Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Solvated-Electron Initiated Rapid Polymerization at Ambient-Temperature: A case of Monomer Solubility

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Materials and Methods

Measurements. ^{1}H and ^{13}C NMR spectra for all samples were obtained using Bruker Avance III spectrometer (600 MHz), using deuterated chloroform or deuterated dimethyl sulfoxide as solvents. All NMR spectra were compared with literature where possible. Gel permeation chromatography (GPC) was performed on a Shimadzu Prominence with chloroform as the solvent at 40 °C and 1 mL/min flow rate. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) was performed using TA Instruments Q20 and Q50 (10°C/min). XPS spectra was obtained using Kratos Analytical AMICUS spectrometer. CW ESR spectra were obtained using Bruker ELEXYS E580 FT-EPR.

Materials. Hexamethylphosphoramide (99%), sodium (99.9%), styrene (>99%), vinylcyclohexane (>99%), ethyl methacrylate (99%), acrylonitrile (>99%), styrene oxide (97%), benzoyl peroxide (70%), methyl acrylate (99%), methyl methacrylate (99%), methyl crotonate (98%), methyl cinnamate (99%), butyl methacrylate (99%), benzyl methacrylate (96%) and phenyl methacrylate (97%) were purchased from Sigma Aldrich.

Experimental. Our experimental set-up was based on Schlenk techniques for preparing solvated electrons coupled with cannula transfer under controlled environment as developed by Whitesides and co-workers[1]. The set-up is schematically shown below (Figure S1). A graduated addition funnel was used to quantify the volume of the solvated electrons added., while the cannula was used to mitigate transfer of any undissolved metals – a key requirement in challenging the Jedlinski's potassium anion where partial dissolution of the metal was required.

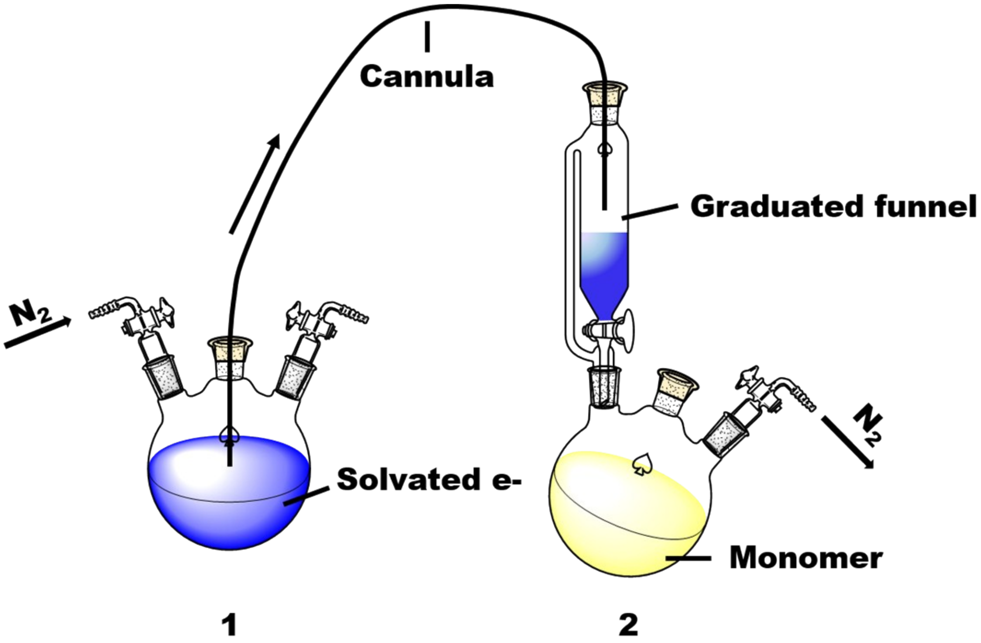

Figure S1: Setup for transferring solvated electrons into monomer. Setup 1 is used to prepare e^-_{sol} while Setup 2 is used for polymer synthesis.

Preparing solvated electrons. A 500 ml three neck flask was flame dried and partially filled with molecular sieves. Two exits were closed using rubber septum while the remaining exit was attached to a glass valve connected to a Schlenk line. With the valve open, the flask was heated above 300°C (measured using infrared thermometer) with a propane burner. Vacuum was then applied while the flask was constantly heated for *ca* 30 minutes to activate the molecular sieves. After cooling to ambient temperature, the flask was back-filled with ultra-high purity (UHP) N_2 and then charged with hexamethylphosphoramide (HMPA) through the rubber septum using a syringe. After equilibration for at least 20 hours, the HMPA was ready to use. A 50 ml three neck flask containing a magnetic stir bar (Figure S1) was flame dried under a stream of UHP N_2. 0.02g of Na was thoroughly rinsed with hexanes then quickly introduced into the flask while maintaining an inert atmosphere through positive N_2 pressure. The flask was then charged with 20 ml anhydrous HMPA and the mixture was stirred under an inert atmosphere. To prevent adventitious contaminants from the N_2 stream, flow was stopped as soon as a blue hue formed on the metal surface (*ca.* 15-20 seconds after introduction of the solvent).

Preparing monomer. Monomer stabilizers were removed by adsorption onto a column of Celite as previously reported.[2] A second setup containing a three neck round bottom flask, a graduated addition funnel, a stirrer, a rubber septum and a ground-glass gas valve (Setup 2, Figure S1) was assembled and flame dried under an inert atmosphere. The round bottom flask was then charged with 2 ml of anhydrous HMPA followed by 2 ml of monomer and degassed.

Synthesis. The transfer of solvated electrons into the graduated funnel was setup as shown in Figure S1. The flask containing the blue solution was pressurized with N_2, then cannula was introduced but not immersed into the solvated electrons, allowing flow through the cannula for *ca.* 0.5 minutes. The other end of the cannula was then inserted into the rubber septum on the graduated funnel. The exit valve was then momentarily opened to relieve internal pressure and the cannula was then immersed into solvated electrons, allowing transfer into the graduated funnel. After desired amount is transferred, the cannula was then removed from the solution to stop flow, followed by disconnection from the setup. Amount of initiator used was calculated considering a 1:1 stoichiometric relation to Na although surface oxidation is expected during the transfer process. The reactants were then quenched in methanol with concomitant precipitation of the polymer.

Kinetics experiment. An aliquot was withdrawn from the polymerizing reaction periodically. The extracted solution was immediately diluted with Chloroform-D at ambient conditions followed by NMR analysis. Conversion was calculated by comparing integrals between characteristic monomer and polymer peaks.

Sequential addition. 1 ml of styrene was polymerized in solvated electrons (6 ml) by direct injection (monomer-initiator ratio = 20). After 8 minutes, 1 ml of methyl acrylate was introduced, turning the solution from red to light yellow in color. After 25 minutes, another 1 ml of methyl acrylate was charged into the solution. The reactants were then quenched in methanol after 1 hour.

Calculating $k_{p.}$ Assuming an addition polymerization and all of the solvated electrons introduced into styrene initiates polymerization, we can estimate the rate of change of monomer concentration as;[3]

$$\frac{dM}{dt} = k_p[M][I]$$

Whereby [4] is the monomer concentration, *t* is time, [*I*] is initiator concentration and k_p.

Calculating Δδ. The difference in Hansen solubility parameters or the solubility parameter distance (Ra) is given by,[5]

$$\Delta\delta = \sqrt{4(d_{D1} - d_{D2})^2 + (d_{P1} - d_{P2})^2 + (d_{H1} - d_{H2})^2}$$

$d_{D,}$ $d_{P,}$ and d_H are the dispersion, polar and hydrogen bond components of the Hansen solubility parameter.

Characterization of Polystyrene (PS):

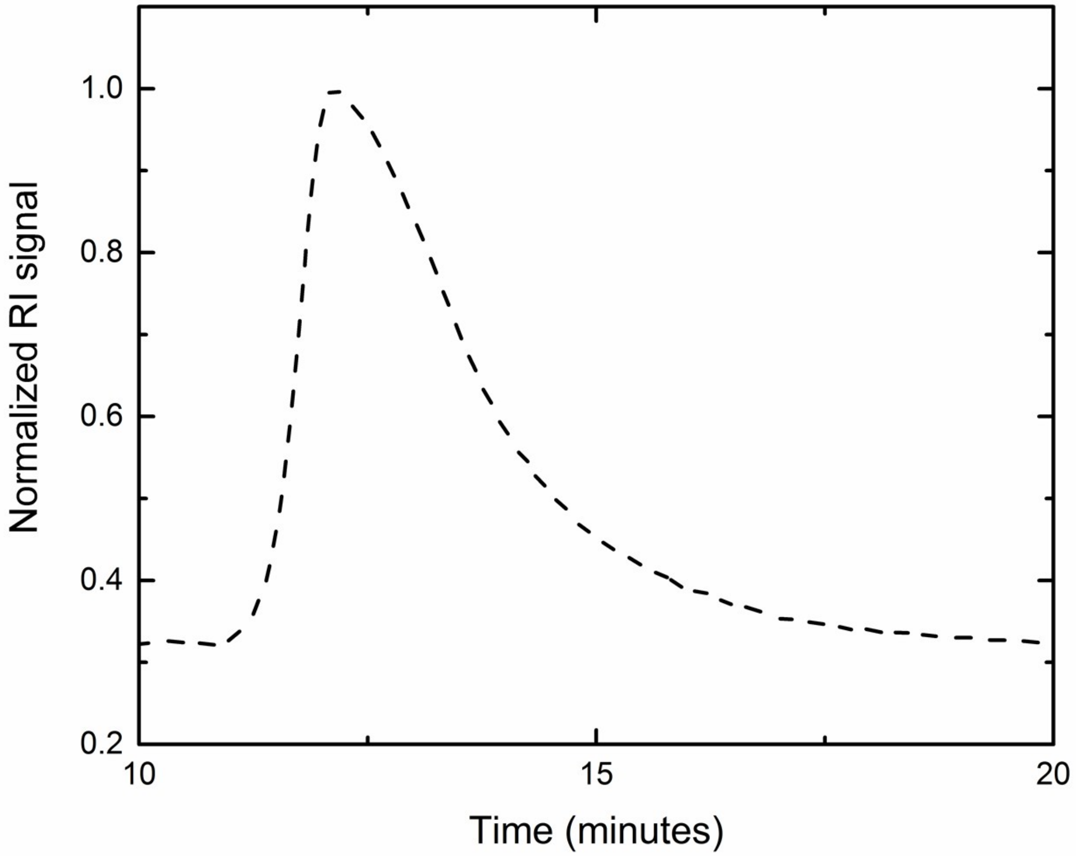

Figure S2: Gel permeation chromatogram of polystyrene synthesized by direct injection of monomer into solvated electrons at different reaction times. M_n = 191,000 g/mol, M_w = 449,000 g/mol, PDI: 2.3.

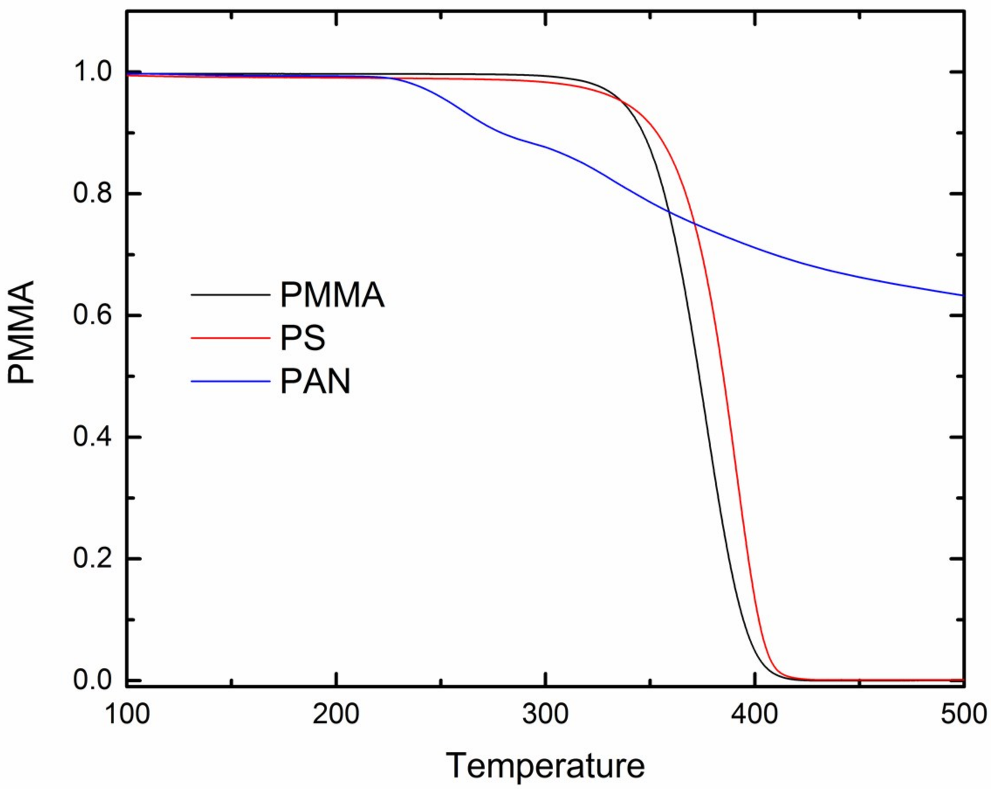

Figure S3: Thermogravimetric analysis (TGA) of PS, PMMA and PAN.

