

Supporting Information

Kinetically-Controlled Photo-Induced Phase Separation for Hybrid Radical/Cationic Systems

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23 Figure S1 shows stress as a function of strain for photopolymerized systems before and after
24 thermal-cure. At low irradiation intensity, each polymer system with 1:1, 7:3, or 9:1 DOX:BA
25 demonstrate similar stress and strain behavior before and after thermal-curing. Each sample
26 photocured at 100 mW cm⁻² show slightly different maximum stress and reduced elongation at
27 break by approximately 1% before thermal post-cure. For irradiation intensity of approximately
28 1500 mW cm⁻², thermally-cured phase-separated systems (1:1 and 7:3 DOX:BA) exhibit higher
29 Young's modulus likely due to increased DOX conversion and perhaps small changes in the
30 interaction between soft/hard domains. Additionally, thermal curing these latter systems leads to
31 reduced elongation at break perhaps due to increased brittleness of these materials when compared
32 to those of only UV-cured. For single-domain polymers (9:1 DOX:BA) photocured at 1500 mW
33 cm⁻², the application of thermal post-cure results in similar Young's modulus with slightly lower
34 elongation at break compared to those of only UV-cured. Even though the application of thermal
35 cure increases oxetane conversion of each system more than 50% when photocured at different
36 irradiation intensities (Figure 3), stress and strain profiles for each system do not significantly
37 change. This behavior suggests that the overall mechanical properties are primarily dependent on
38 UV-established polymer morphology before thermal-cure.

