point.

The compressive modulus of the LLC compatibilized materials was measured from stress strain curves obtained with dynamic mechanical analysis (TA instruments DMA Q800 series) and previously established methods.^[12] Dehydrated disks were placed into the compressive clamp on the DMA and compressed at a rate of 1 N/m to a maximum force of 15 N. The compressive modulus was determined from the stress/strain curves of the DMA test runs. Glass transition temperature (T_g) analysis was carried out using the DMA equipped with a gas cooling accessory for sub-ambient material testing. Dehydrated sample materials underwent a 1 Hz oscillation of constant 0.1% strain while the temperature was ramped from -80°C to 60°C at 2°C/min. T_g was determined by plotting both the storage modulus and $\tan \delta$ as a function of temperature.

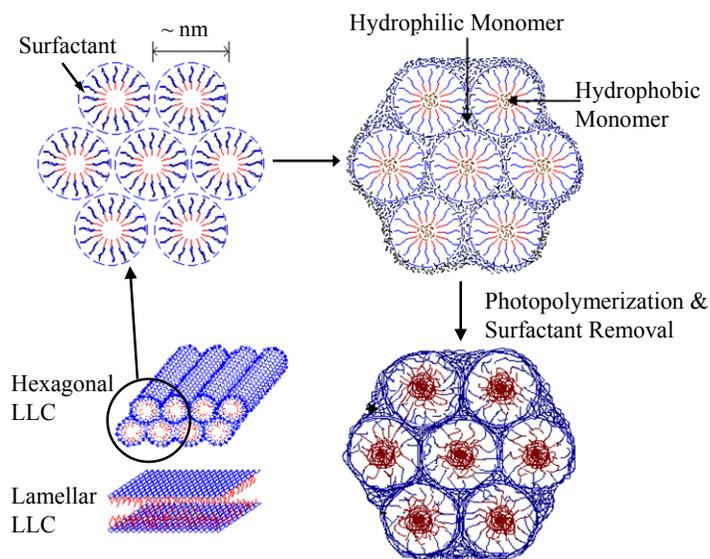


Figure 2. Diagram of the templating process with LLC mesophases. Clockwise from bottom left: Hexagonal and lamellar LLC structures; 2D hexagonal LLC with surfactant; addition of hydrophilic and hydrophobic monomers; photopolymerized material with segregated domains for each polymer constituent

Results

Phase Behavior

To test the compatibilizing effects of a LLC template on the copolymerization of immiscible blends, formulations of PEGDA and HDDA were mixed with increasing concentrations of Brij 56 surfactant. The process of copolymerizing and compatibilizing a blend of hydrophobic and hydrophilic monomers within an LLC is given in Figure 2 above. Figure 3 shows a phase diagram determined from PLM images for a 40 wt% mixture of 3:1 by weight PEGDA:HDDA in surfactant/water LLC formulations, as well as photopolymerized sample materials of each solution. With 0wt% surfactant (isotropic), there is a large degree of phase separation that occurs before and during polymerization resulting in a material that does not hold together as pictured in Fig. 3. By increasing the concentration of Brij 56 to 20 and 30 wt% (micellar phase), a small increase in compatibility can be observed in Fig. 3, including an increase in material adherence after the surfactant is removed. However, there is still a great deal of deformation and phase separation in these samples resulting in a low quality polymeric material. At 40 wt% surfactant there is the appearance of a hexagonal LLC phase in the blend solution. The corresponding material polymerized within the hexagonal LLC template appears very homogeneous, mechanically stable, and has excellent interfacial adhesion even upon surfactant removal.