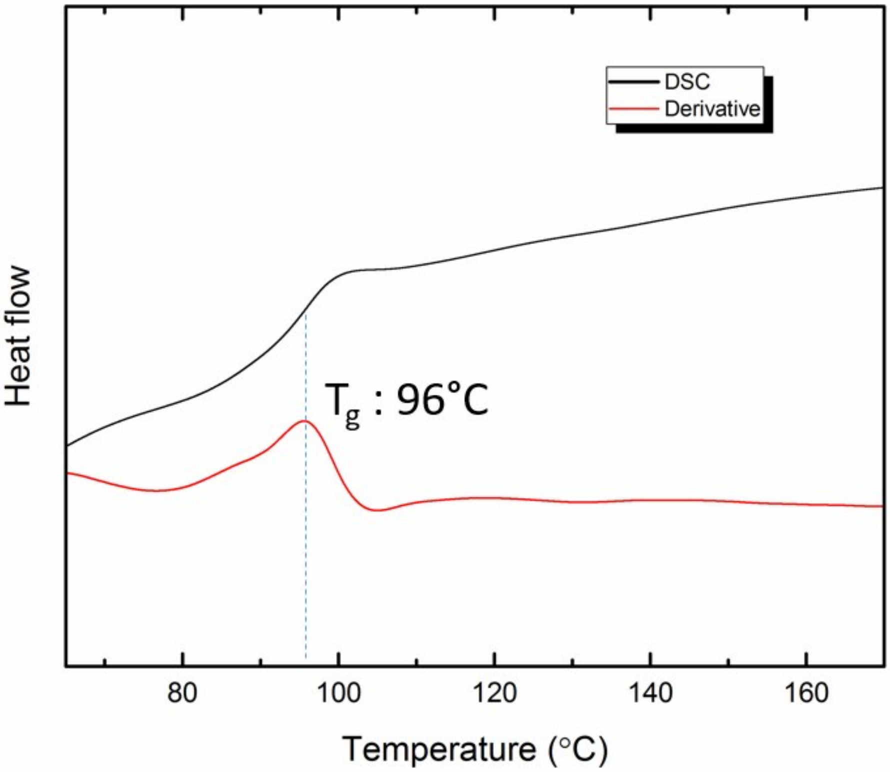

Figure S4: DSC of 56:1 polystyrene

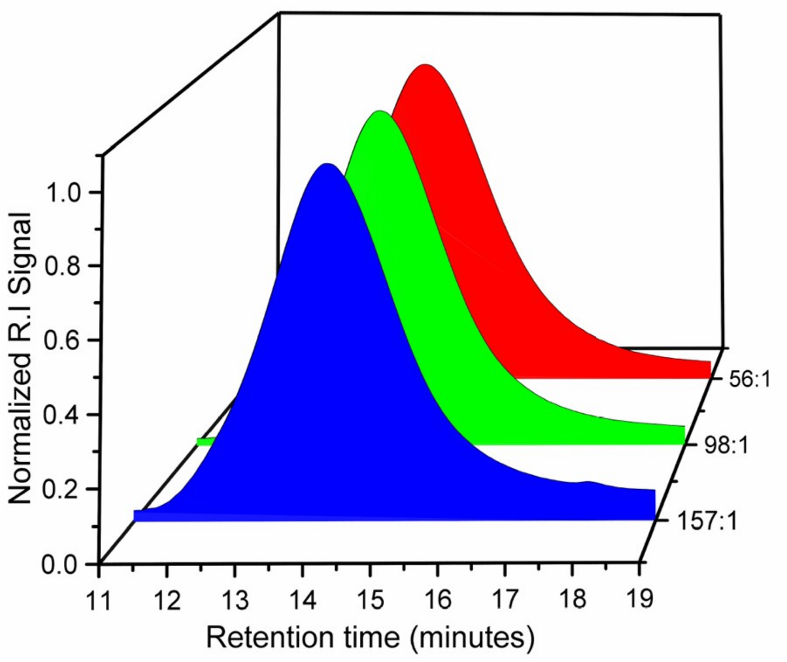

Figure S5: GPC traces of polystyrene synthesized at varying monomer: initiator ratio.

Thermogravimetric analysis (TGA) of the obtained polystyrene showed a degradation peak centered at 391°C. The glass transition temperatures, $T_{g,}$ of the resulting polystyrene were 96 °C, 106 °C, and 102 °C in the order of decreasing initiator concentration. From the Flory-Fox equation, the glass transition temperature of a polymer increases with molecular weight and approaches an asymptote at $T_{g,\infty}$. The observed T_g for the highest monomer molar ratio, deviates from the Flory-Fox equation[6], in part due to the presence of a low molecular weight adduct as seen in the GPC trace (kink at ~18 minutes retention time), that corresponded to a Mw ≈ 12,000 g/mol.

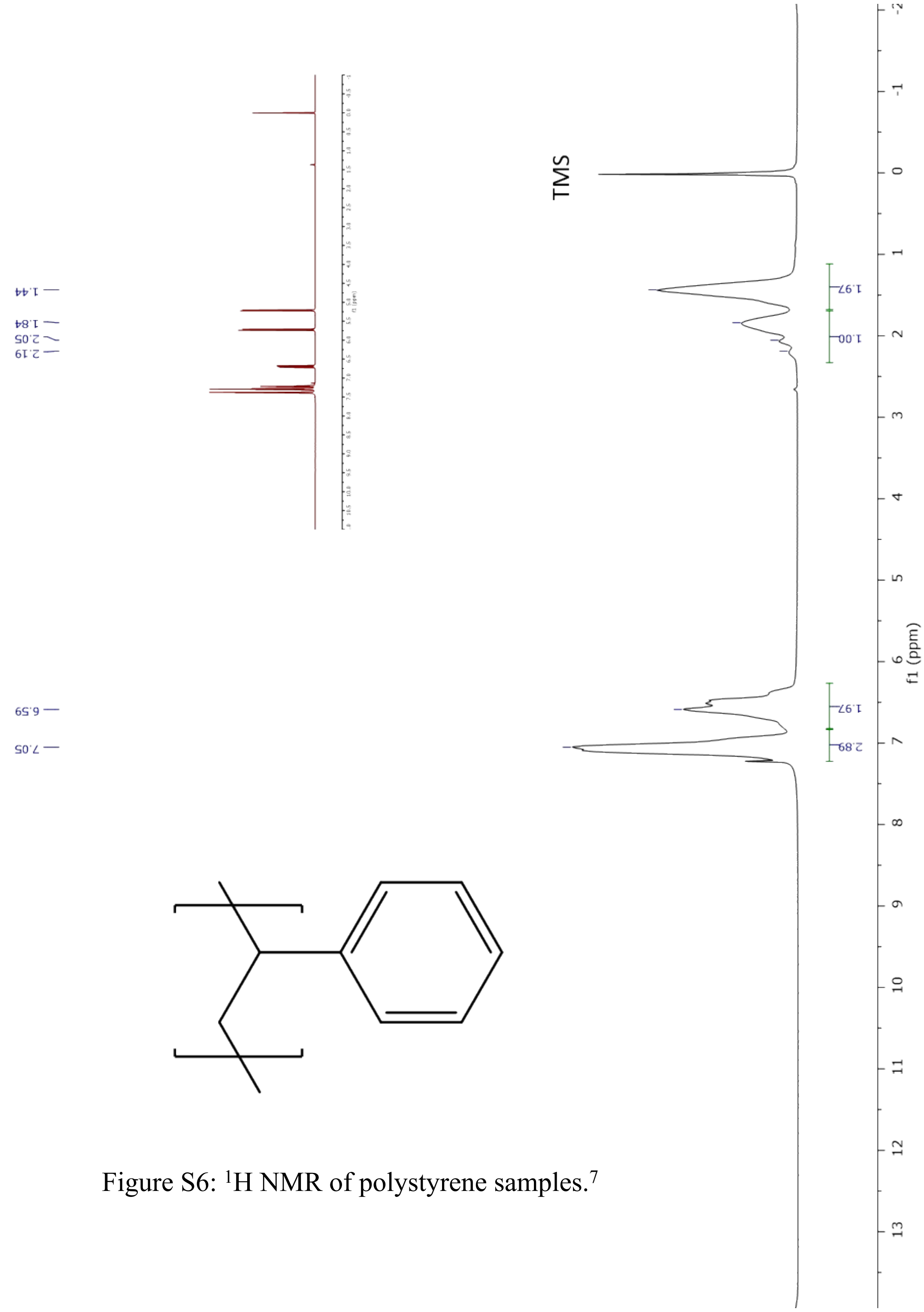

Figure S6: ^{1}H NMR of polystyrene samples.[7]

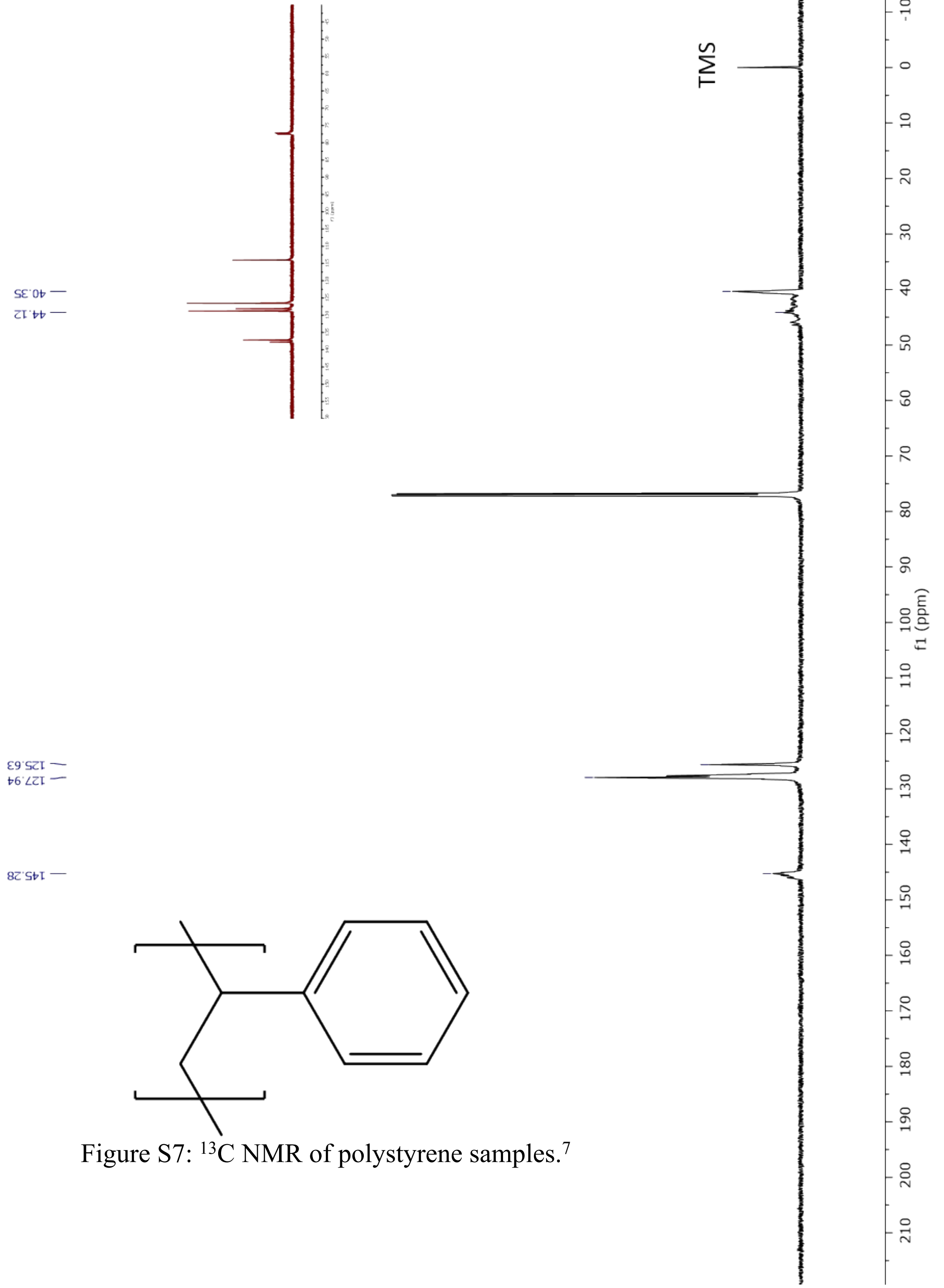

Figure S7: ^{13}C NMR of polystyrene samples.[7]

