Electronic Supplementary Material (ESI) for Polymer Chemistry.

ELECTRONIC SUPPLEMENTARY INFORMATION

Poly(alkylene itaconate)s – An interesting class of polyesters with periodically located *exo*-chain double bonds susceptible to Michael addition

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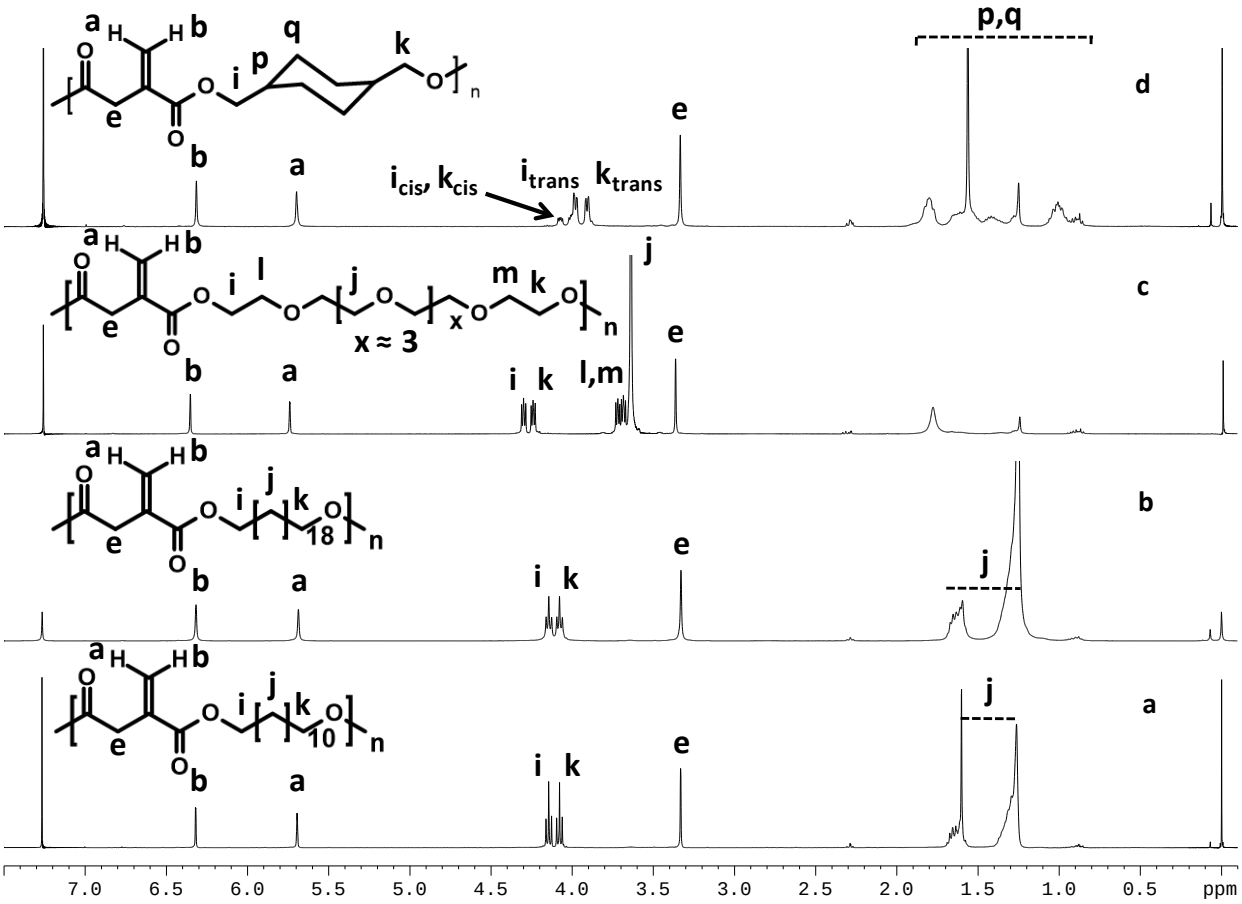

Figure S1: ^{1}H NMR spectra of the parent linear polyesters, poly(dodecyl itaconate) (**PDI**) (a), poly(icosyl itaconate) (**PII**) (b), poly(oligoethyleneoxy itaconate) (**PEOI**) (c) and poly(CDM-itaconate) (**PCDMI**) (d). All the spectra were recorded in $CDCl_3$.

