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Accessing photo-based morphological control in phase-separated, cross-linked networks through delayed gelation

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Abstract

This work presents an approach to extend the period for phase separation, independent of temperature, in ambient phase-separating photopolymerizations based on the copolymerization of structurally similar mono- and di-vinyl monomers. Copolymer resins composed of triethylene glycol dimethacrylate (TEGDMA) and ethylene glycol methyl ether methacrylate (EGMEMA) were modified with a thermoplastic prepolymer, poly(butyl methacrylate). With increasing EGMEMA modification into the bulk TEGDMA resin, there is a decrease in the initial reaction rate, which increases the time for development of compositionally different phases prior to network gelation. The period between phase separation and gelation was probed through optical and rheological measurements, and it was extended from 22 s in a TEGDMA resin to 69 s in a TEGDMA:EGMEMA copolymer, allowing these materials to be processed under a wide range of UV-irradiation intensities ($300 \mu\text{W cm}^{-2}$ – 100 mW cm^{-2}), which provided an additional degree of control over the resulting phase separated domain size and morphology.

GRAPHICAL ABSTRACT

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Keywords

photopolymerization; heterogeneous polymers; phase separation

INTRODUCTION

The application of heterogeneous polymer networks has been explored extensively for applications ranging from membrane development, holographic polymers, biomaterials and liquid crystal-based displays[1–5]. Heterogeneous networks are necessary in these applications as the desired bulk properties cannot be achieved from a single polymeric network or precursor[6]. However, the heterogeneous morphology can significantly alter critical properties such as strength and appearance. Therefore it is necessary to design approaches to develop heterogeneous networks where the resulting morphology is easily tunable. The traditional approach to forming heterogeneous networks includes blending of two different polymers, which involves a large mechanical and often thermal input to effectively create defined heterogeneous structure[6, 7].

Polymerization induced phase separation (PIPS) has been explored as a more elegant approach to develop network heterogeneity[8–16]. With PIPS, phase-separated structure is formed from an initially homogeneous state by the diffusion of partially or totally immiscible phases during a polymerization. Since the polymerization causes an increase in overall free energy and promotes phase separation, PIPS eliminates the need for external apparatus to form the heterogeneous structure. Understanding the balance between thermodynamic and kinetic constraints, or more simply stated, the competition between phase separation and the polymerization, is essential if precise design of heterogeneous networks is desired[17]. Thermodynamic factors influencing PIPS include miscibility between components and the system entropy[18]. Kinetic constraints on PIPS include physical properties such as viscosity that can limit the diffusion and de-mixing of immiscible phases.

One approach to directly control the kinetic constraints during PIPS is to use photo-irradiation as the mechanism of initiation. With photo-initiation, the rate at which the polymer network forms can be controlled precisely through photo-initiator selection and irradiation conditions, and there is enhanced spatial and temporal control over the polymerization. These benefits make photo-induced PIPS an attractive approach to design heterogeneous networks especially for *in situ* applications. It should be noted, that there is often an observed decrease in optical clarity of materials that undergo PIPS, which could limit the application of photo-irradiation and cause a gradient in material properties.

Photo-initiation has been used in conjunction with PIPS to control heterogeneous morphology for the development of polymer-dispersed liquid crystals (PDLC)[2–4, 19–21], and is effective for tailoring properties such as transmittance, driving voltage and contrast ratio. These studies have utilized linear based polymeric systems where the liquid crystal fraction is quite high ranging from 60–80 wt%, meaning there is a low polymer fraction in the PDLC, resulting in elastically weak materials[2–4, 20, 21].

Unfortunately, limited work has been done using photo-PIPS to form materials with a significant polymer fraction since the physical limitations to phase separation are more significant, especially if multi-functional monomers are in use[8, 11, 22]. Specifically, the conversion-dependent increase in resin viscosity during polymerization will suppress morphological development, even if not at thermodynamic equilibrium. In linear polymerizations, suppression of morphology development typically coincides with the onset of autodeceleration[8, 10], while in cross-linked resins this limit is observed at the onset of network gelation[16, 23]. Some examples of cross-linked PDLC materials formed via PIPS have demonstrated phase development that proceeds via liquid-gel de-mixing post-network gelation[3, 21], however in cross-linked networks with a high polymer fraction, it has been well studied that the amount of network development prior to gelation impacts the limiting domain size and morphology[8, 12, 24–27]. To minimize this limitation to morphology development elevated temperature is often used to enhance the diffusion of phases by reducing viscous effects[10, 12, 16, 22, 24–26]. The introduction of thiol compounds that act as chain transfer agents during the reaction are also used to delay gelation and minimize this limitation to morphology development[28]. While both are effective, the structure of the thiol utilized may change the relative miscibility in a heterogeneous system, and thus further complicate the analysis of phase separation, and the use of elevated temperature limits the use in ambient applications.

Here, we demonstrate an approach that allows heterogeneous morphology to be readily controlled in the formation of moderate to densely cross-linked, phase-separated networks formed by photopolymerization. A dimethacrylate resin modified with thermoplastic prepolymer, utilized in previous studies[29, 30] is modified by the addition of a structurally similar mono-methacrylate comonomer. The addition of the mono-vinyl decreases the viscosity as well as the conversion-dependent physical limitations to diffusion of immiscible phases during polymerization. This is different from other approaches that utilize the polymerization of comonomers to create limited miscibility during the reaction to promote PIPS[13, 14, 31], as we use the presence of a comonomer to increase the time between phase separation and gelation, but to the extent possible, not to alter miscibility. This permits a broader range of phase morphologies and processing conditions that can be utilized to form cross-linked, phase-separated networks.