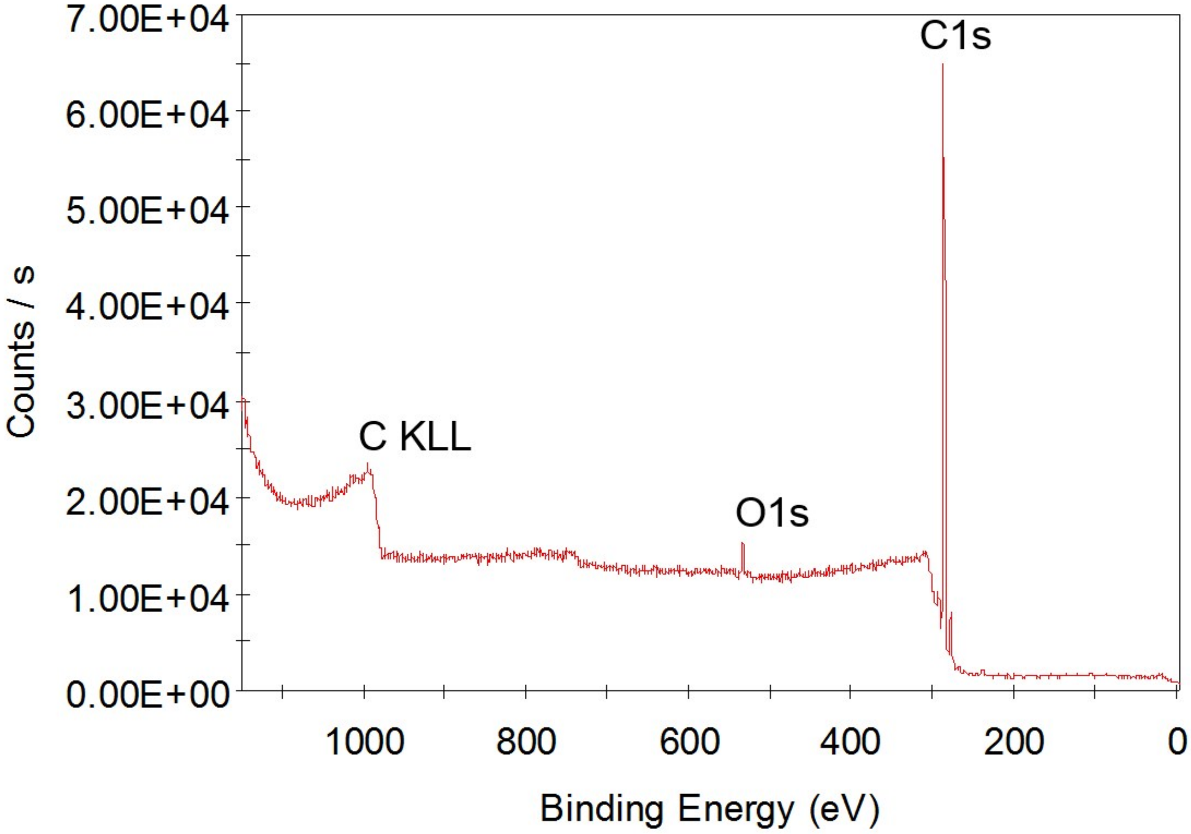

Figure S8: X-ray photoelectron spectrum of polystyrene.

Poly(methyl methacrylate) (PMMA):

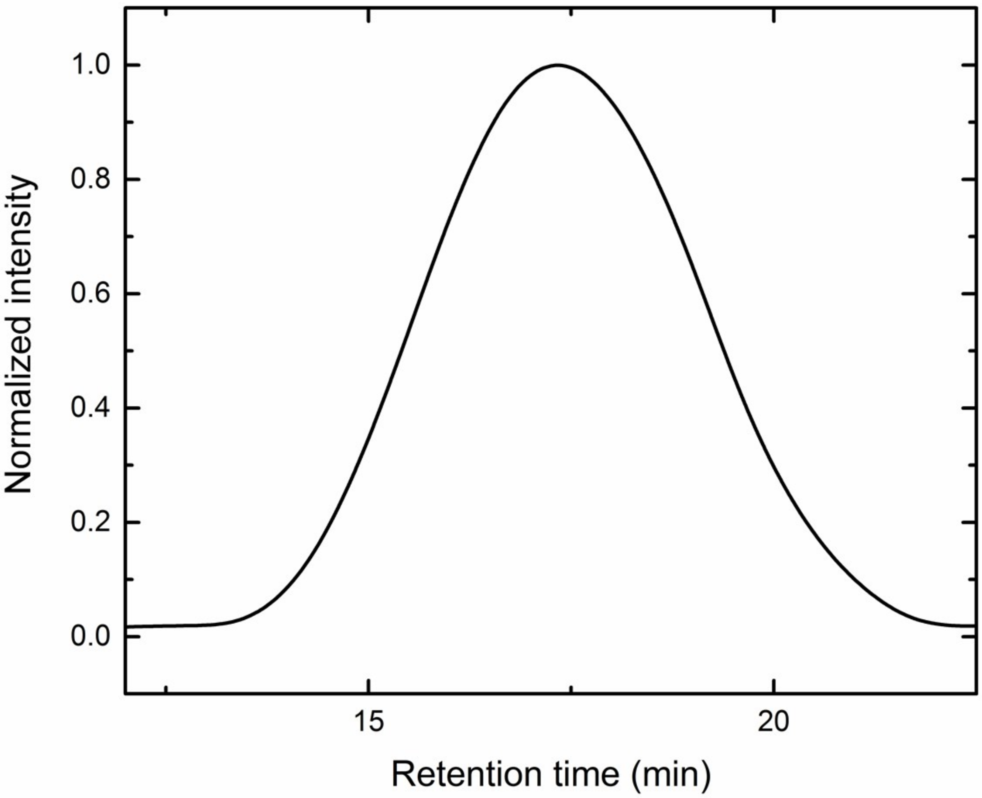

Figure S9: GPC of poly(methyl methacrylate).

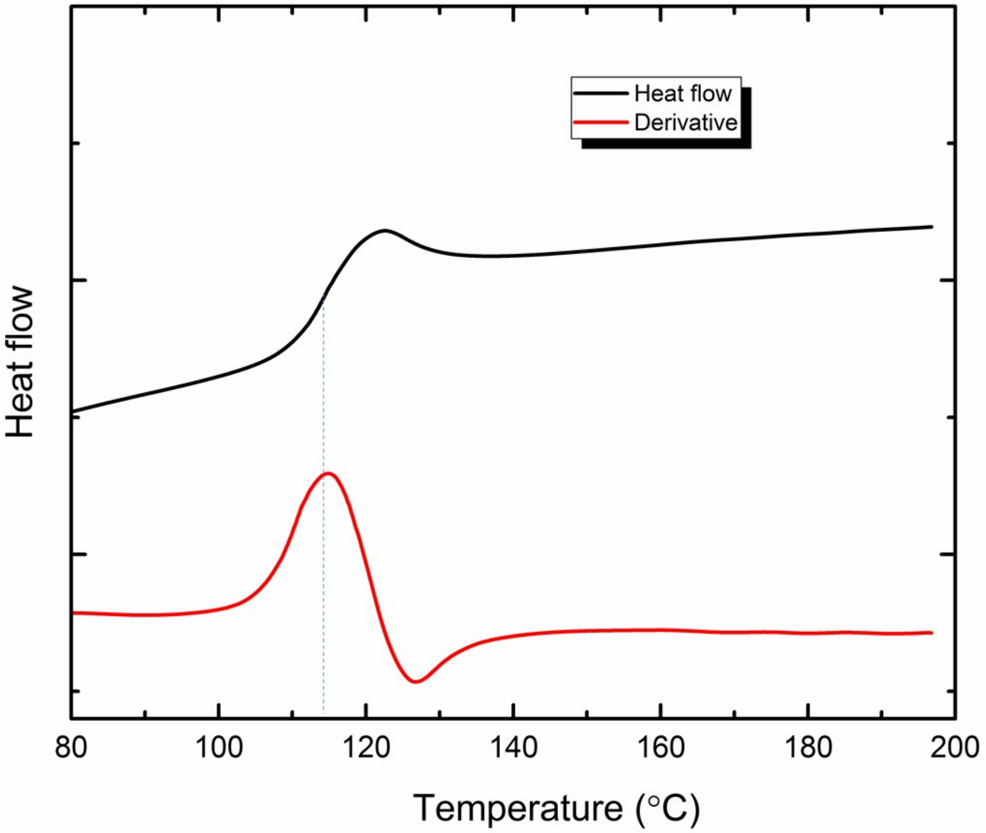

Figure S10: DSC of poly(methyl methacrylate).

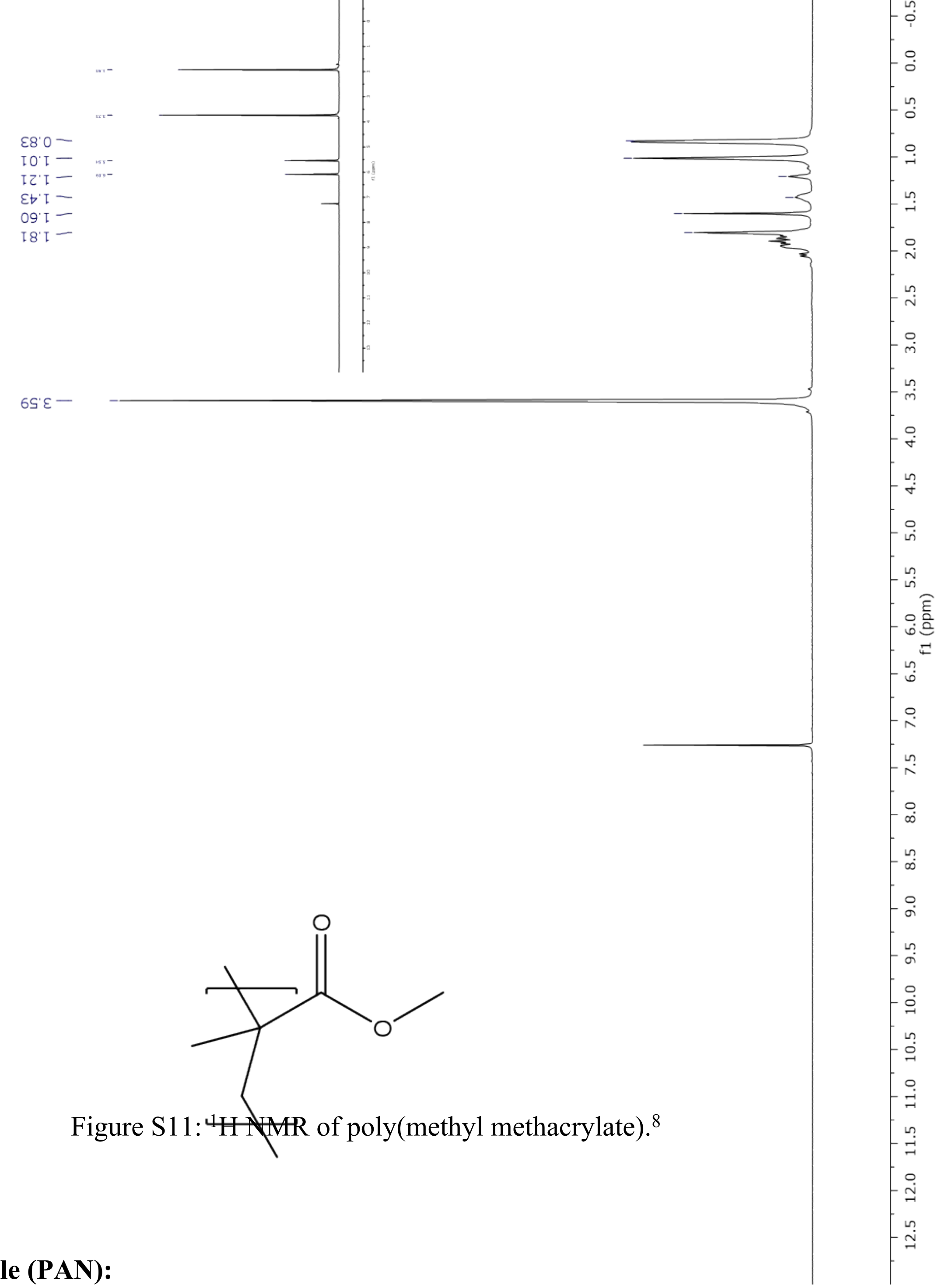

Figure S11: ^{1}H NMR of poly(methyl methacrylate).[8]