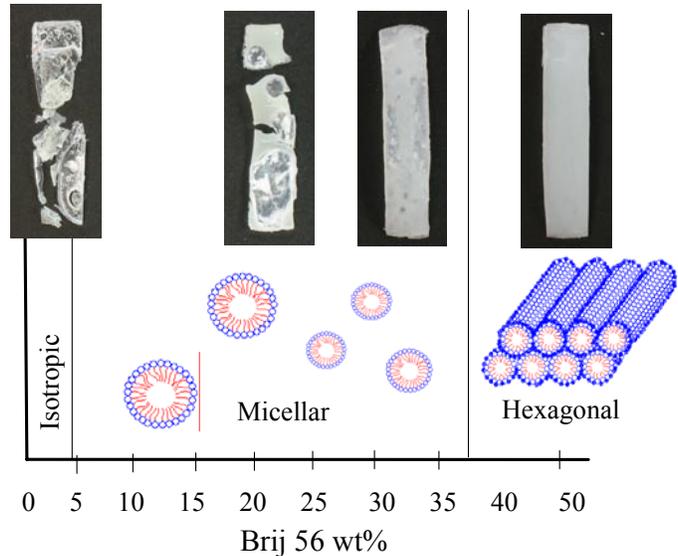


Figure 3. Phase diagram of a 40 wt% 3:1 blend of PEGDA and HDDA in water at 25C with increasing concentrations of Brij 56 surfactant. Insets are digital photographs of the 40% 3:1 blends made with (from left to right) 0%, 20%, 30%, and 40% Brij 56 surfactant.

Although there is an apparent trend between the compatibility of the PEGDA and HDDA blends and increasing surfactant concentrations (Fig. 3, 0-30 wt%), the considerable improvement of the 40% Brij 56 sample over the 30% sample suggests that the degree of compatibilization is not solely due to the linear addition of the surfactant in these solutions. By self assembling into an array of nanometer sized hydrophilic and hydrophobic domains, it is expected that the hexagonal LLC provides a stable configuration for the segregation of the two immiscible monomers on the nanometer scale. This highly structured template for the polymerization serves to greatly reduce phase separation before and during polymerization, resulting in a material with substantially improved physical properties.

Network Swelling

By increasing the compatibility between immiscible HDDA and PEGDA through the use of a hexagonal LLC template, it is expected that the resulting material will act as a homogeneous polymer blend of miscible monomers with properties intermediate of each homopolymer. Due to the vastly different polarity and swelling potentials of HDDA and PEGDA in aqueous solutions, the overall swelling was investigated to assess the swelling contributions of each monomer in the network. Materials were fabricated using 40 wt% Brij 56 surfactant to yield the hexagonal mesophase in each blend. Figure 4A shows the degree of swelling for the LLC compatibilized materials as the ratio of PEGDA and HDDA is varied. Swelling was normalized to the highest swelling material (0% HDDA), and a general decrease in the overall water uptake is observed as HDDA is increased in the monomer formulation. Though it is expected that water absorptivity of the PEGDA/HDDA/LLC networks will decrease with increasing HDDA content due to the preferential swelling of water to PEGDA, the linearity with which swelling depends on monomer concentration is noteworthy.

Mechanical Strength

Similar to swelling tests, mechanical testing was performed on the PEGDA/HDDA/LLC networks to determine the contributions of each monomer in the network. As HDDA is increased in the monomer blend, Figure 4B shows an increase in the compressive modulus of hexagonal LLC polymerized disks (fabricated with the same formulation concentrations used in the swelling tests). Again, the trend displayed in Figure 4b is expected given the large difference in modulus between PEGDA and HDDA. However, the direct dependence of the modulus measurements on the monomer composition is indicative of the high degree of compatibility between the two monomers within the blended polymer system.

