Electronic Supplementary Information for

Divergent Silylium Catalysis Enables Facile Poly(vinyl chloride) Upcycling to Poly(ethylene-*co*-styrene) Derivatives

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1. General Considerations

All polymerization reactions were set up under anaerobic and anhydrous conditions in a Vacuum Atmospheres OMNI glovebox under a dinitrogen atmosphere. Benzene and toluene were sparged with UHP argon (Praxair) and dried by passage over Q-5 and molecular sieves using a JCMeyer solvent purification system. Poly(vinyl chloride) (PVC) (Aldrich, M_n = 67.6 kDa, $Đ$ = 1.76) was dried under reduced pressure at 110 °C for 24 h prior to use. Painted PVC toys were ground into a powder using a blender and dried under reduced pressure at 110 °C for 24 h prior to use. Triphenylmethylium terakis(pentaflouorophenyl)borate ($[Ph_3C][B(C_6F_5)_4]$) and anhydrous grade triethyl silane, *o*-, *m*-, and *p*-xylene were purchased from Aldrich and used as received. $CDCl_3$ and tetrachloroethane-d_2 were purchased from Cambridge Isotope Laboratories and used as received. Isolated yields for prepared vinyl aromatic copolymers were estimated using theoretical yields calculated as follows: $mmol_{PVC} \times \{(mol\%_{PE} \times MW_{PE}) + (mol\%_{PS} \times MW_{PS})\}$.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian 400-MR 2-Channel NMR spectrometer and referenced against residual solvent resonances. IR spectra were recorded on an Agilent Cary 630 FTIR spectrometer equipped with a single reflection diamond (Di) ATR module. Polymer molecular weights and dispersities were determined using an Agilent 1260 Infinity II GPC instrument calibrated with monodisperse polystyrene standards at 140 °C in 1,2,4-tricholorbenzene. Differential scanning calorimetry (DSC) traces were recorded using a Perkin-Elmer DSC 8000 instrument and processed with a Pyris software. The DSC measurements were made at a heating rate of 10 °C/min and a dinitrogen flow rate of 20 ml/min, and T_g values were obtained from the midpoint of the glass transition in the second heating curve. Thermogravimetric analyses (TGA) were carried out on a Mettler Toledo TGA/DSC+ instrument at a heating rate of 10 °C/min and a dinitrogen flow rate of 40 ml/min. Elemental analyses were carried out on a Thermo Flash 2000 Elemental Analyzer. Energy-dispersive X-ray spectroscopy (EDX) measurements were made on a Thermo Scientific Helios G4 PFIB UXe instrument equipped with an Oxford UltimMax 170 Silicon Drift Detector (500,000 counts at 6kV and 0.8nA) and processed with a Aztec software.

2. General Procedures for Synthesis of ES Derivatives

2.1 Synthesis of poly(ethylene-*co*-styrene): In a glovebox, $[Ph_3C][B(C_6F_5)_4]$ (10.4 mg, 0.011 mmol, 0.5 mol%), PVC (136.4 mg, 2.182 mmol, 1 equiv), Et_3SiH (0.38 mL, 2.379 mmol, 1.1 equiv), benzene (2.13 mL, 24 mmol, 11 equiv) and stir bar were charged into a 2 dram vial equipped with a Teflon-coated cap. The vial was sealed and secured with electrical tape, taken out of the glovebox, and placed inside a Chemglass high-throughput tray that was preheated at 110 °C. After stirring for 1 h, the reaction mixture was quenched with isopropanol (15 mL), which resulted in precipitation of white solids. The solids were allowed to settle and the supernatant was decanted away. The polymer was then dried at 160 °C for 1 h under dynamic vacuum (85.9 mg, 91% yield).

2.2 Synthesis of poly(ethylene-*co*-styrene) from PVC toys: In a glovebox, a 2 dram vial equipped with a Teflon-coated cap was charged with $[Ph_3C][B(C_6F_5)_4]$ (10.3 mg, 0.011 mmol, 7.5 wt%), Et_3SiH (0.38 mL, 2.379 mmol), benzene (2.13 mL, 24 mmol), and a powdered mixture of blue-, green-, yellow- and grey-colored PVC lizard toys (137.1 mg). The vial was sealed and secured with electrical tape, taken out of the glovebox, and placed inside a Chemglass high-throughput tray that was preheated at 110 °C. After stirring for 1 h, the reaction mixture was quenched with isopropanol (15 mL), which resulted in precipitation of white solids. The solids were allowed to settle and the supernatant was decanted away. The polymer was then dried at 160 °C for 1 h under dynamic vacuum.

2.3 Benchtop synthesis of poly(ethylene-*co*-styrene): A 20 mL scintillation vial was charged with a stir bar and $[Ph_3C][B(C_6F_5)_4]$ (10.6 mg, 0.011 mmol, 0.5 mol%) inside a glovebox. The vial was removed from the glovebox, and Et_3SiH (0.38 mL, 2.379 mmol, 1.1 equiv) and benzene (2.13 mL, 24 mmol, 11 equiv) (both stored outside the glovebox) were added on a bench top. The mixture was stirred for 1 min and transferred to a 2 dram vial equipped with a Teflon coated cap containing pre-weighed PVC (136.7 mg, 2.187 mmol, 1 equiv) (stored outside the glovebox). The vial was sealed and secured with electrical tape, and placed inside a Chemglass high-throughput tray that was preheated at 110 °C. After stirring for 1 h, the reaction mixture was quenched with isopropanol (15 mL), which resulted in precipitation of white solids. The solids were allowed to settle and the supernatant was decanted away. The polymer was then dried at 160 °C for 1 h under dynamic vacuum (83.4 mg, 88% yield).