Polyacrylonitrile (PAN):

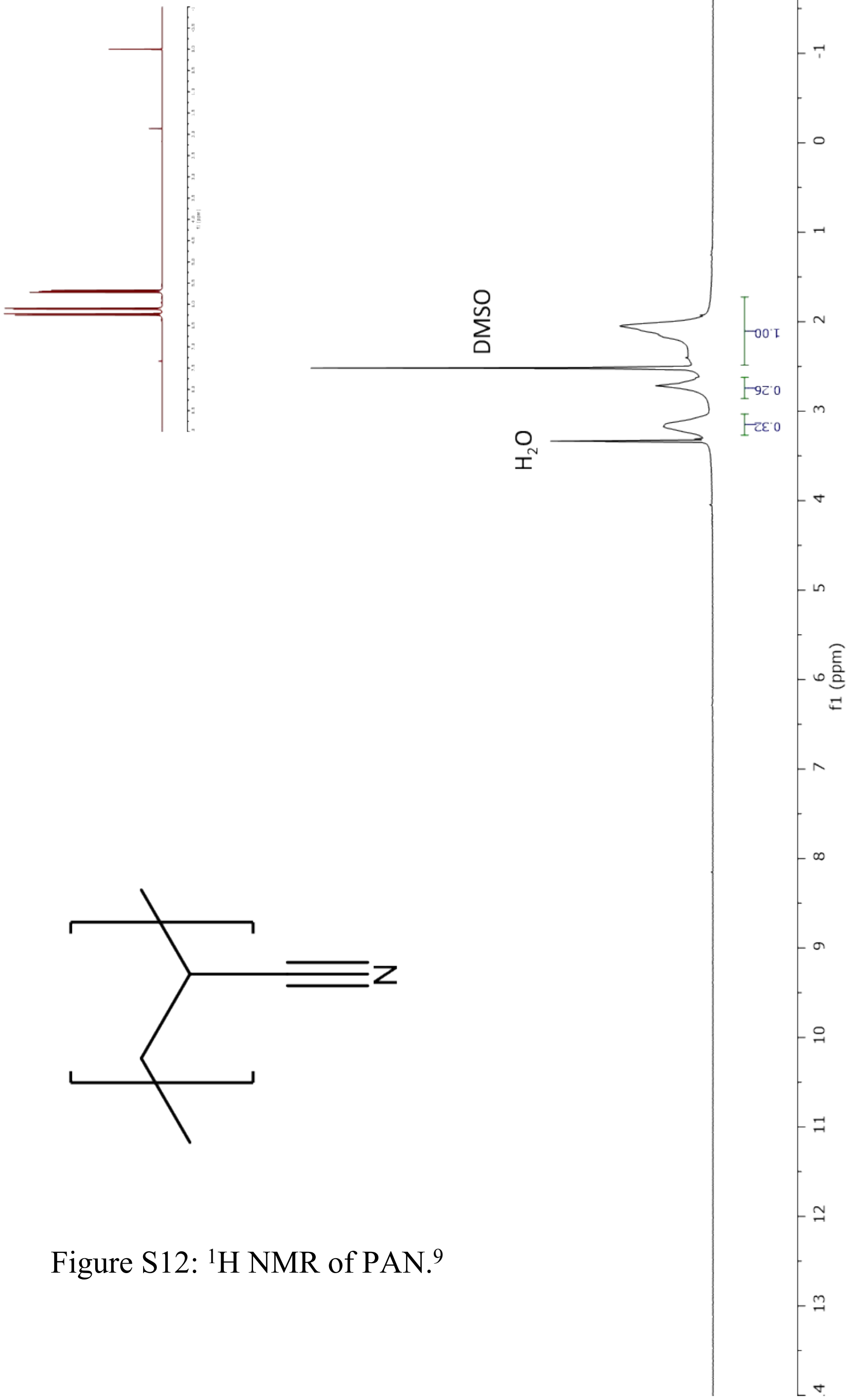

Figure S12: ^{1}H NMR of PAN.[9]

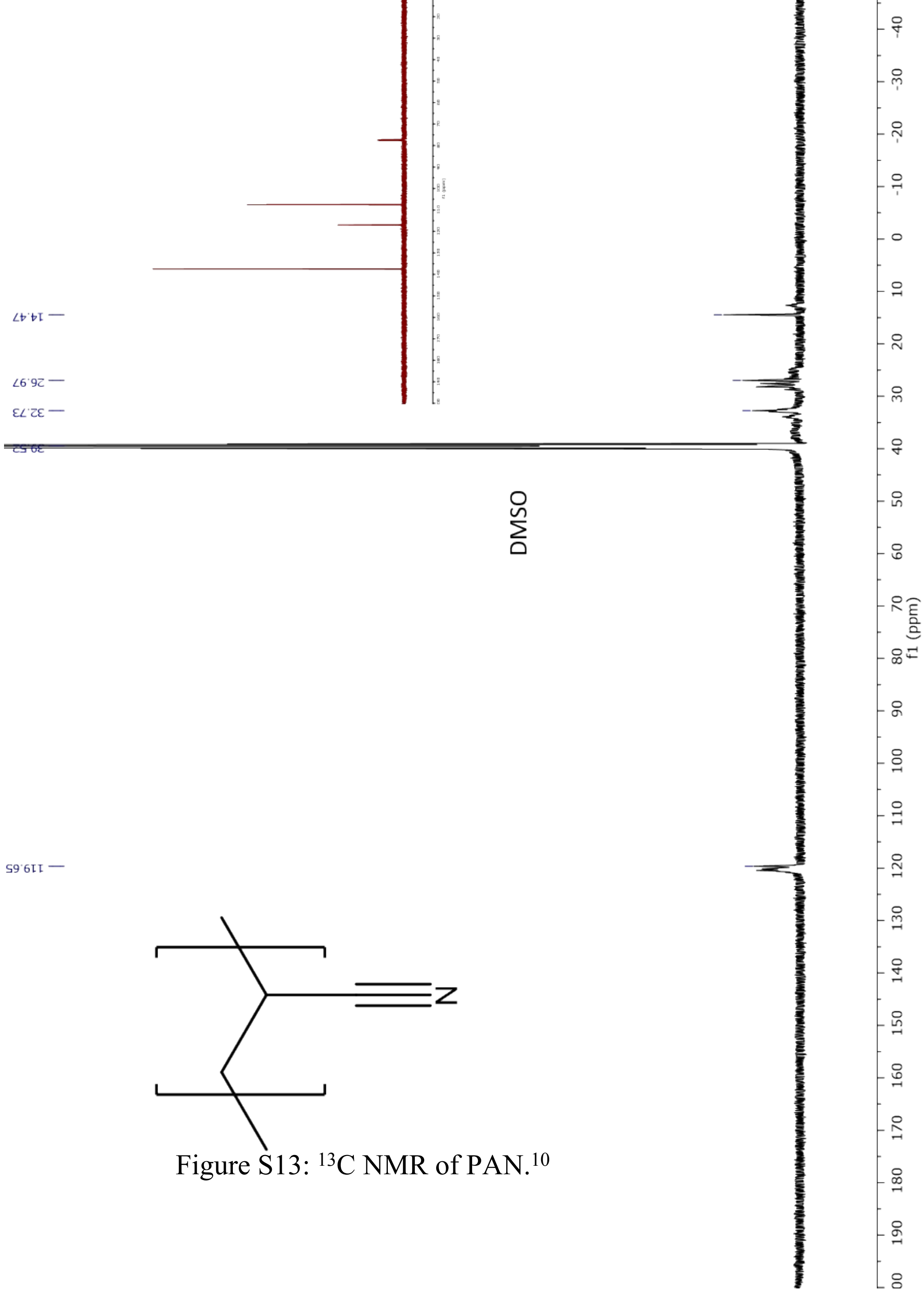

Figure S13: ^{13}C NMR of PAN.[10]

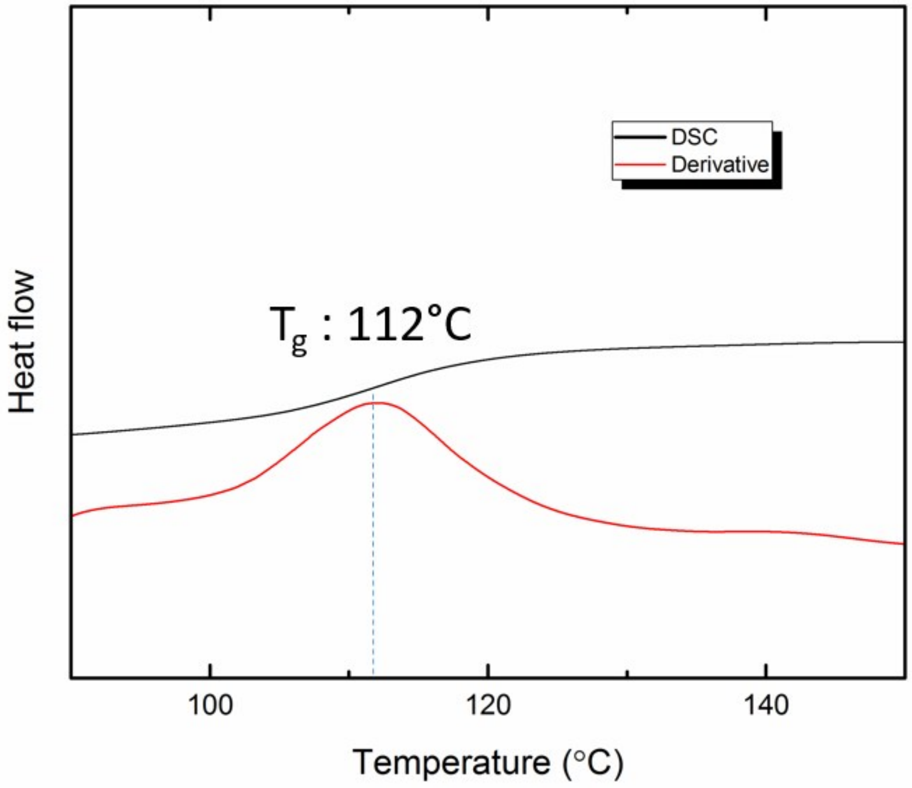

Figure S14: DSC of PAN.