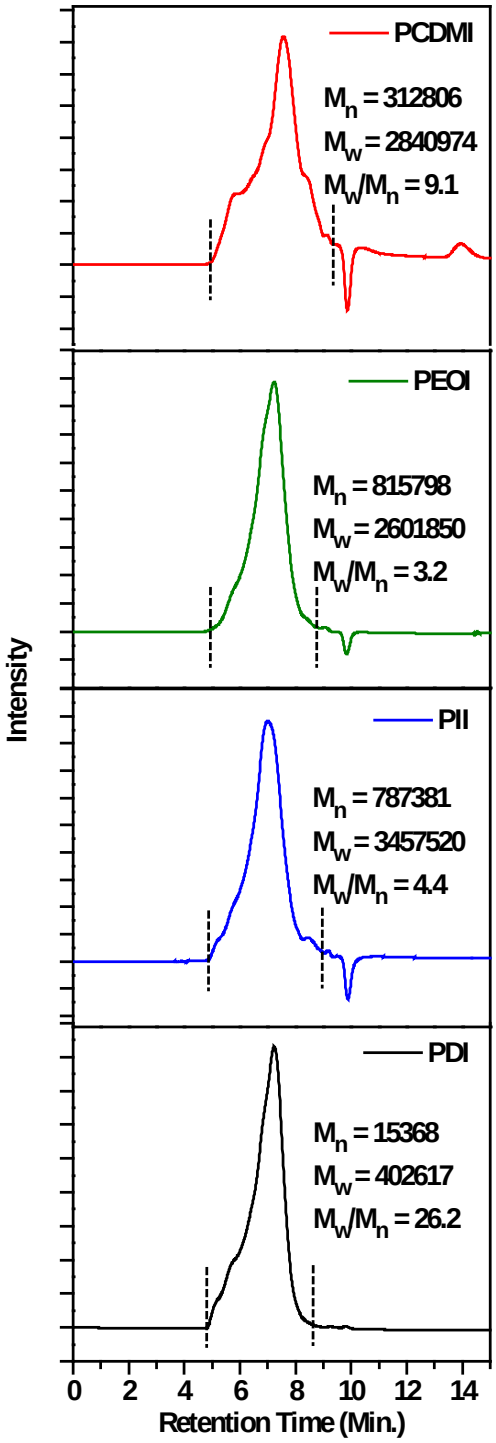

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Figure S2: Stack plot of the GPC chromatograms of the parent polyesters recorded using $CHCl_3$ as the eluent. The molecular weights were estimated using polystyrene-based standard calibration curve. The unusually high molecular weight and PDI of some samples is probably a reflection of the formation of some microgels, which are of small enough dimension that they pass through the 0.45 µm filter.

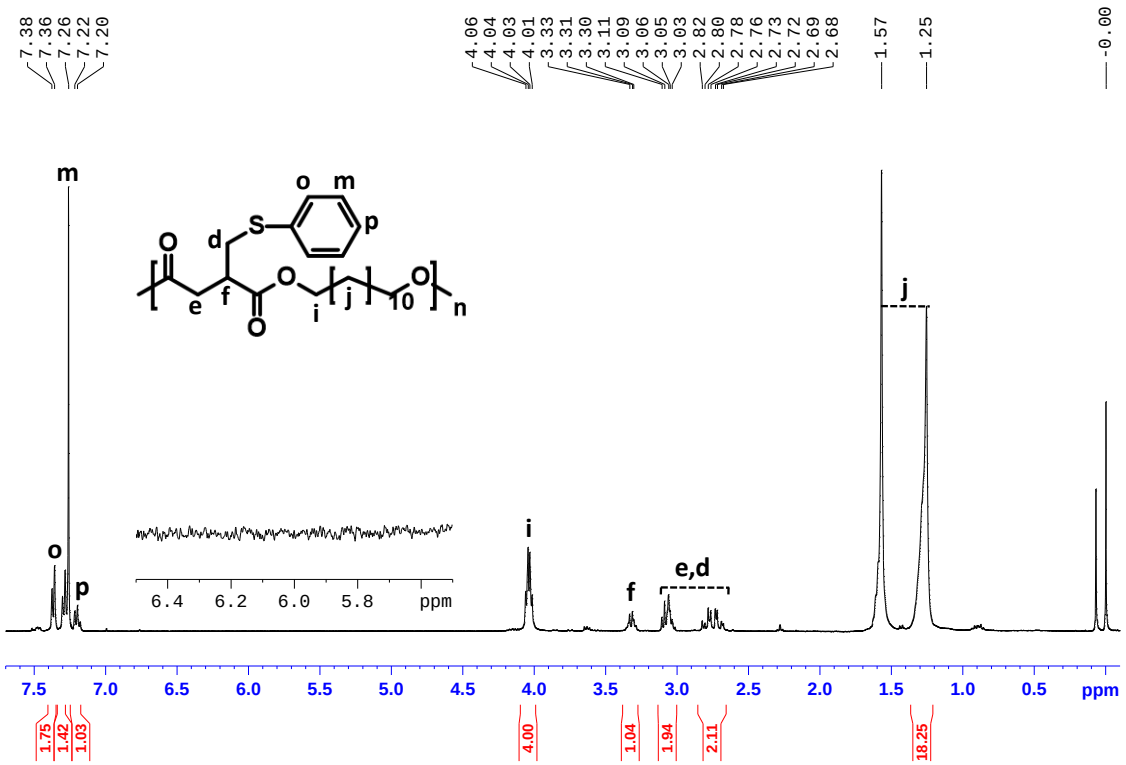

Figure S3(a): [1]H NMR spectra of PDI-TP. The expanded region from 5.5 to 6.5 ppm clearly reveals the complete disappearance of the olefinic protons suggesting that the Michael addition is nearly quantitative.

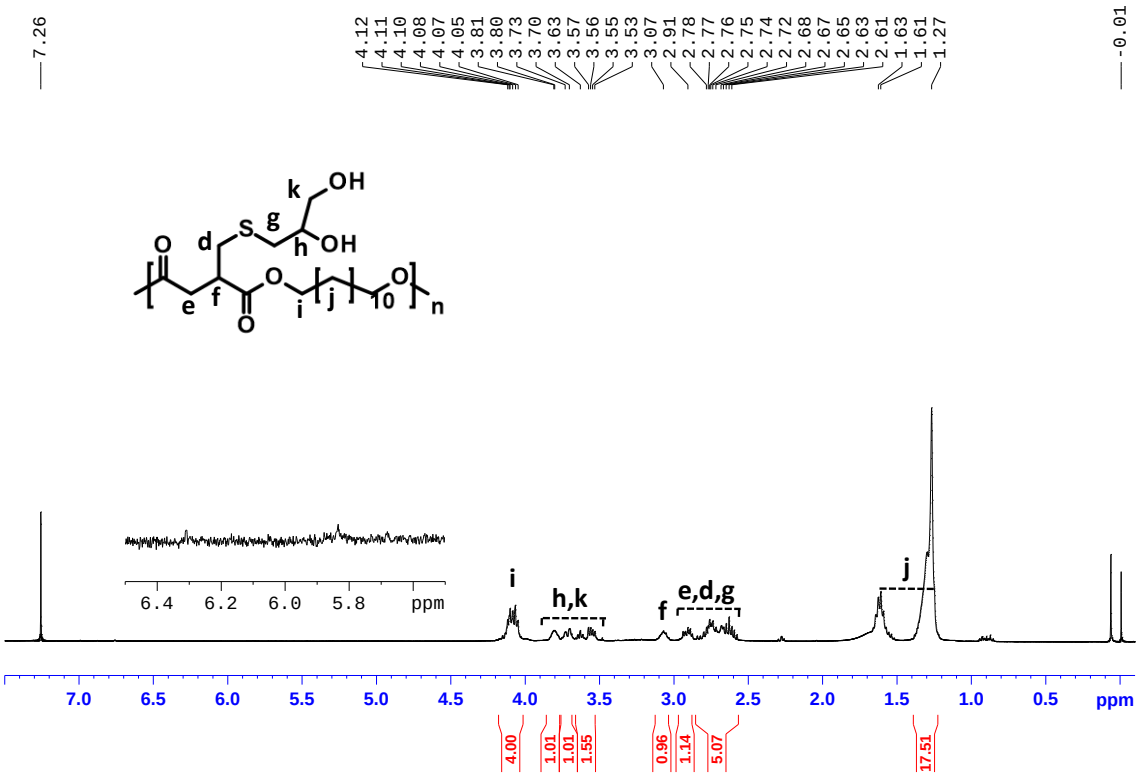

Figure S3(b): [1]H NMR spectra of PDI-TG.

