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ELECTRONIC SUPPLEMENTARY INFORMATION

Post-polymerisation Modification of Bio-derived Unsaturated Polyester Resins via Michael Additions of 1,3-dicarbonyls

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Submitted to *Polymer Chemistry*

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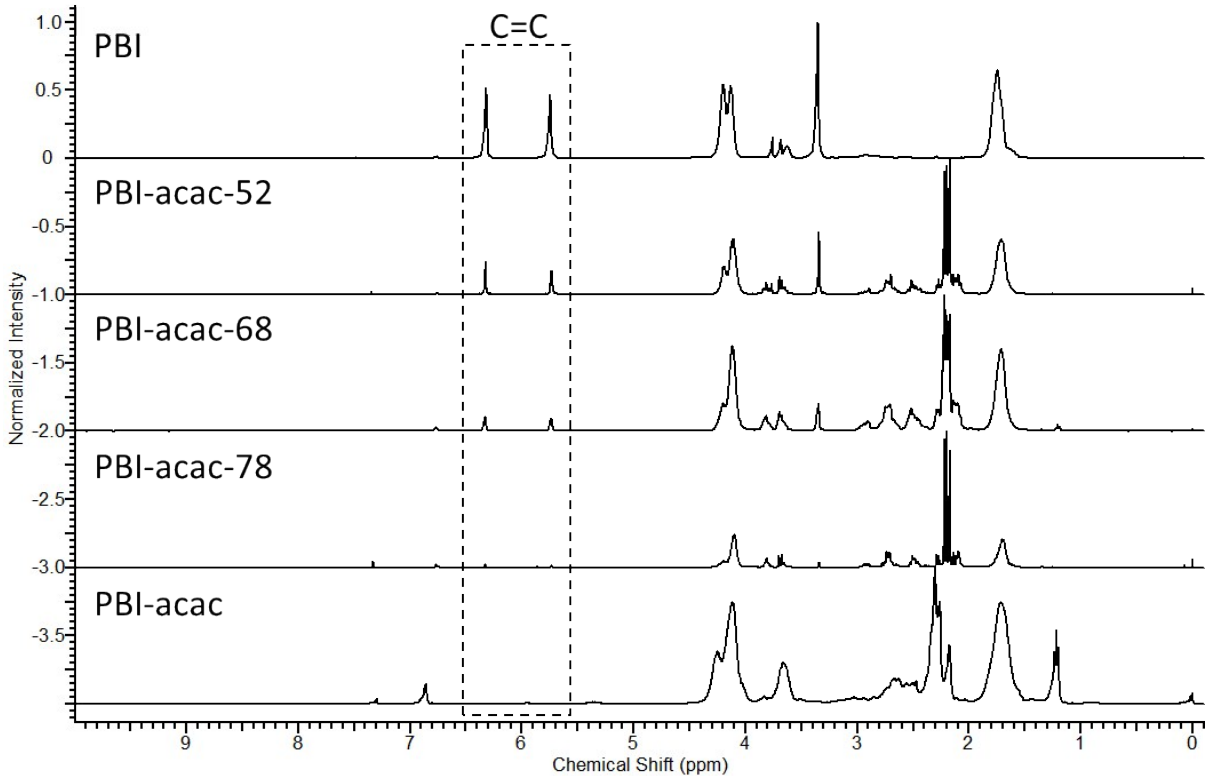

Figure S1: Partial addition of acetylacetone (Hacac) monitored by ^{1}H-NMR spectroscopy. PBI (top): unsaturated polyester backbone (0% of C=C have undergone addition of Hacac); PBI-acac-52 (second from top): partial addition of Hacac whereby 52% of the original C=C in PBI has undergone Michael addition with Hacac; PBI-acac-68: 68% of C=C has reacted with Hacac; PBI-acac-78: 78% of C=C has reacted with Hacac or undergone isomerisation to mesaconate; PBI-acac: >99% of C=C has reacted with Hacac or undergone isomerisation to mesaconate. ^{1}H-NMR collected in $CDCl_3$.

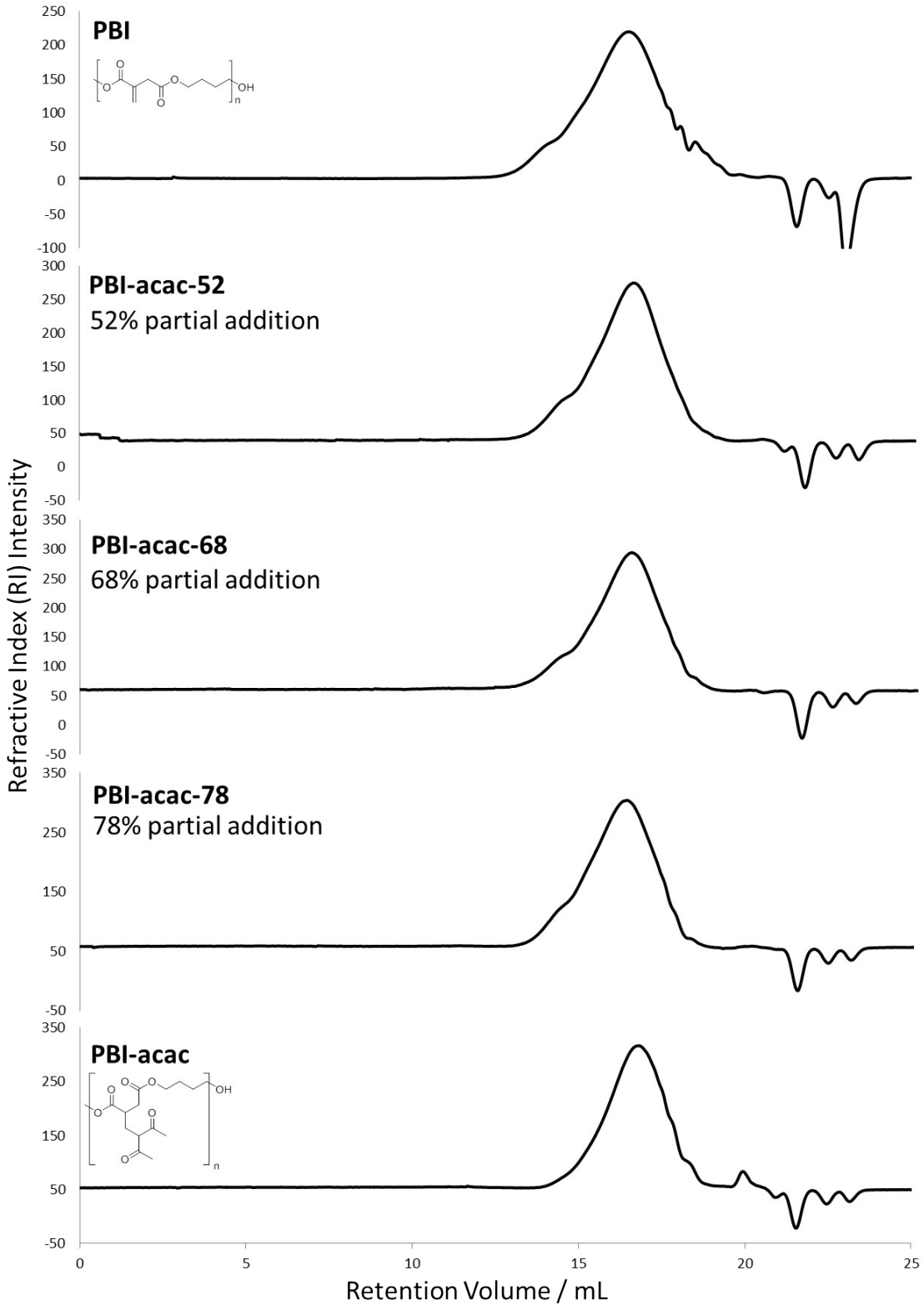

Figure S2: GPC chromatograms (Refractive Index Detector, THF eluent, polystyrene standard) for the addition of Hacac to PBI. PBI (top): unsaturated polyester backbone (0% of C=C have undergone addition of Hacac); PBI-acac-52 (second from top): partial addition of Hacac whereby 52% of the original C=C in PBI has undergone Michael addition with Hacac; PBI-acac-68: 68% of C=C has reacted with Hacac; PBI-acac-78: 78% of C=C has reacted with Hacac; PBI-acac: >99% of C=C has reacted with Hacac.