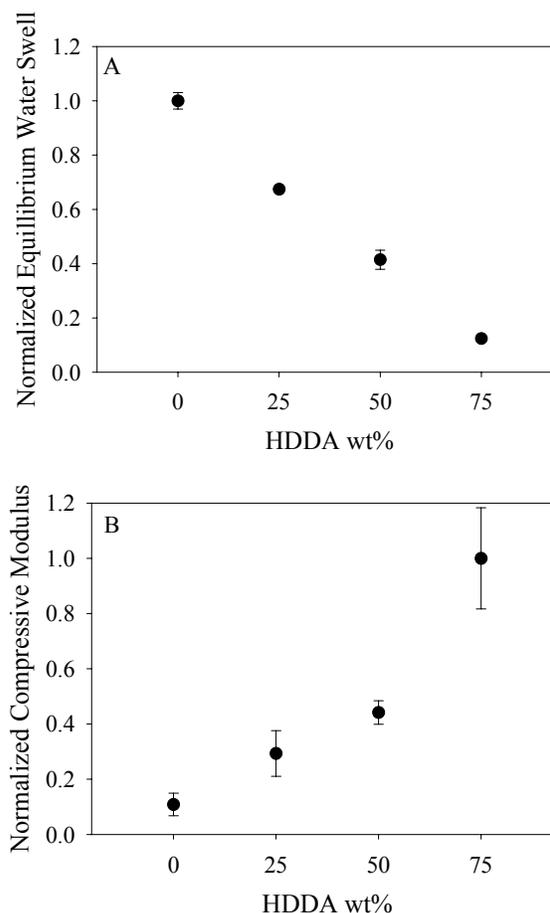


Figure 4. Normalized (A) equilibrium weight percent water and (B) compressive modulus of HDDA/PEGDA (40wt%) materials with increasing HDDA monomer composition. All samples were compatibilized with 40wt% Brij 56 surfactant to yield a hexagonal LLC polymer template. Surfactant and water are removed post polymerization, and samples are normalized to the largest value of each figure.

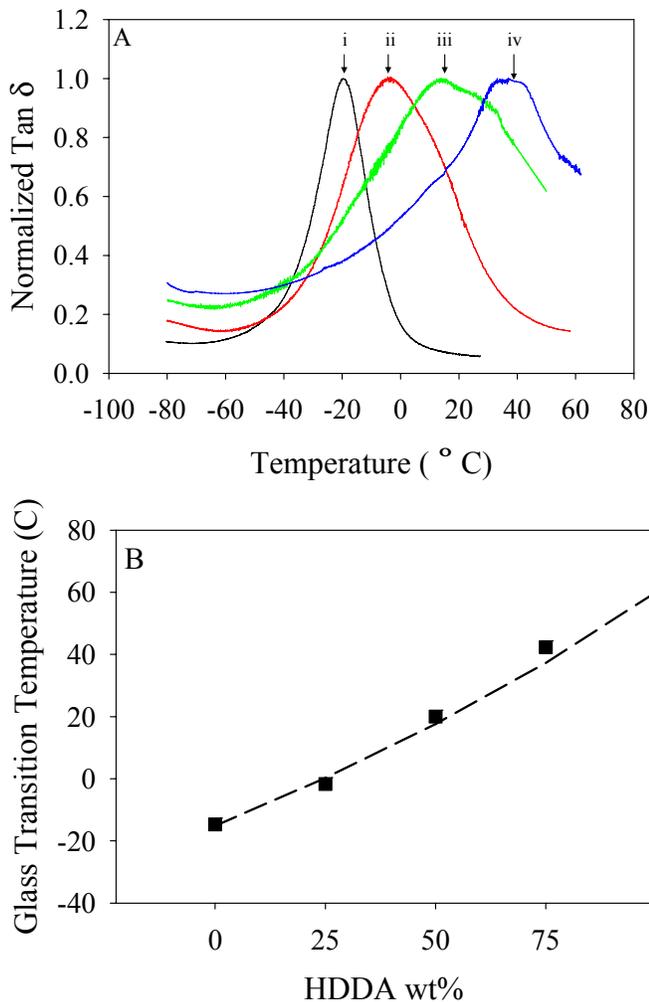


Figure 5. (A) Tan δ / temperature profiles of HDDA/PEGDA (40wt%) materials with: i) 0% HDDA, ii) 25% HDDA, iii) 50% HDDA, iv) 75% HDDA, compatibilized with 40% Brij 56 (hexagonal LLC) normalized with the peak value of each profile. (B) T_g of HDDA/PEGDA materials compatibilized with 40% Brij 56. Ideal mixing T_g calculated from the Fox equation is shown as the dashed line.

general broadening of the tan δ peak itself. Pure (100%) HDDA exhibits a broad tan δ profile with a T_g that is greater than the materials displayed in Figure 5A. Thus the change in both the height and position of the tan delta curves reflects the overall compositional change in the system as the monomer portion of the PEGDA/HDDA/LLC formulations approaches 100% HDDA.

The LLC fabricated materials were further analyzed by plotting the T_g of the formulations against the composition of the monomer blend for each material. Figure 5B shows a fairly linear increase in T_g as HDDA is increased indicating additive contributions of each monomer in the material, characteristic of a highly compatible system. Another measure of the miscibility in polymer blends is the application of the Fox equation (Eq. 1 below) that accounts for changes in T_g with the composition

Glass Transition Temperature

To probe the type of network generated by the co-photopolymerization of immiscible PEGDA and HDDA within the hexagonal LLC, the glass transition temperature (T_g) was determined for materials of increasing HDDA. T_g is a highly informative parameter for polymer blended systems as small changes in network composition or structure will typically result in a dramatic shift in the materials T_g profile. Specifically, the compatibility between constituents in a polymer blend can be directly related to the number of peaks observed in the material's tan δ profile, a common analysis plot in which the peak of the tan δ curve vs. temperature is accepted as the material's T_g. Incompatible systems typically result in two or more tan δ peaks while truly compatible blends should only exhibit one peak.

