

Characterization of heterogeneity in polymerization-induced phase-separated all methacrylate systems: DMA and reaction kinetics

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Introduction

Hybrid, multi-phase polymeric structures, which normally combine properties of the individual phases, have been largely applied in the industry with great success where materials with tailorable mechanical properties, controllable shrinkage and shrinkage stress are desired¹. Such polymers find applications in the most diverse fields: liquid-crystal displays,² in the production of high-impact polystyrene,³ paints and coatings, auto-parts and dental restorative materials.⁴ Heterogeneity can be introduced with the addition of pre-polymers which then swell in a secondary monomer matrix (sequential formation of interpenetrating polymer networks, IPNs) or by combining monomers with various degrees of miscibility (simultaneous formation of IPNs).⁵ In addition to the thermodynamics of interaction between two network components, reaction kinetics determines the onset of phase-separation, the structure and the viscoelasticity of such networks.⁶ In a simple example of a binary mixture of components A and B (all monomer or a combination of monomer and polymer), as the polymerization progresses, the free energy of mixing (ΔG_m) increases, leading to the formation of A-rich domains dispersed in a secondary B-rich phase, each with a unique kinetic profile. The possibility for diffusion of the A-rich phase then depends on the delayed gelation of the B-rich phase, and that will determine domain size and distribution.⁷ Therefore, the potential extent of stress relaxation (or void formation) at the domain interfaces, and ultimately, the overall volumetric shrinkage, can be controlled by reaction kinetics, which is in turn achieved by fine tuning the composition and/or processing conditions.

For all monomeric systems, it is classically accepted that non-interfering polymerization mechanisms must be used with each component to avoid chemical interactions and produce distinct networks.^{5, 6} This dual mechanism approach allows for fine control of not only the sequence of network formation but also the rate of polymerization of each component nearly independently, therefore their individual role on phase-separation can be reliably determined. In epoxy/methacrylate sequential polymerizations, the extent of phase-separation, as well as the domain size distributions, as determined by the breadth of the tan delta peak obtained in dynamic mechanical analysis, have been shown to be a function of the molecular rigidity and extent of cure (*i.e.*, network formation) achieved by the component that reacts first.⁷ For example, in the case where the epoxy-rich phase was allowed to polymerize first, its network formation imposes diffusion challenges to the second component (methacrylate), in an effect known as IPN vitrification, which may lead to smaller phase-separated domains to be formed, as evidenced by narrower tan delta peaks.⁷

One underexplored approach to obtain heterogeneous networks is the use of blends of marginally compatible monomers that, polymerized via a single route (pure free radical, for example), show increasing incompatibility as network development progresses. The initial degree of compatibility of any two given monomers depends, amongst other factors, on steric constraints⁶ and the strength of intermolecular interactions, particularly hydrogen bonding.⁸ Without the addition of pre-polymers, the influence of hydrogen bonding interactions on the phase separation behavior has also been demonstrated in hybrid networks formed by 2-hydroxyethyl methacrylate and vinyl ethers, although in this case, the fact that only one of the monomers presented hydrogen bonding capability led to an increase in the Flory Huggins χ -parameter, therefore favoring phase-separation.⁹

The aim of this study was to evaluate the influence of composition (ratio of di- to mono-methacrylate) on the polymerization induced phase-separation behavior of all methacrylate model monomers, as determined by their kinetic profiles and glass transition temperature. We hypothesized that: 1. the magnitude of phase-separation increases with increasing mono-methacrylate concentrations; 2. phase-separation is suppressed in mixtures containing the non-hydrogen bonding dimethacrylate, at all formulations.

Materials and Methods

Isodecyl methacrylate (IDMA, Aldrich, Milwaukee, WI) was added to Bisphenol A diglycidyl dimethacrylate (BisGMA, ESSTECH, Essington, PA) in concentrations ranging from 10-90 mol% (BIDMA XX-YY, where XX corresponds to BisGMA mol% and YY corresponds to IDMA mol%). Materials were made photopolymerizable by the addition of 2,2-dimethoxy-2-phenylacetophenone (DMPA, Aldrich) at 0.1 wt%. All materials were used as received.

Disc-shaped specimens (0.5 mm thick) were molded between glass slides, subsequently fixed in an optical bench. Materials were irradiated with an UV source (filtered for 365 ± 10 nm, Novacure, EXFO, Mississauga, ON) for 15 min at 30 mW/cm^2 . Fiber optic cables transmitted a near-IR beam through the sample and the integrated area corresponding to the 6165 cm^{-1} methacrylate $=\text{CH}_2$ first overtone peak was followed in real time (Nexus 870 IR Spectrometer, Thermo Scientific, Waltham, MA) to obtain reaction kinetics. Prior to the onset and throughout the UV-activated photopolymerization process, the specimen was exposed to the broadband output (400-800 nm) of a collimated 200 W mercury-xenon beam (Oriel, Stratford, CT). Simultaneously, 400, 500 and 600 nm light transmission was recorded by a UV-Vis spectrometer (USB 2000, Ocean Optics, Dunedin, FL) and temperature was followed with the aid of a thermocouple embedded in the specimen (Figure 1). The percent light transmission reduction during the course of polymerization was used to estimate the onset and magnitude of phase separation. These results were plotted against conversion.