PS-b-PMMA

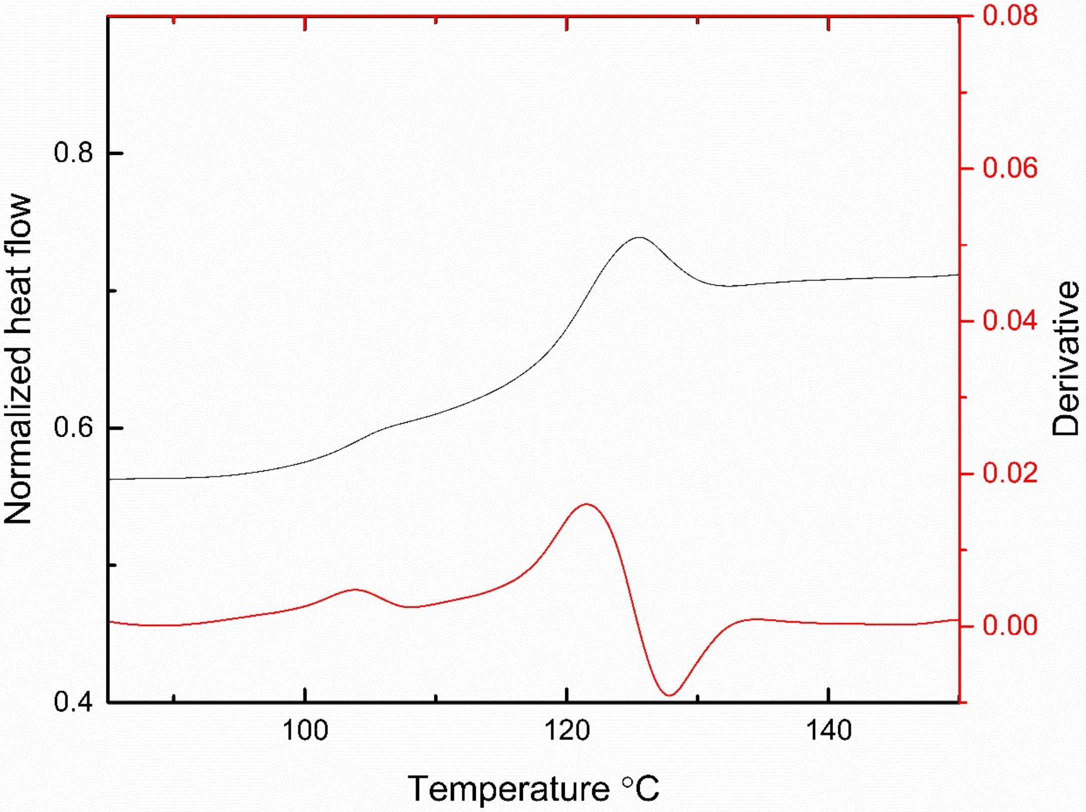

Figure S15: DSC of PS-b-PMMA.

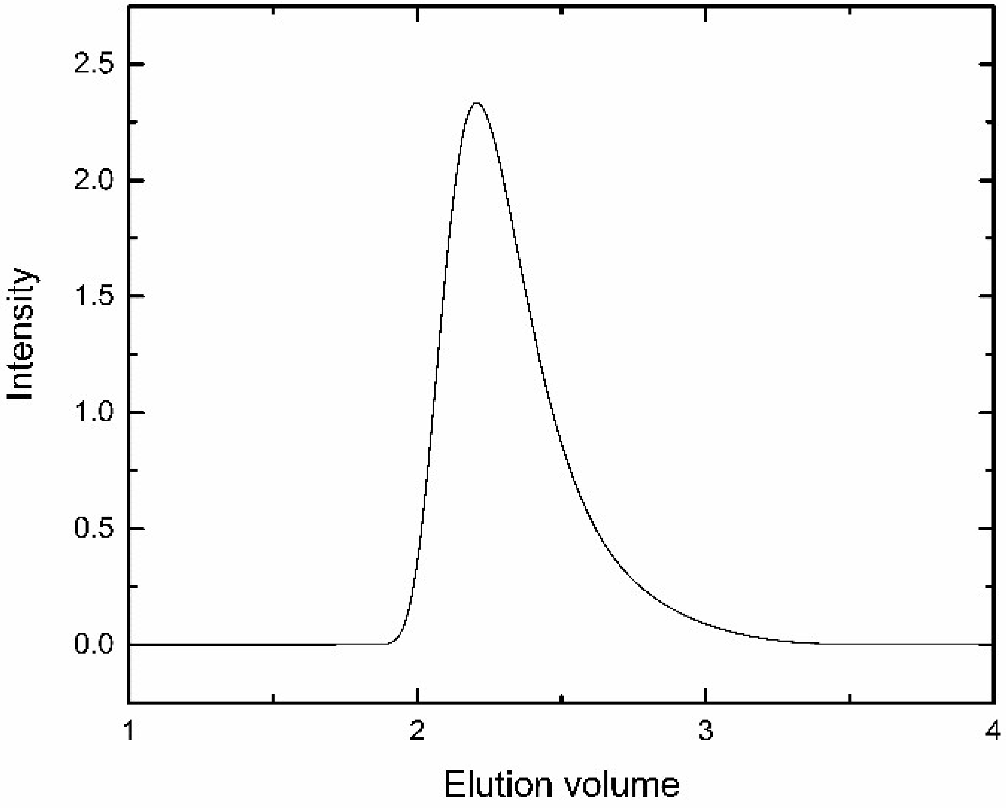

Figure S16: GPC of PS-b-PMMA. (Mw = 121,000 g/mol, PDI = 1.5)

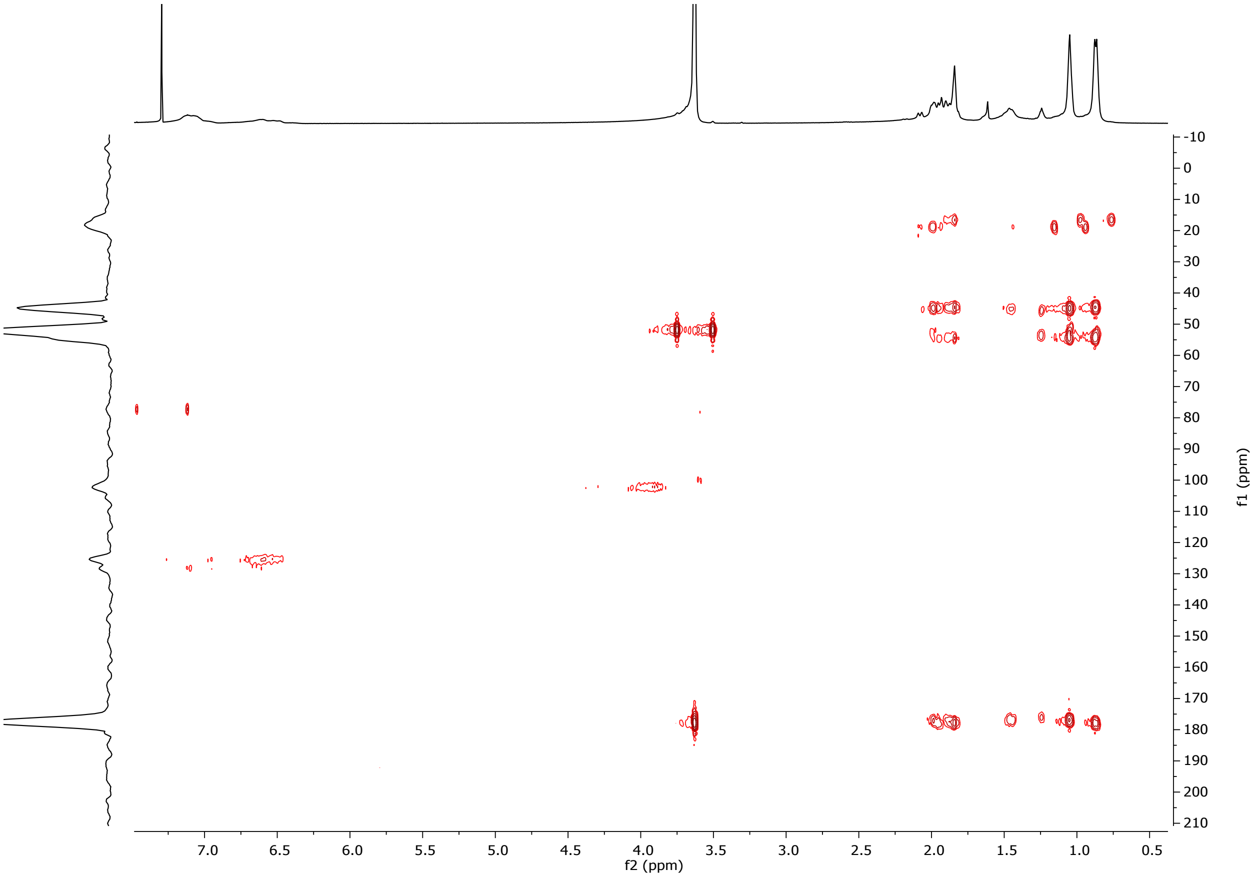

Figure S17: Heteronuclear Multi Bond Correlation (HMBC) NMR of PS-b-PMMA.

Characterization of polyacrylates

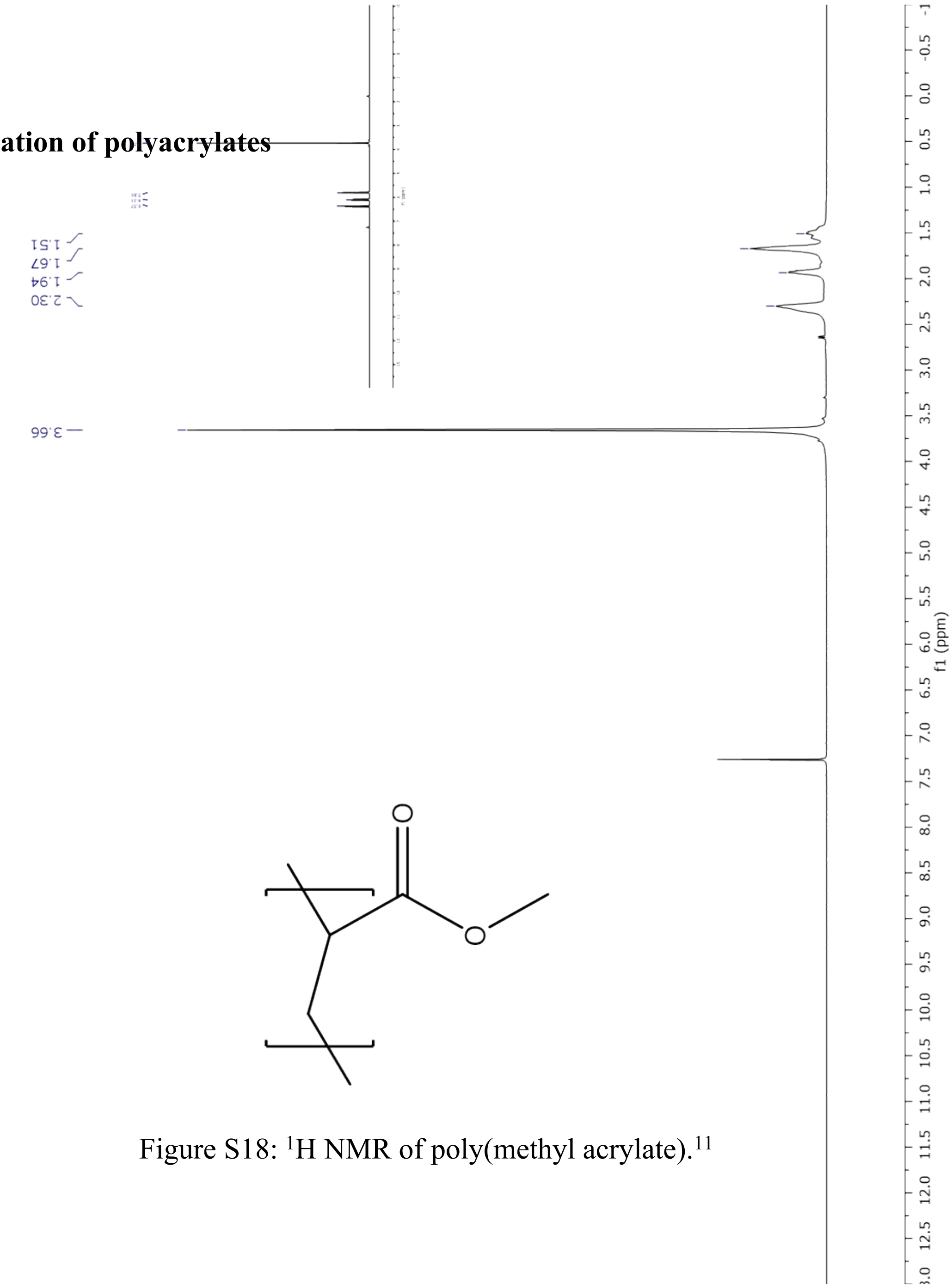

Figure S18: ^{1}H NMR of poly(methyl acrylate).[11]

