Supporting information for

Toward Sustainable SLA 3D Printing: Glycerol-Based 1,3-Diether-2-Methacrylates with Solvent Capability for In Situ Polymer Blend Formation

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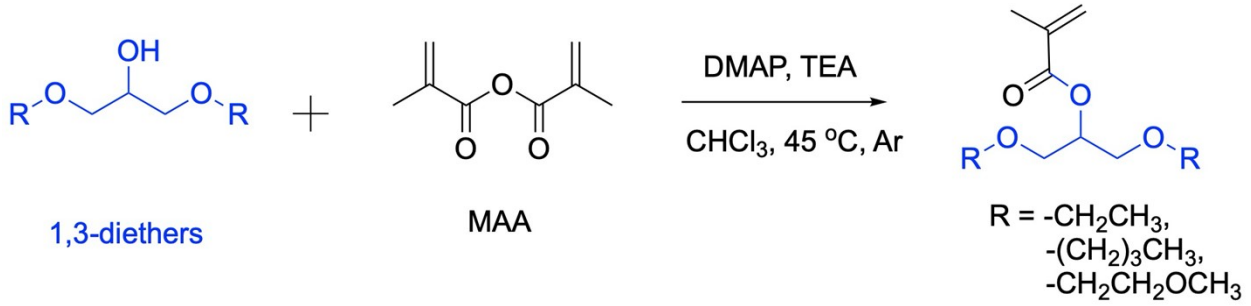
1. Detailed Synthesis of Symmetric 1,3-Diether-2-Methacrylates

The general synthesis of 1,3-diether-2-methacrylate monomers was carried out as follows. DEP, DMEP, or DBP (20 g, 1 eq) and 0.1 eq of DMAP were added to a 250 mL round-bottom flask. $CHCl_3$ (60 mL) and Et_3N (1.5 eq) were introduced under an Ar atmosphere, followed by the dropwise addition of 1.1 eq of MAA at room temperature. The resulting mixture was stirred at 45 °C for 24 h. The reaction mixture was then diluted with $CHCl_3$ and washed several times with saturated $NaHCO_3$ and water, followed by drying over $MgSO_4$. The solvent was removed by rotary evaporation under reduced pressure, and the product was further dried under vacuum overnight. The general synthesis of these monomers is illustrated in **Figure S1**.

DEP was prepared in 82.1% yield as a clear, yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.16 – 6.13 (m, 1H), 5.59 (q, J = 1.5 Hz, 1H), 5.18 (p, J = 5.2 Hz, 1H), 3.66 – 3.62 (m, 4H), 3.59 – 3.50 (m, 4H), 1.98 – 1.95 (m, 3H), 1.20 (t, J = 7.0 Hz, 6H).

DBP was prepared in 84.3 % yield as a clear, yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.13 (s, 1H), 5.58 – 5.55 (m, 1H), 5.17 (p, J = 5.2 Hz, 1H), 3.61 (d, J = 5.2 Hz, 4H), 3.51 – 3.41 (m, 4H), 1.95 (s, 3H), 1.57 – 1.50 (m, 4H), 1.40 – 1.32 (m, 4H), 0.91 (t, J = 7.4 Hz, 6H)

DMEP was prepared in 80.0 % yield as a clear, yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.12 – 6.10 (m, 1H), 5.56 (p, J = 1.5 Hz, 1H), 5.20 (p, J = 5.2 Hz, 1H), 3.70 – 3.58 (m, 8H), 3.51 (t, J = 4.7 Hz, 4H), 3.35 (s, 6H), 1.94 – 1.92 (m, 3H).



Scheme S1. General synthesis of 1,3-Diether-2-Methacrylates

2. Tables

Table S1. Hansen solubility parameters (HSP) of PS and PMMA polymers.

Polymers	δ_d ((MPa)$^{1/2}$)	δ_p ((MPa)$^{1/2}$)	δ_h ((MPa)$^{1/2}$)	R_0 ((MPa)$^{1/2}$)
PS	18.5	4.5	2.9	8
PMMA	18.6	10.5	5.1	8

δD: dispersion forces
δP: polar interactions
δH: hydrogen-bonding interactions
R_0: interaction radius

Table S2. Tensile properties of the 3D printed pure polymers and their blends

Sample	Tensile Strength (SEM)[1] (MPa)	Elongation at Break (SEM)[1] (%)	Young Modul (SEM)[1] (MPa)
Poly(MAA-DEP)	1.61 (±0.097)	142.94 (±7.75)	7.67 (±0.29)
Poly(MAA-DEP)/WPS (5wt)	3.50 (±0.285)	24.19 (±1.53)	22.64 (±1.78)
Poly(MAA-DEP)/WPS (10wt)	3.67 (±0.159)	91.45 (±6.70)	29.82 (±1.01)
Poly(MAA-DEP)/PS (45K) (10wt)	2.17 (±0.088)	29.01 (±0.55)	12.61 (±0.49)
Poly(MAA-DBP)	1.41 (±0.150)	22.87 (±2.68)	8.25 (±0.28)
Poly(MAA-DBP)/WPS (10wt)	3.83 (±0.177)	19.92 (±0.61)	30.69 (±2.45)
poly(MAA-DMEP)	0.70 (±0.084)	42.90 (±6.82)	2.17 (±0.09)
Poly(MAA-DMEP)/WPS (10wt)	2.31 (±0.127)	26.69 (±2.72)	19.81 (±0.42)
Poly(MAA-DEP)/PMMA (5wt)	1.80 (±0.156)	159.20 (±14.21)	6.61 (±0.09)
Poly(MAA-DEP)/PMMA (10wt)	3.06 (±0.242)	154.3 (±19.27)	10.02 (±1.13)