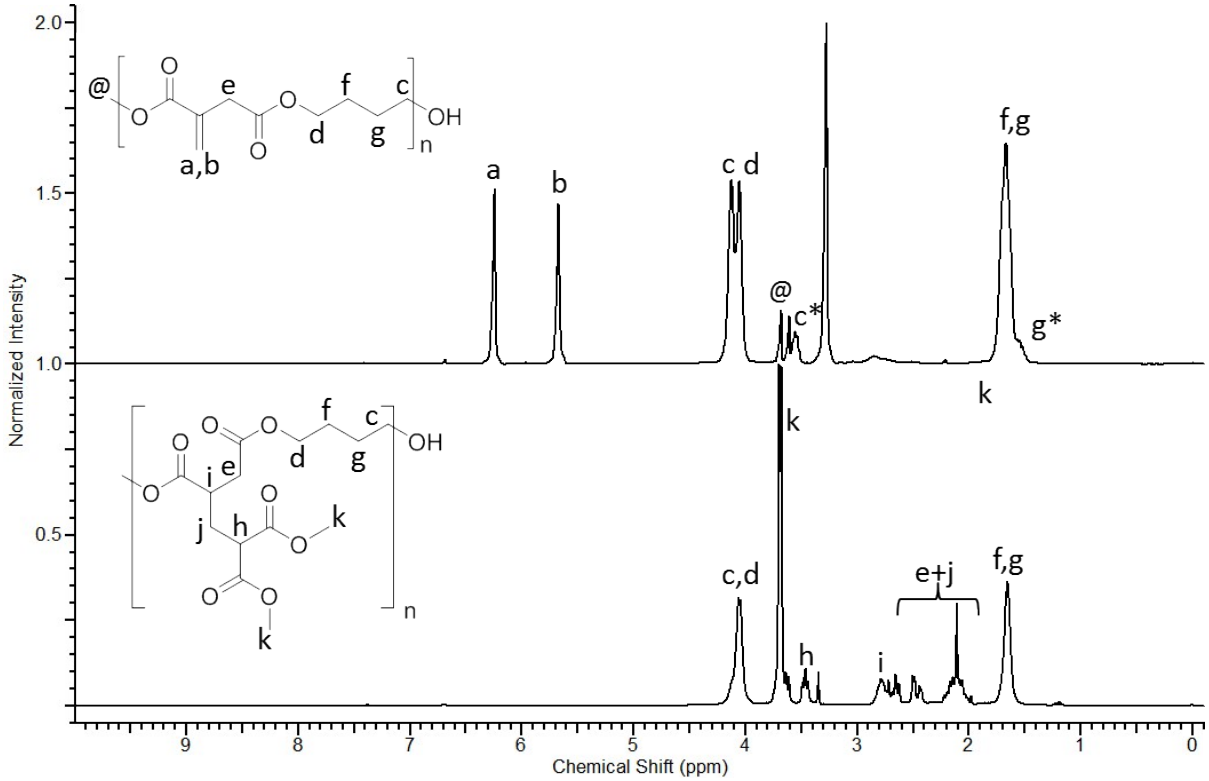

Figure S3: ^{1}H-NMR spectra, with assignments, for PBI before (top) and after (bottom) dimethyl malonate (DMM) addition. ^{1}H-NMR collected in $CDCl_3$, @ refers to ^{1}H-signals as a result of the CH_3 of the methyl ester end-group, * refers to the CH_2s of the diol when as an end group.

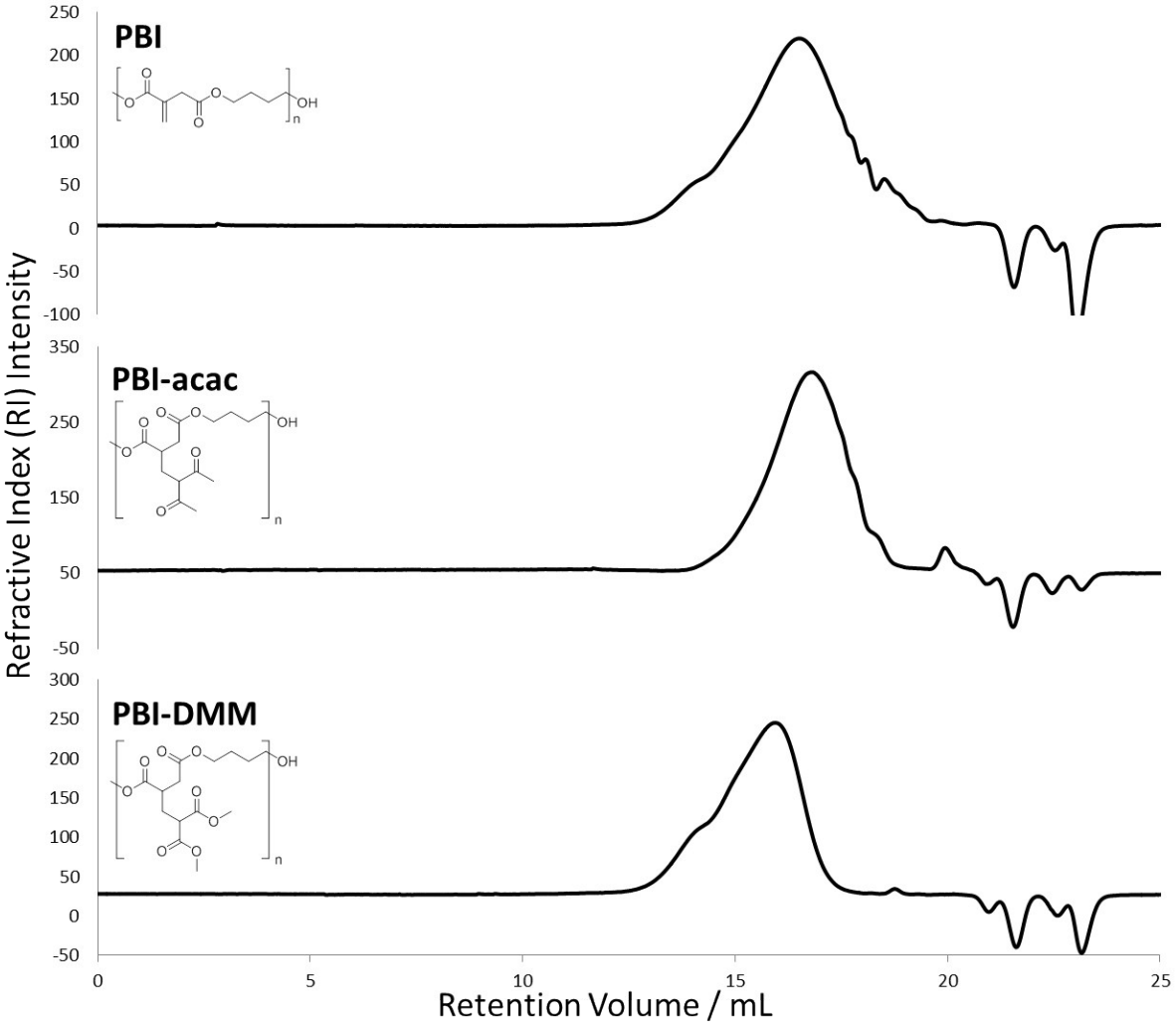

Figure S4: GPC chromatograms (Refractive Index Detector, THF eluent, polystyrene standard) for the addition of Hacac (middle) or DMM (bottom) to PBI (top).