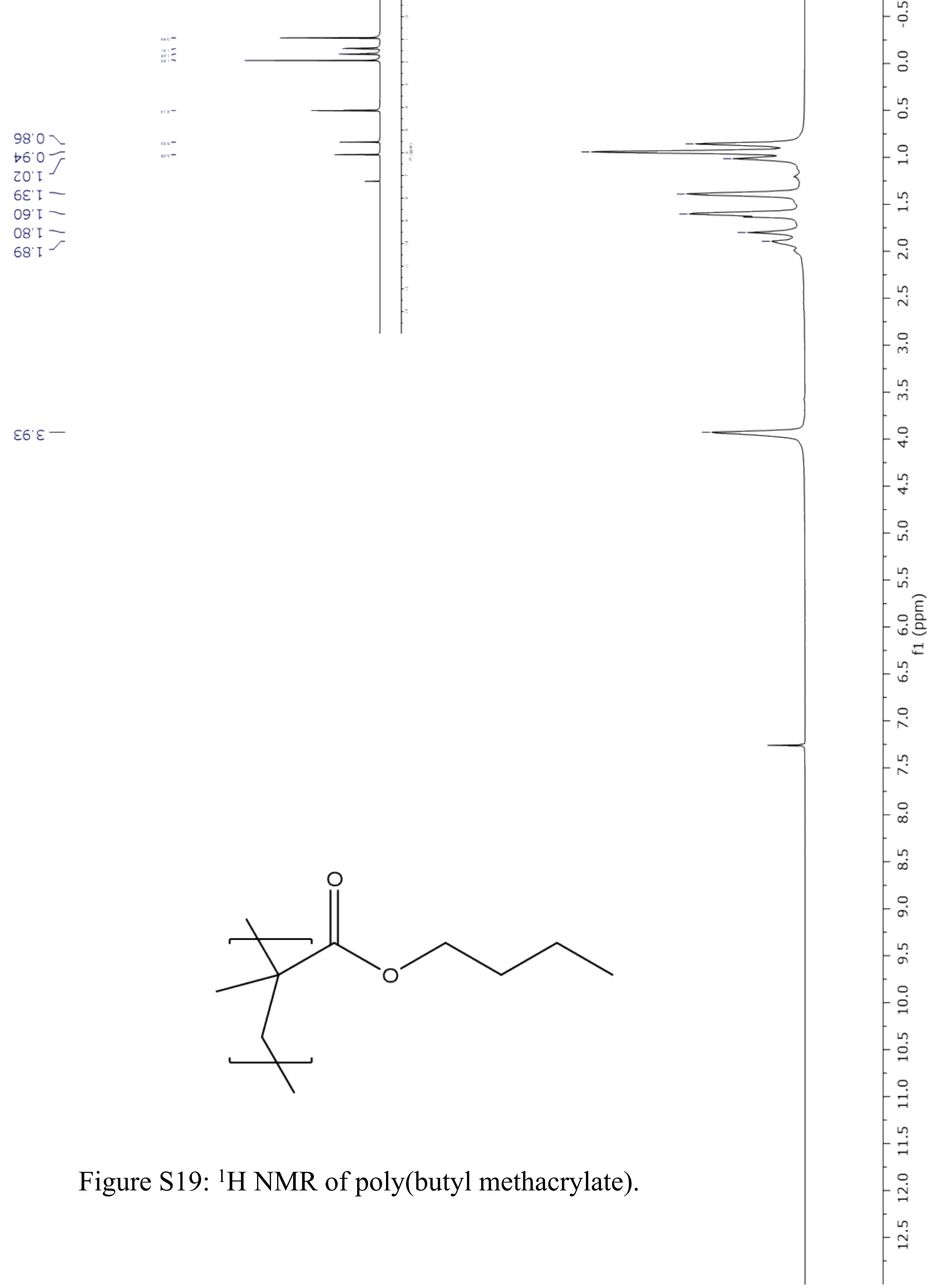

Figure S19: ^{1}H NMR of poly(butyl methacrylate).

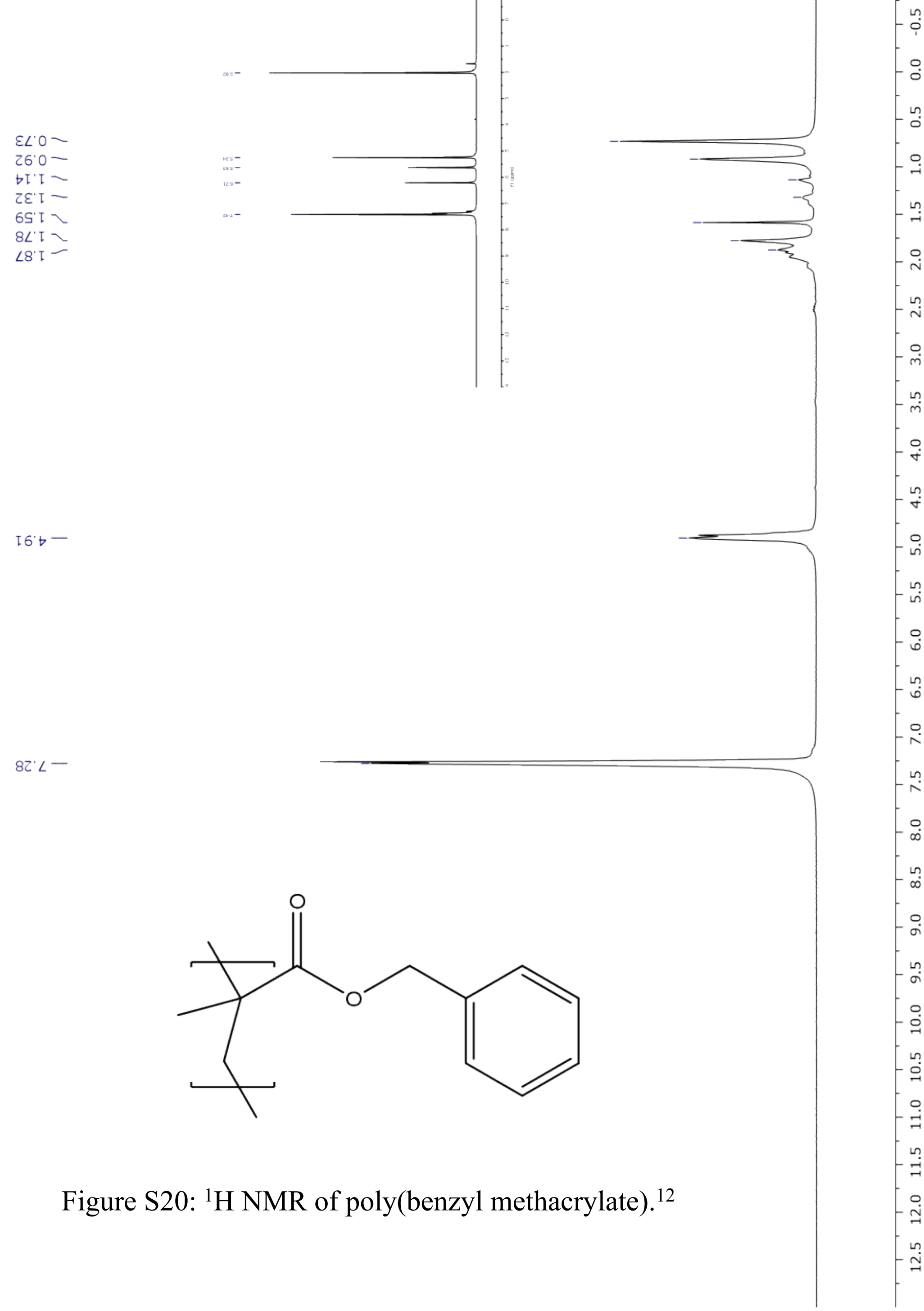

Figure S20: ^{1}H NMR of poly(benzyl methacrylate).[12]

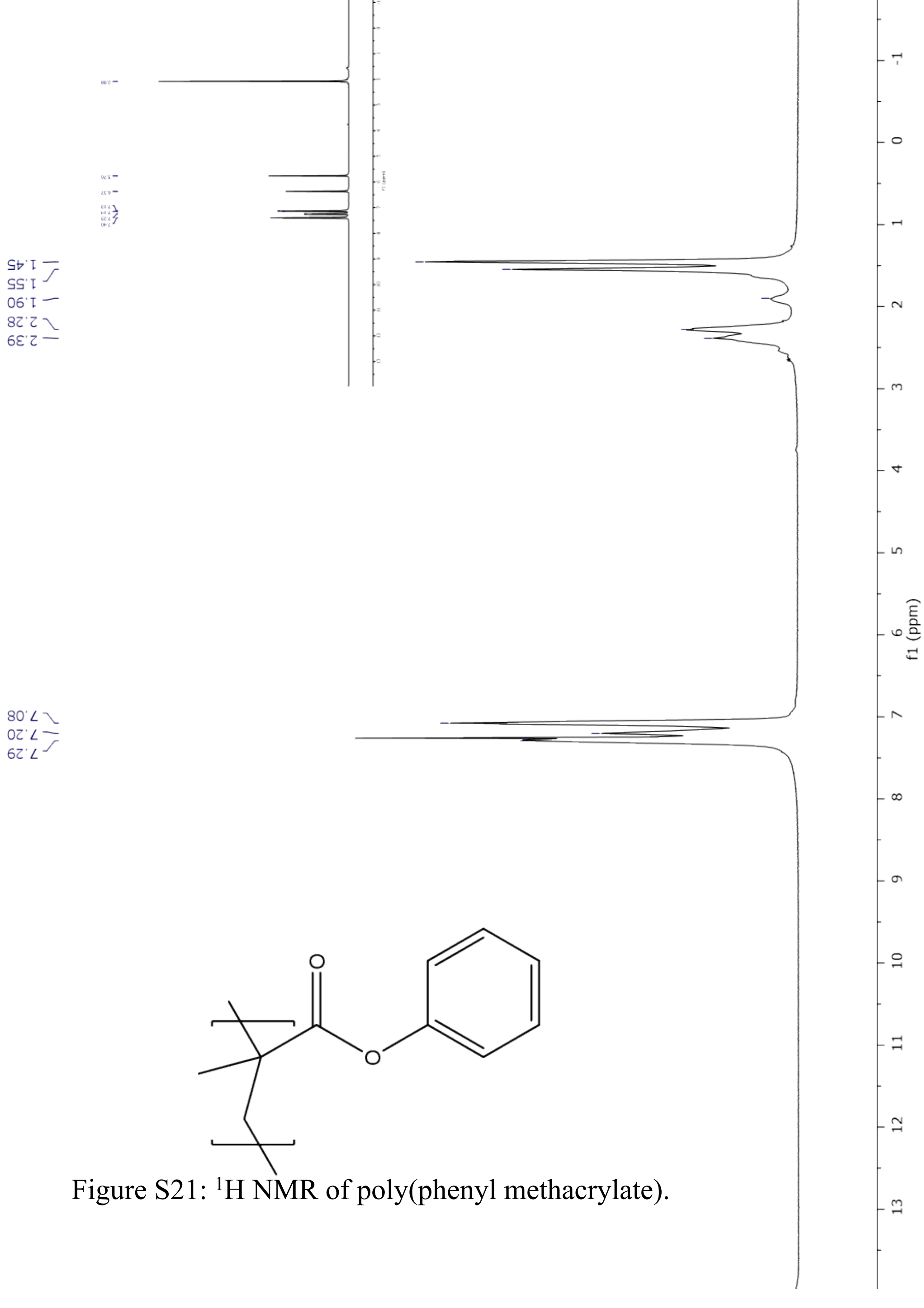

Figure S21: ^{1}H NMR of poly(phenyl methacrylate).