2.4 Synthesis of poly(ethylene-*co*-toluene): $[Ph_3C][B(C_6F_5)_4]$ (5.0 mg, 0.005 mmol, 0.25 mol%), PVC (136.0 mg, 2.176 mmol, 1 equiv), Et_3SiH (0.38 mL, 2.379 mmol, 1.1 equiv), toluene (2.53 mL, 24 mmol, 11 equiv) and stir bar were charged into a 2 dram vial equipped with a Teflon-coated cap. The vial was sealed and secured with electrical tape, taken out of the glovebox, and placed inside a Chemglass high-throughput tray that was preheated at 110 °C. After stirring for 5 min, the reaction mixture was quenched with isopropanol (15 mL), which resulted in precipitation of white solids. The solids were allowed to settle and the supernatant was decanted away. The polymer was then dried at 160 °C for 1 h under dynamic vacuum (76.6 mg, 72% yield).

2.5 Synthesis of poly(ethylene-*co*-*o*-xylene): Reaction was carried out using procedures analogous to that of poly(ethylene-*co*-toluene) (70.5 mg, 61% yield).

2.6 Synthesis of poly(ethylene-*co*-*m*-xylene): Reaction was carried out using procedures analogous to that of poly(ethylene-*co*-toluene) (47.8 mg, 41% yield).

2.7 Synthesis of poly(ethylene-*co*-*p*-xylene): Reaction was carried out using procedures analogous to that of poly(ethylene-*co*-toluene) (59.0 mg, 55% yield).

3. NMR Spectroscopy

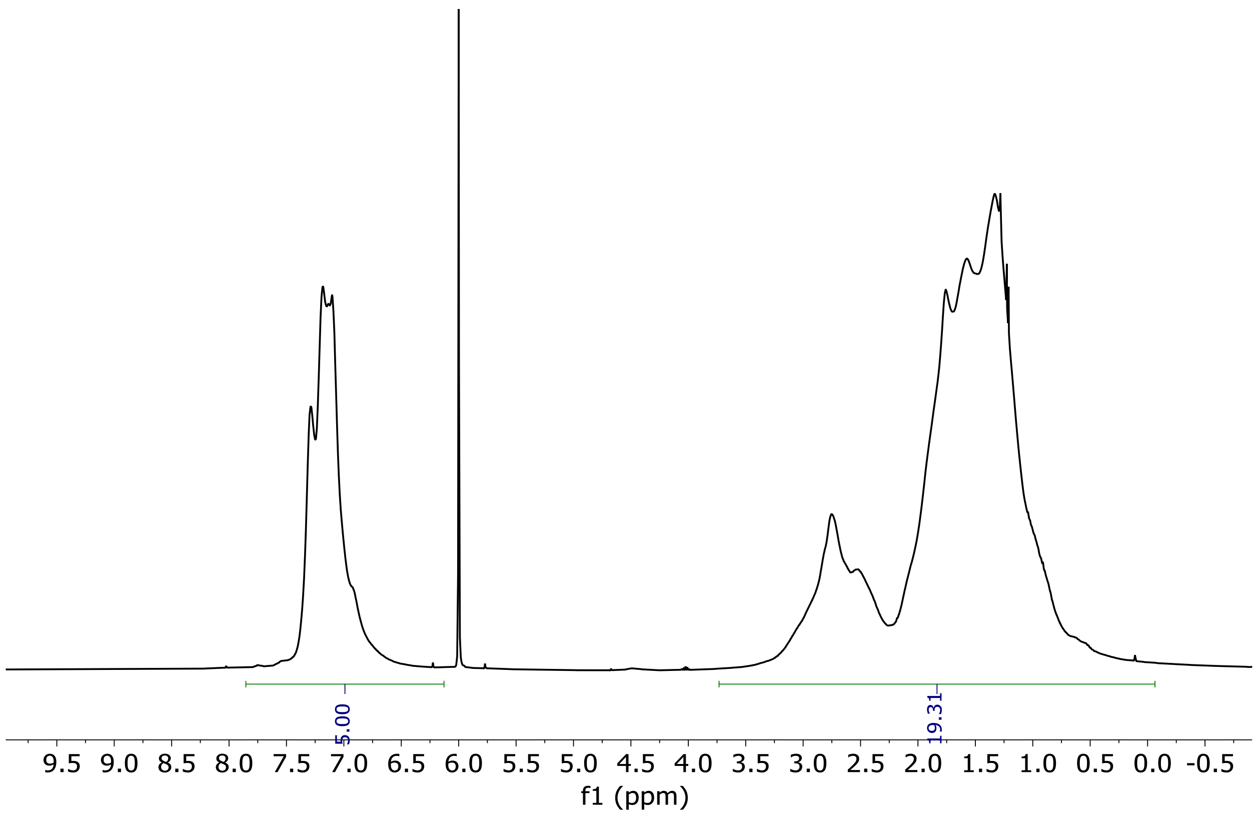

Fig. S1 ^{1}H NMR spectrum of poly(ethylene-*co*-styrene) in tetrachloroethane-d_2.