EXPERIMENTAL

Materials

Ethylene glycol methyl ether methacrylate (EGMEMA, Aldrich) was added to triethylene glycol dimethacrylate (TEGDMA, Esstech) to form the bulk comonomer matrix. The amount of EGMEMA added was varied to increase the fractional contribution of double bonds present in the matrix from EGMEMA. For example, the 50:50 TEGDMA:EGMEMA designation indicates that half of the double bonds in the resin originate from each monomer; it does not indicate a molar ratio of the two monomers.

To induce phase separation, 20 wt% of poly(butyl methacrylate) (PBMA, Aldrich) was added to the comonomer matrices. This prepolymer has $M_w \sim 337,000$ Da and $T_g \sim 22.4 (\pm 2.5$ °C). The photoinitiator utilized in all studies was 2,2-dimethoxy-2-phenylacetophenone

(DMPA), which absorbs in the UV-region. The photoinitiator loading was maintained at 0.5 wt% (relative to the comonomer/prepolymer mass). A UV irradiation source was utilized in all studies to initiate polymerization ($\lambda=365 \pm 10\text{nm}$). All polymerizations were conducted at ambient temperature (22–25 °C).

Methods

Dynamic Mechanical Analysis—All samples ($8.0 \times 5.5 \times 1.0\text{ mm}$; $n=3$) were photopolymerized under ambient conditions and then post-cured at 180°C to ensure a total methacrylate conversion greater than 90%, and eliminate any possibility of additional cure occurring during the thermal analysis. A dynamic mechanical analyzer (DMA, TA Q800) was used in tension mode under 0.01% strain with a frequency of 1 Hz. After allowing the sample to equilibrate at –50°C for 20 min, the chamber temperature was raised to 200°C at a rate of 3°C min^{–1}, and then held isothermally for 20 min. The temperature was then brought back to –50°C at the same rate to verify consistency in the $\tan \delta$ data. Results presented here are from the initial ramp in temperature.

Differential Scanning Calorimetry—A differential scanning calorimeter (DSC, Perkin Elmer Pyris Series Diamond) was utilized to measure the glass transition temperature of linear poly(EGMEMA), post-ambient cure, which cannot be analyzed via DMA. A disc-shaped sample (6.5 mm diameter, 0.80 mm thickness) with mass of ~15mg was photocured ($I_0=5\text{mW cm}^{-2}$) prior to DSC analysis. The sample was placed in a 50 μL , thin-walled aluminum pan, and an empty pan of the same dimension was utilized as a reference. The sample was allowed to equilibrate at –120°C and then brought to a temperature of 50°C at a rate of 10°C min^{–1}. It was then cooled back down to –120°C and the procedure was repeated.

Kinetic Analysis—Bar-shaped specimens of dimensions $8.0 \times 5.5 \times 1.0\text{ mm}$ (*length* $\times$ *width* $\times$ *thickness*) sandwiched between glass slides were photopolymerized *in situ* to probe reaction rate development during polymerization. To measure the reaction rate, a FTIR spectrometer was utilized (Thermo Scientific, Nicolet 6700). The dynamic change in methacrylate peak area in the near-IR ($=\text{CH}_2$ first overtone at 6165 cm^{–1}) was used to calculate degree of conversion and reaction rate. All experiments were conducted with 2 cm^{–1} resolution.

Photo-Rheometry—A parallel-plate rheometer (TA Ares) was coupled to an in-house designed optical attachment that allowed for simultaneous measurement modulus development and methacrylate conversion, which has been described in detail in other work[28, 32]. The gel point was assigned as the G'/G'' crossover point[33]. Methacrylate conversion was measured utilizing a FTIR spectrometer (Thermo Scientific, Nicolet 6700) equipped with near-IR fiber optic cables. The near-IR source was directed through the center of the sample, and conversion was calculated using the same approach as in the kinetic analyses. This attachment also allowed for *in-situ*, uniform UV-irradiation of the sample. The samples were sandwiched between two quartz plates (22 mm diameter) and thickness was maintained at 300 μm . A chamber was constructed for nitrogen purging, and each sample was purged while the quartz plates were separated by 1.5 mm for 1 h. This was done

to remove all dissolved oxygen and avoid any oxygen-inhibited edge effects, which would confound the rheological data.

Viscosity Measurements—The same rheometer utilized for gel-point determination was used to measure the initial viscosity of comonomer/prepolymer solutions. A steady rate sweep test (strain-controlled) was performed on samples with 0.200 mm thickness and 22 mm diameter. The initial rate in the tests was 0.1 s^{-1} and the final rate was 1000 s^{-1} .

Optical Property Development During Polymerization—Disc-shaped samples were fixed to an optical bench used to monitor dynamic changes in optical properties during polymerization. The samples, which were sandwiched between a glass slide and coverslip, had dimensions of 20 mm diameter and 240 μm thickness. The samples were irradiated with a UV-curing light source ($\lambda=365 \pm 10\text{nm}$), to initiate the polymerization. Near-IR fiber optic cables were used to measure methacrylate conversion during polymerization under the same conditions as noted previously with a FTIR spectrometer (Thermo Scientific, Nicolet 6700). A broadband light source that emits visible light ($\lambda=400\text{--}800\text{nm}$) was transmitted through the material during polymerization, and a UV/Vis portable spectrometer (Ocean Optics, USB 2000) was used to monitor dynamic changes in visible light transmission, specifically the intensity of 600nm light transmitted through forming material. Since DMPA does not absorb above 380 nm[34] the visible light source acts as a probe independent of the photoinitiator and does not affect the reaction kinetics.