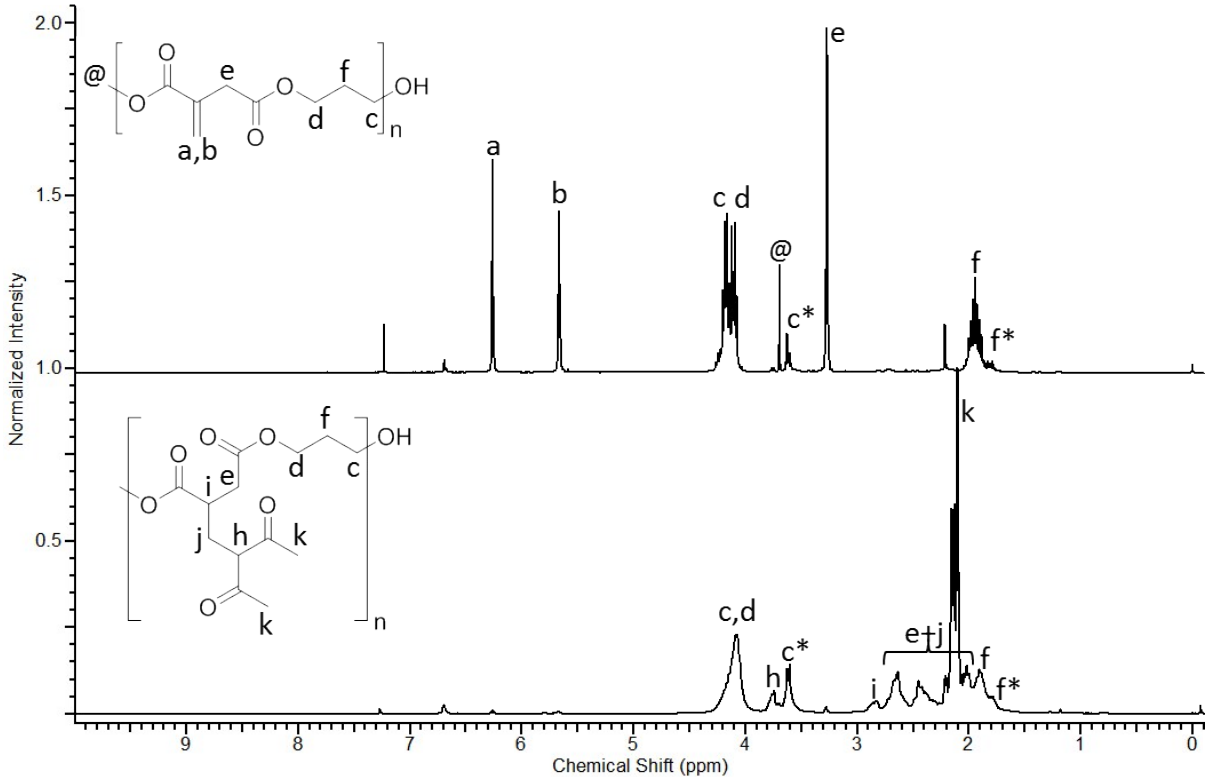

Figure S5: ^{1}H-NMR spectra, with assignments, for PPI before (top) and after (bottom) Hacac addition. ^{1}H-NMR collected in $CDCl_3$, @ refers to ^{1}H-signals as a result of the CH_3 of the methyl ester end-group, * refers to the CH_2s of the diol when as an end group. Note that the PPI sample used for the above spectra was of a low degree of polymerisation, required to produce a soluble sample, while the PPI-acac shown was synthesised using a cross-linked insoluble PPI backbone but through Hacac addition resulted in a sample of sufficient solubility for NMR analysis.

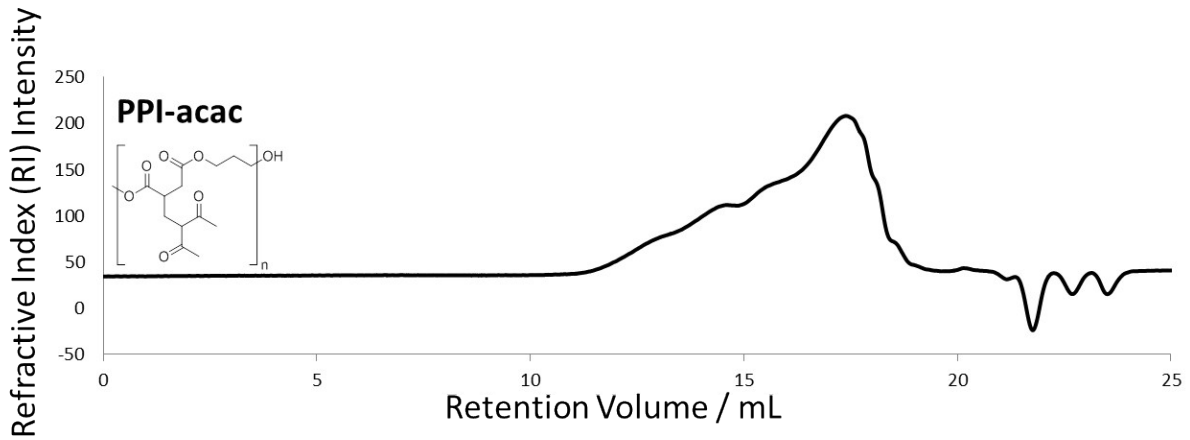

Figure S6: GPC chromatograms (Refractive Index Detector, THF eluent, molecular weights estimated via triple detection and a polystyrene standard) for the addition of Hacac to PPI (formally as a cross-linked insoluble sample, hence the high level of microgel observed in the sample following Hacac addition).

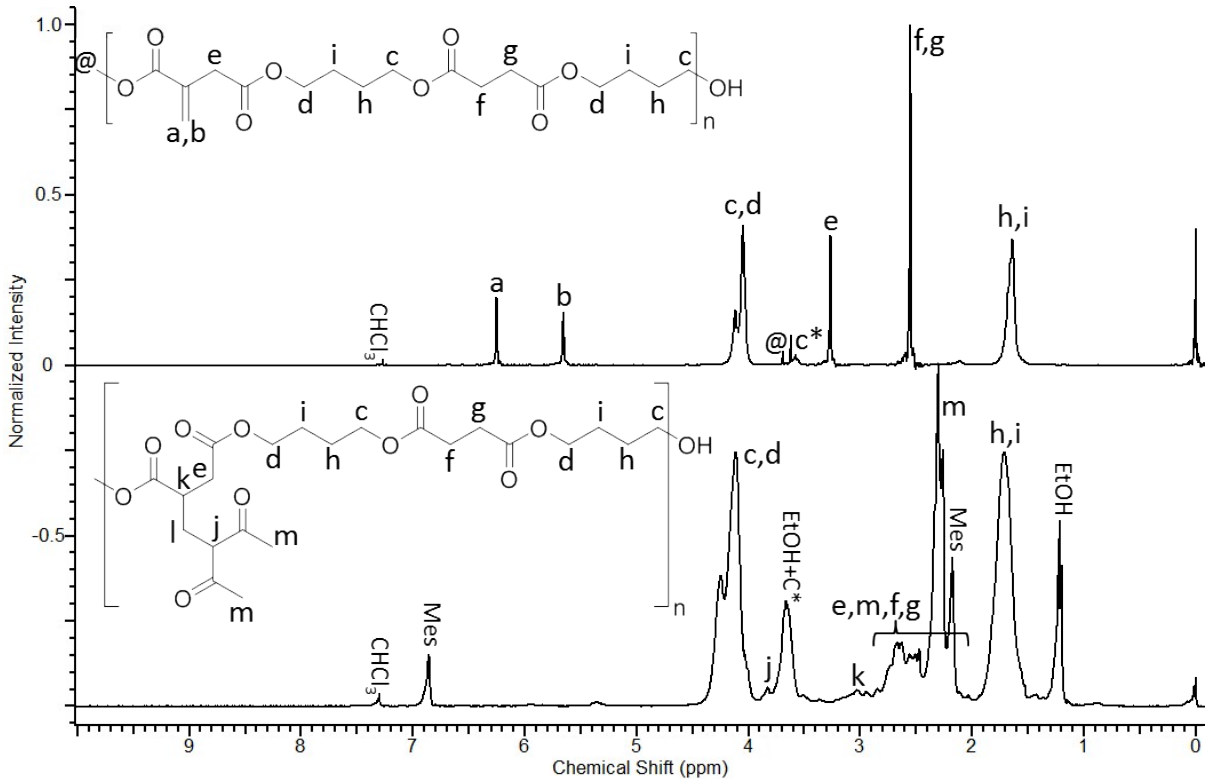

Figure S7: ^{1}H-NMR spectra, with assignments, for PBIBS before (top) and after (bottom) Hacac addition. ^{1}H-NMR spectra collected in $CDCl_3$, @ refers to ^{1}H-signals as a result of the CH_3 of the methyl ester end-group, * refers to the CH_2s of the diol when as an end group. Note: residual ethanol (EtOH) was present as a result of solubility issues encountered during the work-up of this sample.

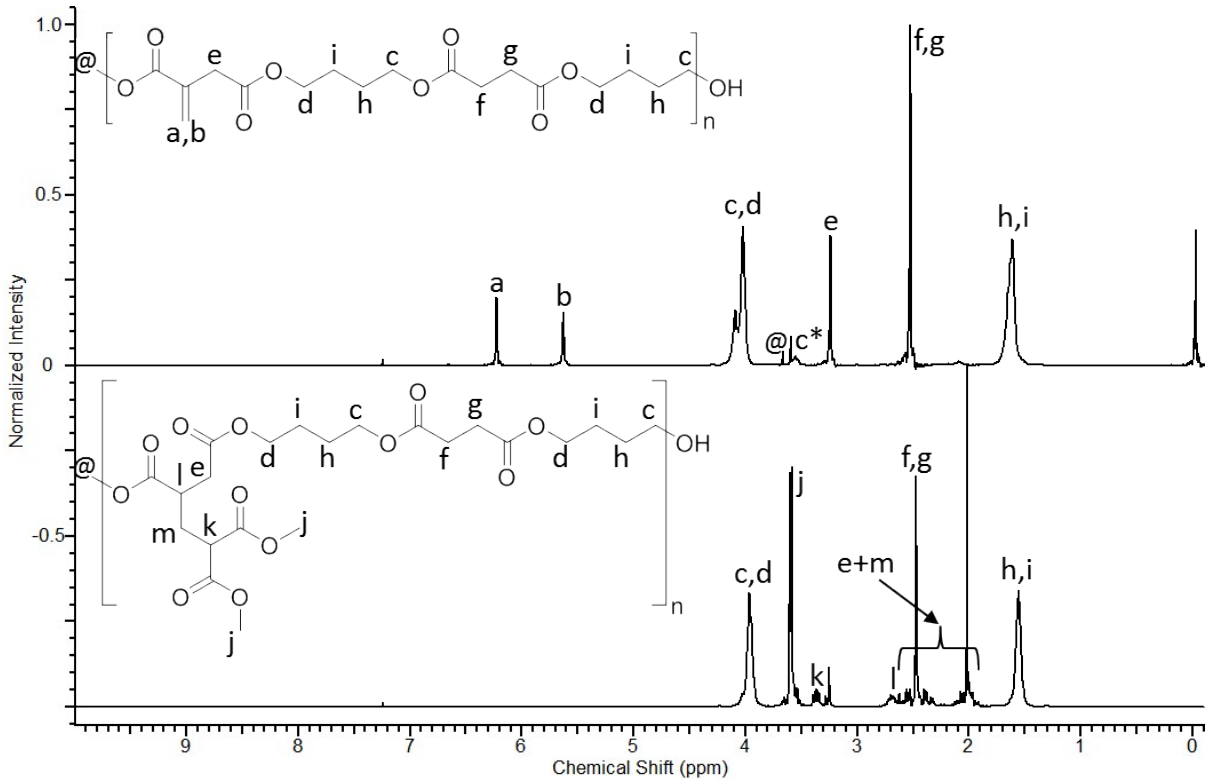

Figure S8: ^{1}H-NMR spectra, with assignments, for PBIBS before (top) and after (bottom) dimethyl malonate (DMM) addition. ^{1}H-NMR collected in $CDCl_3$, @ refers to ^{1}H-signals as a result of the CH_3 of the methyl ester end-group, * refers to the CH_2s of the diol when as an end group.