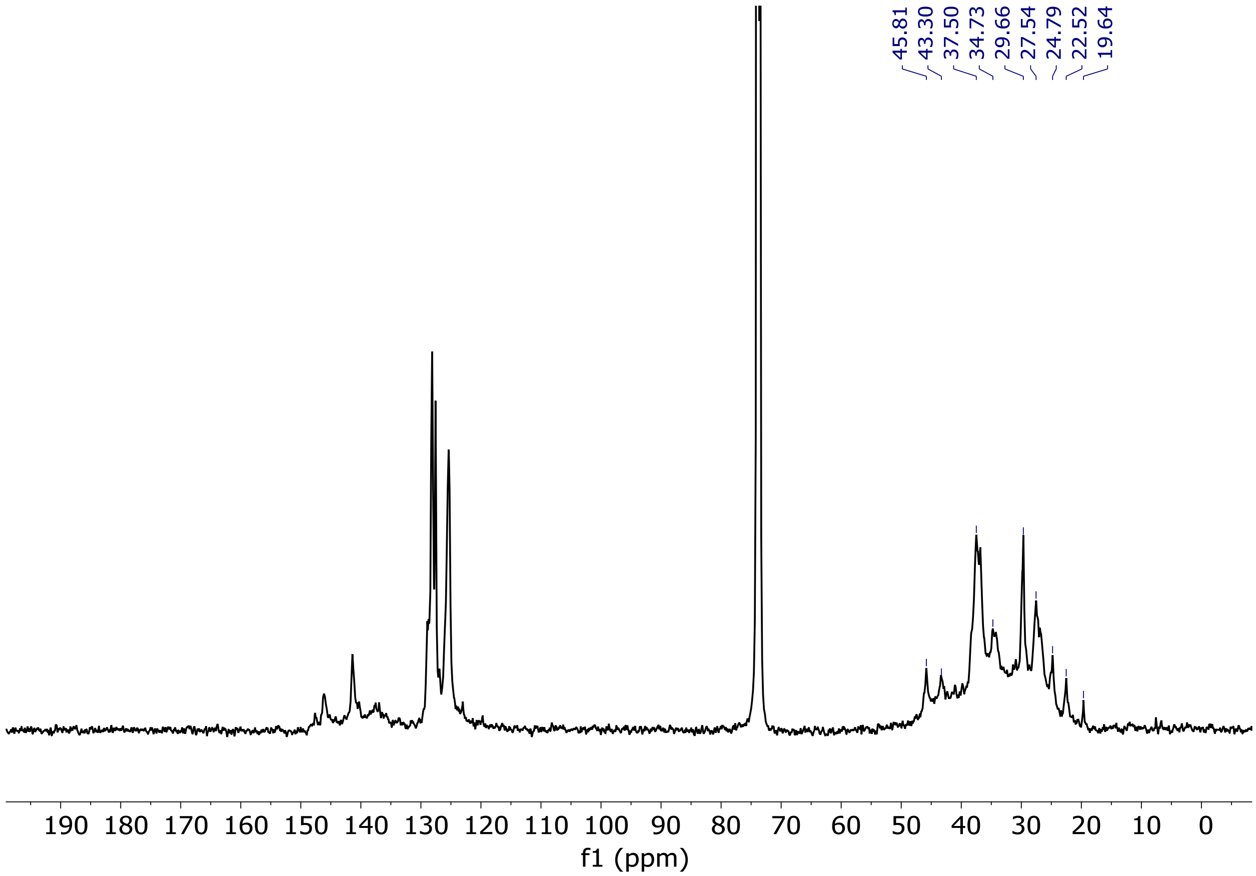

Fig. S2 $^{13}C\{^{1}H\}$ NMR spectrum of poly(ethylene-*co*-styrene) in tetrachloroethane-d_2.

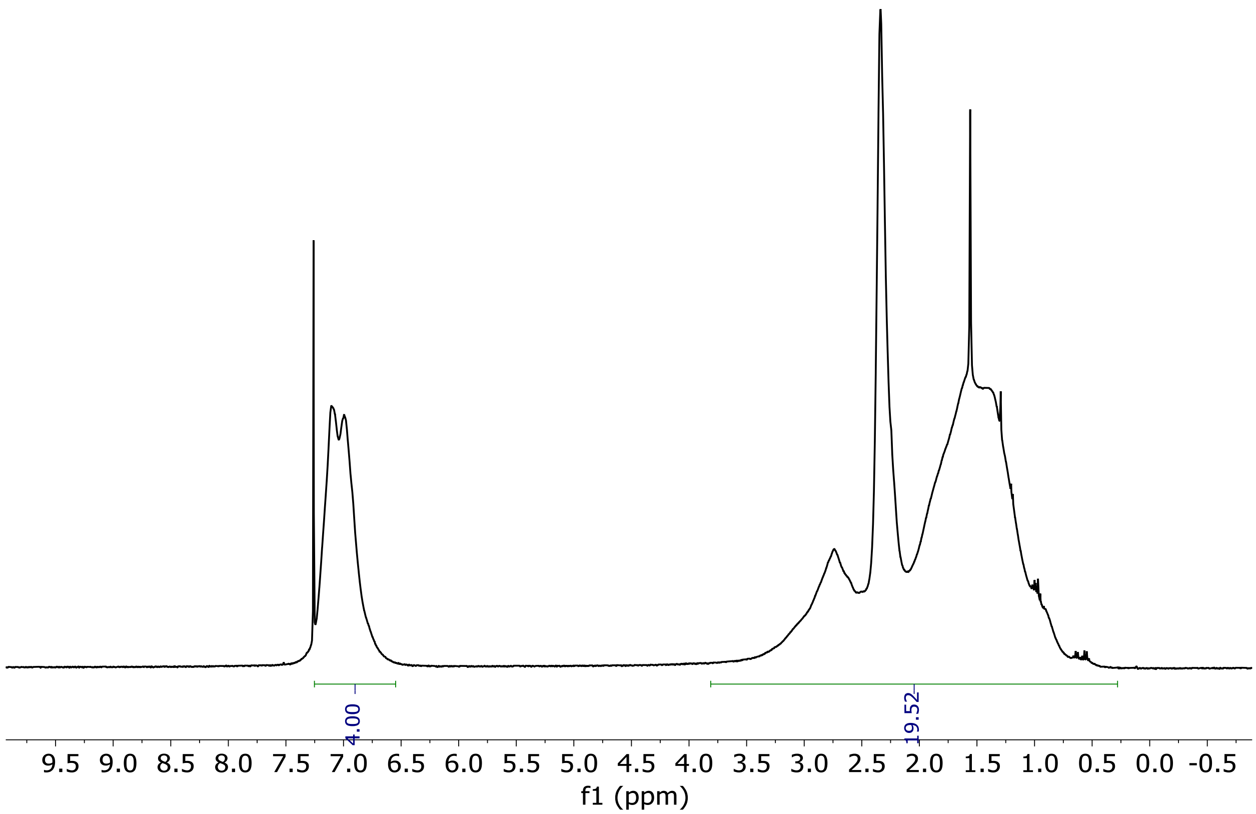

Fig. S3 ^{1}H NMR spectrum of poly(ethylene-*co*-toluene) in $CDCl_3$.