Atomic Force Microscopy—Atomic force microscopy (AFM, Easy Scan 2 Nanosurf) was used to image heterogeneous networks post ambient photopolymerization. All images were collected in tapping mode using conical tapping mode AFM probes with a spring constant of 50 N m^{-1} (Aspire CT-170). The images presented in this manuscript are phase contrast maps.

RESULTS AND DISCUSSION

Dynamic Mechanical Analysis (DMA)

To detect multi-phase structure post-cure, $\tan \delta$ profiles were evaluated with DMA. This was first done on copolymer networks without prepolymer (PBMA) to ensure no phase separation occurred from the bulk copolymerization of TEGDMA and EGMEMA. In the bulk copolymers, all $\tan \delta$ profiles display one broad asymmetric peak, indicating single-phase network structure (Appendix Figure A.1). With increasing EGMEMA modification, the main peak in the $\tan \delta$ profile shifts to lower temperatures from 161°C for bulk poly(TEGDMA) to 139°C and 105°C in 75:25 and 50:50 TEGDMA:EGMEMA resins respectively. This is expected, as the decrease in overall cross-linking will decrease the T_g . The peak breadth and presence of a slight shoulder at lower temperatures are attributed to the heterogeneous nature of methacrylate based cross-linking polymerizations, and specifically the formation of cycles[35]. This is supported by the fact that the contribution of the shoulder to the total area underneath the $\tan \delta$ curve is equivalent independent of the degree of EGMEMA modification. The linear poly(EGMEMA) in bulk was found to have a broad T_g from $0\text{--}20^\circ\text{C}$. While this does correlate with observed shoulders, and could

indicate a degree of separation between the mono- and di-vinyl monomers, other experiments presented in this study indicate that no distinct phase separation occurs without the introduction of prepolymer.

When PBMA is introduced into the comonomer matrix multi-phase structure, as detected by multiple peaks in the $\tan \delta$ profile, is observed (Figure 1), indicating the formation of compositionally different phase-separated structures. A loading level of 20 wt% PBMA was chosen to induce phase separation since in previous studies with all-dimethacrylate resins, this was found to induce significant phase separation during polymerization[29, 30].

In all phase-separated matrices, the first peak in the $\tan \delta$ profile lies between the T_g of pure PBMA (22.4°C) and bulk copolymer (Appendix Figure A.1). The second peak, which occurs at a higher temperature, falls very close to the bulk copolymer T_g . Table 1 displays the comparison between the T_g of the bulk copolymer resins and the T_g assigned as the copolymer-rich domains in phase-separated networks. The difference in the copolymer-rich T_g compared to the bulk copolymer is not significant, as determined by a paired t-test with a 95% confidence interval. This indicates that a structurally similar network forms in the copolymer-rich regions of the phase-separated networks as in the bulk copolymers, and that the phase separation does not lead to significant differentials in diffusion of either monomer present in the resin. This is expected, since at the initial stages of polymerization all vinyl groups from either EGMEMA or TEGDMA have similar reactivity whether present on a free monomer, pendant vinyl group, or a cross-linker molecule. Propagating radicals will react with these different vinyl groups statistically based on differences in concentration, but are not influenced by any differences in affinity for the either of the monomers.

With this observation, it is expected that a phase rich in copolymer and a phase rich in copolymer/prepolymer form during PIPS. To estimate the composition of each phase, a modified version of the Fox equation[36] was utilized (Equation 1).

$$\%PBMA = \left(\frac{T_g^{Copolymer} - T_g^{NewPhase}}{T_g^{Copolymer} - T_g^{PBMA}} \right) * 100 \quad (1)$$

Using this relationship, the relative composition (wt%) of PBMA in the copolymer rich phase and the prepolymer rich phase was found for phase-separated networks at varying levels of EGMEMA modification. In all cases, the copolymer-rich phase has minimal PBMA present, consistently at a level of 10 wt% or less. However, the level of PBMA in the prepolymer-rich phase varied based on the degree of EGMEMA modification (Figure 2).

As the degree of cross-linking decreases, the PBMA mass fraction in the prepolymer-rich phase increases. This is the first indication that the diffusion of small molecules during PIPS differs based on the initial resin viscosity and the degree of cross-linking present in the matrix. Similar trends of PBMA weight fraction increasing in prepolymer-rich domains with EGMEMA modification is observed when the materials are formed under more rapid or slower irradiation conditions ($I_0=20 \text{ mW cm}^{-2}$ or $300 \mu\text{W cm}^{-2}$ – Appendix Figures A.2 and A.3). At the lowest irradiation conditions tested, there is only a significant difference in the

PBMA mass fraction in the 100:0 modified matrix, which is lower than that of the 50:50 and 75:25 modified systems. At such a low rate of network formation, only the most densely cross-linked system imposes significant limitations to diffusion of immiscible phases.

Viscosity and Kinetics of Reaction

The viscosity of each comonomer/prepolymer solution, prior to polymerization was measured using a parallel plate viscometer (Table 2). With increasing dimethacrylate fraction in the bulk comonomer resin, there is a gradual associated increase in viscosity. Additionally, the introduction of prepolymer significantly increases resin viscosity as compared to the control matrices.

Knowing these significant differentials in initial solution viscosities (Table 2), the polymerization kinetics were analyzed using FTIR spectroscopy. The dynamic change in rate of polymerization (R_p) was calculated from the real-time conversion data. The kinetic rate profiles for polymerizations conducted at $I_0=5\text{mW cm}^{-2}$ are shown for the control copolymer resins (Appendix Figure A.4) and the phase separating resins (Figure 3).