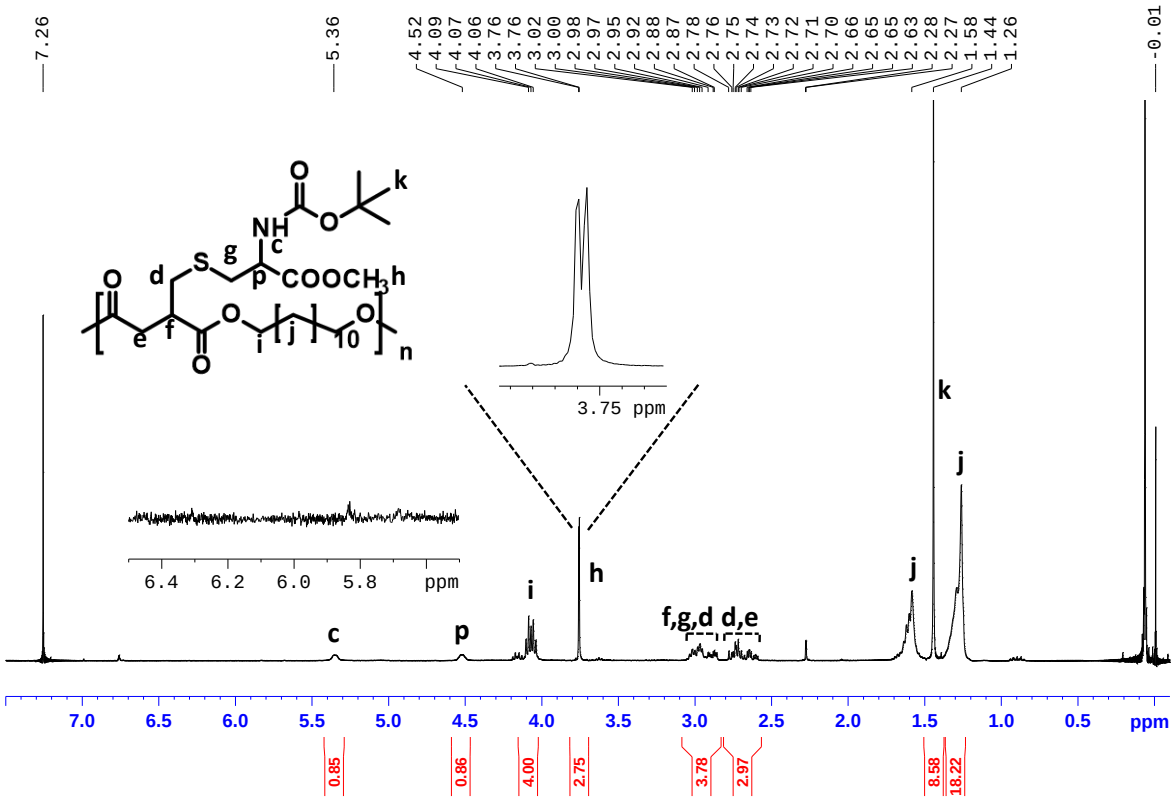

Figure S3(c): ^{1}H NMR spectra of PDI-CYS. It is interesting that the protons of the methyl ester of the cysteine unit appear as two distinct peaks of equal intensity; despite the fairly remote location of the methyl ester group with respect to the new sterogenic center that is formed, two distinct peaks are observed reflecting the two diastereomeric forms.