[1] Standard error of the mean (SEM)

3. Figures

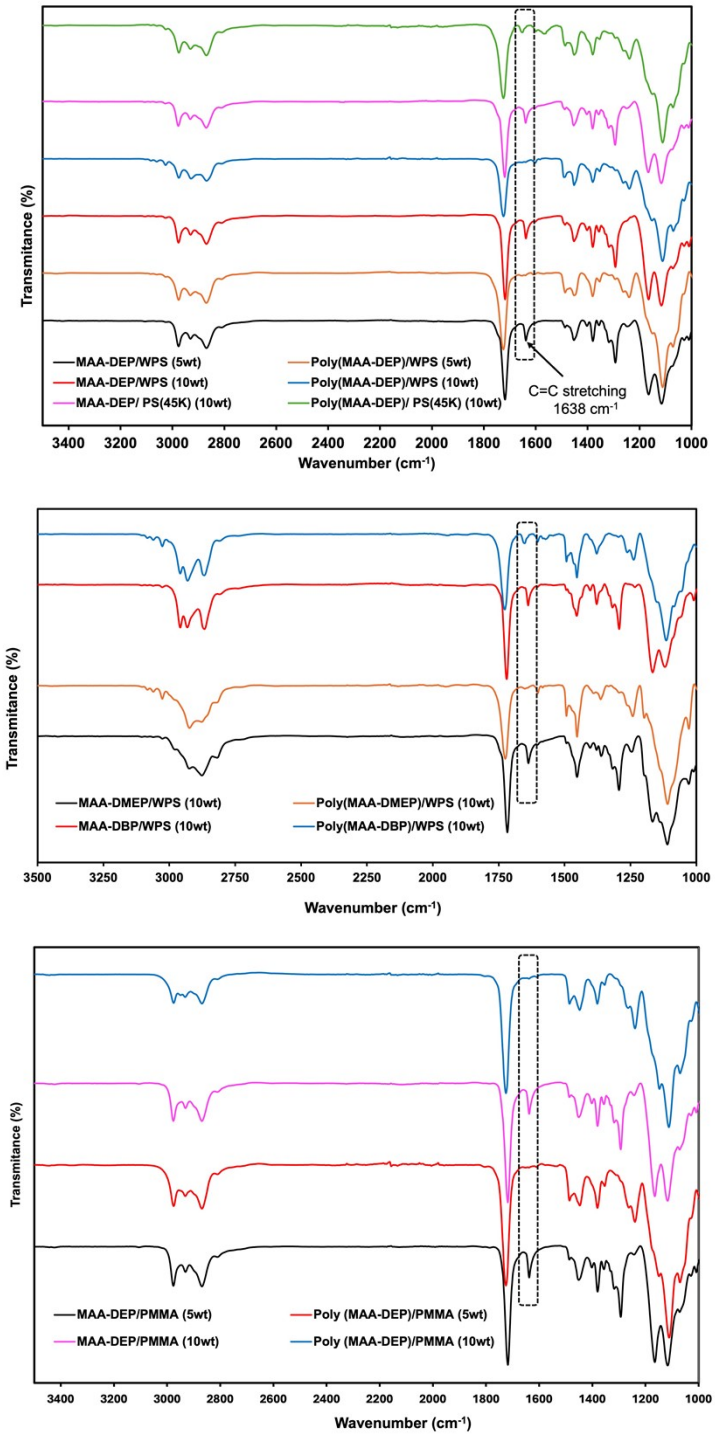


Figure S1. FTIR spectra of poly(1,3-diether-2-methacrylate)/thermoplastic blends.