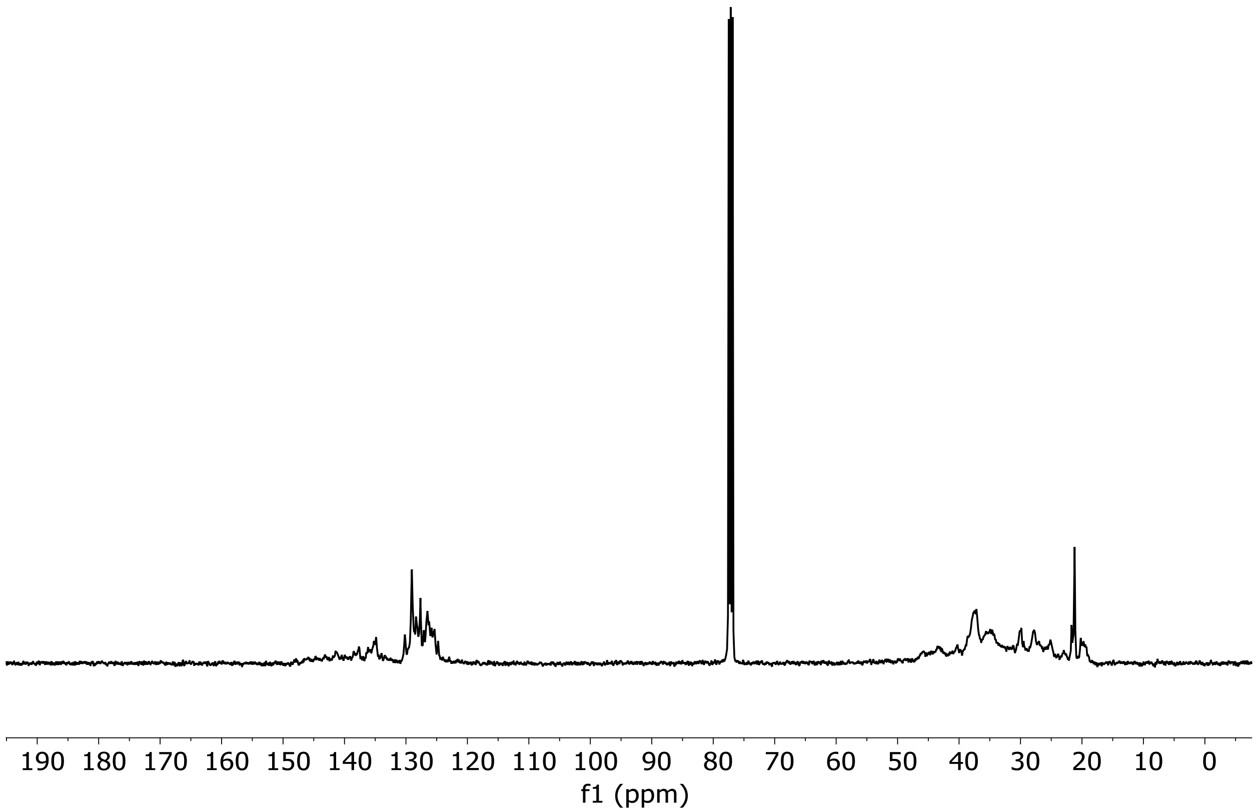

Fig. S4 $^{13}C\{^1H\}$ NMR spectrum of poly(ethylene-*co*-toluene) in $CDCl_3$.