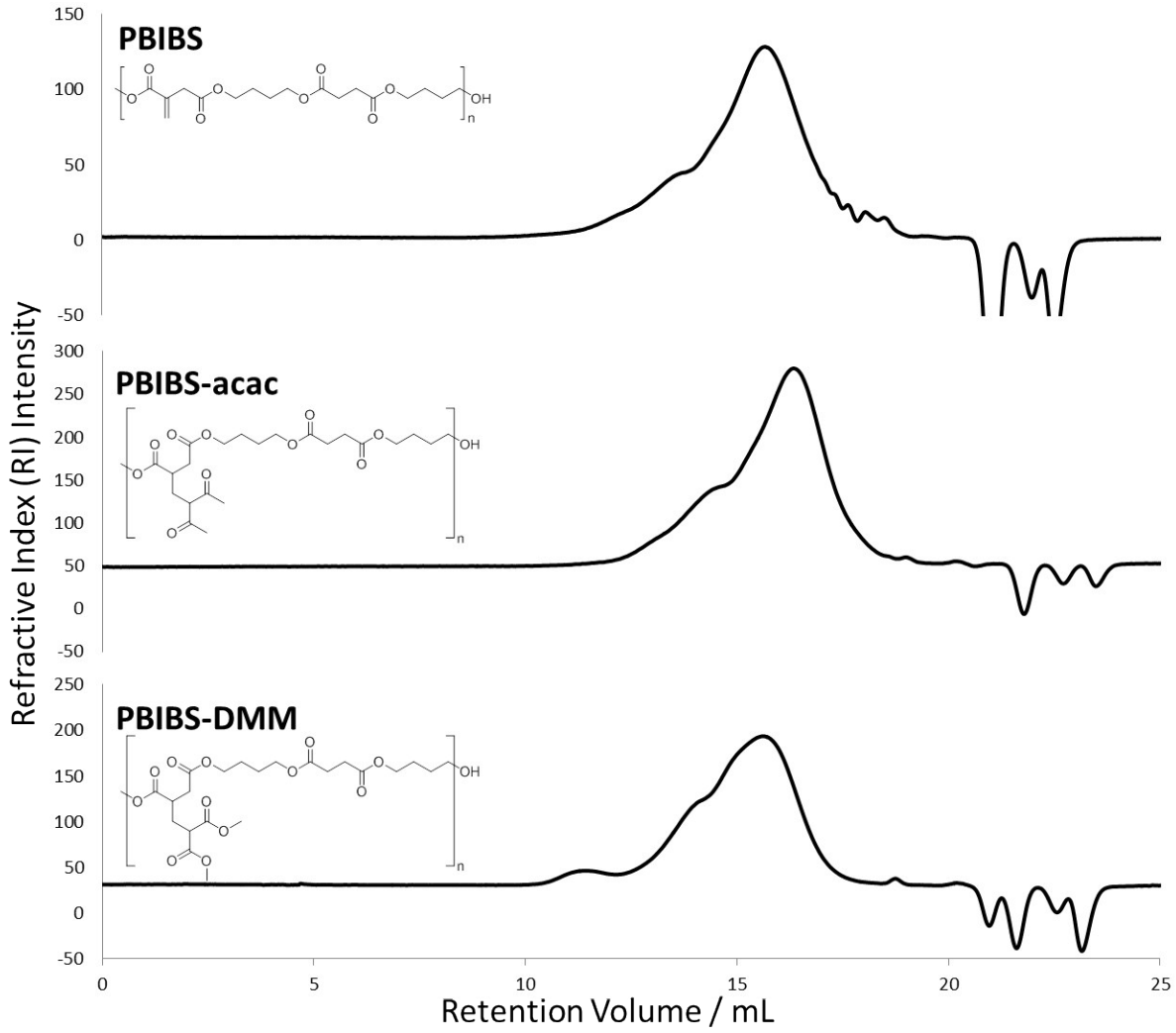

Figure S9: GPC chromatograms (Refractive Index Detector, THF eluent, polystyrene standard) for the addition of Hacac (middle) or DMM (bottom) to PBIBS (top).

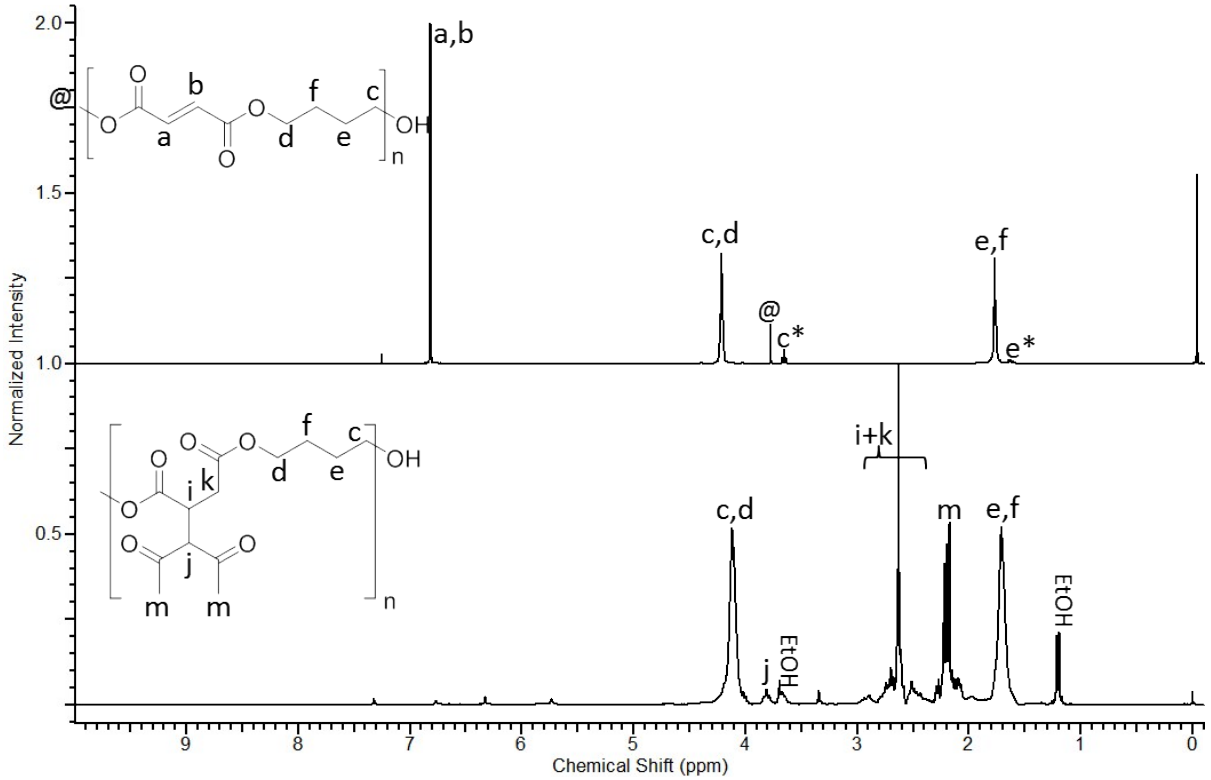

Figure S10: ^{1}H-NMR spectra, with assignments, for PBFu before (top) and after (bottom) Hacac addition. ^{1}H-NMR spectra collected in $CDCl_3$, @ refers to ^{1}H-signals as a result of the CH_3 of the methyl ester end-group, * refers to the CH_2s of the diol when as an end group. Note: residual ethanol (EtOH) was present as a result of solubility issues encountered during the work-up of this sample.