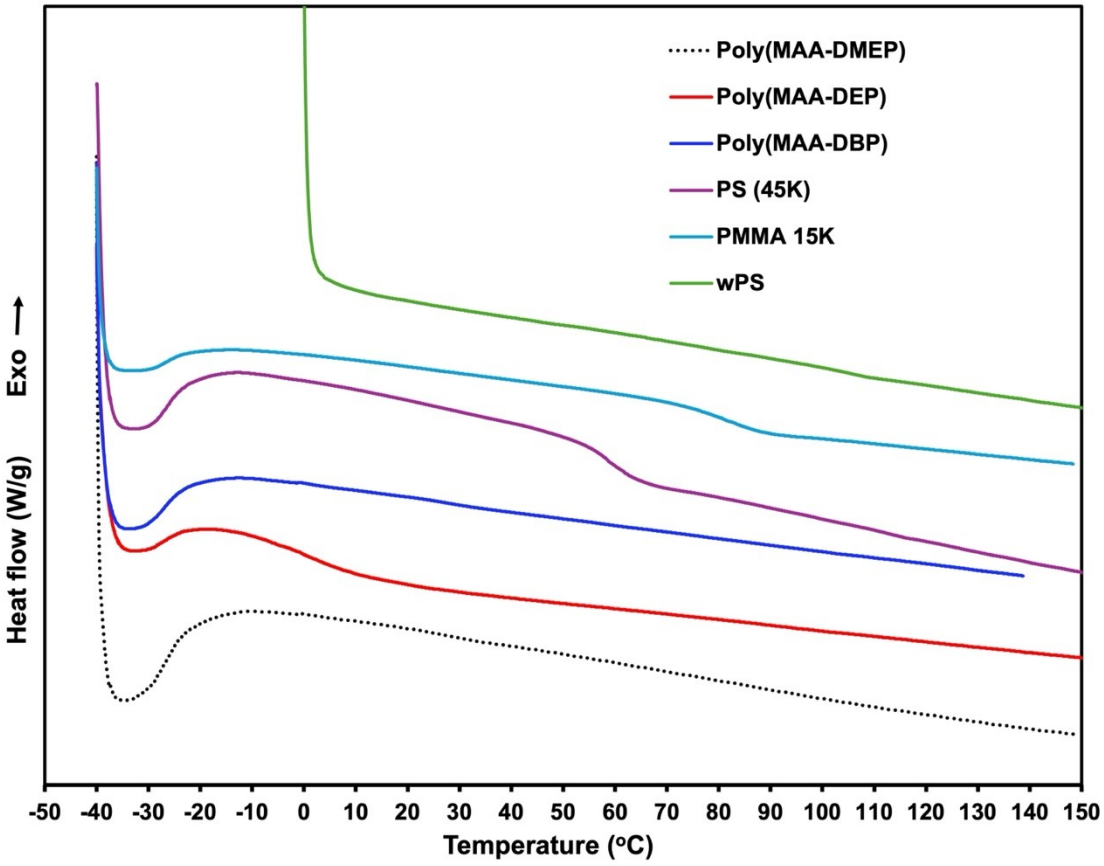


Figure S2. DSC thermograms of pure polymers.

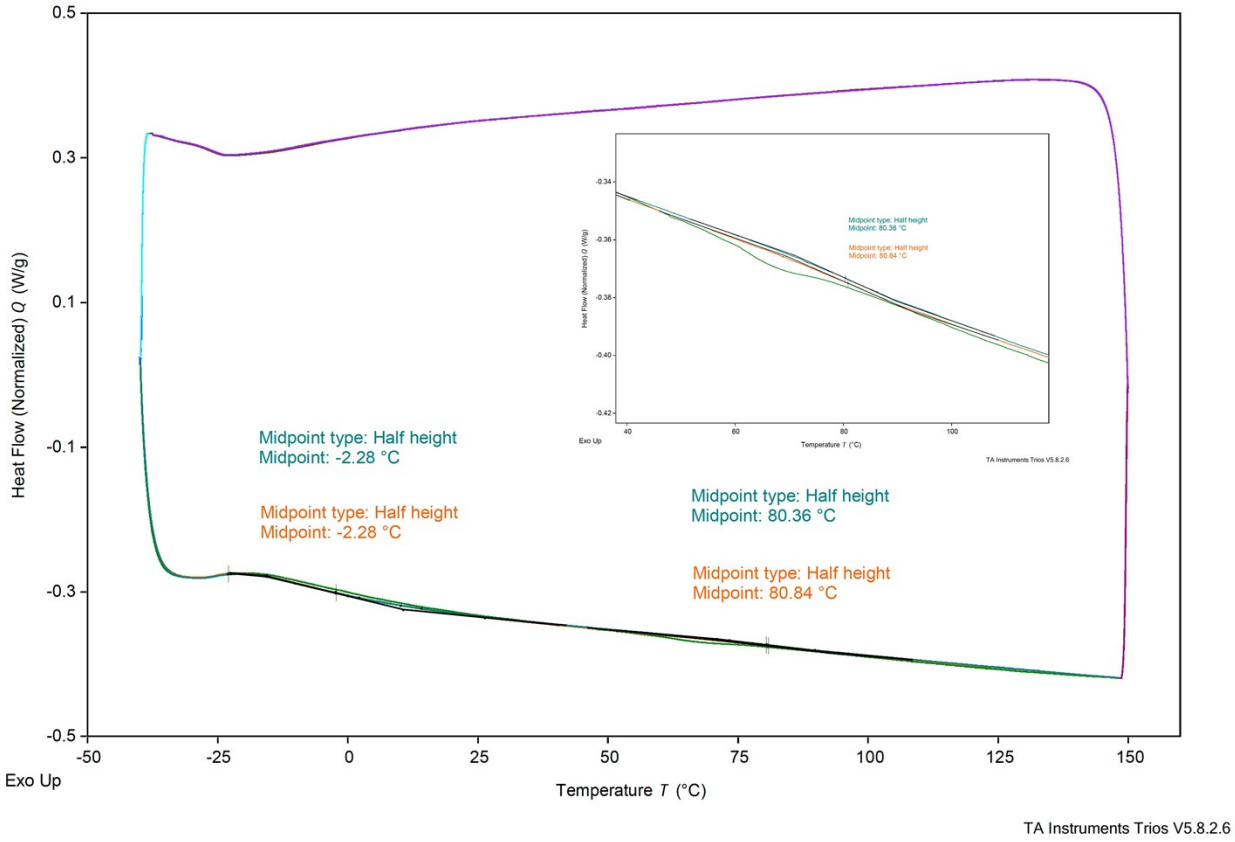


Figure S3. DSC thermograms of Poly(MAA-DEP)/WPS (5wt%)