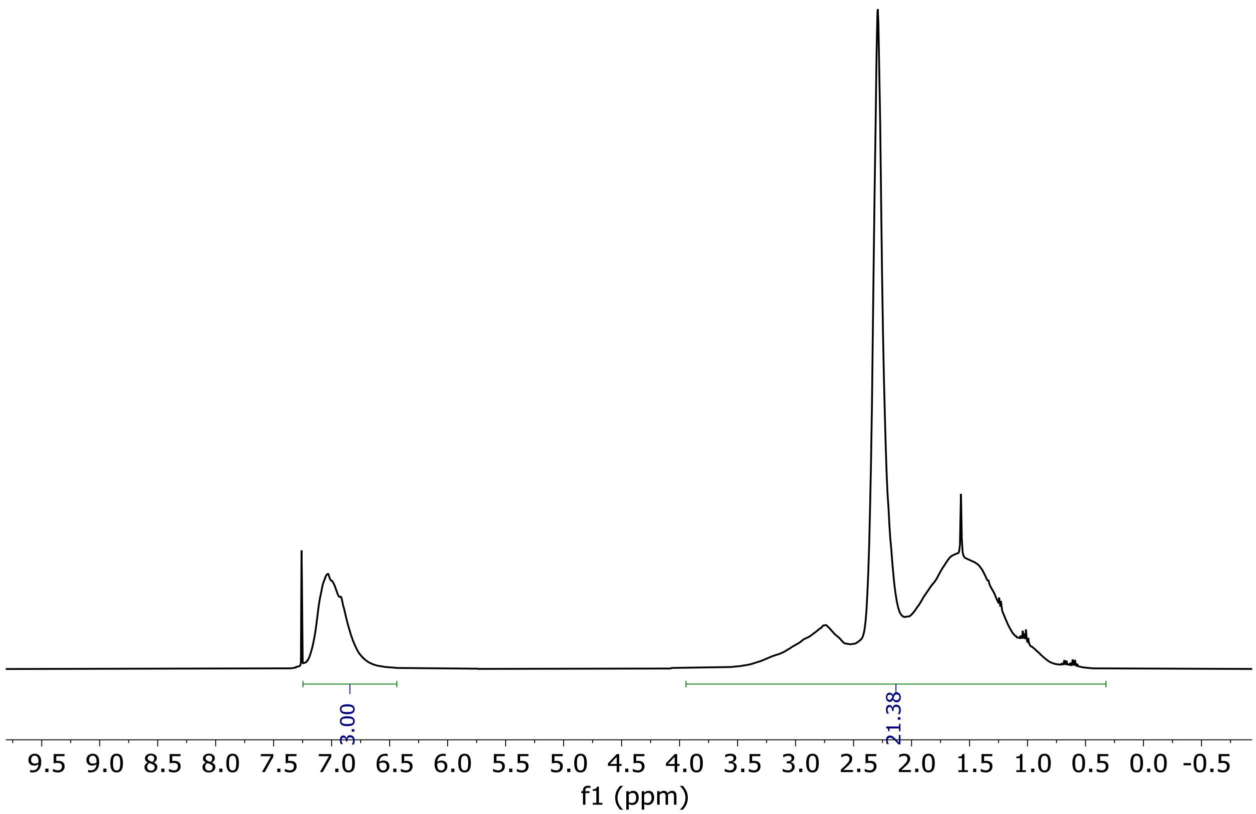

Fig. S5 ^{1}H NMR spectrum of poly(ethylene-*co*-*o*-xylene) in $CDCl_3$.

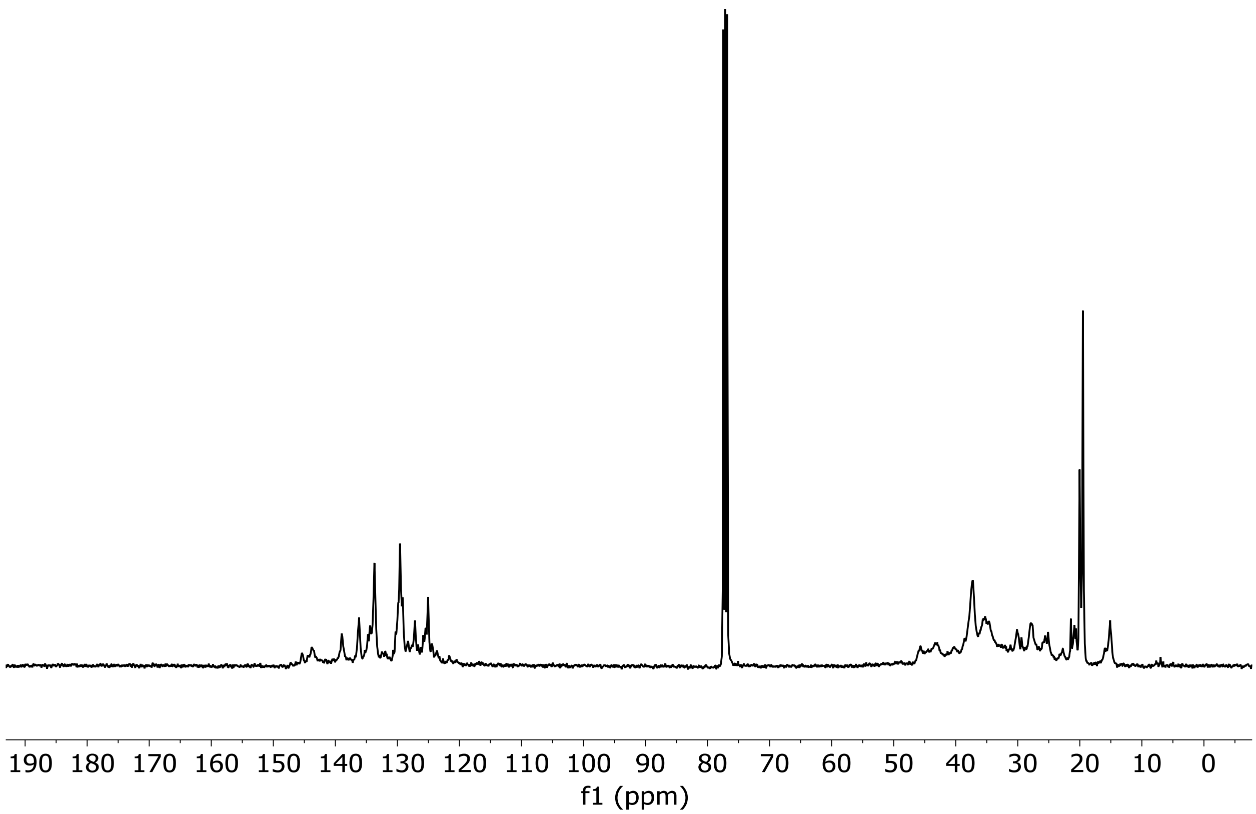

Fig. S6 $^{13}C\{^{1}H\}$ NMR spectrum of poly(ethylene-*co*-*o*-xylene) in $CDCl_3$.