All reaction rate profiles, regardless of degree of EGMEMA or PBMA modification display an autoacceleration period typical of a cross-linking polymerization[37, 38]. In both the control and PBMA modified networks, the initial rate in the 100:0 matrix is largest, as it has a higher initial viscosity that favors diffusion limited termination earlier in the reaction. Since the resin viscosity decreases with EGMEMA addition (Table 2), it is not until a higher extent of polymerization that the viscosity is high enough to limit termination and allow for increase in overall polymerization rate in the 75:25 and 50:50 matrices. This is why with increasing EGMEMA modification, the maximum rate of polymerization (R_p^{max}) and presumably the onset of vitrification are delayed in the reaction[39], which leads to an increase in final degree of methacrylate conversion. (This behavior is observed in both control and PBMA-modified polymerizations.)

Certain aspects of the polymerization kinetics are altered significantly by the phase separation induced by PBMA modification (Figure 3) compared to the control matrices (Appendix Figure A.4). First, at all levels of EGMEMA modification, during PIPS the absolute value of R_p is reduced compared to the control polymerizations due to the significant increase in viscosity by introducing PBMA into the matrix, thus limiting diffusion of all species in the reaction medium. Second, in all phase-separating reactions the autoacceleration period is expanded compared to the control matrices. The period during which a relatively high R_p is observed extends for a much larger portion of the reaction, and results in a higher limiting conversion than in the non-phase-separating counterparts. This expanded period is likely a result of the formation of compositionally different domains, which will undergo local autoacceleration behavior at different points of the polymerization, and thus enhance the observed bulk autoacceleration behavior. Contributing to this behavior is the delayed vitrification in the prepolymer-rich phase as a consequence of the relatively low prepolymer T_g . The same kinetic trends amongst varying degrees of EGMEMA modification were observed at lower ($I_0=300\text{ }\mu\text{W cm}^{-2}$) and higher ($I_0=20\text{mW cm}^{-2}$) irradiation intensities tested (Appendix Figures A.5, A.6).

The observed kinetic profile supports the phase composition findings (Figure 2). With a delayed autoacceleration period, the 50:50 modified matrices have an extended opportunity for diffusion of small molecules (i.e. small radicals and monomer, though likely not prepolymer to any significant degree) to a much later extent of reaction. This allows for thermodynamic diffusion of TEGDMA and EGMEMA monomer out of the prepolymer rich domains, to form a phase more concentrated in PBMA. Since the mono- and di-vinyl monomers used in this study were intentionally selected to have structural similarity, we do not expect selective diffusion of either monomer out of the prepolymer-rich domains based on affinity. However, since only free monomer can diffuse, there is likely that slightly more of the EGMEMA diffuses into copolymer-rich domains prior to gelation. This potential variation in diffusion, however, does not make a significant impact on the composition of copolymer rich domains as the pure copolymer T_g and copolymer-rich T_g 's in phase-separated networks are equivalent at varying levels of EGMEMA modification (Table 1).

Onset of Phase Separation & Gelation Measurements

The period of time that occurs between phase separation and gelation is critical in a system that undergoes PIPS, as diffusion is suppressed after macrogelation. Previously, we have shown that in a purely dimethacrylate based phase-separating polymerization, maximizing the extent of network development between phase separation and network gelation is highly favorable as it allows for the formation of co-continuous network morphology and maximizes the level of internal polymerization stress reduction[30]. Therefore, to validate that the diffusion potential during PIPS is increased pre-gelation with EGMEMA modification as implied by the results thus far, the onset of phase separation and gelation need to be characterized directly.

The onset of network gelation and the onset of phase separation were measured in PBMA modified comonomer matrices utilizing photo-rheometry and changes in optical density, respectively. The onset of network gelation was assigned as the G'/G'' crossover point[33], measured coincidentally with coupled near-IR conversion and photo-rheometry. The onset of phase separation during polymerization was taken as the point at which a decrease in the visible light transmission ($\lambda=600\text{nm}$) was observed as measured by UV/Vis analysis with an optical bench set-up. Although these two points were measured independently and in different apparatuses, the irradiation conditions and sample geometry were nearly identical so reasonable comparisons can be made between the two. The measured degree of conversion at these two different reaction benchmarks is shown in Table 3.

The onset of phase separation is nearly instantaneous with the polymerization, occurring at roughly 1–4% methacrylate conversion independent of the level of EGMEMA modification. This indicates that in all resins, the polymerization leads to limited miscibility early on in the reaction. The gelation behavior, however, varies with the degree of EGMEMA modification. For reference, the gel point conversion for the three different control copolymer resins, 100:0, 75:25, and 50:50 TEGDMA:EGMEMA, occur at 3.4, 4.5 and 6.3% methacrylate conversion respectively. This behavior is expected of the control matrices, as the mono-vinyl modification is known to modestly delay network gelation to higher degrees of conversion. However, when PIPS occurs in the matrix, gelation is delayed significantly from

that of the control, and that delay corresponds to an additional 10–20% overall methacrylate conversion occurring in the pre-gel state.

It is difficult to probe the exact origin of the substantial and reproducible delay in gelation with respect to conversion observed in the 75:25 TEGDMA:EGMEMA, 20 wt% PBMA network when compared to the other matrices undergoing PIPS. This is likely due to the nature of the phase-separated domains formed as well as the local differentials in the polymerization kinetics. If a dispersed phase structure forms, the network formation in the continuous domain determines the bulk gel point. If the volume fraction of dispersed domains is small, then the polymerization proceeds mostly in the continuous phase, and gelation is observed earlier in the reaction. However, if a fully co-continuous domain structure is formed, gelation will be delayed substantially until one of the continuous domains gels, which has been shown experimentally[30]. Depending on the kinetic rate differential between the two phases formed, as well as any additional diffusion of monomer that occurs early on in the reaction, the delay in gelation may vary substantially between the different copolymer-based resins.