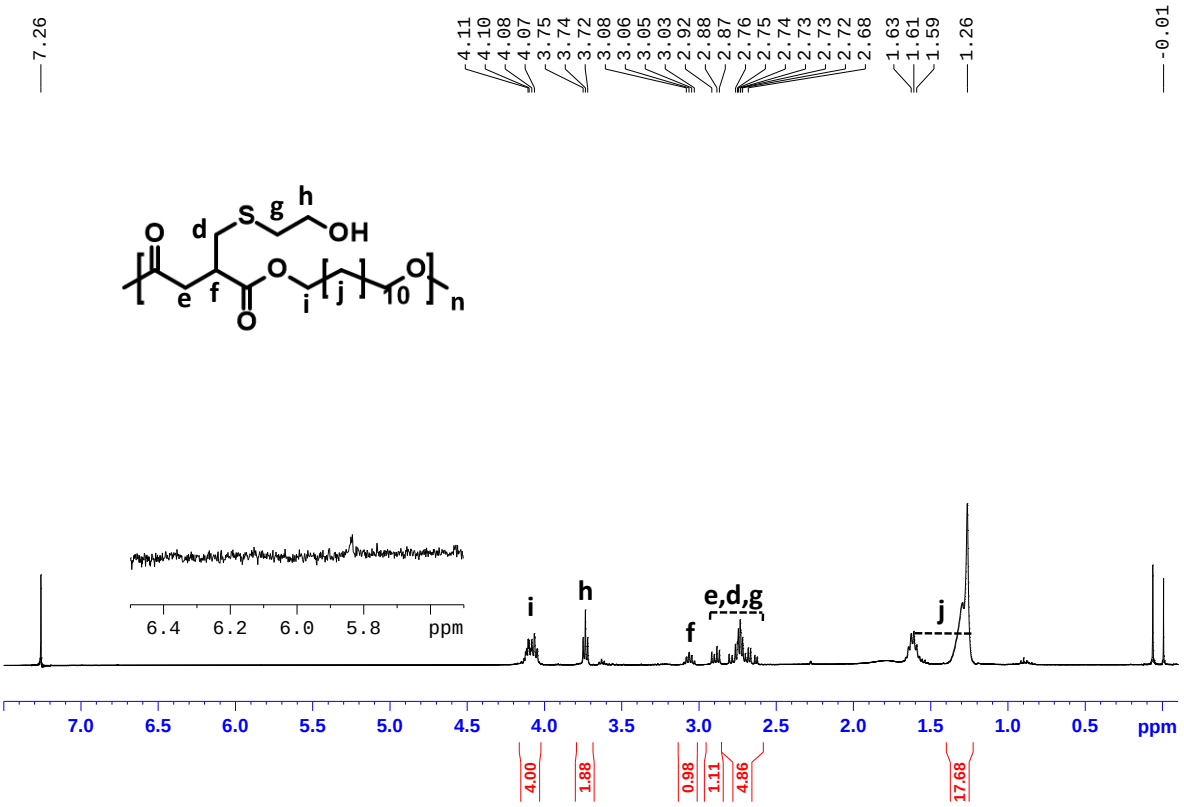

Figure S3(d): ^{1}H NMR spectra of PDI-ME.

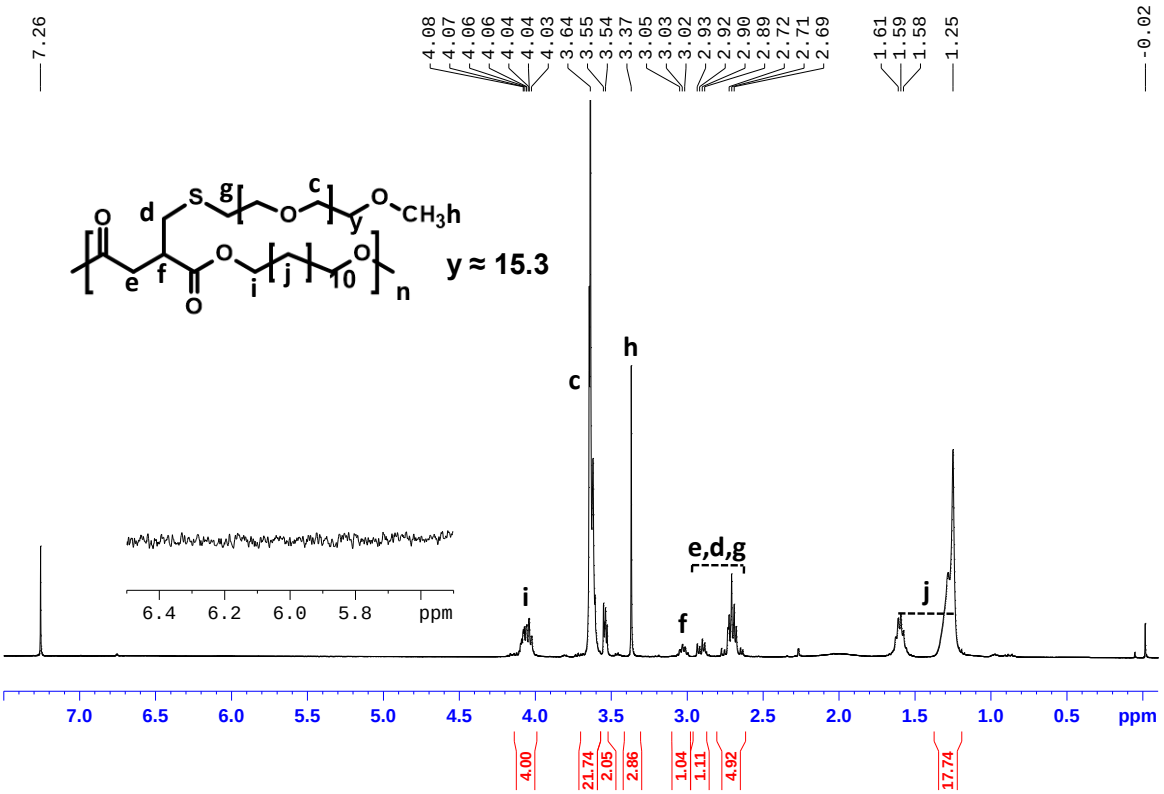

Figure S3(e): ^{1}H NMR spectra of PDI-PEG750. It is evident that the Michael reaction has gone to completion as the ratio of the intensity of the peak due to the terminal CH_3O- group of the grafted PEG segment (marked 'h') to the peak due the methylene protons adjacent to the ester group (marked 'i') matches reasonably well with the expected value (4:3).