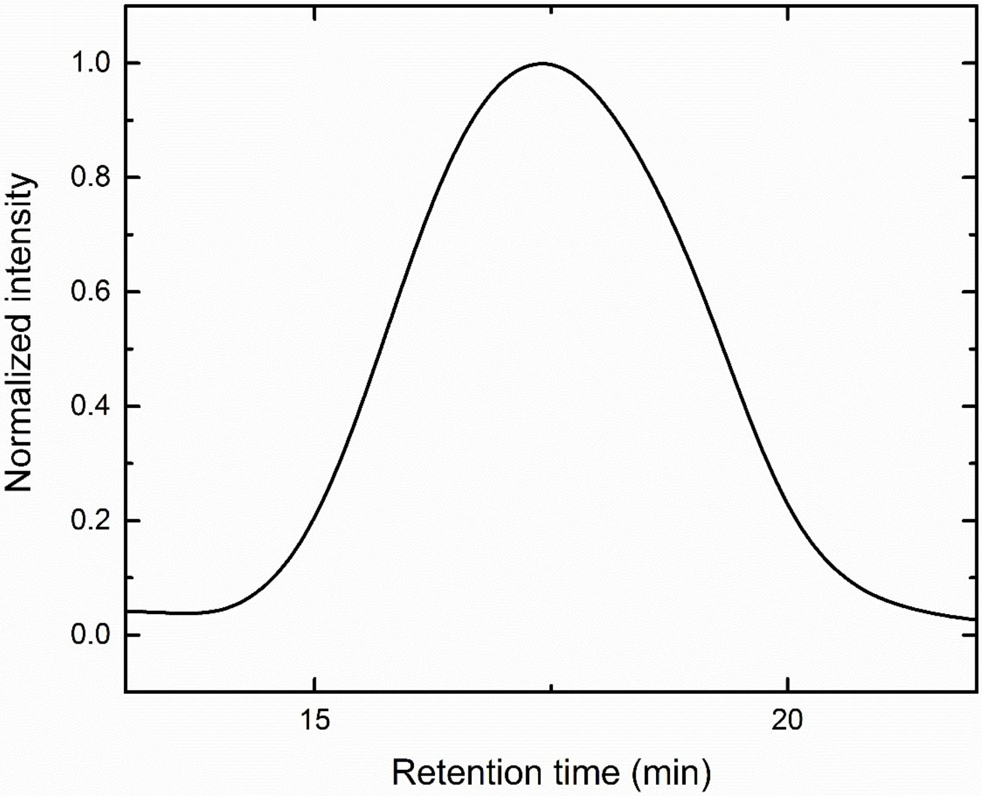

Figure S22: GPC of poly(methyl acrylate).

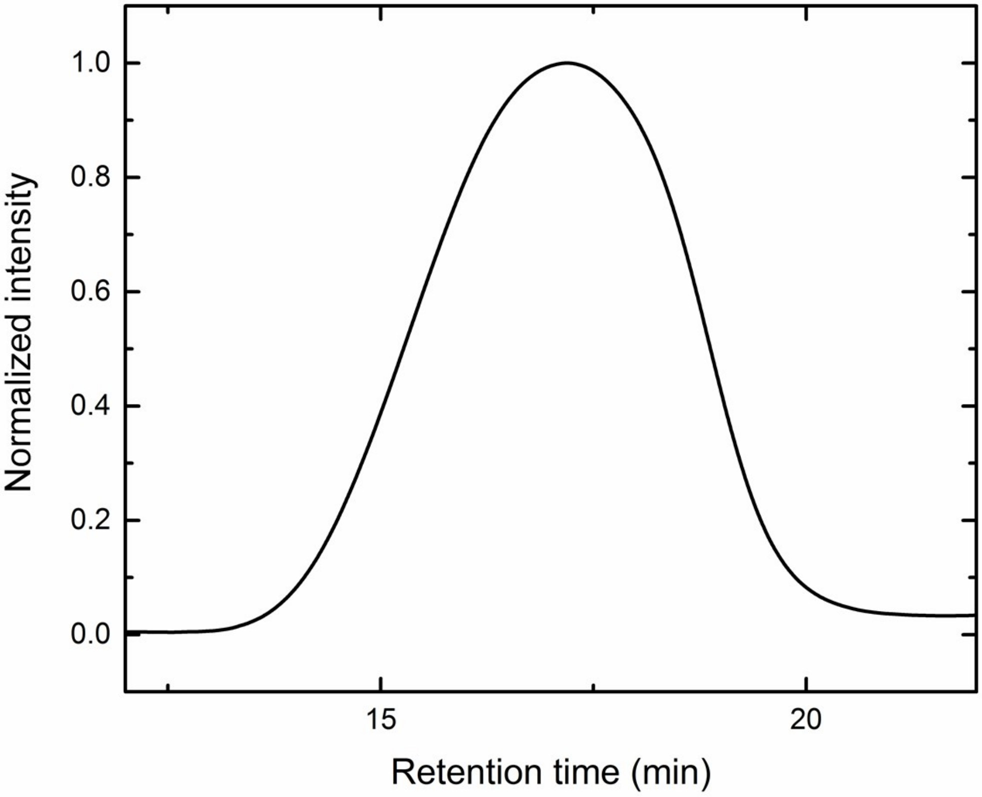

Figure S23: GPC of poly(butyl methacrylate).

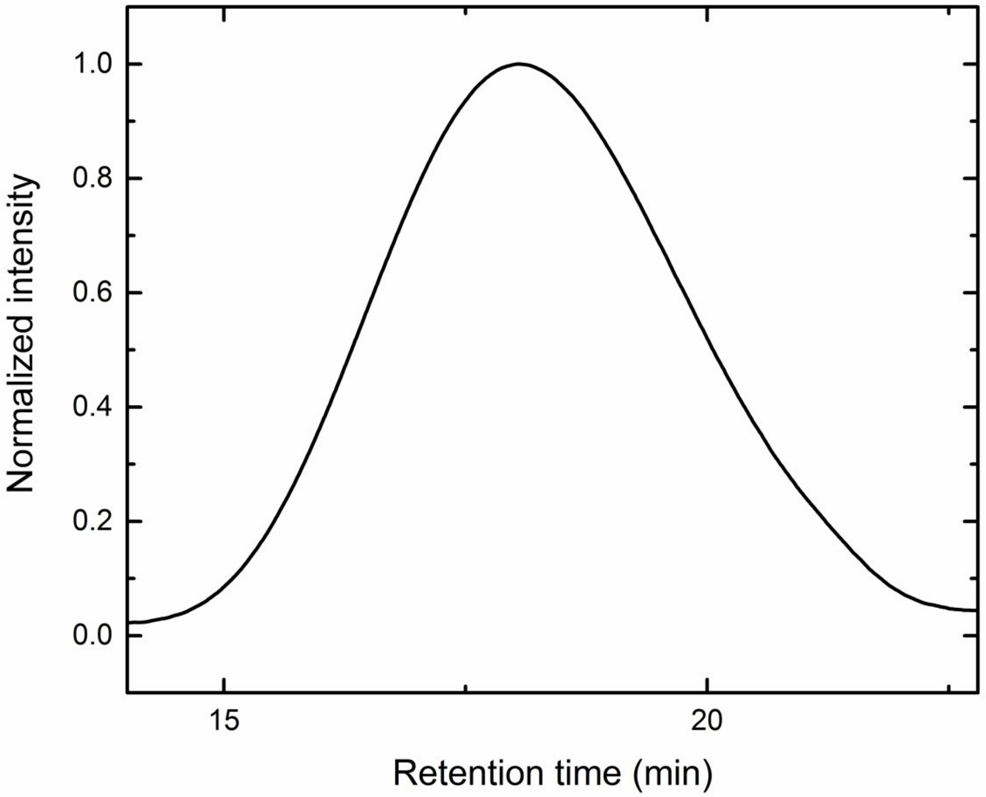

Figure S24: GPC of poly(benzyl methacrylate).

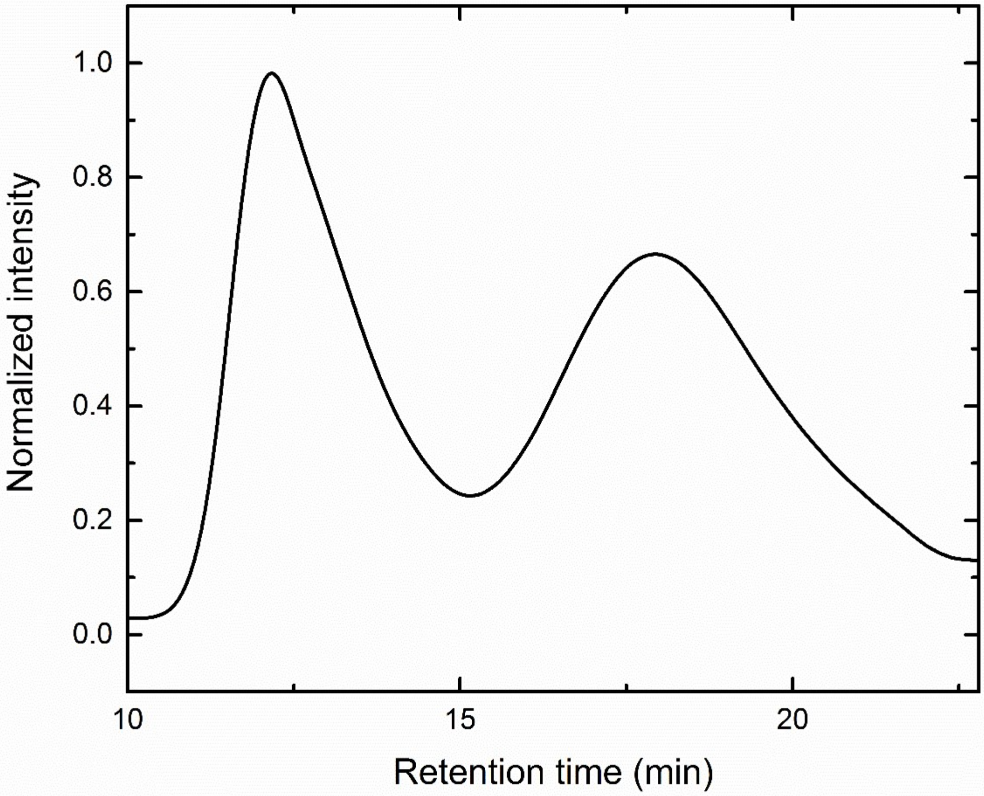

Figure S25: GPC of poly(phenyl methacrylate).

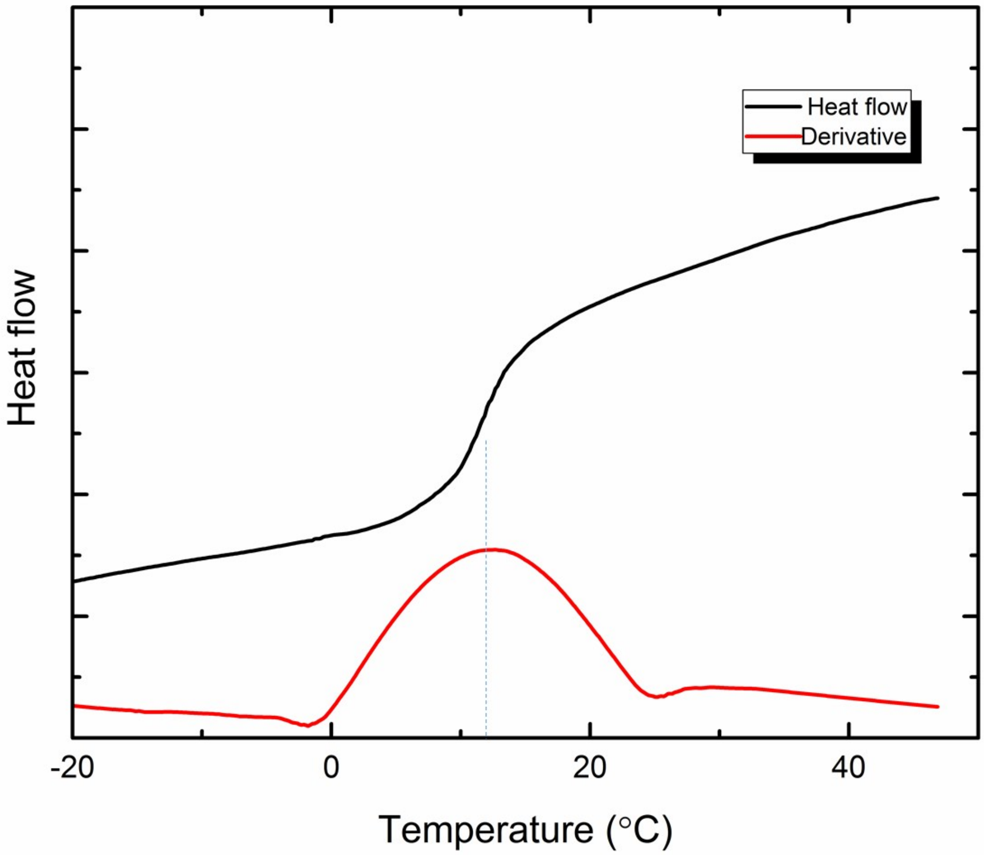

Figure S26: DSC of poly(methyl acrylate).