While the extent of conversion that occurs between phase separation and gelation is important, it is again helpful to relate the extent of conversion between these reaction benchmarks to time intervals, since both the reaction kinetics (Figure 3) and the resulting phase compositions (Figure 2) vary significantly with extent of EGMEMA modification. The amount of time between these two reaction benchmarks was calculated based on the kinetics of the reaction, and are also presented in Table 3.

With increasing EGMEMA modification, there is increasing elapsed time between phase separation and gelation, and this increase is most significant when increasing the modification from the 75:25 to the 50:50 matrix. This supports the previous results on purity of phases formed. The error in these measurements becomes larger with increasing degree of cross-linking, which is again a consequence of the heterogeneous nature of dimethacrylate polymerizations that become more significant in a bulk TEGDMA resin[37, 38]. The extended period between phase separation and gelation in the EGMEMA-modified systems is very promising as it presents an approach, independent of temperature, to extend the time for diffusion of partially miscible components during PIPS.

Monitoring phase separation during polymerization and corresponding phase-structure post-cure

With a longer interval available for phase separation, especially in the 75:25 and 50:50 matrices, it is likely that distinctly phase-separated networks can be formed under a broad range of irradiation conditions. Previous approaches to morphology control with photo-irradiation in PIPS have only explored UV curing intensities less than 1 mW cm^{-2} [3, 10] and visible light intensities less 4 mW cm^{-2} [8, 11] so as not to suppress the phase separation due to diffusion constraints imposed by a rapidly forming network. Here, since the EGMEMA modification expands the time interval available for phase separation, the processing conditions under which phase-separated networks can form may be greater.

To explore this possibility, the phase separation and resulting heterogeneous morphology of 50:50 and 75:25 matrices modified with PBMA were monitored using a real-time light transmission technique and atomic force microscopy, when formed at three different irradiation intensities ($I_0 = 20 \text{ mW cm}^{-2}$ - high, 5 mW cm^{-2} - intermediate, $300 \mu\text{W cm}^{-2}$ - low).

The real-time light transmission technique used in this study characterizes the changes in visible light transmission during polymerization. The onset of turbidity is used as a sign of phase separation during polymerization, as it indicates whether a material has domains of differing refractive indices (RI)[9]. During PIPS, two main factors will lead to differences in RI. The first will be the difference in relative methacrylate conversion between the phases formed. In a pure comonomer resin, as methacrylate conversion increases, the RI will increase in a linear manner. Therefore, domains polymerizing at nonequivalent rates and with different degrees of local conversion during PIPS will have disparity in RI. For reference, the RI's of initial comonomers and fully cured copolymer resins without PBMA are included in the Appendix (Table A.1) [40]. The second factor that contributes to local disparity in RI is the compositional differences between domains. We have characterized that two phases form during the polymerization; one highly rich in comonomer and the other composed of a varied mixture of comonomer and PBMA. The pure prepolymer, PBMA, has a RI of $\sim 1.4804 (\pm 6\text{E-}4)$, which will either increase or decrease the local RI depending on the relative mass fraction of PBMA and extent of methacrylate conversion.

The formation of micro-sized domains may also lead to a decrease in the level of light transmission during polymerization. Post gelation, due to diffusion constraints, there should be no significant changes in morphology shape or size. Therefore, significant changes in light transmission behavior after macro-gelation are likely due changes in the RI differential between phases.

The light transmission during polymerization of the 75:25 TEGDMA:EGMEMA copolymer as well as the 75:25 matrix modified with PBMA is displayed in Figure 4 at varying irradiation intensities. The control matrix, 75:25 TEGDMA:EGMEMA does not experience any significant change in visible light transmission during polymerization, as there is no significant local difference in RI. In the matrices with PBMA that undergo PIPS, turbidity is observed very early in the reaction. This results from two phases of differing refractive indices at the onset of phase separation. The degree of light transmission continues to decrease as diffusion of partially miscible components, as well as the kinetic development of the two phases occurs at non-equivalent rates, increasing the refractive index disparity. This is followed by a period where the intensity of light transmission is recovered. Here, polymerization approaches limiting conversion in both phases and differences in RI based on extent of reaction are minimized. The final degree of clarity is based on compositional and extent of conversion differences between the two phases formed.

To demonstrate that the phase separation process and significant increase in turbidity during PIPS does not alter the degree of conversion measurements, we selected a material with an even more extreme optical density increase during polymerization to validate our real-time conversion calculations (the details of this experiment are included in the Appendix). The

result was that the final methacrylate conversion did not vary when measured with or without the use of an internal standard. This demonstrates that despite the increase optical density associated with PIPS, excellent penetration efficiency of the near-IR wavelengths leads to negligible signal loss and also verifies that any dimensional change as a consequence of polymerization shrinkage does not alter the conversion measurement. Therefore, the use of the dynamic change in methacrylate peak in the near-IR is valid for the material systems tested here.

At varying irradiation intensities similar qualitative behavior with regards to changes in light transmission are observed, but the minimum value of light transmission varies significantly. Additionally, the rate at which light transmission decreases within the material is slower at higher irradiation intensities (i.e. the minimum light transmission is not observed until later stages in the reaction).