Bar-shaped specimens (1x3x20 mm) were photoactivated with an UV source (filtered for 365 ± 10 nm, Novacure) for 15 min at 30 mW/cm^2 , and checked for conversion. To avoid artifacts caused by continued polymerization during the thermo cycle in the DMA, all specimens were placed in a vacuum oven at $150 \text{ }^\circ\text{C}$ for 8 hours or until conversion reached 95% or higher. Then, the bars were attached in tension to a DMA (Q80, TA Instruments, New Castle, DE) and subjected to -50 to $200 \text{ }^\circ\text{C}$ cycles at 1 Hz to obtain tan delta curves and T_g of the tested materials.

Results and discussion

The dynamic polymerization curves obtained in NIR for BisGMA combined with increasing ratios of IDMA are shown in Figure 2. All curves show typical features of free-radical polymerization, such as autoacceleration, autodeceleration and limiting functional group conversion. For IDMA concentrations ranging from 70-90 mol%, three distinct stages can be observed in the kinetic profile, with progressively reduced slopes, which strongly suggests the presence of two different composition phases, polymerizing independently. It can be inferred that a BisGMA-rich phase is formed early in the process, once the first portion of the conversion x rate of polymerization curves (Figure 2) reveals polymerization rates much faster than what would be expected from the homopolymerizations of both the less reactive monomethacrylate (IDMA) or BisGMA itself. In the case of BisGMA homopolymerizations, the backbone rigidity and the very high viscosity given by strong hydrogen bonding interactions¹⁰ cause the polymerization to progress at slower rates than the ones observed in the first portion of the kinetic curves for groups containing 70-90 mol% IDMA. This means that the non-hydrogen bonding IDMA improved media mobility in the BisGMA-rich domains, leading to autoacceleration at later stages in conversion. This would normally reflect in a higher conversion at $R_{p_{max}}$, which is not observed here. However, this is easily reconciled by the fact that the unreacted vinyl group overall concentration is kept high by the second, IDMA-rich phase, in which rates of polymerization are one order of magnitude lower than the ones observed in the first portion of the kinetic curve. This sequence of events favors phase-separation, once the more rigid, BisGMA-rich phase polymerizes first, while rigidity increase is not only less significant but is also delayed in the second, IDMA-rich phase, which then has extended opportunity to flow and rearrange in its own domain. The fact that the specimens in those groups were visibly opaque upon photoactivation indicates polymerization-induced phase-separation using pure free-radical, all monomeric systems.

The dynamic mechanical analysis results showed that increasing monomethacrylate concentration causes a significant decrease in storage modulus, as well as a shift of the glass transition to lower temperatures (Figure 3). This was expected based on the additive effect of the low T_g given by the flexible, non-crosslinking IDMA ($-41\text{ }^{\circ}\text{C}$)¹¹ in comparison with that from BisGMA ($145\text{ }^{\circ}\text{C}$),¹² even though IDMA-rich compositions presented higher overall conversion.

DMA analysis is very sensitive to heterogeneity in polymer networks¹³, as determined by the breadth of the tan delta peak. The presence of multiple tan delta peaks indicates phases with distinct Tg's, therefore, with very different compositions. Peaks with shoulders (or convoluted tan delta peaks) indicate 2 phases, though with a narrower composition distribution. Broader tan delta peaks indicate either a greater number of phases or a broader compositional distribution in, for example, gradient block co-polymers. Narrower peaks are correlated with more homogeneous networks, as is the case with thiol-ene polymerizations⁷. Crosslinked dimethacrylates generally produce polymers with significant structural heterogeneity (as opposed to the compositional heterogeneity observed in phase-separated systems), due to the differences in local crosslink density that relate back to microgel precursor to network formation, which was true for all compositions studied here (and explains the relatively broad tan delta peaks observed). However, for IDMA concentrations ranging from 70-90 mol%, more significant broadening of the tan delta curves were observed (determined by the width at half-height), even more markedly for 70 and 80% IDMA groups, where two peaks were discernable, though partially convoluted. This strongly suggests the formation of two phases with large discrepancies in composition, while it can be inferred that the two phases formed in the BisGMA/IDMA 10/90 mol% material (as shown by the kinetic profile) present a closer match.