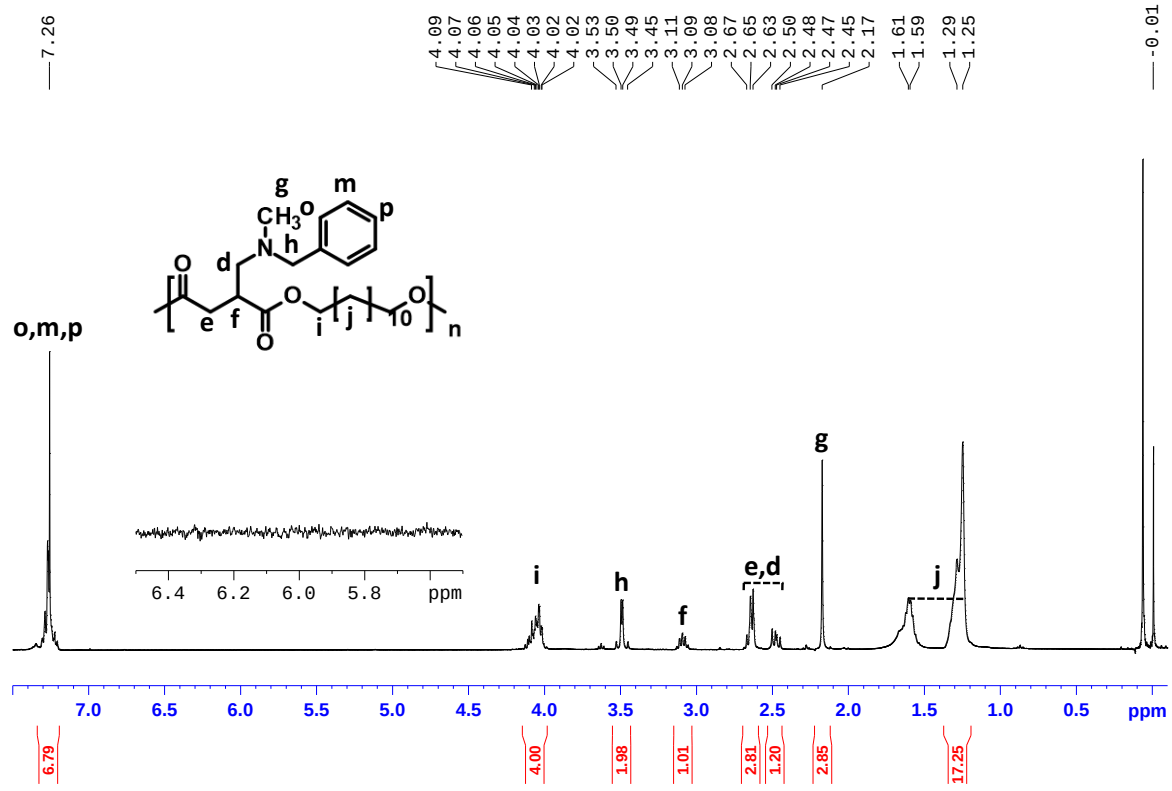

Figure S4(a): ^{1}H NMR spectra of PDI-MBA.

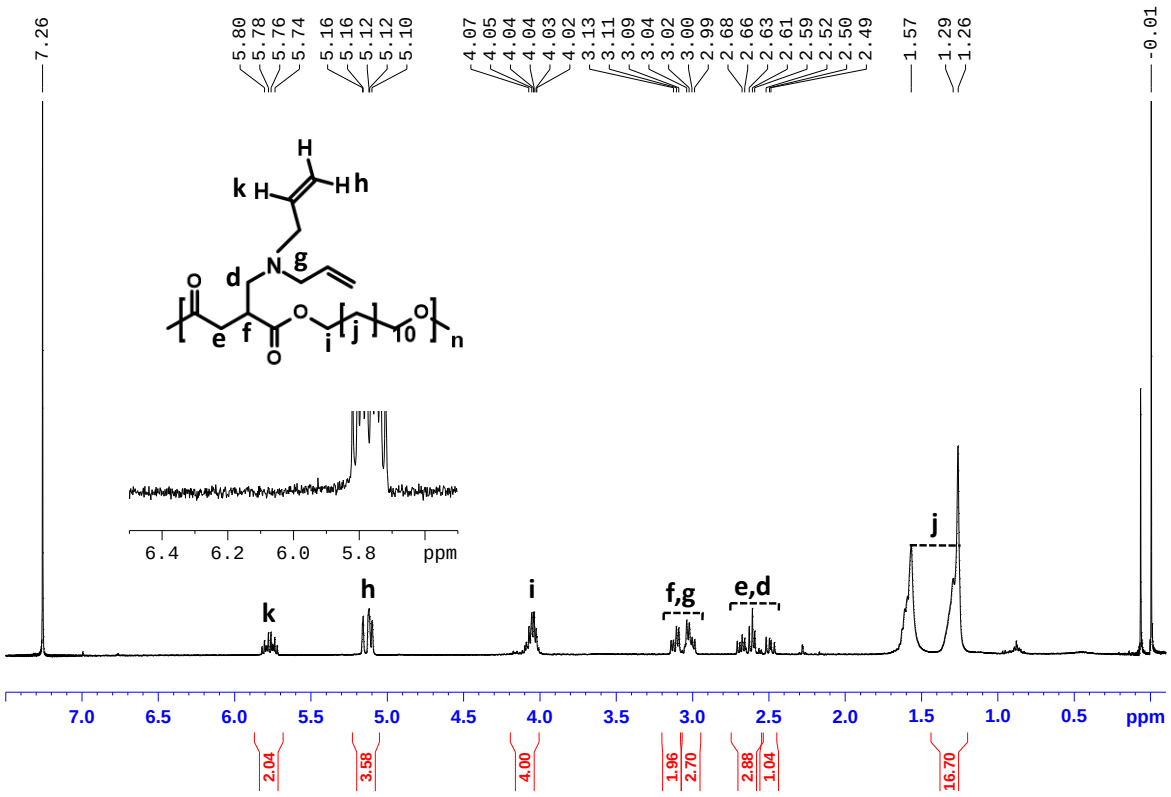

Figure S4(b): ^{1}H NMR spectra of PDI-DAA.