The resulting morphology of the 75:25 matrices modified with PBMA was characterized with AFM (Figure 5). There is an observed decrease in the size of phase-separated domains as a function of irradiation intensity. The resulting domain size was calculated by taking a weighted average of segments in both the x and y -direction with similar phase angles. At low and intermediate irradiation intensities, the domain sizes are relatively similar (Low: $2.2 \pm 1.6 \mu\text{m}$, Intermediate: $2.7 \pm 1.9 \mu\text{m}$). But the size of phase-separated domains decreases ($0.60 \pm 0.45 \mu\text{m}$) significantly at the high irradiation intensity, $I_0=20\text{mW cm}^{-2}$. This is not unexpected, as with increasing light intensity, the time for diffusion and morphological development decreases, minimizing the time for coalescence of the incipient phase-separated domains, making them smaller.

In the 50:50 modified polymerizations, similar differences in light transmission during polymerization (Figure 6) and domain size (Figure 7) are observed as in the 75:25 modified matrices. In this material with increasing irradiation intensity, the resulting domain size decreases steadily from $3.3 \pm 2.5 \mu\text{m}$, $2.5 \pm 1.5 \mu\text{m}$, to $0.81 \pm 0.62 \mu\text{m}$ for low, intermediate and high irradiation intensities, respectively. Again, the minimum value of light transmission also increases with irradiation intensity.

When compared to the 75:25 resins, the 50:50 modified matrices have a more dramatic loss of light transmission during polymerization at the irradiation intensities tested. This correlates nicely with the final phase composition results presented earlier (Figure 2). Since in the 50:50 modified matrices, a more concentrated PBMA-rich phase is formed than in the 75:25 counterpart, there will be a more significant disparity in refractive index between the comonomer-rich and comonomer/PBMA-rich phase. The increased diffusion potential in the 50:50 matrices permits the formation of a phase more concentrated in PBMA. While the reduction in transmitted visible light ($\lambda=600\text{nm}$) is as great as 50% in some polymerizations, since the materials in these experiments end up close to an optically thin film state, no significant decrease is noted in the overall degree of conversion through the material thickness. However, if applying these reactions to optically thick materials, the decrease in light transmission could create issues in obtaining uniform bulk properties.

The results of light scattering experiments and morphology characterization for 100:0 TEGDMA:EGMEMA polymerizations are included in the appendix (Figures A.7–8). In these matrices, the optical development during PIPS does not vary significantly as a result of irradiation intensity. The resulting phase structure is also constant across the three different polymerization rates (Figure S.8). The morphology appears co-continuous and the average domain size is $0.5 - 1.5 \mu\text{m}$ at all three irradiation intensities. (Low: $0.82 \pm 0.57 \mu\text{m}$, Intermediate: $1.28 \pm 0.92 \mu\text{m}$, High: $0.66 \pm 0.50 \mu\text{m}$). The high cross-link density in the bulk matrix reduces the time interval available for phase separation via diffusion. Therefore, no distinct difference in morphology is observed at varying kinetic regimes since diffusion is limited uniformly under all irradiation conditions.

The significant differences in light transmission behavior as a function of irradiation intensity in the 50:50 and 75:25 modified matrices highlights significant advantages with these phase-separating polymerizations. In these matrices the increased interval for diffusion pre-gelation permits irradiation intensity to be utilized as a key control parameter to vary phase structure. It is possible that the differential in reaction rate between the two phases formed varies with irradiation intensity, which would also contribute to the increased scattering observed. In the lower irradiance polymerizations, primary radical diffusion is not limited in initial stages of the reaction, so the polymerization can proceed primarily in the copolymer rich regions that effectively have a much higher double bond concentration and will be thermodynamically preferred. This is difficult to show experimentally, since both phases rely on the conversion of methacrylate functional groups so their individual conversions cannot be monitored separately. In some phase-separating reactions studied previously, two distinct kinetic regimes have been observed during polymerization, one example being based in the copolymerization of a monomethacrylate and a dimethacrylate with limited miscibility[31]. These distinct and separate regimes make it much simpler to assign the order of polymerization of the two phases formed. We do not observe two distinct kinetic regimes and it is likely that our phases polymerize simultaneously but at differing rates. Since our current kinetic approaches can only monitor bulk methacrylate conversion as a function of time, future studies in this area should probe the dynamic difference in local methacrylate conversion.

As stated, phase structure control through photo-PIPS has only been demonstrated over a limited range of irradiation intensities, and not at all at UV-irradiation intensities above 1 mW cm^{-2} . With the system presented here, we have already demonstrated that we can use photo-PIPS in high irradiation (20 mW cm^{-2}) UV photopolymerizations. To further demonstrate the range of kinetic conditions available for curing this material system, the 50:50 TEGDMA:EGMEMA, 20 wt% PBMA resin was cured under ambient conditions at $I_0=100 \text{ mW cm}^{-2}$. The phase structure post-ambient cure is displayed in Figure 8. From this image, it can be seen that PIPS is not suppressed and dispersed phase structure with domains on the order of $0.98 \pm 0.62 \mu\text{m}$ in size, similar to what is observed for the same resin cured at $I_0=20 \text{ mW cm}^{-2}$ (Figure 7C), forms. Although this indicates that a limit in the size of domains formed has been reached (i.e. the size scale cannot be pushed to nanoscale domains by further increasing the irradiation intensity), it shows that this material system can be applied to create phase-separated networks cured under much more rapid conditions than have been explored previously.