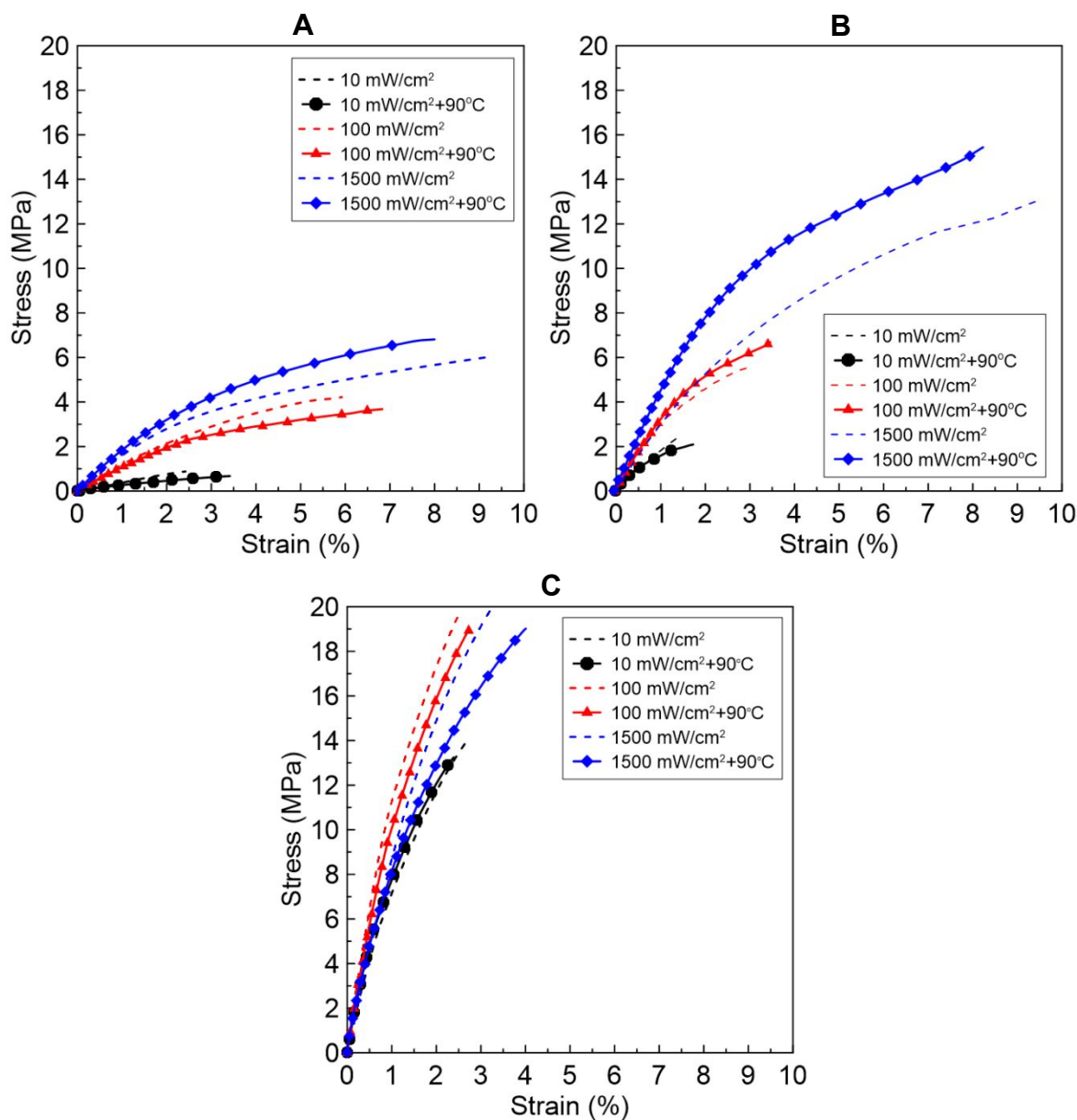


Figure S1. Stress-Strain profiles in tensile mode at room temperature of polymer systems with DOX:BA ratios of a) 1:1, b) 7:3, and c) 9:1. Dashed lines represent polymers UV-cured only and solid lines represent polymer both UV- and thermally-cured.

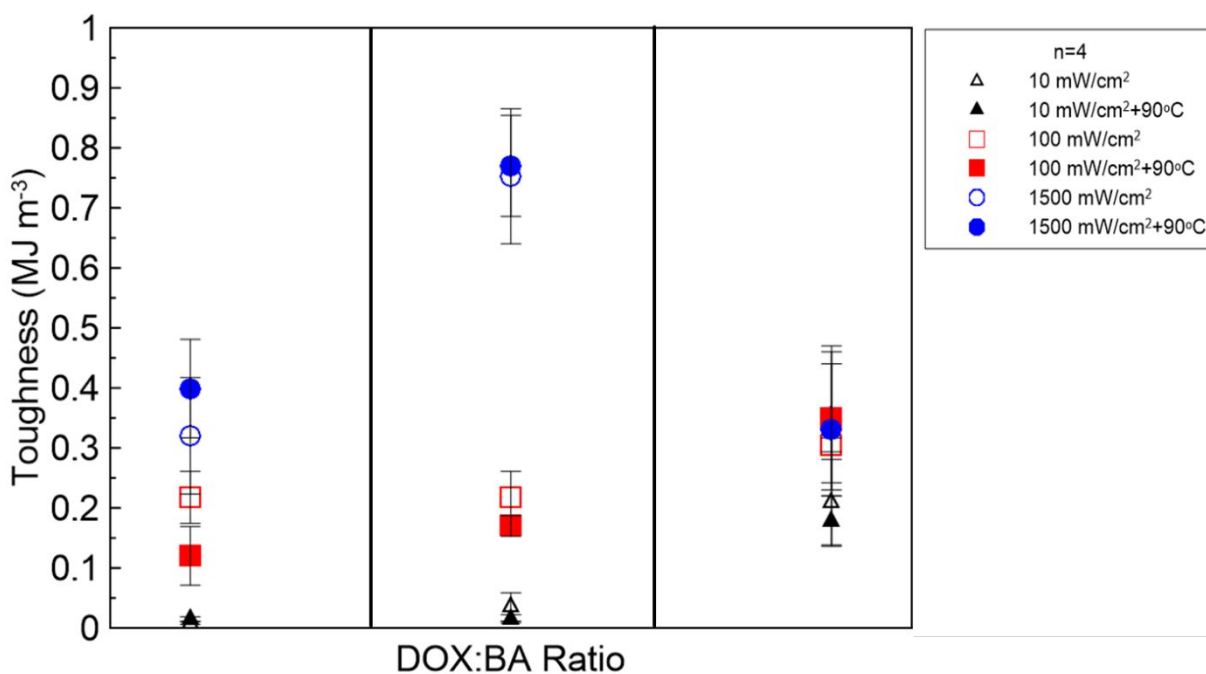


Figure S2. Toughness of polymers for UV-cured systems (open symbols) and post UV-thermally cured systems (closed symbols). Each experiment was conducted 4 times with error bars representing standard deviation.