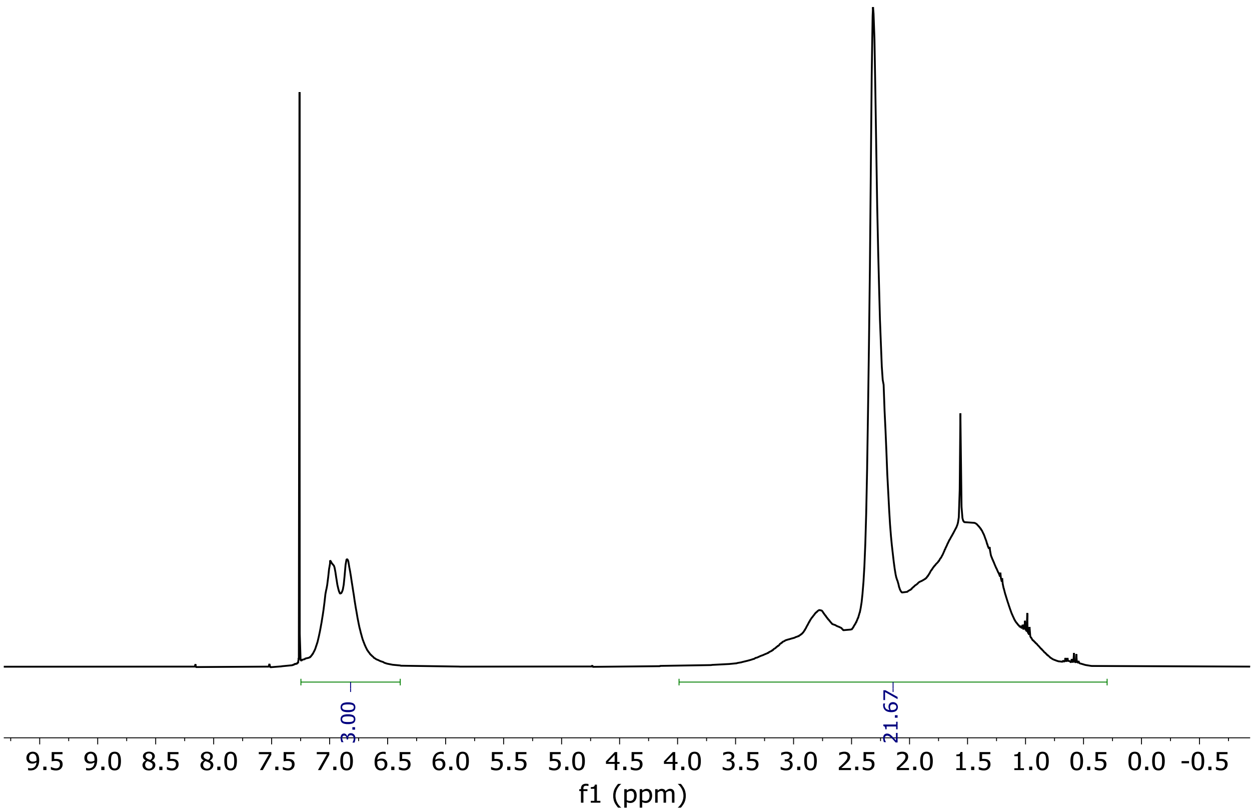

Fig. S7 ^{1}H NMR spectrum of poly(ethylene-*co*-*m*-xylene) in $CDCl_3$.

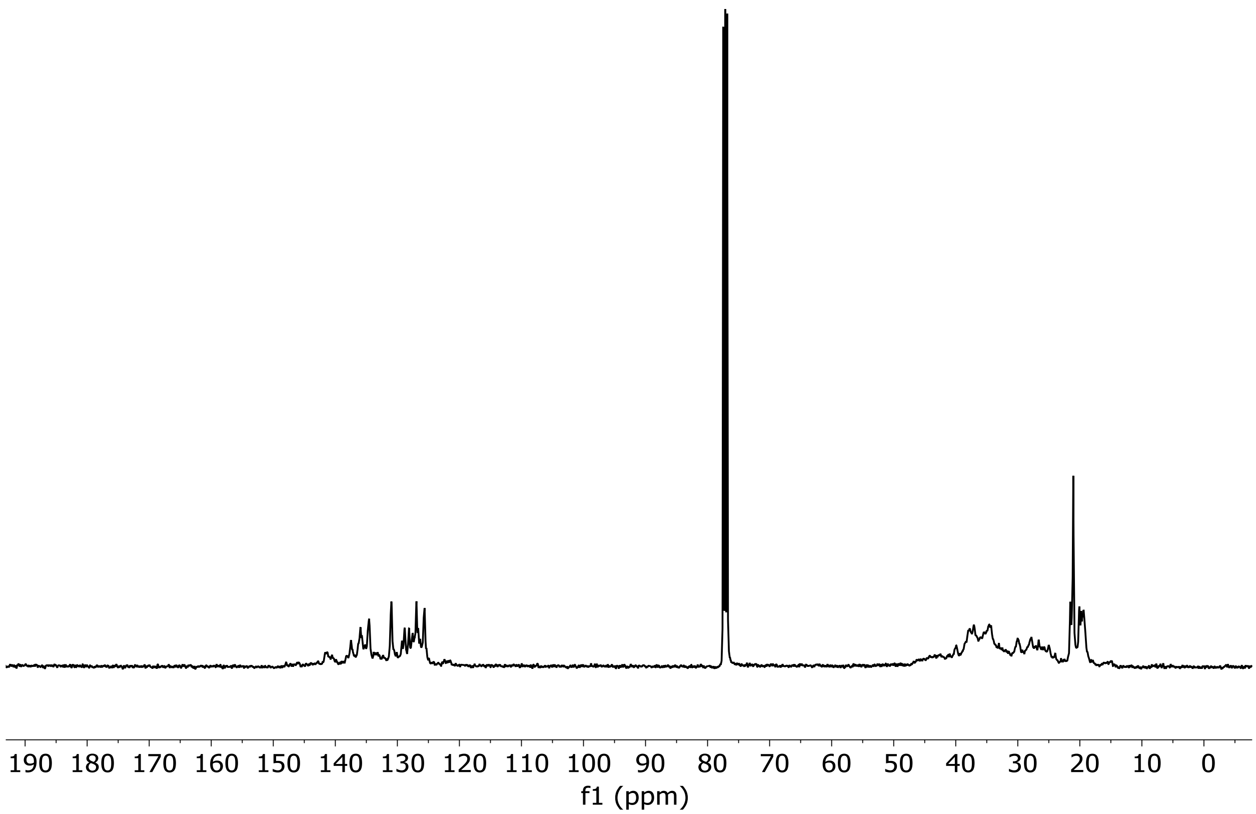

Fig. S8 $^{13}C\{^{1}H\}$ NMR spectrum of poly(ethylene-*co*-*m*-xylene) in $CDCl_3$.