Blends of PEGDA and HDDA were again polymerized within the confinements of the hexagonal LLC phase similar to the swelling and mechanical tests above. Figure 5A shows tan δ profiles of these materials (normalized to the peak value in each curve) as the ratio of HDDA to PEGDA is increased in the monomer formulation. The single peak profiles obtained in Figure 5A is further evidence that the immiscible monomers photopolymerized within the LLC are extremely compatible. In addition, as HDDA is increased in the monomer blend, there is an incremental shift in the peak of each profile to a higher temperature, as well as a

of a multi-component system. The Fox equation assumes ideal volume mixing of each monomer in the system, and therefore, materials that follow this relationship are considered to exhibit high miscibility between monomer components.^[14]

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad \text{Eq. 1}$$

In Equation 1, w_1 and w_2 are the weight fractions and T_{g1} and T_{g2} are the glass transition temperatures of the pure polymer systems of PEGDA and HDDA respectively. The T_{g1} of the 40% PEGDA dehydrated systems was obtained from repeated testing of this material. Due to the inability to fabricate a 40% HDDA system, the T_{g2} value was extrapolated from the data in Figs. 5A,B. It should be mentioned that in all of the above tests (swelling, mechanical, T_g) a 100% HDDA sample was not feasible due to the inherent nature of the hexagonal LLC.^[15] The experimentally determined T_g points in Figure 5B closely track the relationship of the Fox equation (Fig. 5B, dashed line) suggesting that the PEGDA and HDDA form a very miscible or compatible system when photopolymerized within the hexagonal LLC.

Discussion

From previous research in polymer blends and immiscible multi-component polymer systems, it has been stated that the only way to achieve physical characteristics typical of miscible polymer blends with systems of two or more crosslinking polymers is through the formation of a specific type of polymer blend, an interpenetrating network (IPN).^[2] In the present study, the linear dependence of physical properties on polymer composition demonstrates that the compatibilization and polymerization of PEGDA and HDDA, two crosslinking polymer systems, leads to materials with properties equivalent to that of a compatibilized polymer blend.^[16] It follows then, that the physical behavior observed for the PEGDA/HDDA LLC compatibilized materials is indicating that a type of IPN is being generated with the LLC templating method.

The distinction that separates an IPN from a typical polymer blend can be found in the general definition, describing these materials as interlocking polymer networks that occur by non-interfering polymerization reactions, with little to no “crossover” crosslinking or covalent bonds between the two polymer systems.^[4, 17] It is reasonable to assume that the polar PEGDA monomers and the non-polar HDDA monomers are confined to the hydrophilic and hydrophobic domains respectively of the hexagonal LLC. A small degree of crossover polymerization between the two systems is expected due to the fact that both monomers possess acrylate functionality and will readily co-polymerize. This crossover polymerization will be minimized by the physical separation of the two components within the LLC, and by definition, a pseudo IPN will be generated. Evidence supporting the possibility of IPN formation can be observed in the polarized light microscopy images taken before and after polymerization with the PEGDA/HDDA compatibilized materials. Such images demonstrate that the hexagonal LLC ordering is present throughout the photopolymerization process indicating that the respective structure and separated phase domains also remain intact.^[11] The retention of the phase separated domains in the LLC reinforces the premise that there is a limited degree of migration and cross-polymerization between the two components, and that the two forming networks remain fairly independent, similar to an IPN type material.

Conclusion

In summary, it has been shown that LLCs can be used in the fabrication of new polymeric materials due to their inherent ability to act as both a polymerization template and as a compatibilizing agent for immiscible polymer blends. In this study, materials fabricated from a mixture of two incompatible crosslinking monomers polymerized within a hexagonal LLC demonstrated the physical properties of a compatible polymer blend. Specifically, the blended polymer systems exhibited swelling, mechanical, and T_g behavior that was linearly proportional to the monomer composition of the material, indicative of an IPN type material.

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