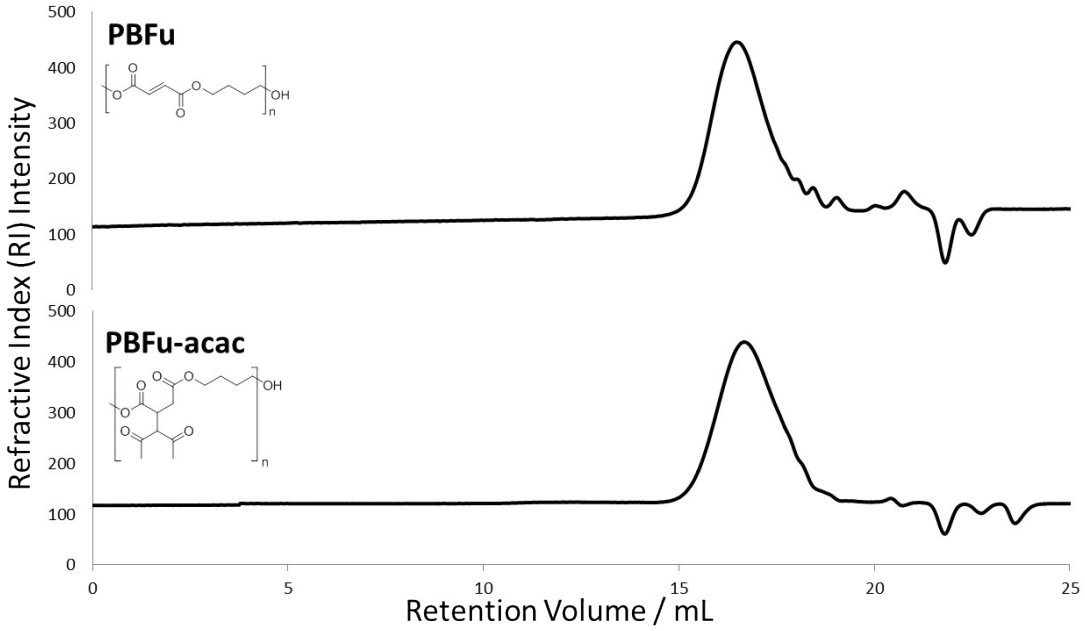

Figure S11: GPC chromatograms (Refractive Index Detector, THF eluent, polystyrene standard) for the addition of Hacac (bottom) to PBFu (top).

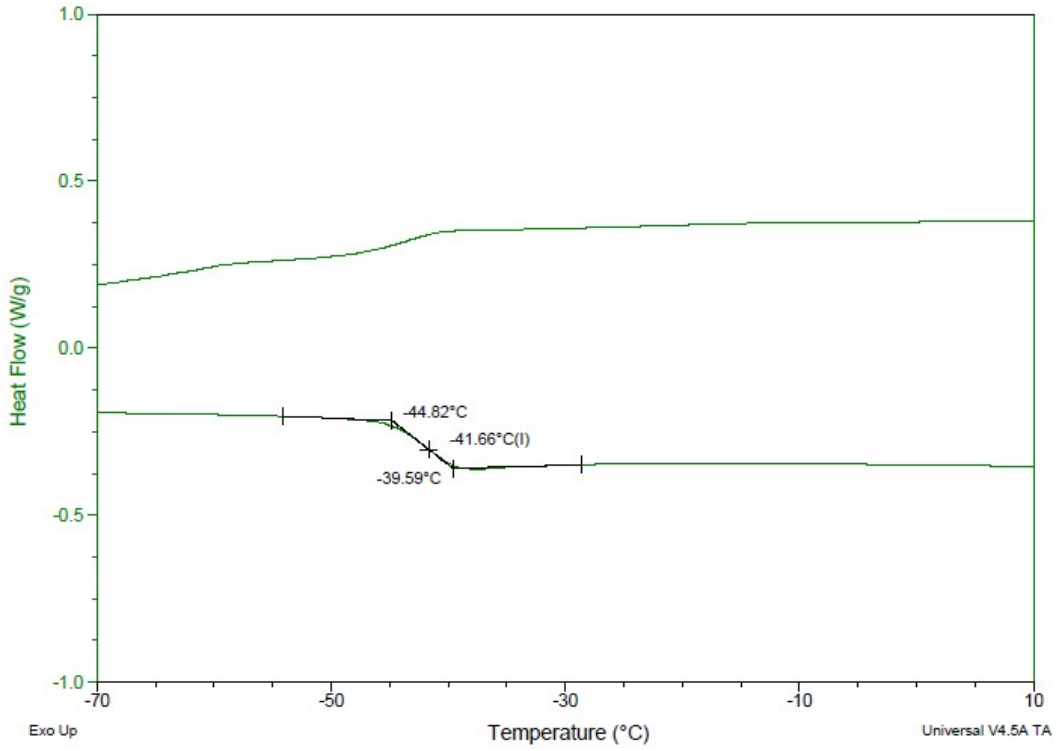

Figure S12: Modulated DSC thermogram of PBI; the scans were run at a heating rate of 10 deg/min. DSC thermogram collected in duplicate to ensure reproducibility, the value for T_g given in the manuscript was the average of the duplicate thermograms. No melt observed.

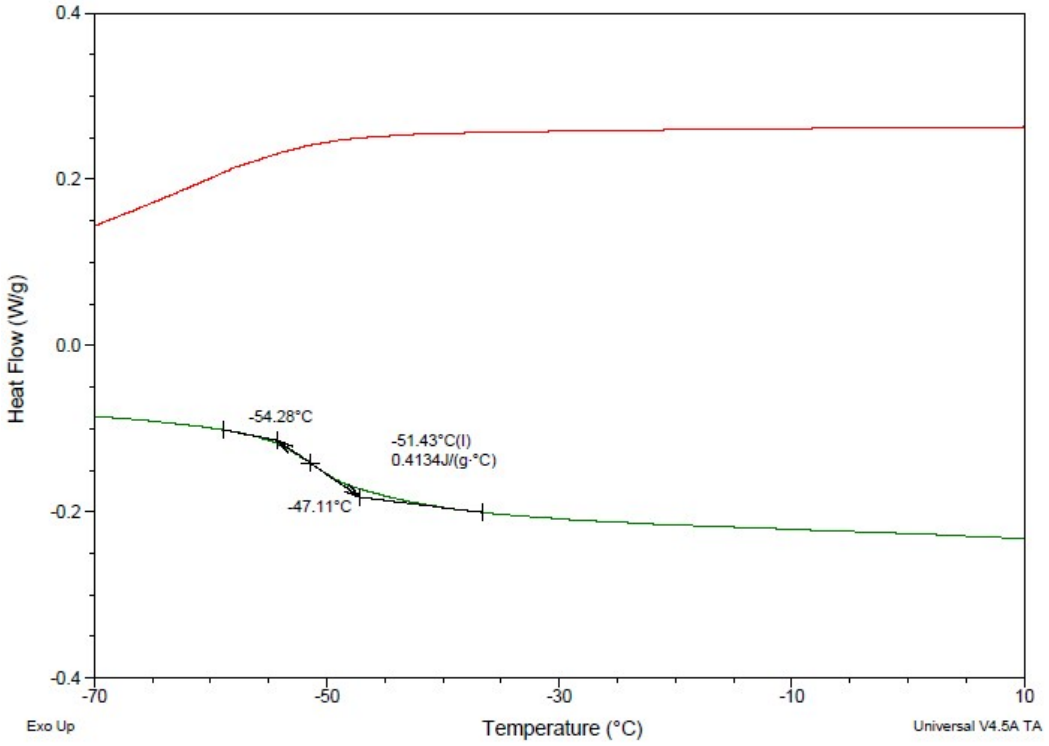

Figure S13: Modulated DSC thermogram of PPI; the scans were run at a heating rate of 10 deg/min. DSC thermogram collected in duplicate to ensure reproducibility, the value for T_g given in the manuscript was the average of the duplicate thermograms. No melt observed.