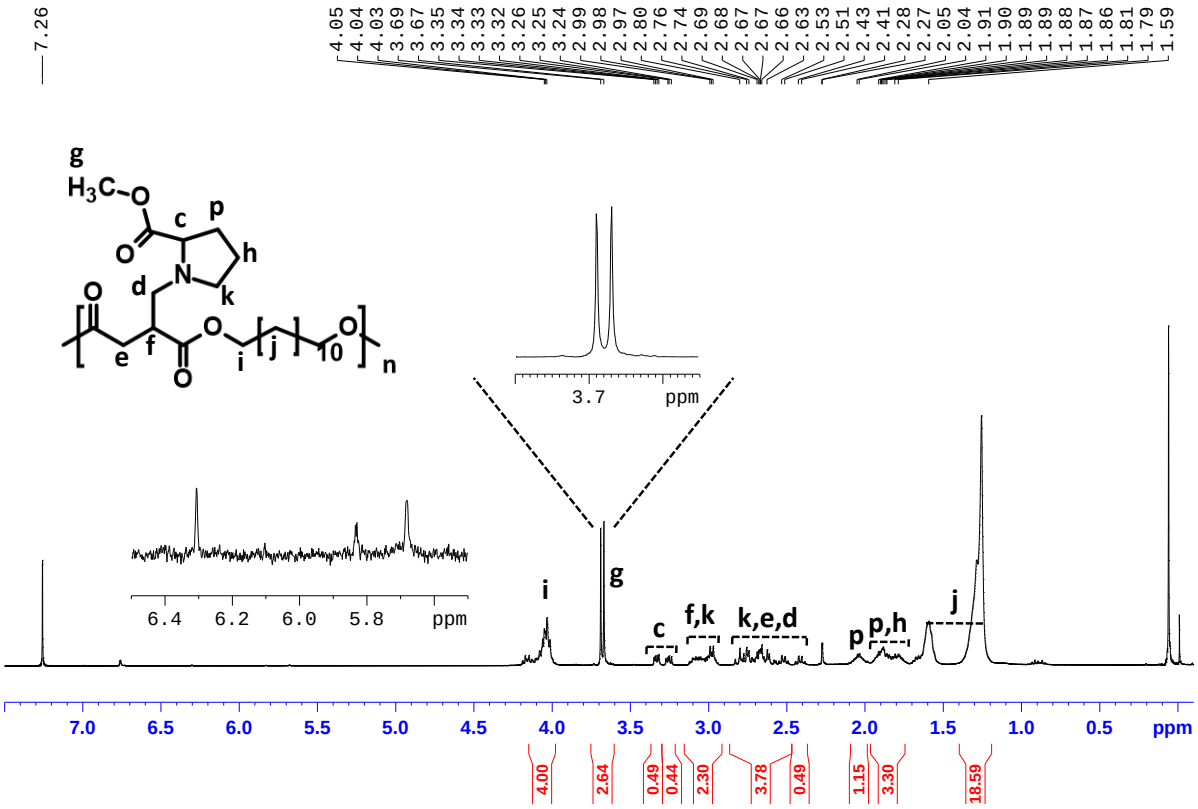

Figure S4(c): ^{1}H NMR spectra of PDI-PRO. Expansion of the region from 5.5 ppm to 6.5 ppm indicates very small presence of the olefinic protons; conversion of the Michael reaction was calculated to be 99%. Similar to PDI-CYS, protons of the methyl ester of the proline unit appear as two distinct peaks of equal intensity indicating the presence of the two diastereomeric forms after Michael addition.

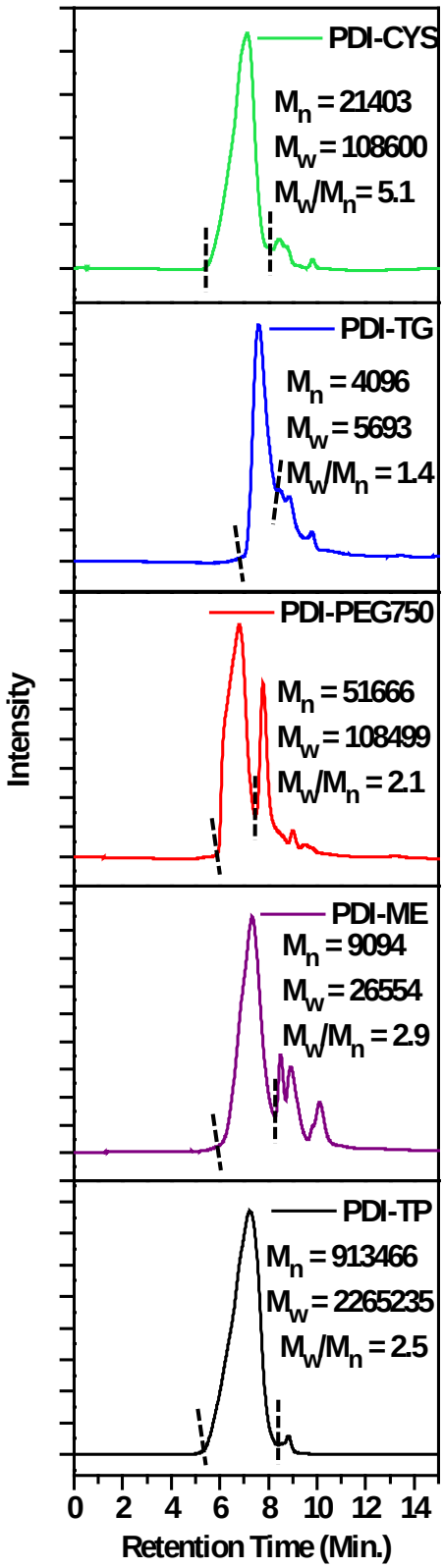

Figure S5(a): Stack plot of the GPC chromatograms of the various thiolated polyesters recorded using $CHCl_3$ as the eluent. The molecular weights were estimated using polystyrene-based standard calibration curve. The unusually high molecular weight and PDI of some samples is probably a reflection of the formation of some microgels, which are of small enough dimension that they pass through the 0.45 µm filter.