CONCLUSIONS

These results highlight some of the advantages and control that can be exploited by introducing monomethacrylate modification into a phase-separating, methacrylate-based polymerization. In an exclusively dimethacrylate resin, there is little control offered by adjusting the irradiation intensity. The formation of high concentrations of cross-linked microgels during the pre-gel stage of the reaction prohibits significant diffusion during the phase-separation process[41, 42], meaning little control is offered by changing the reaction conditions.

In the EGMEMA modified resins, the decrease in initial reaction rate (Figure 3) increases the time for diffusion prior to gelation (Table 3) such that distinctly phase-separated structure forms much more readily and larger domains, which are also more concentrated in prepolymer can form. This effect becomes exaggerated in the lowest intensity polymerizations, where there is a significant loss of light transmission in the materials (Figures 4, 6). This extended period prior to gelation allows processing of bulk, cross-linked, phase-separated networks to be conducted at a much wider range of irradiation intensities. Previous work has been limited to UV processing at or below 1mW cm^{-2} , whereas the current materials still produce phase-separated morphologies at intensities as high as 100mW cm^{-2} .

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APPENDIX

Validation of Double Bond Conversion Calculations without Internal Standard

A homogeneous resin composed of isodecyl methacrylate (IDMA) and BisGMA in a 7:3 mole ratio, has previously been shown to undergo PIPS along with a drop in the light transmission at 600 nm, which is due to the distinctly different compositions and refractive indices of the phases formed. In that system, light transmission rapidly approaches 0 % by 5 % conversion and remains nearly opaque throughout the polymerization process. [31]. For that IDMA/BisGMA resin, the final degree of conversion was measured with NIR spectroscopy in a 0.5 mm thick specimen disk with and without use of an internal reference (the NIR aromatic C-H band at 4623 cm^{-1} was used as the internal standard as validated by Stansbury et al. [43]). The result was that the final IDMA/BisGMA conversion was $84.5 \pm 1.0\%$ while the analogous measurement employing the aromatic internal reference was $86.2 \pm 0.3\%$. This demonstrates that despite the increase optical density associated with PIPS, excellent penetration efficiency of the near-IR wavelengths leads to negligible signal loss and also verifies that any dimensional change as a consequence of polymerization shrinkage does not alter the conversion measurement. Considering that the IDMA/BisGMA resin undergoes more dramatic and irreversible optical density change compared with the

TEGDMA-based prepolymer-modified resins used in the current study at only a 240 μm specimen thickness, the conversion data reported here can be reasonably assumed reliable.

Refractive Index

The refractive index (n_D^{22}) of each comonomer/prepolymer resin was measured with a refractometer (Atago T2). Fully cured refractive indices were found by extrapolation of the copolymer/prepolymer refractive indices measured at varying extents of conversion. The refractive index of PBMA was found by extrapolation from increasing concentrations of PBMA in TEGDMA monomer (Table S.1).

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Highlights

We explore phase separation in a comonomer matrix modified with linear polymer.

The ratio of comonomers is varied to increase diffusion during phase separation.

Heterogeneous morphology is controlled with photo- irradiation intensity.

Increasing irradiation intensity decreases heterogeneous domain size.

Phase separated morphology is formed under very rapid polymerization conditions.

Figure 1.

Tan delta profiles, post-cure of TEGDMA:EGMEMA copolymer resins modified by 20 wt% PBMA. All samples were photopolymerized ($I_0=5\text{mW cm}^{-2}$) under ambient conditions and thermally post-cured at 180°C prior to analysis.

Figure 2.

Weight fraction of PBMA in copolymer/prepolymer rich phase post-polymerization (n=3). Weight fraction calculated using shift in T_g as measured by DMA and applying a modified version of the Fox equation. All samples were photocured under ambient polymerization conditions ($I_0=5\text{mW cm}^{-2}$) and thermally post cured at 180°C prior to analysis.

Figure 3. Polymerization rate development in TEGDMA:EGMEMA matrices modified by 20 wt% PBMA ($I_0=5mW\ cm^{-2}$). R_{pmax} is observed in the reaction approximately 51, 51 or 78 s after initiation for the 100:0, 75:25 and 50:50 modified resins, respectively.

Figure 4.

Real-time changes in visible light transmission during polymerization at varying light intensities for 75:25 TEGDMA:EGMEMA, 20 wt% PBMA polymerizations. Polymerization initiated via UV-irradiation at varying intensities $\lambda=365\text{nm}$. Visible light transmission monitored at $\lambda=600\text{nm}$, which acts independent of the photoinitiating light source.

Figure 5. Phase morphology of 75:25 TEGDMA:EGMEMA, 20 wt% PBMA networks cured at varying light intensities, post-polymerization. (A) $I_0=300 \mu\text{W cm}^{-2}$ (B) $I_0= 5 \text{ mW cm}^{-2}$ (C) $I_0=20 \text{ mW cm}^{-2}$. Scale bar = $10\mu\text{m}$.

Figure 6.

Real-time changes in visible light transmission during polymerization at varying light intensities for 50:50 TEGDMA:EGMEMA, 20 wt% PBMA polymerizations. Polymerization initiated via UV-irradiation at varying intensities $\lambda=365\text{nm}$. Visible light transmission monitored at $\lambda=600\text{nm}$, which acts independent of the photoinitiating light source.

Figure 7.

Phase morphology of 50:50 TEGDMA:EGMEMA, 20 wt% PBMA networks cured at varying light intensities, post-polymerization. (A) $I_0=300 \mu\text{W cm}^{-2}$ (B) $I_0= 5 \text{ mW cm}^{-2}$ (C) $I_0=20 \text{ mW cm}^{-2}$. Scale bar = $10\mu\text{m}$.