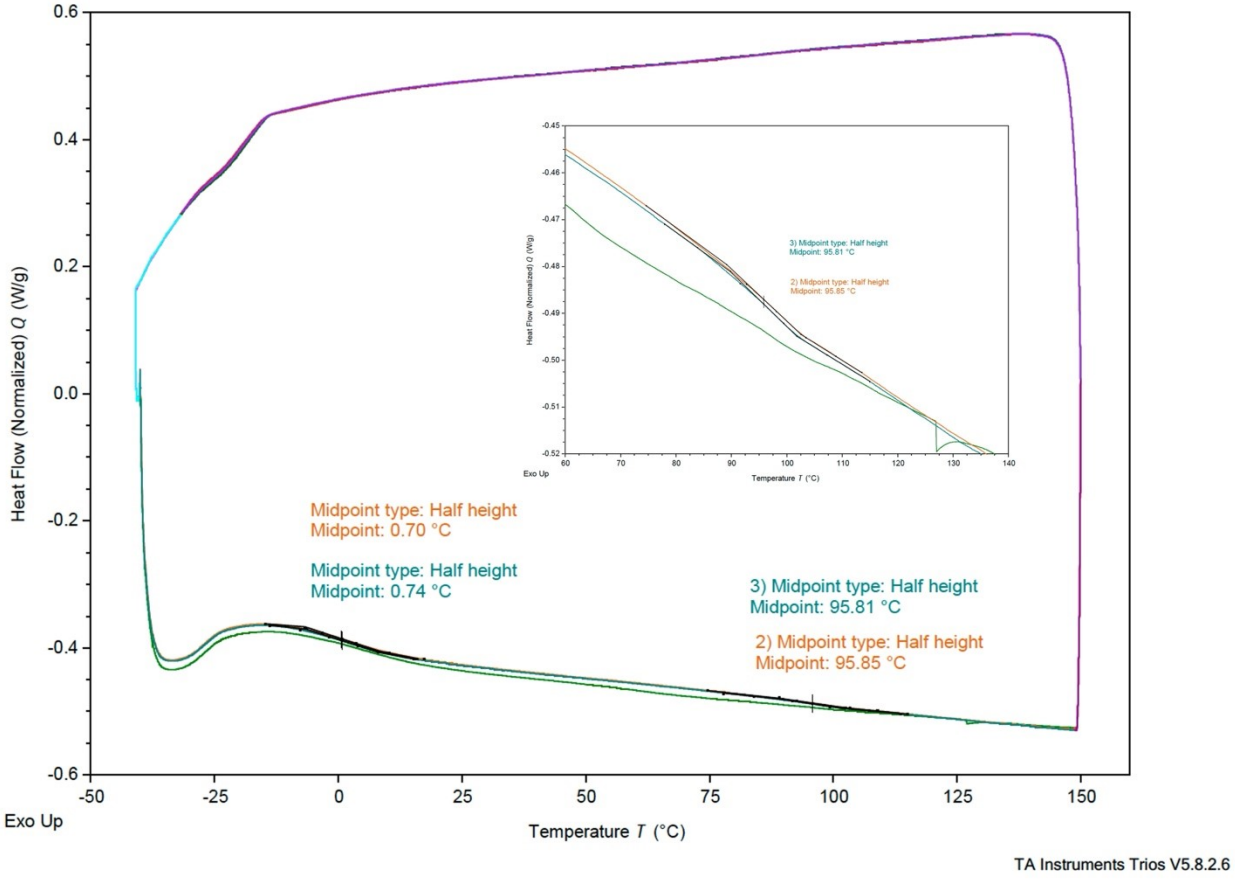


Figure S4. DSC thermograms of Poly(MAA-DEP)/WPS (10wt%)