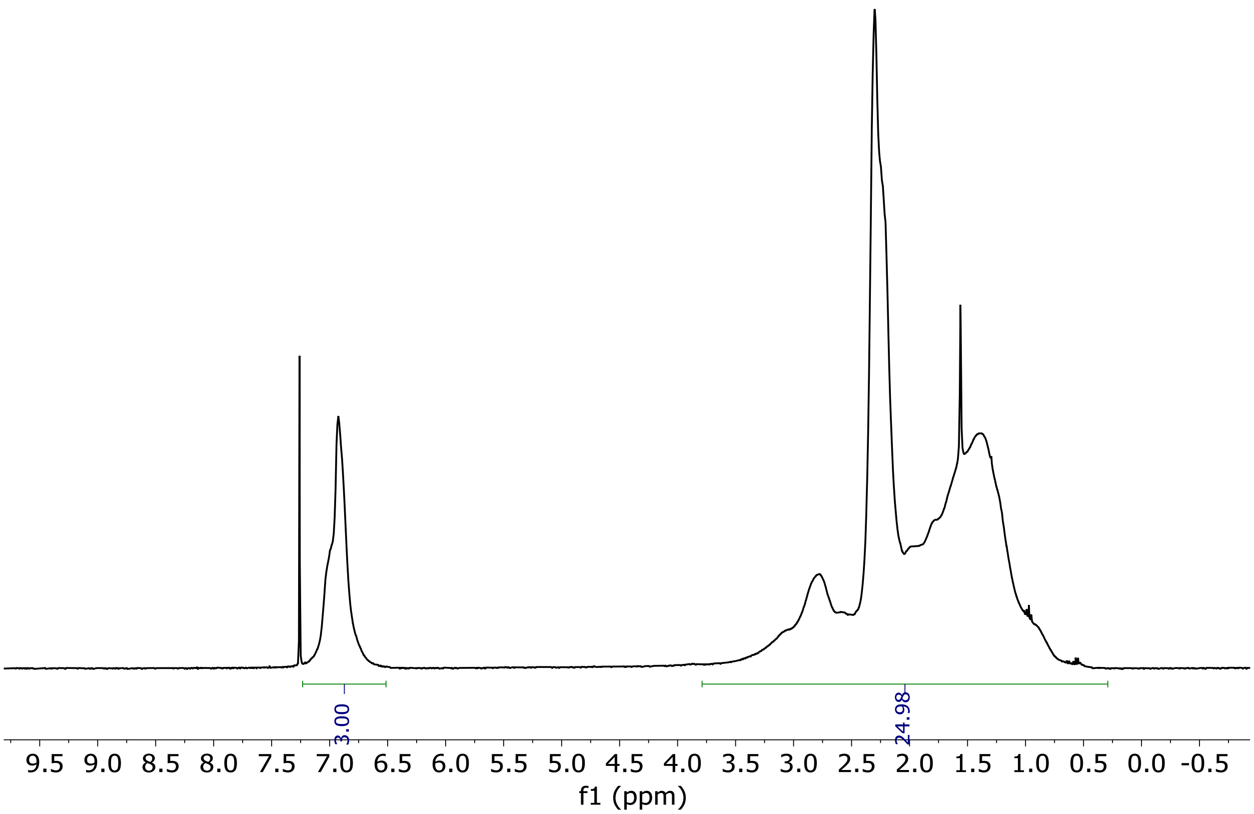

Fig. S9 ^{1}H NMR spectrum of poly(ethylene-*co*-*p*-xylene) in $CDCl_3$.