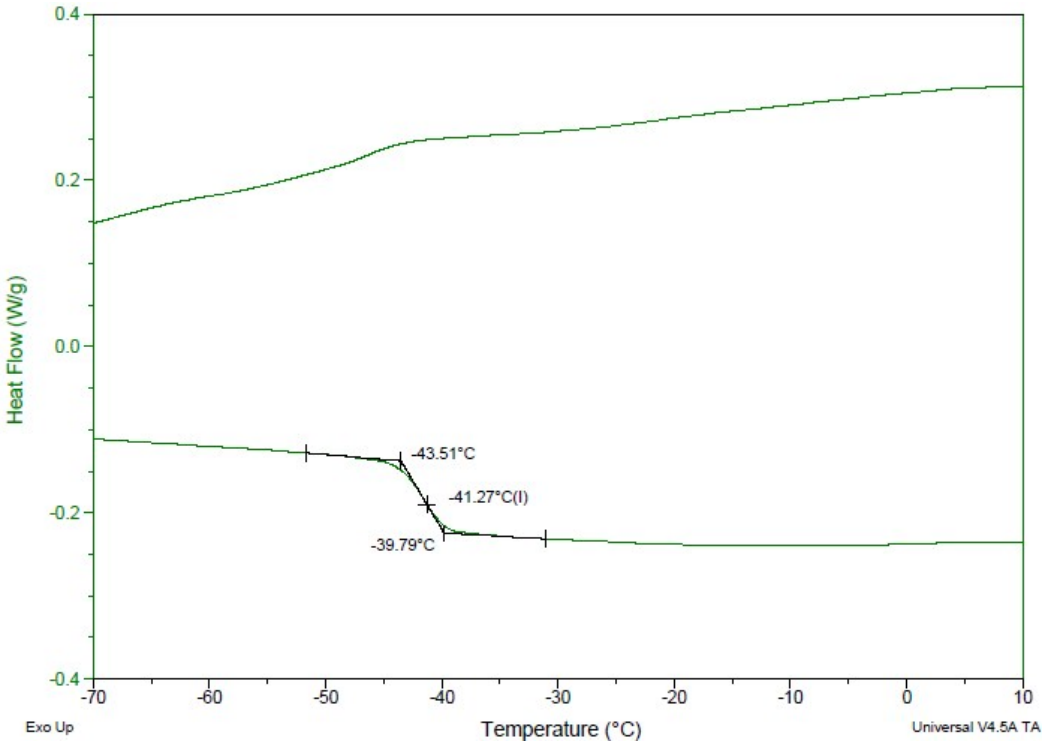

Figure S14: Modulated DSC thermogram of PBIBS; the scans were run at a heating rate of 10 deg/min. DSC thermogram collected in duplicate to ensure reproducibility, the value for T_g given in the manuscript was the average of the duplicate thermograms. No melt observed.

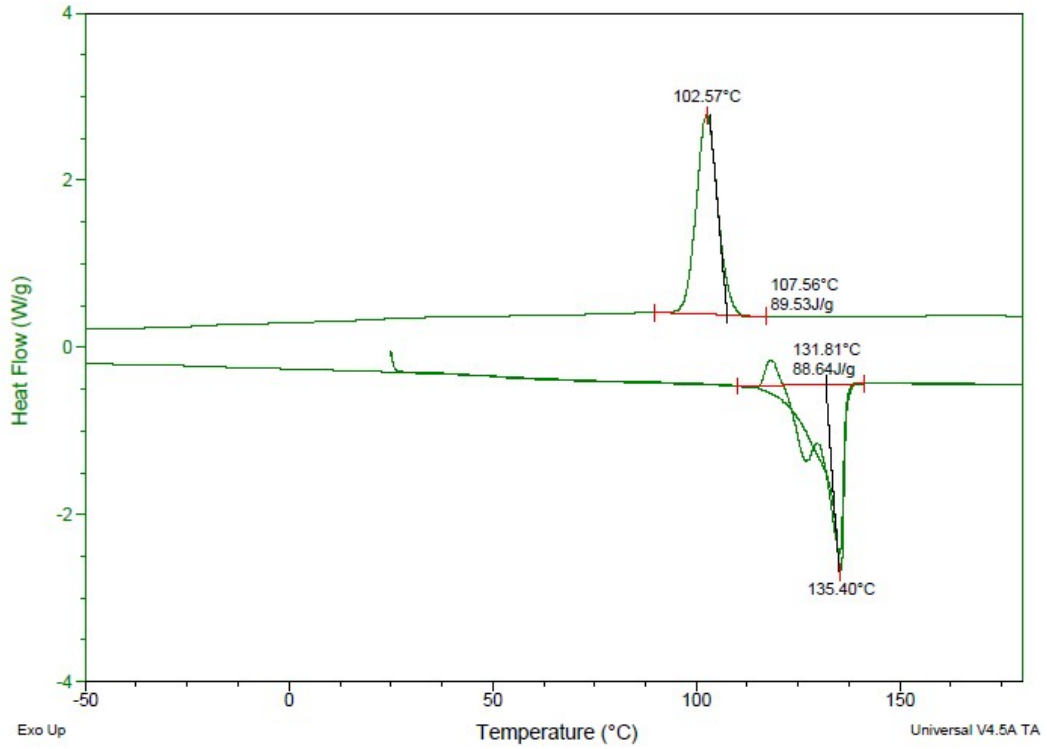

Figure S15: Modulated DSC thermogram of PBFu; the scans were run at a heating rate of 10 deg/min. DSC thermogram collected in duplicate to ensure reproducibility, the value for T_g given in the manuscript was the average of the duplicate thermograms. No T_g observed.

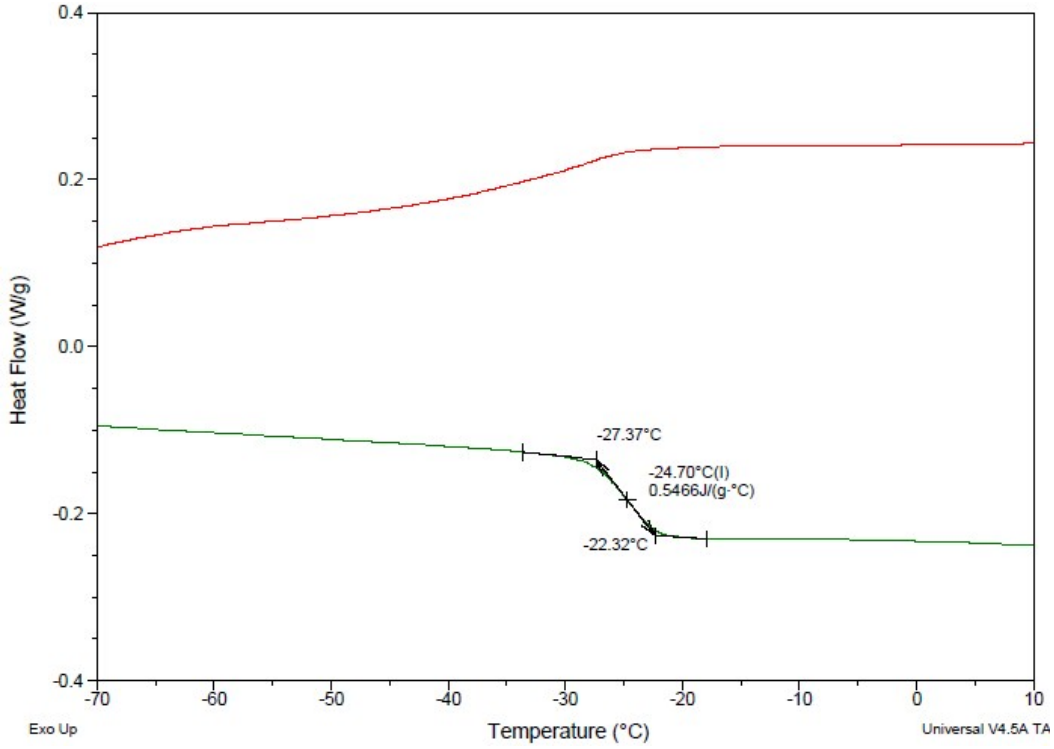

Figure S16: Modulated DSC thermogram of PBI-acac; the scans were run at a heating rate of 10 deg/min. DSC thermogram collected in duplicate to ensure reproducibility, the value for T_g given in the manuscript was the average of the duplicate thermograms. No melt observed.

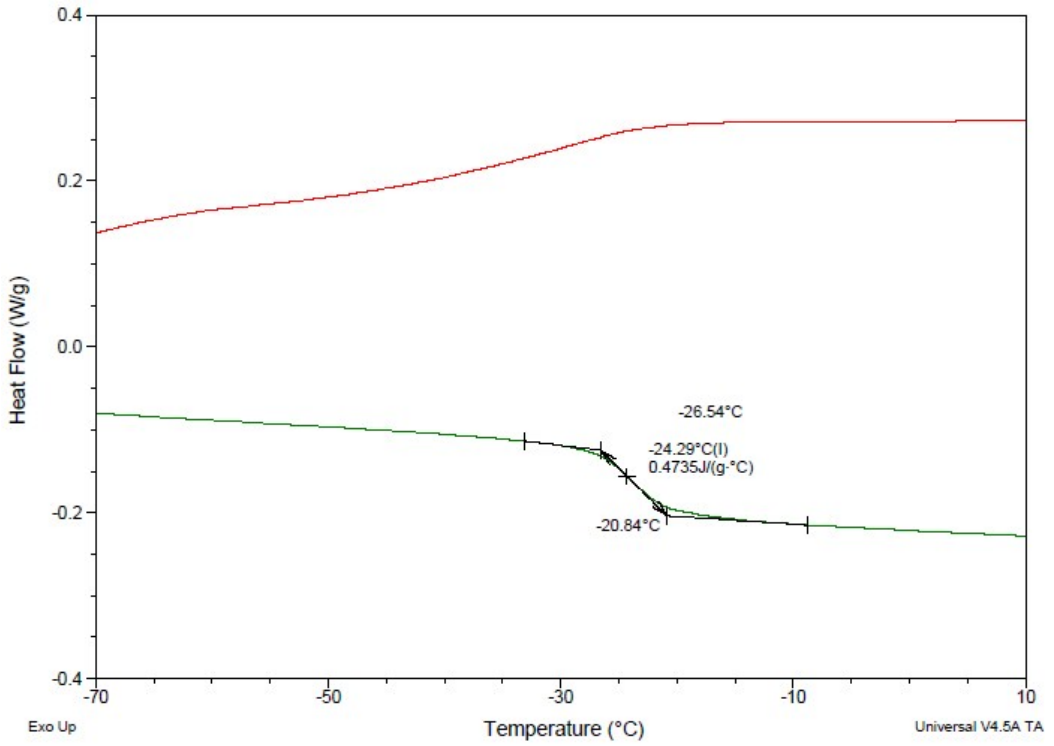

Figure S17: Modulated DSC thermogram of PPI-acac; the scans were run at a heating rate of 10 deg/min. DSC thermogram collected in duplicate to ensure reproducibility, the value for T_g given in the manuscript was the average of the duplicate thermograms. No melt observed.