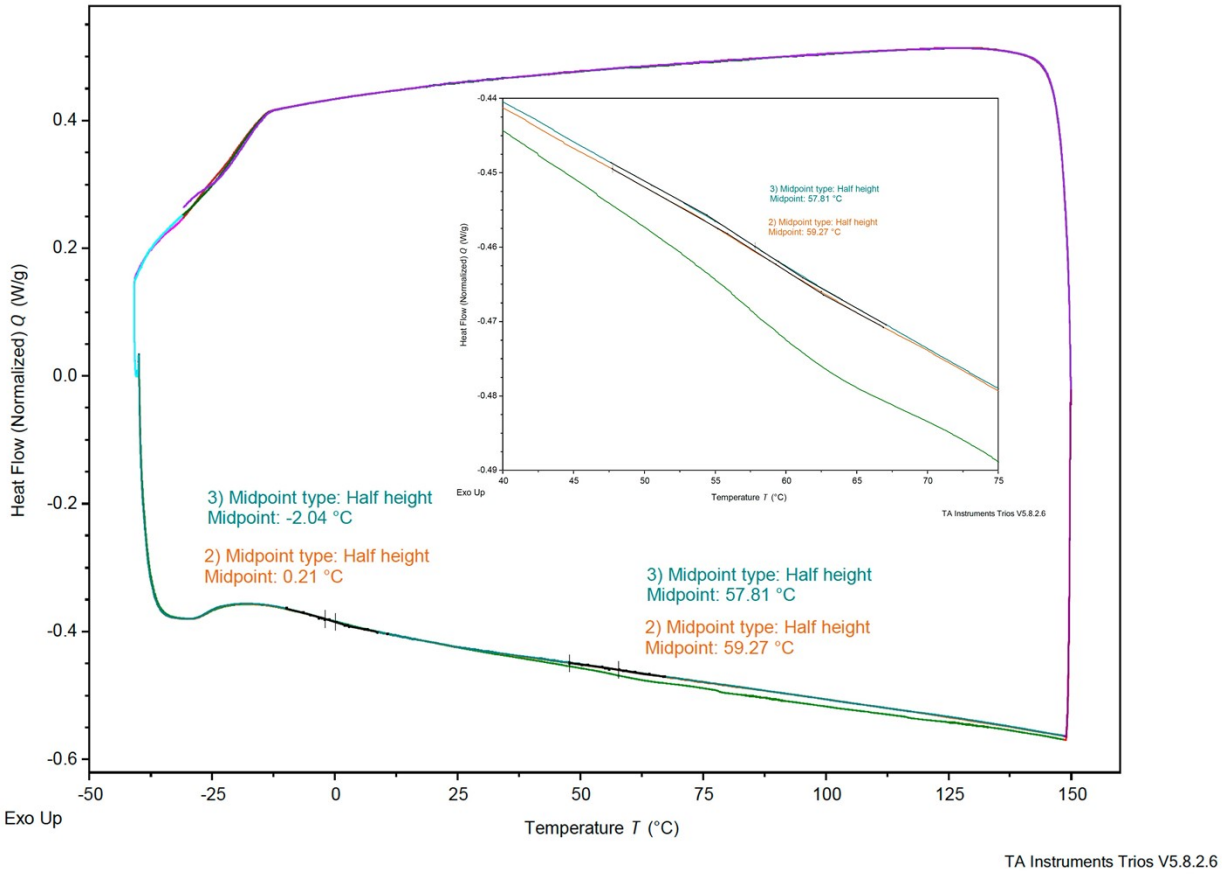


Figure S5. DSC thermograms of Poly(MAA-DEP)/PS (45K) (10wt%)

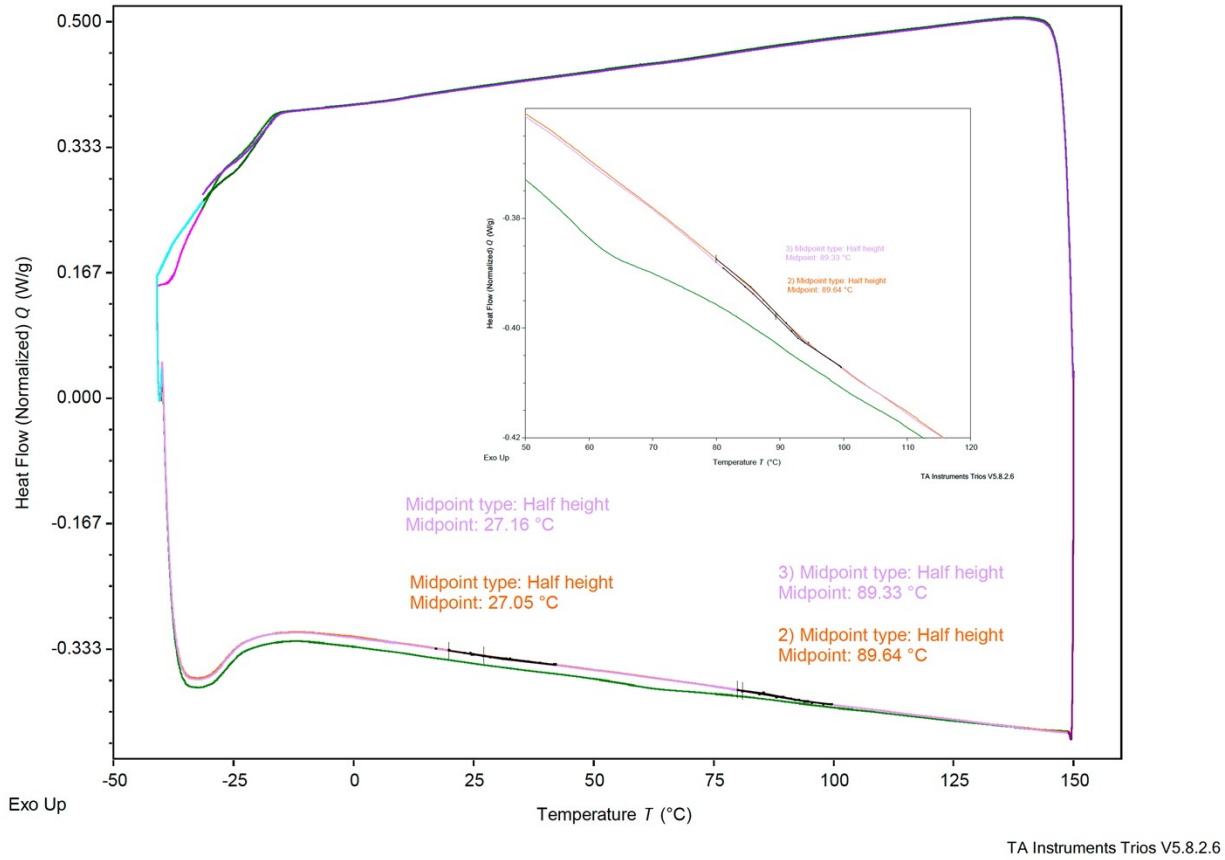


Figure S6. DSC thermograms of Poly(MAA-DBP)/WPS (10wt%)