For the groups where IDMA concentration was lower than 60 mol% in relation to BisGMA, the two-staged kinetic profile was not observed and both degree of conversion and polymerization rate decreased with increasing BisGMA content. In the same fashion, DMA results did not show evidence of multiple phase formation, with all materials presenting a single, narrower tan delta peak compared to the higher IDMA concentrations. The specimens in those groups were apparently clear upon polymerization, which does not necessarily mean they formed homogeneous polymers, but rather that the domain size, if present, is smaller than visible light wavelengths (which, according to the Rayleigh scattering theory, would lead to light scattering only in the UV range) or that the different phases present relatively similar compositions and, therefore, similar refractive indices.⁷

One factor that clearly explains the differences observed in the polymerization behavior and DMA results for groups with IDMA concentrations' ranging from 20-60 mol% or from 70-90 mol% is the strong hydrogen bonding interactions given by the presence of hydroxyl groups

in BisGMA.¹⁰ Hydrogen bonding, as well as the degree of crosslinking, have been demonstrated to affect the miscibility in IPNs formed either by the sequential polymerization of incompatible pre-polymerized networks or by the combination of two or more immiscible pre-polymers.^{14, 15} Since hydrogen bonding relates to the polar character of a molecule, it is expected that two species with similar hydrogen bonding capacity are more likely to be miscible. In one study on polyurethane/epoxy IPN nanocomposites, hydrogen bonding given by PU was able to improve polymer packing and decrease the free volume pore size, therefore, undermining phase mobility/rearrangement after solvent evaporation, and ultimately forming more homogeneous structures.¹⁶ Other authors have observed the same phenomenon, in polycaprolactone^{14, 15} or poly-butyl methacrylate¹⁵ based blends with increasing polymethacrylic acid concentrations, *i.e.*, with increasing hydrogen bonding interactions. In turn, crosslinking, due to its effect on macromolecular mobility, was shown to reduce polymer diffusion during IPN formation, impairing phase rearrangement from its initial heterogeneous state and causing more predominant microphase separation.¹⁵ This means that the discrepancy in hydrogen bonding capacity, as well as the network rigidity at the onset of phase separation, both determine the extent of heterogeneity in co-polymerizations involving marginally compatible species.

Acknowledgements

The donation of part of the monomers used in this study by ESSTECH is greatly appreciated. This study was supported by NIH/NIDCR-2R01DE14227.

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Figures

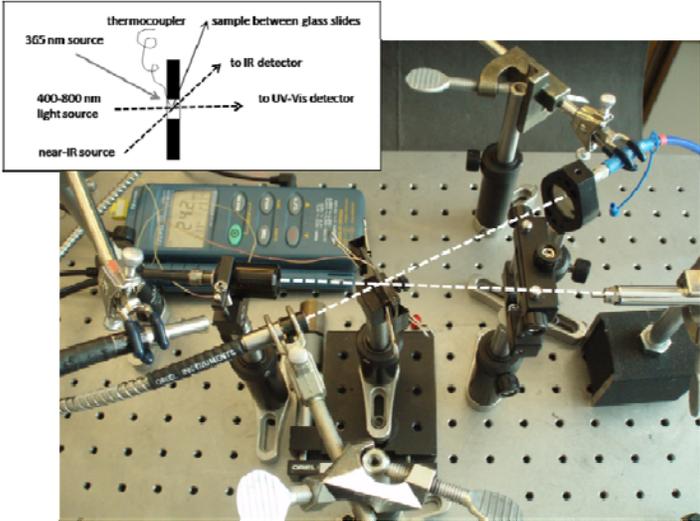


Figure 1: Sample in place for room temperature measurements in the optical bench.

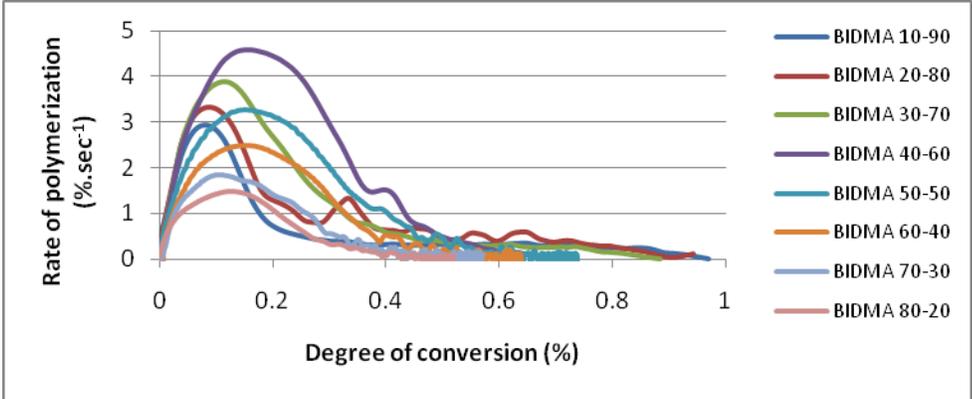


Figure 2: Rate of polymerization as a function of degree of conversion for BisGMA-IDMA series.

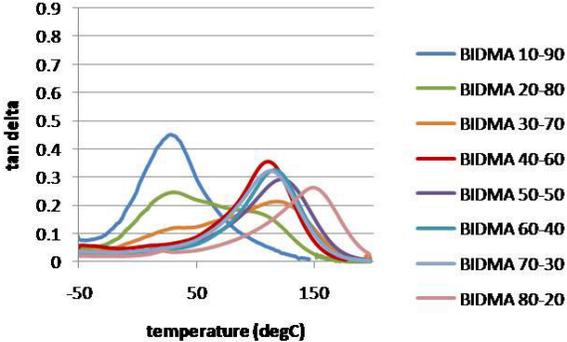


Figure 3: Tan delta for BisGMA-IDMA series at low BisGMA concentrations.