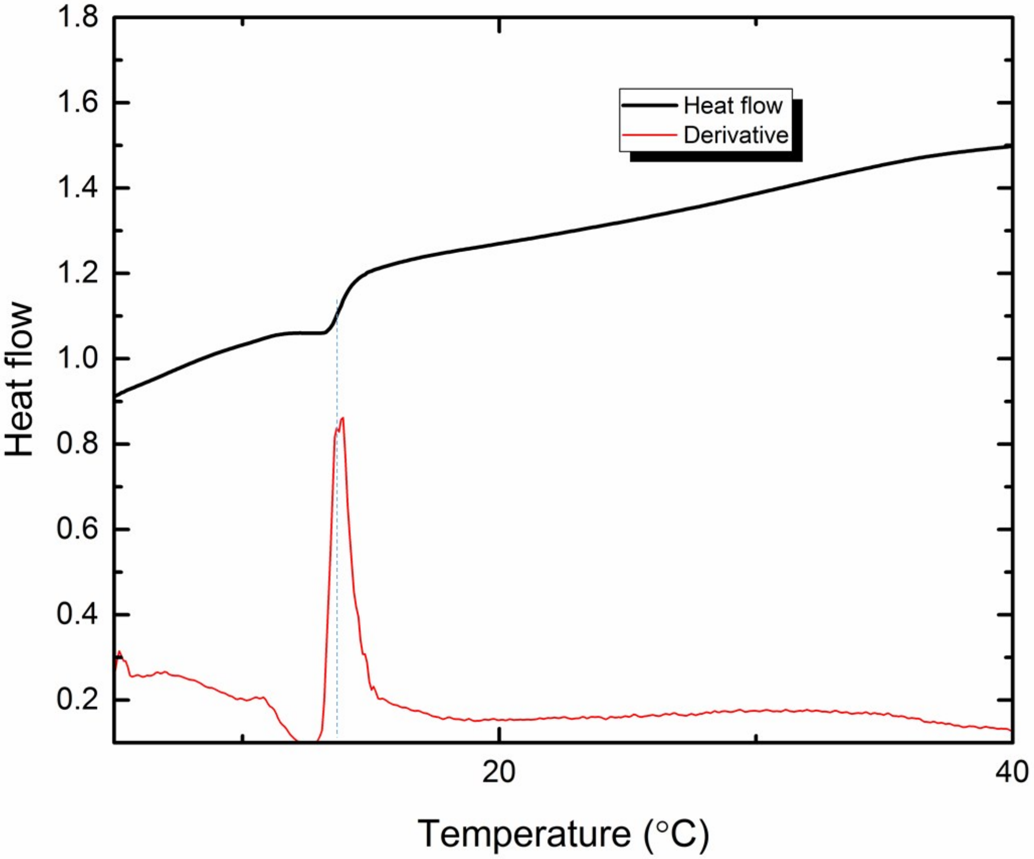

Figure S27: DSC of poly(butyl methacrylate).

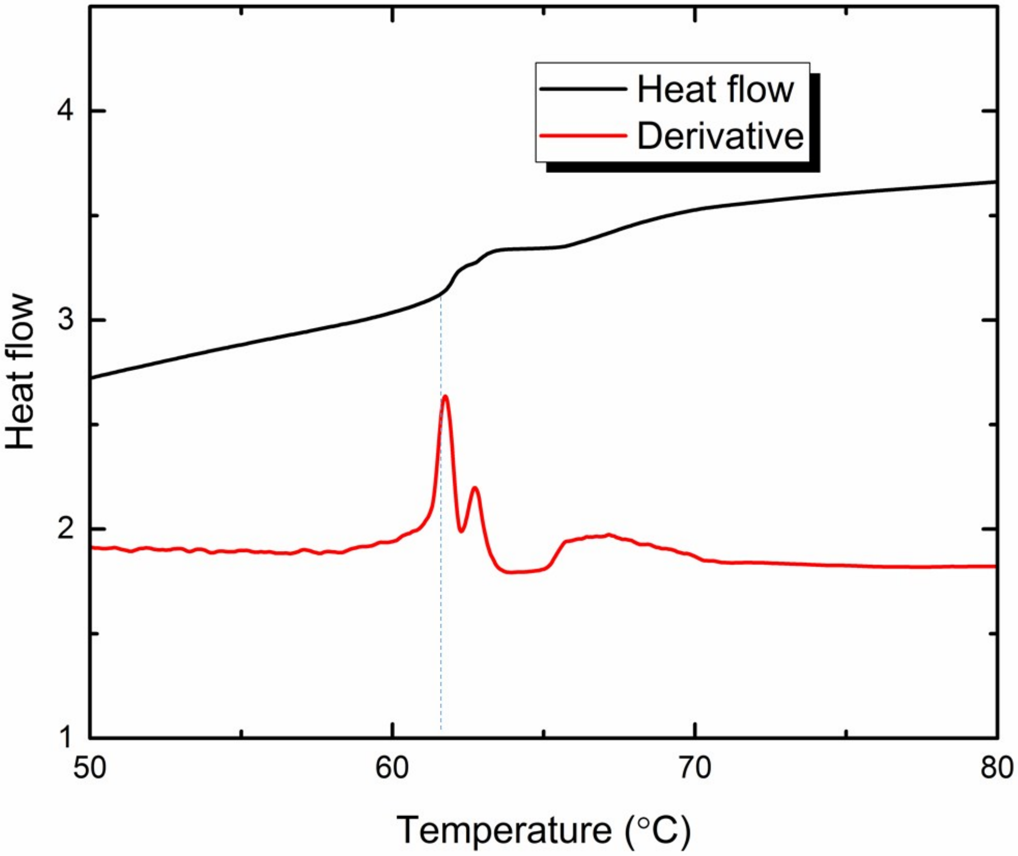

Figure S28: DSC of poly(benzyl methacrylate).

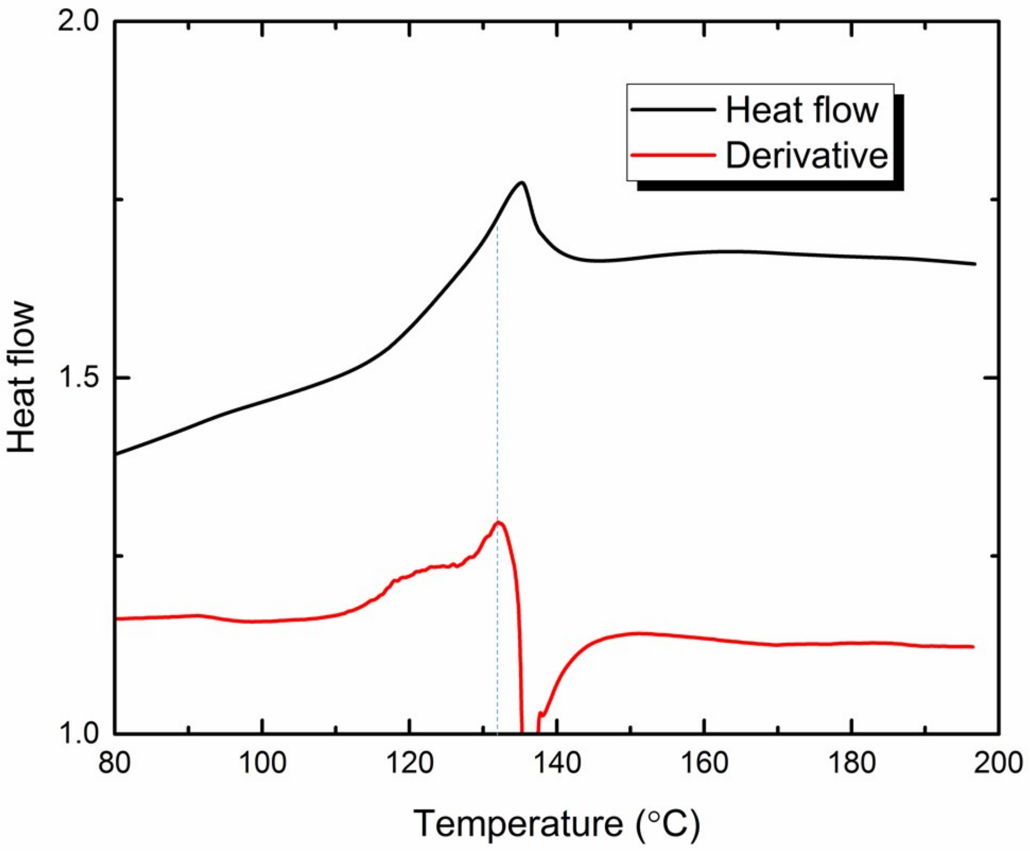

Figure S29: DSC of poly(phenyl methacrylate).

Styrene-methyl acrylate copolymer

Styrene and methyl acrylate were copolymerized by sequential addition, showing the polymerization is ‘living’.

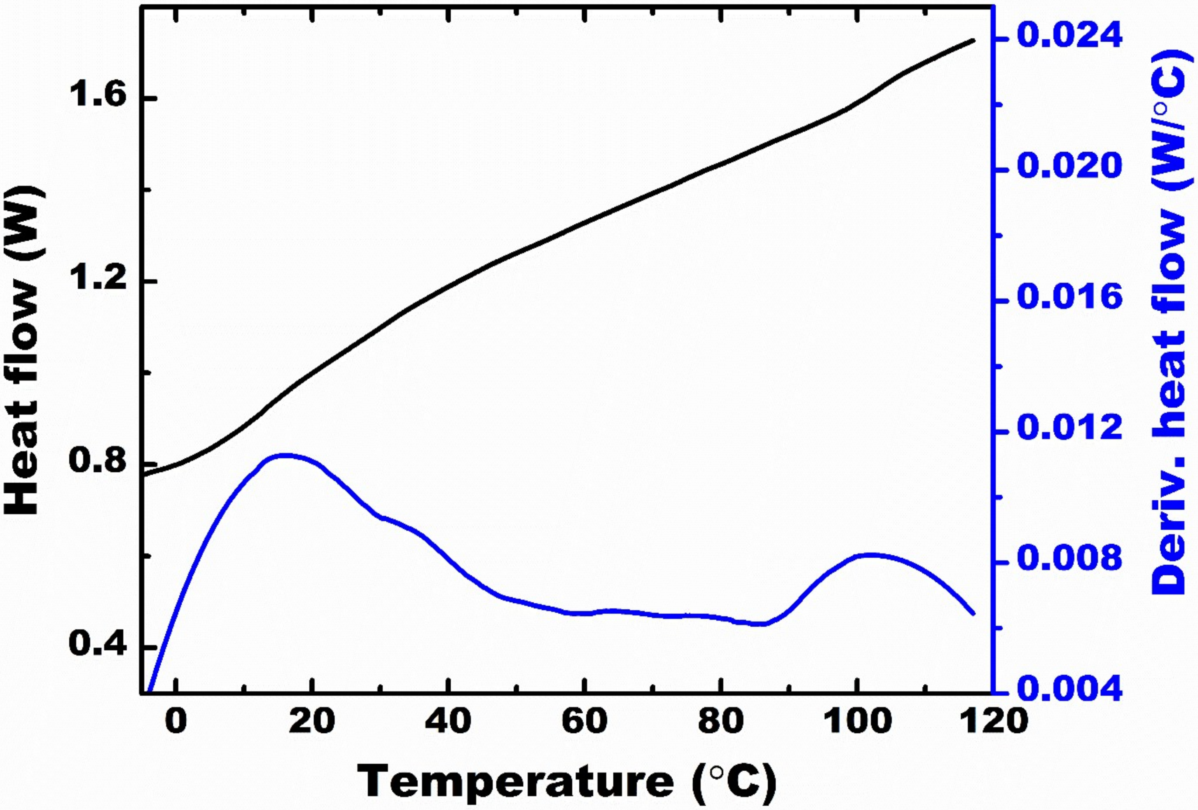

Figure S30: DSC of poly(styrene-b-methyl acrylate).

References

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