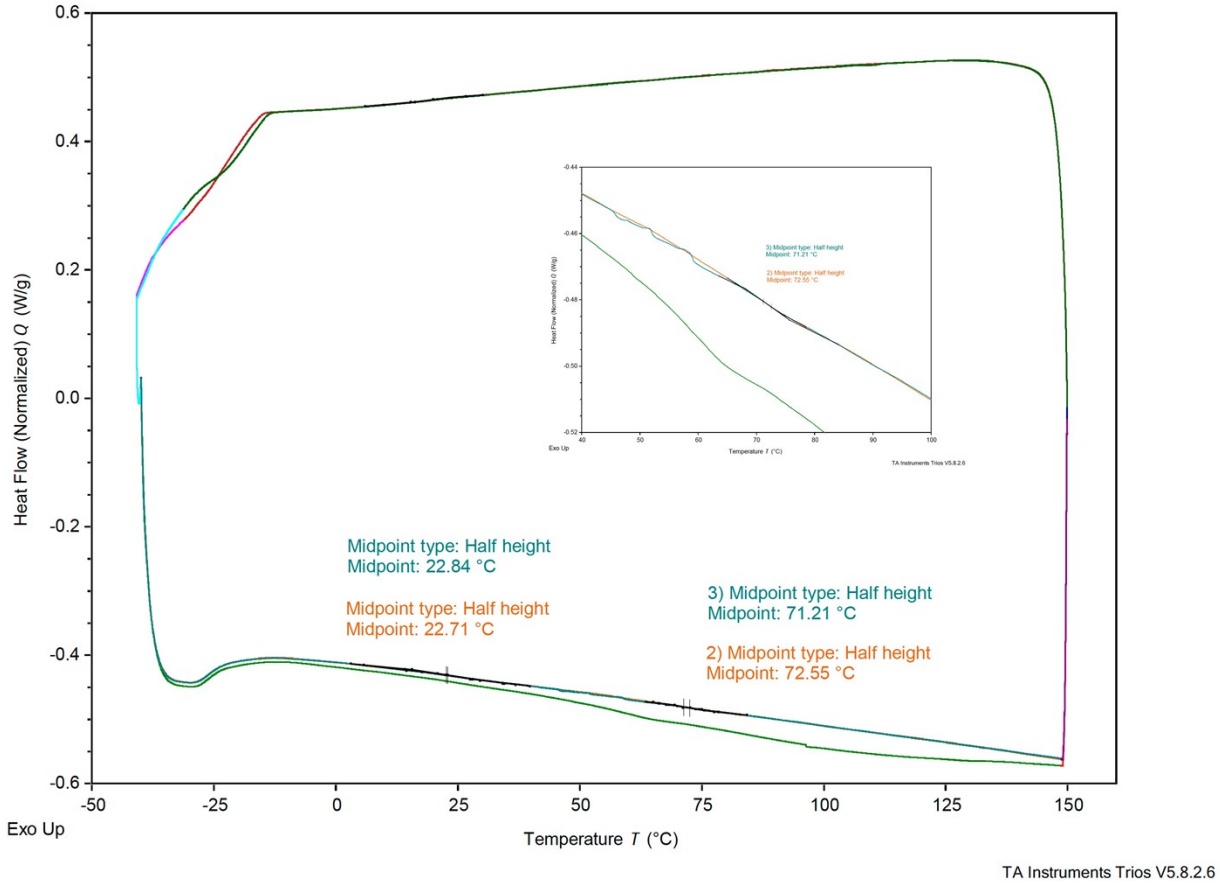


Figure S7. DSC thermograms of Poly(MAA-DMEP)/WPS (10wt%)

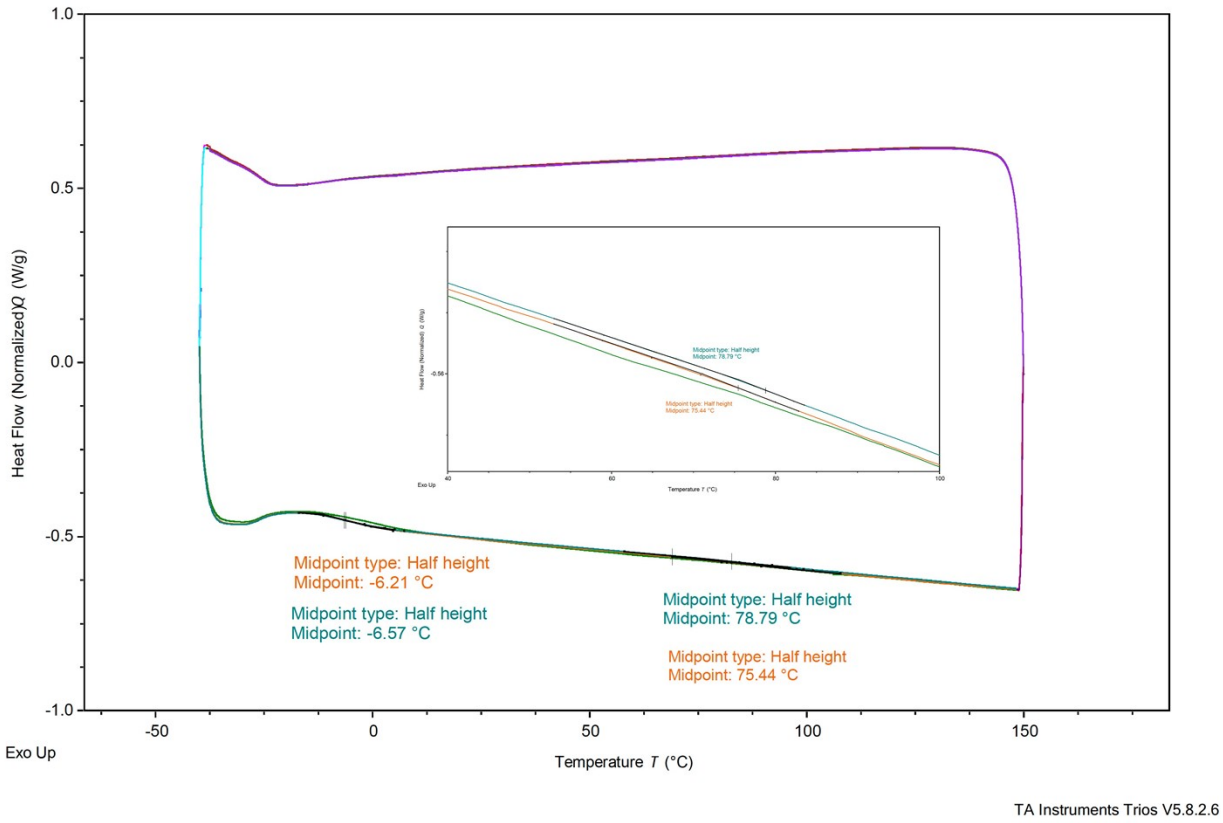


Figure S8. DSC thermograms of Poly(MAA-DEP)/PMMA (5wt%)