Figure 8.
Phase morphology of 50:50 TEGDMA:EGMEMA, 20 wt% PBMA network cured at $I_0=100$ mW cm^{-2} post-polymerization. Scale bar = $5\mu\text{m}$.

FIGURE A.1.

Tan delta profiles, post-cure of copolymer resins, formed of EGMEMA and TEGDMA. The ratios (i.e. 50:50, 75:25) correspond to the percentage of double bonds coming from TEGDMA or EGMEMA respectively. All samples were photopolymerized ($I_0=5 \text{ mW cm}^{-2}$) under ambient conditions and thermally post-cured at 180°C prior to analysis.

FIGURE A.2.

Weight fraction of PBMA in copolymer/prepolymer rich phase post-polymerization ($n=3$). Weight fraction calculated using shift in T_g as measured by DMA and applying a modified version of the Fox equation. All samples were photocured under ambient polymerization conditions ($I_0=20 \text{ mW cm}^{-2}$) and thermally post cured at 180°C prior to analysis.

FIGURE A.3.

Weight fraction of PBMA in copolymer/prepolymer rich phase post-polymerization ($n=3$). Weight fraction calculated using shift in T_g as measured by DMA and applying a modified version of the Fox equation. All samples were photocured under ambient polymerization conditions ($I_0=300\mu\text{W cm}^{-2}$) and thermally post cured at 180°C prior to analysis.

FIGURE A.4.

Polymerization rate development in TEGDMA:EGMEMA matrices ($I_0=5\text{mW cm}^{-2}$). $R_{p\text{max}}$ is observed in the reaction approximately 42, 63 or 116 s after initiation for the 100:0, 75:25 and 50:50 resins, respectively.

FIGURE A.5.

Polymerization rate development in TEGDMA:EGMEMA matrices modified by 20 wt% PBMA ($I_0=300\mu\text{W cm}^{-2}$). R_p^{max} is observed in the reaction approximately 229, 247 or 287 s after initiation for the 100:0, 75:25 and 50:50 modified resins, respectively.

FIGURE A.6.

Polymerization rate development in TEGDMA:EGMEMA matrices modified by 20 wt% PBMA ($I_0=20\text{mW cm}^{-2}$). R_p^{max} is observed in the reaction approximately 25, 29 or 64 s after initiation for the 100:0, 75:25 and 50:50 modified resins, respectively.

FIGURE A.7.

Real-time changes in visible light transmission during polymerization at varying light intensities for 100:0 TEGDMA:EGMEMA, 20 wt% PBMA polymerizations. Polymerization initiated via UV-irradiation at varying intensities $\lambda=365\text{nm}$. Visible light transmission monitored at $\lambda=600\text{nm}$, which acts independent of the photoinitiating light source.

FIGURE A.8.

Phase morphology of 100:0 TEGDMA:EGMEMA, 20 wt% PBMA networks cured at varying light intensities, post-polymerization. (A) $I_0=300 \mu\text{W cm}^{-2}$ (B) $I_0= 5 \text{ mW cm}^{-2}$ (C) $I_0=20 \text{ mW cm}^{-2}$. Scale bar = $10\mu\text{m}$.

TABLE 1

Copolymer T_g in Control Networks and Phase-Separated Networks ($I_0=5\text{mW cm}^{-2}$, $n=3$).

Sample	Copolymer T_g	Copolymer-Rich T_g in Phase-Separated Network
50:50 TEGDMA:EGMEMA	105 (± 7.3) °C	112 (± 1.7) °C
75:25 TEGDMA:EGMEMA	139 (± 5.4) °C	131 (± 2.7) °C
100:0 TEGDMA:EGMEMA	161 (± 4.0) °C	150 (± 10) °C

TABLE 2

Viscosity of Initial Comonomer/PBMA Formulations (n=3)

Sample	Copolymer Viscosity (Pa*s)	Copolymer modified with 20 wt% PBMA Viscosity (Pa*s)
50:50 TEGDMA:EGMEMA	1.9 E-3 ($\pm$ 2.1E-4)	0.23 ($\pm$ 3.2E-3)
75:25 TEGDMA:EGMEMA	3.1 E-3 ($\pm$ 1.5E-4)	0.51 ($\pm$ 8.9E-3)
100:0 TEGDMA:EGMEMA	5.3 E-3 ($\pm$ 1.5E-4)	0.99 ($\pm$ 2.3E-2)

TABLE 3Onset of PIPS and onset of Gelation Conversion Data (n=3, $I_0=300 \mu\text{W cm}^{-2}$)

Sample	Conversion at onset of PIPS (%)	Conversion at onset of network gelation (%)	Average Elapsed time (s)
50:50 TEGDMA:EGMEMA 20 wt% PBMA	1.12 (± 1.14)	16.1 (± 4.1)	65 ($\pm 2.0\text{E-}3$)
75:25 TEGDMA:EGMEMA 20 wt% PBMA	0.92 (± 1.20)	24.6 (± 2.1)	39 (± 1.5)
100:0 TEGDMA:EGMEMA 20 wt% PBMA	4.10 (± 0.80)	14.5 (± 0.6)	22 (± 7.8)

TABLE A.1

Refractive Index of Copolymer Resins in the Monomer and Fully Cured State

Sample	Monomer Refractive Index	Copolymer Refractive Index (% methacrylate conversion)
50:50 TEGDMA:EGMEMA	1.453	1.500
75:25 TEGDMA:EGMEMA	1.457	1.509
100:0 TEGDMA:EGMEMA	1.460	1.530