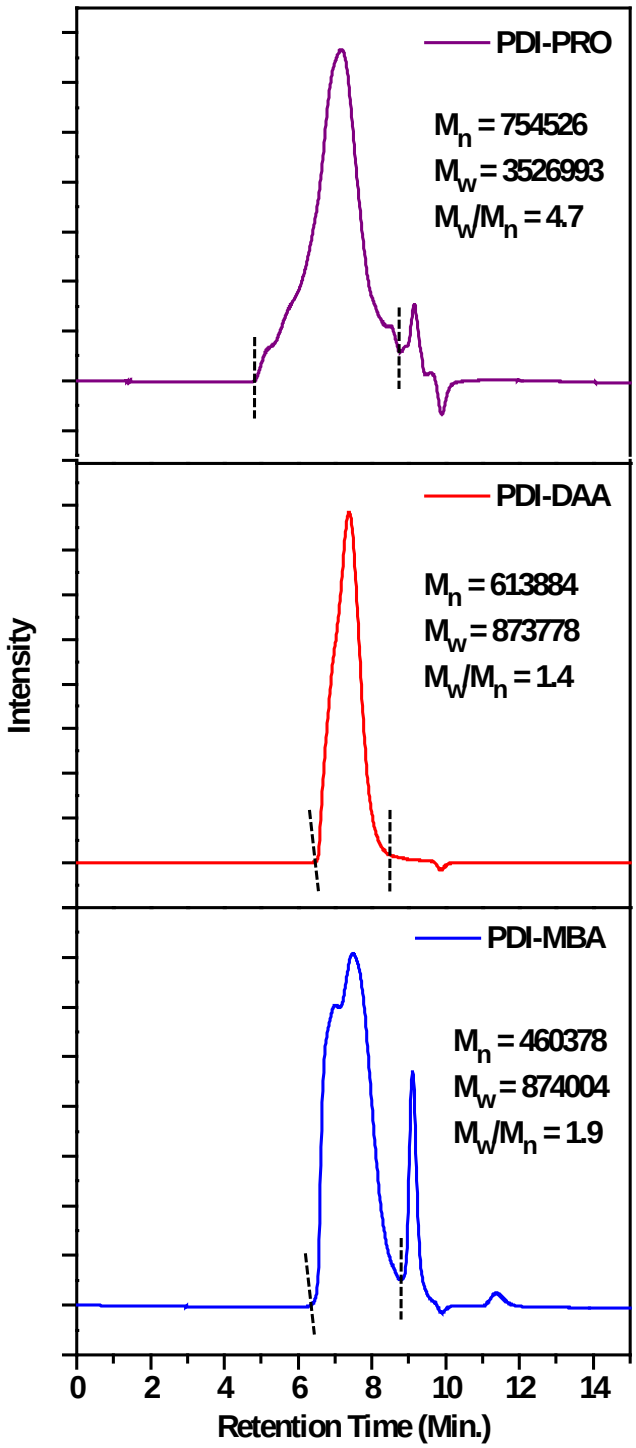

Figure S5(b): Stack plot of the GPC chromatograms of the various amine derivatized polymers recorded using $CHCl_3$ as the eluent. The molecular weights were estimated using polystyrene-based standard calibration curve. The unusually high molecular weight and PDI of some samples is probably a reflection of the formation of some microgels, which are of small enough dimension that they pass through the 0.45 µm filter.

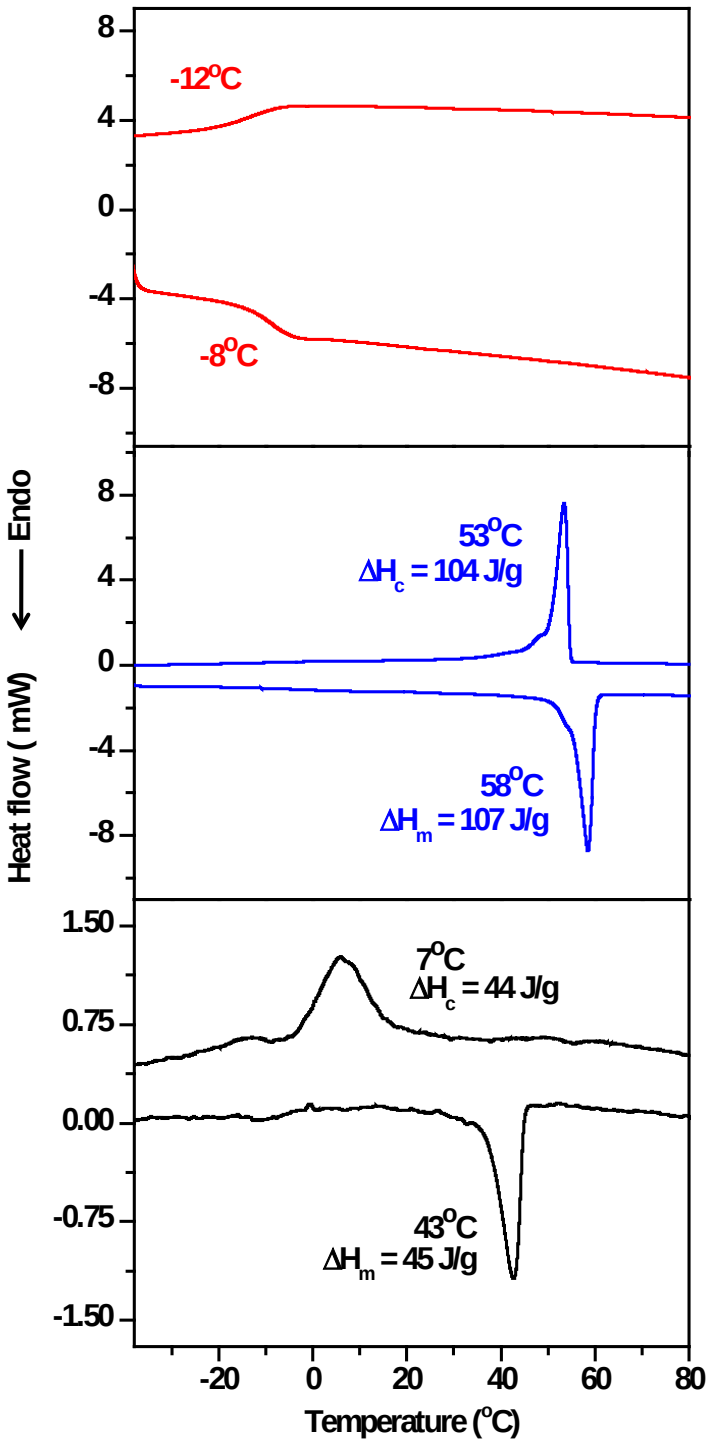

Figure S6: DSC thermograms of **PDI** (black), **PII** (blue) and **PCDMI** (red); the scans were run at a heating rate of 10 deg/min and all the thermograms are completely reproducible.