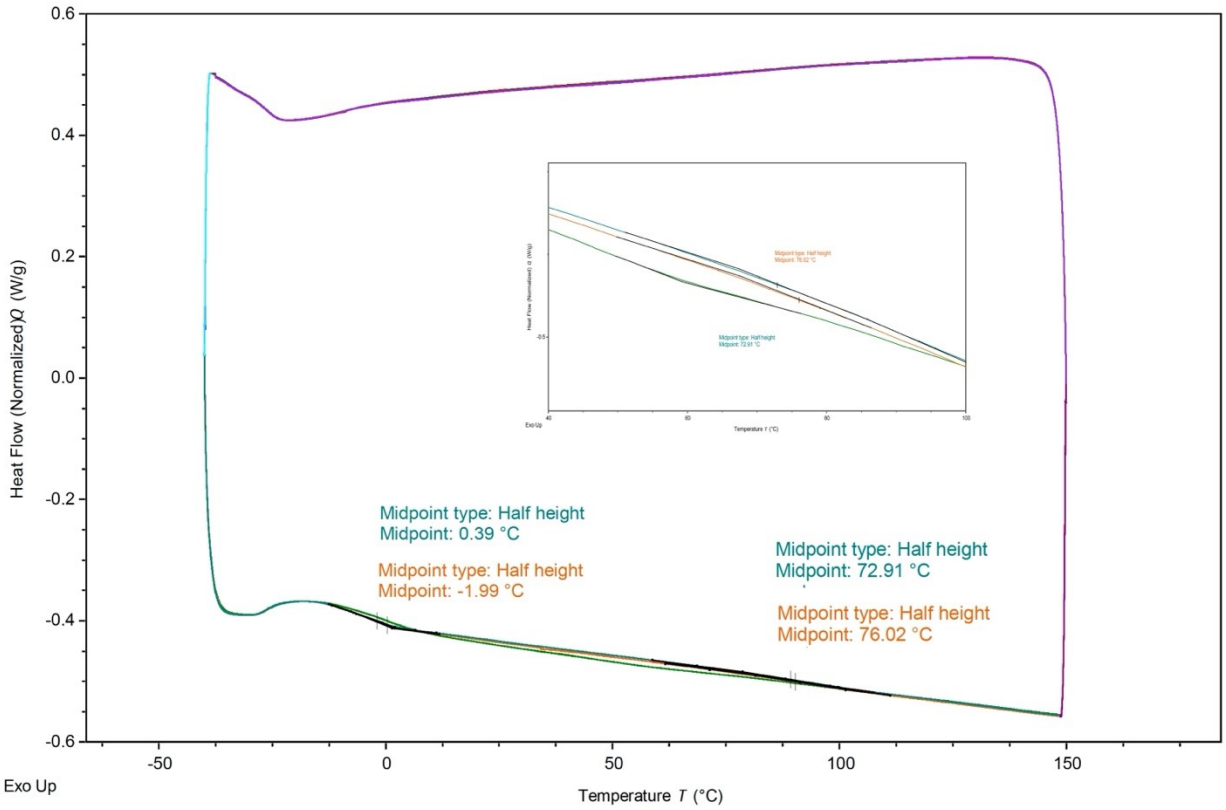


Figure S9. DSC thermograms of Poly(MAA-DEP)PMMA (10wt%)