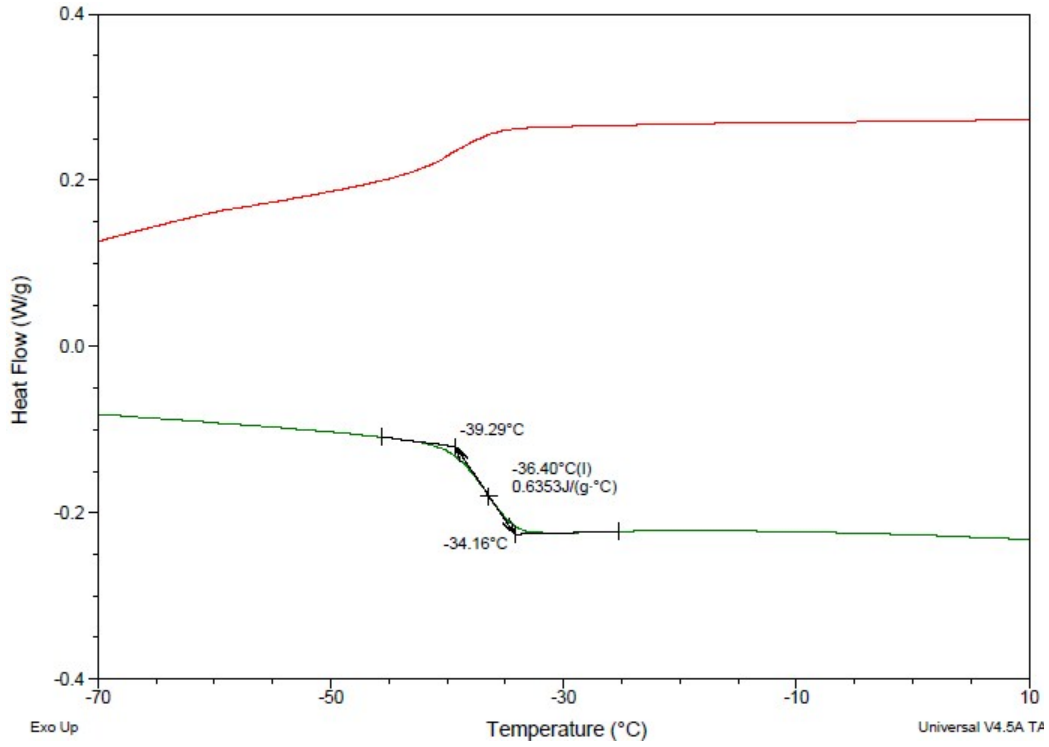

Figure S18: Modulated DSC thermogram of PBIBS-acac; the scans were run at a heating rate of 10 deg/min. DSC thermogram collected in duplicate to ensure reproducibility, the value for T_g given in the manuscript was the average of the duplicate thermograms. No melt observed.

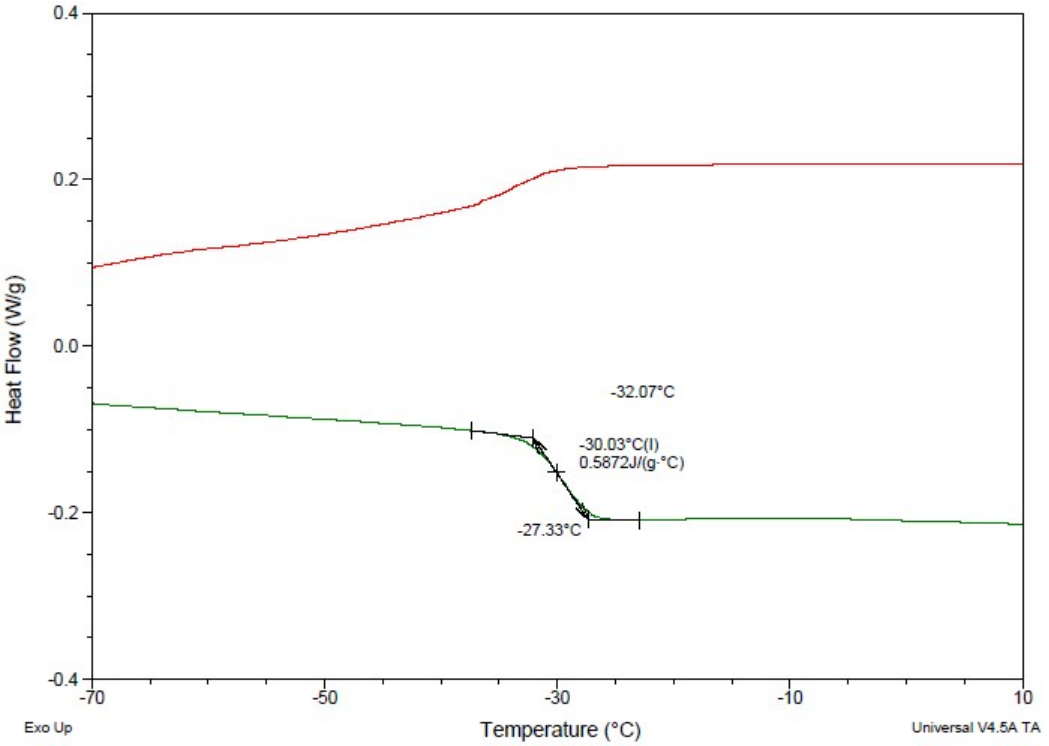

Figure S19: Modulated DSC thermogram of PBI-acac-52; the scans were run at a heating rate of 10 deg/min. DSC thermogram collected in duplicate to ensure reproducibility, the value for T_g given in the manuscript was the average of the duplicate thermograms. No melt observed.

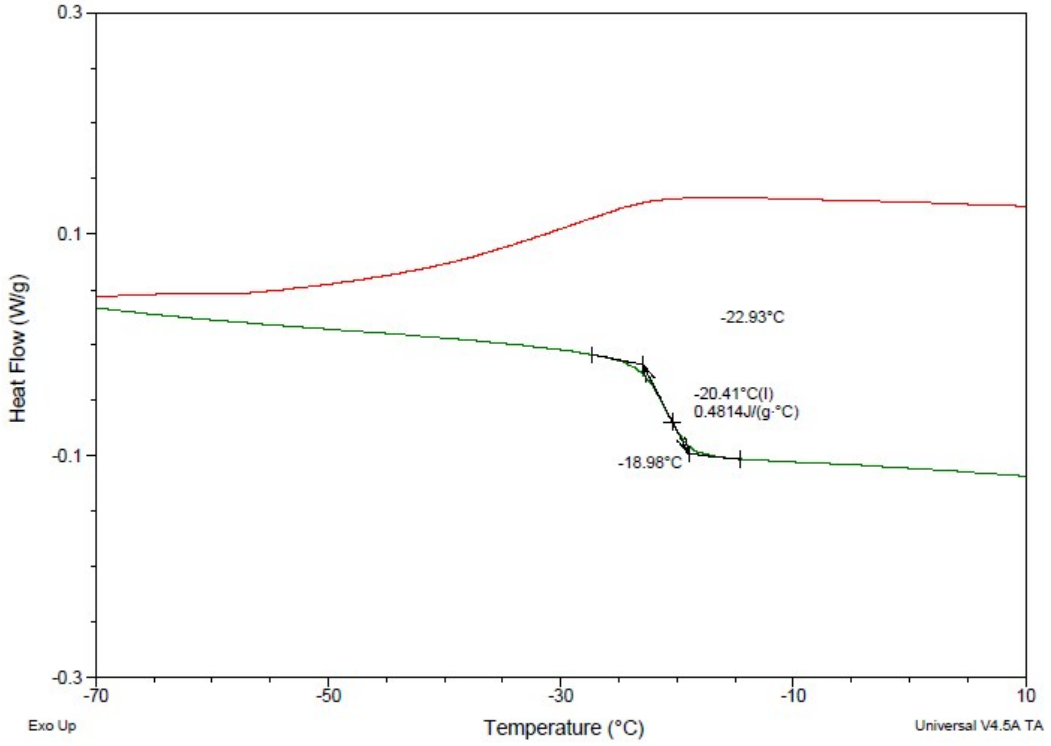

Figure S20: Modulated DSC thermogram of PBI-acac-68; the scans were run at a heating rate of 10 deg/min. DSC thermogram collected in duplicate to ensure reproducibility, the value for T_g given in the manuscript was the average of the duplicate thermograms. No melt observed.