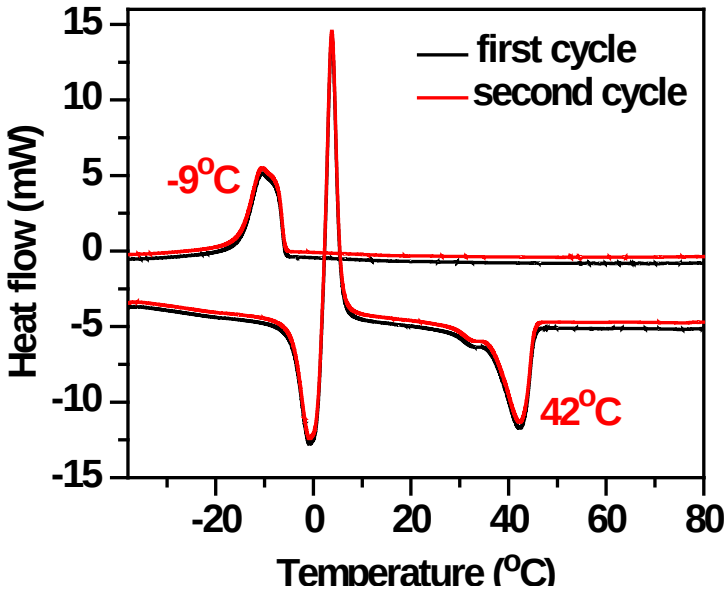

Figure S7(a): DSC thermogram of **PDI**; the scans were run at a heating rate of 10 deg/min and all the thermograms are completely reproducible. The red and black runs have been slightly y-axis displaced for clarity of the reproducibility.

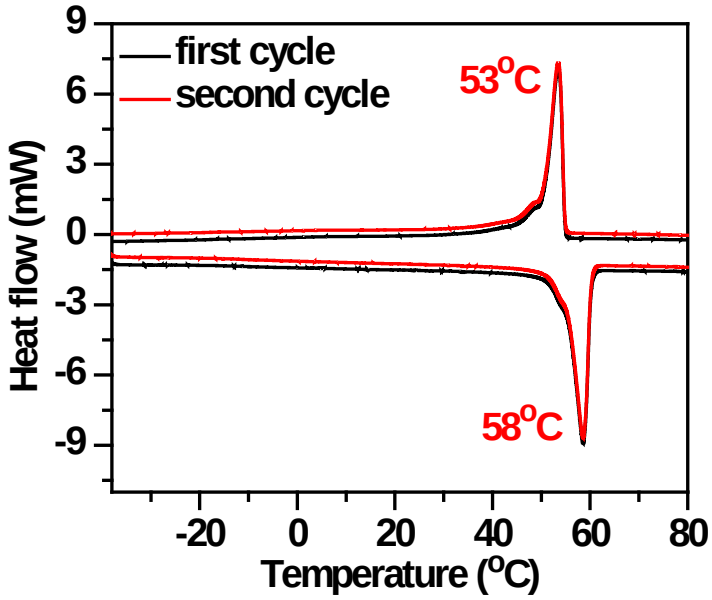

Figure S7(b): DSC thermogram of **PII**; the scans were run at a heating rate of 10 deg/min and all the thermograms are completely reproducible. The red and black runs have been slightly y-axis displaced for clarity of the reproducibility.

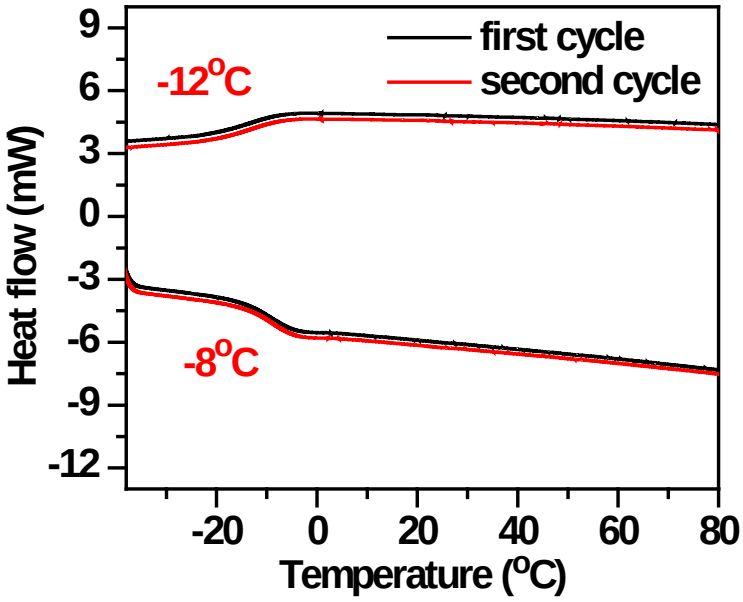

Figure S7(c): DSC thermogram of **PCDMI**; the scans were run at a heating rate of 10 deg/min and all the thermograms are completely reproducible. The red and black runs have been slightly y-axis displaced for clarity of the reproducibility.

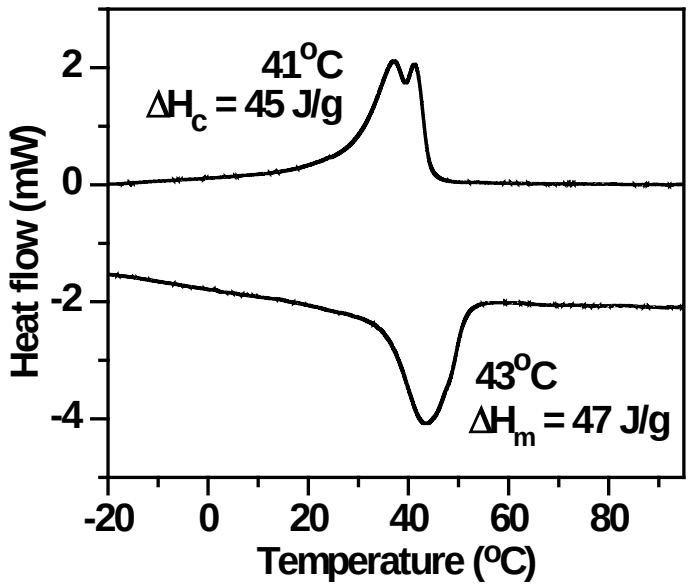

Figure S8: DSC thermogram of PII-PRO; the scans were run at a heating rate of 10 deg/min and all the thermograms are completely reproducible.