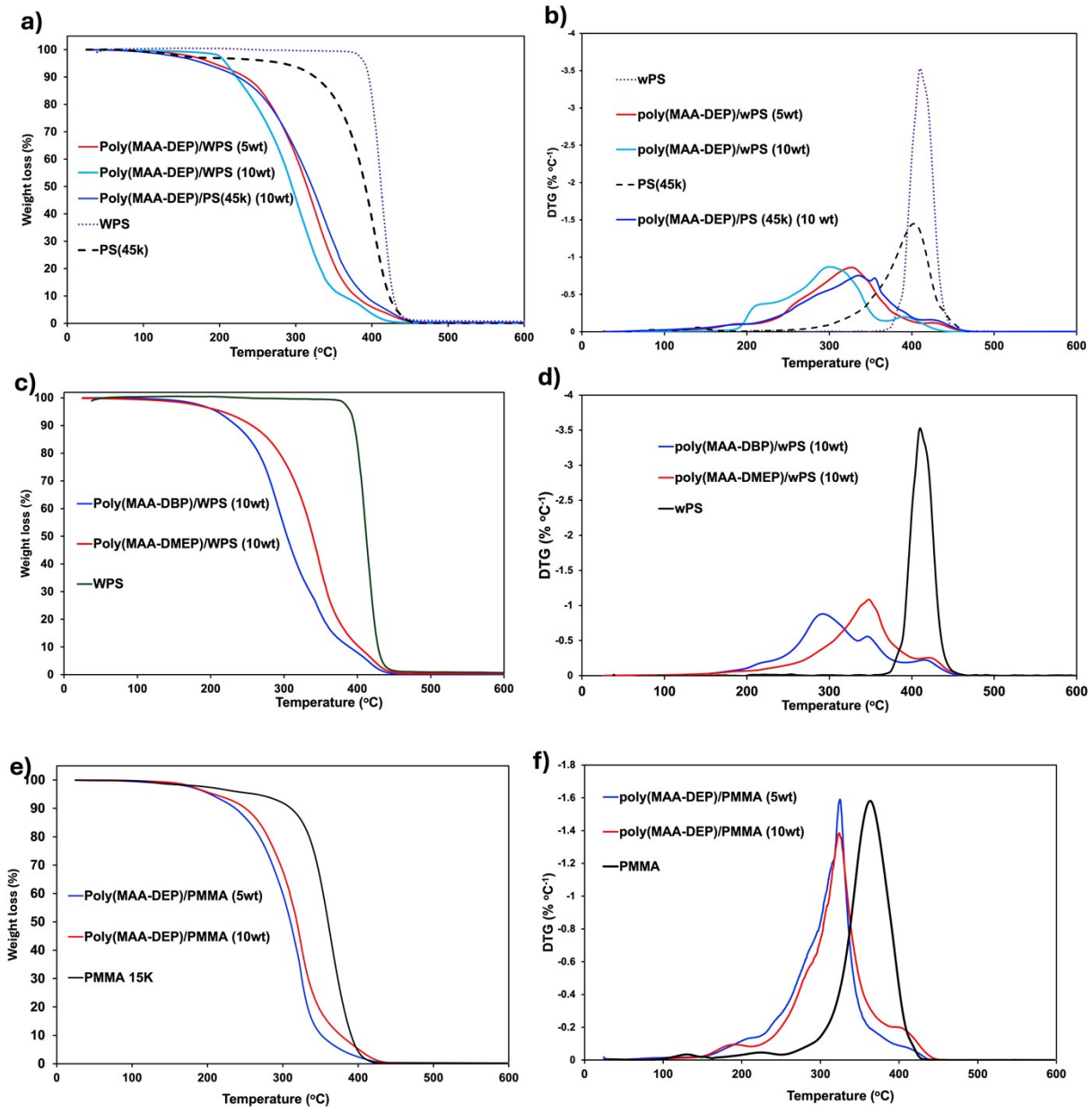


Figure S10. TGA and DTG thermograms of poly(1,3-diether-2-methacrylate)/thermoplastic blends.

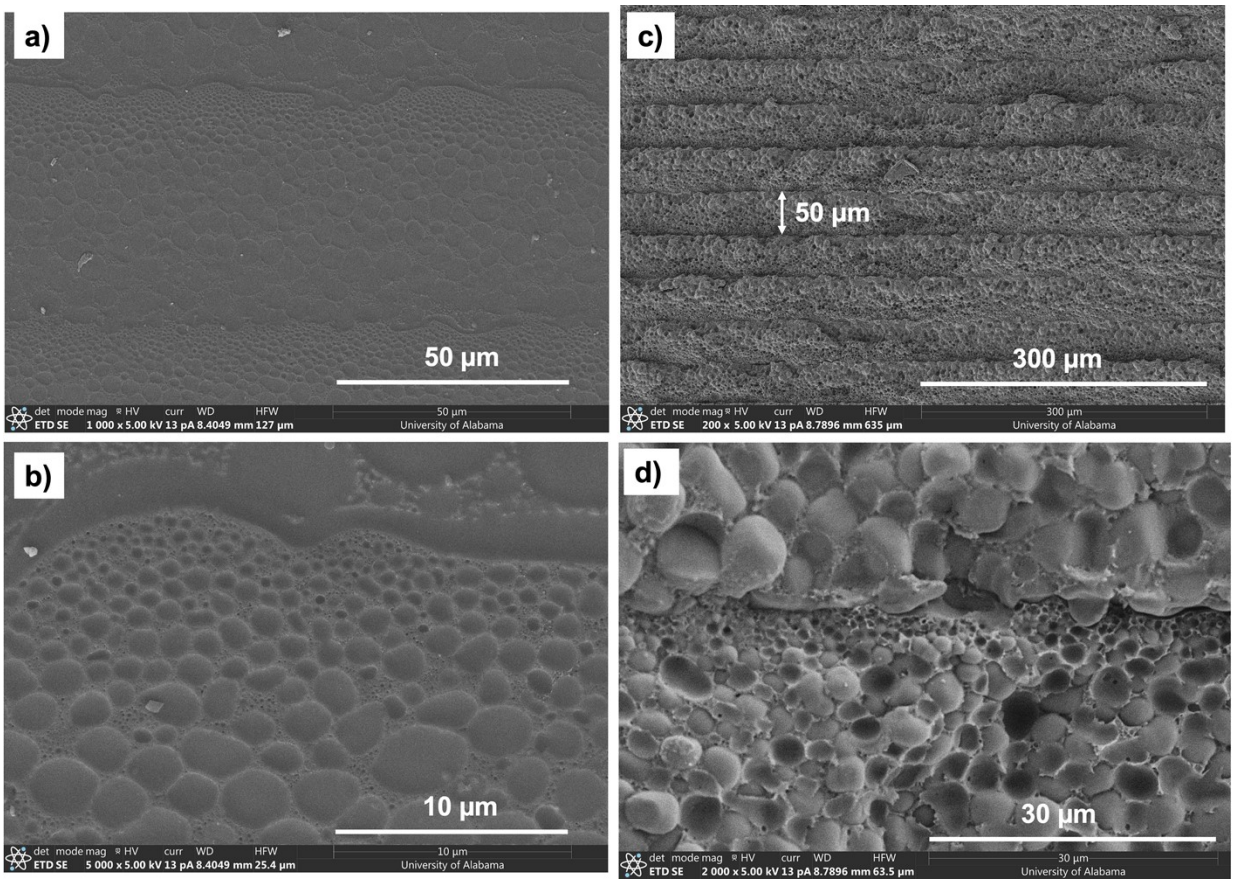


Figure S11. SEM images of cryofracture surface of a and b) poly(MAA-DBP)/WPS (10wt%), c and d) poly(MAA-DMEP)/WPS (10wt%)