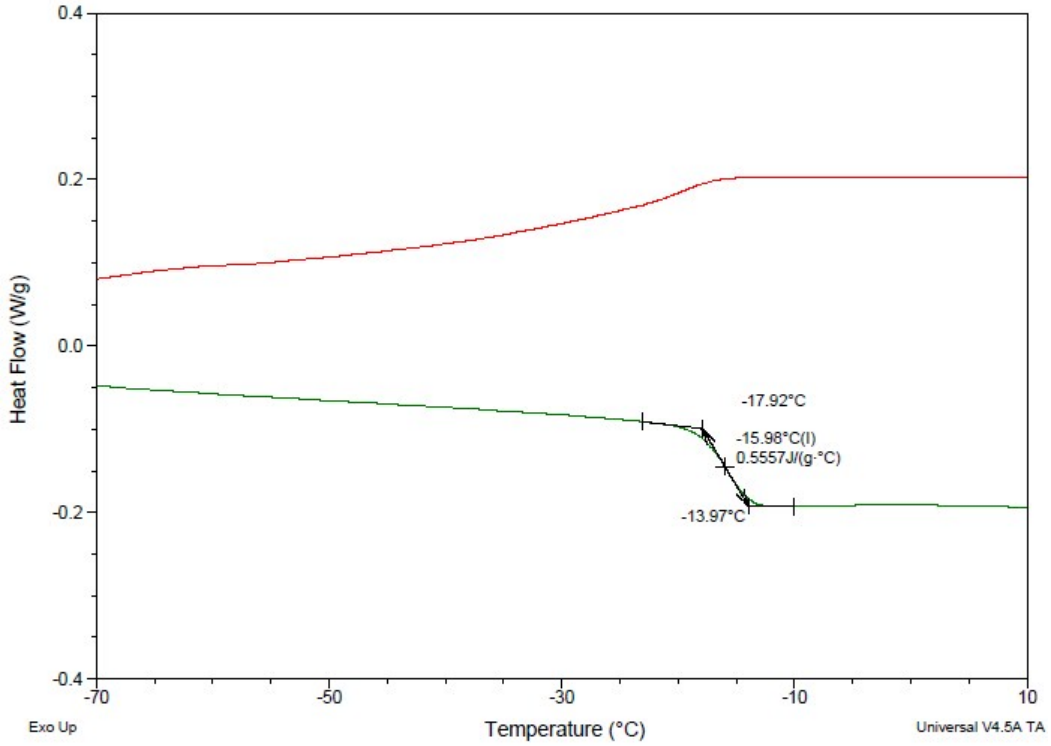

Figure S21: Modulated DSC thermogram of PBI-acac-78; the scans were run at a heating rate of 10 deg/min. DSC thermogram collected in duplicate to ensure reproducibility, the value for T_g given in the manuscript was the average of the duplicate thermograms. No melt observed.

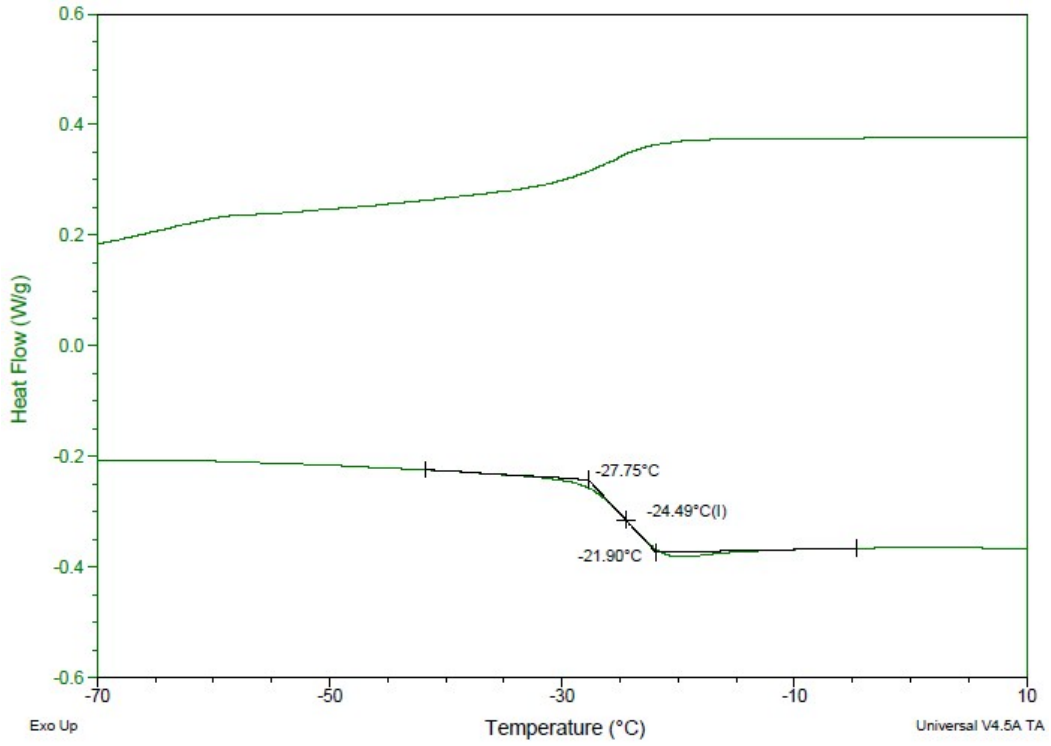

Figure S22: Modulated DSC thermogram of PBI-DMM; the scans were run at a heating rate of 10 deg/min. DSC thermogram collected in duplicate to ensure reproducibility, the value for T_g given in the manuscript was the average of the duplicate thermograms. No melt observed.

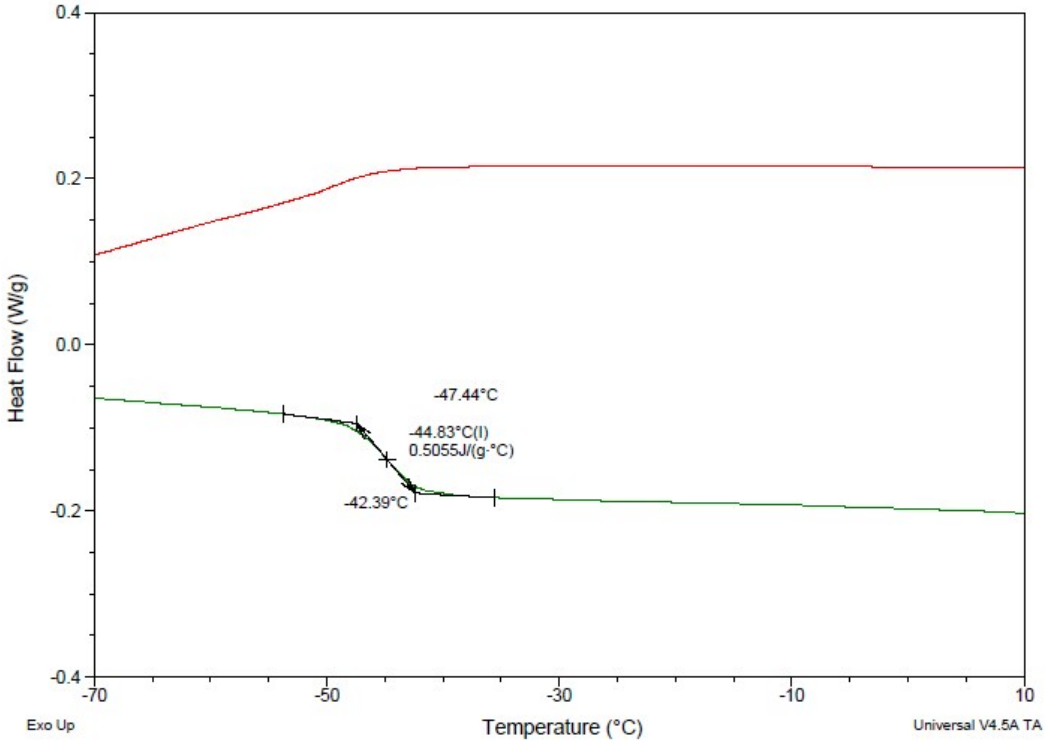

Figure S23: Modulated DSC thermogram of PBIBS-DMM; the scans were run at a heating rate of 10 deg/min. DSC thermogram collected in duplicate to ensure reproducibility, the value for T_g given in the manuscript was the average of the duplicate thermograms. No melt observed.