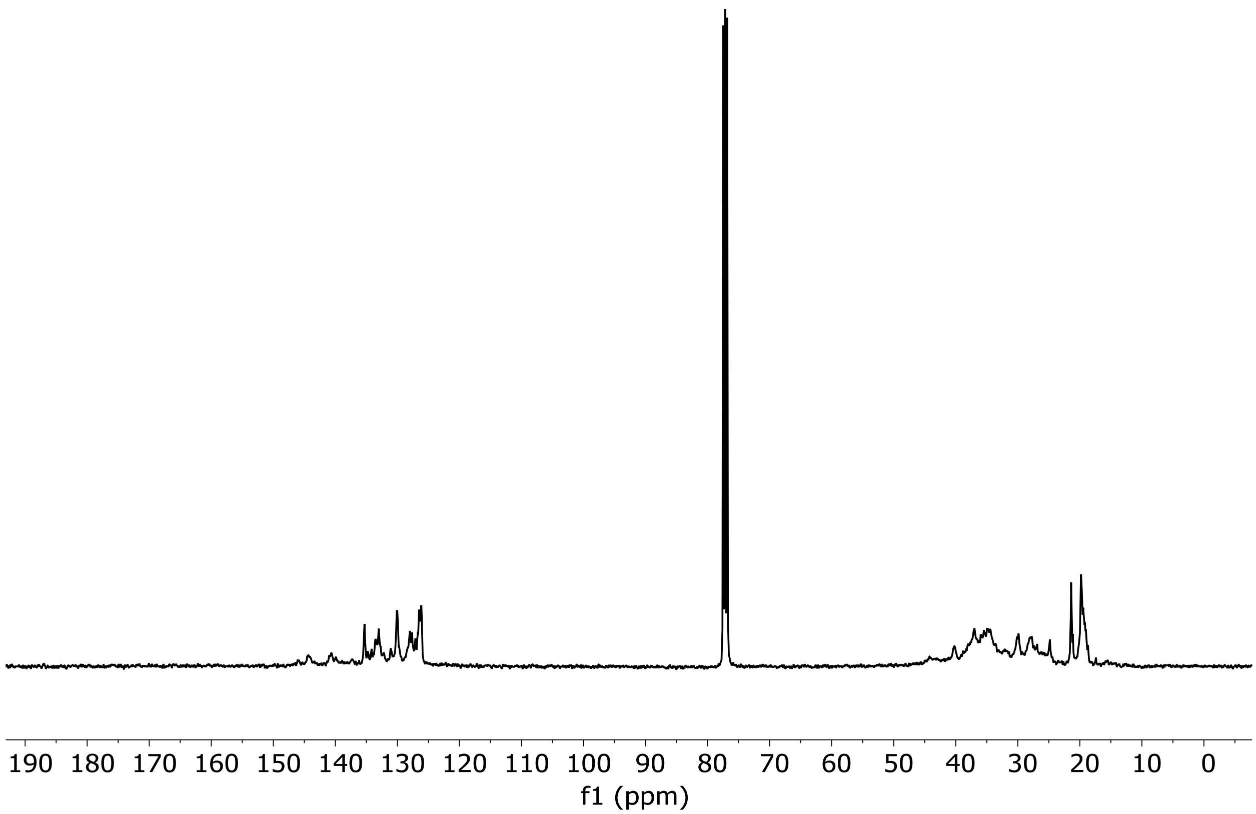

Fig. S10 $^{13}C\{^{1}H\}$ NMR spectrum of poly(ethylene-*co*-*p*-xylene) in $CDCl_3$.

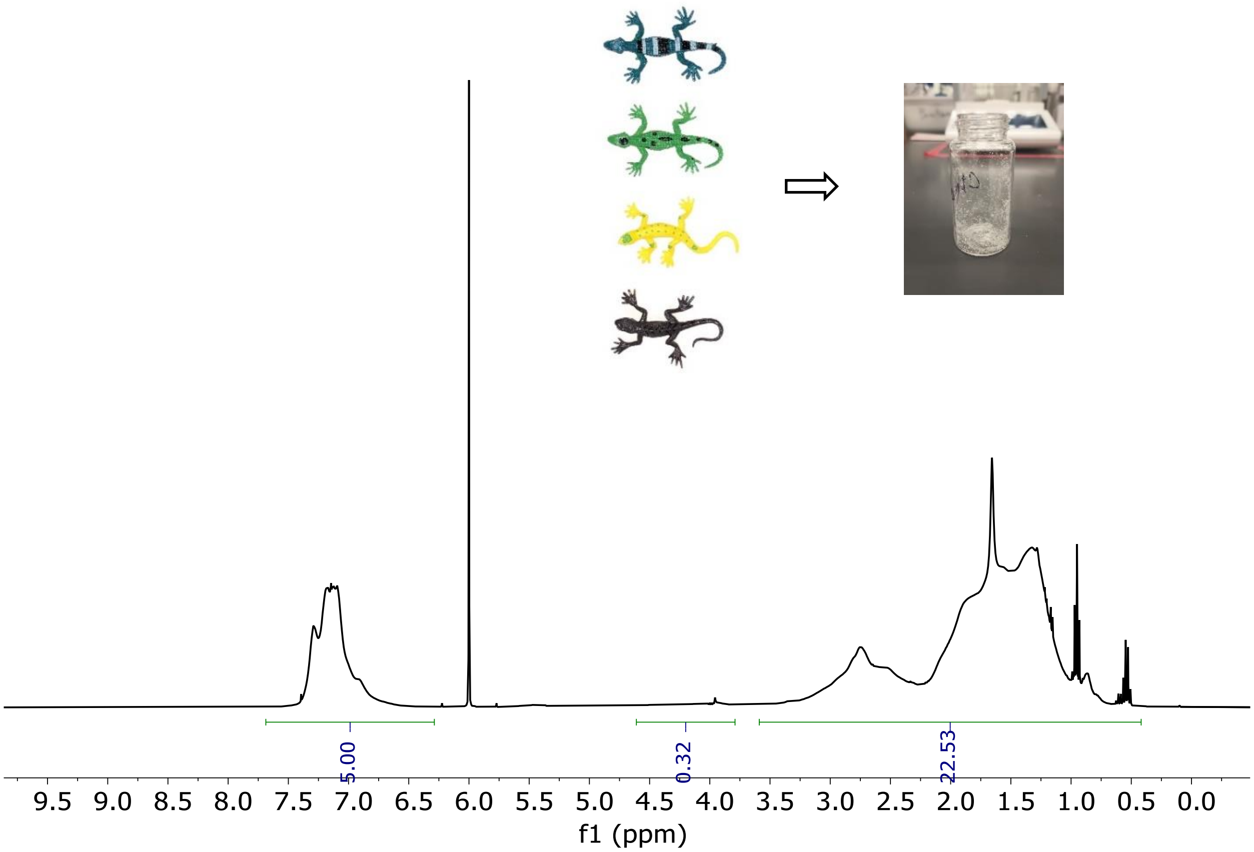

Fig. S11 ^{1}H NMR spectrum, in tetrachloroethane-d_2, of product isolated from tandem hydrodechlorination/Friedel-Crafts alkylation of painted PVC toys.

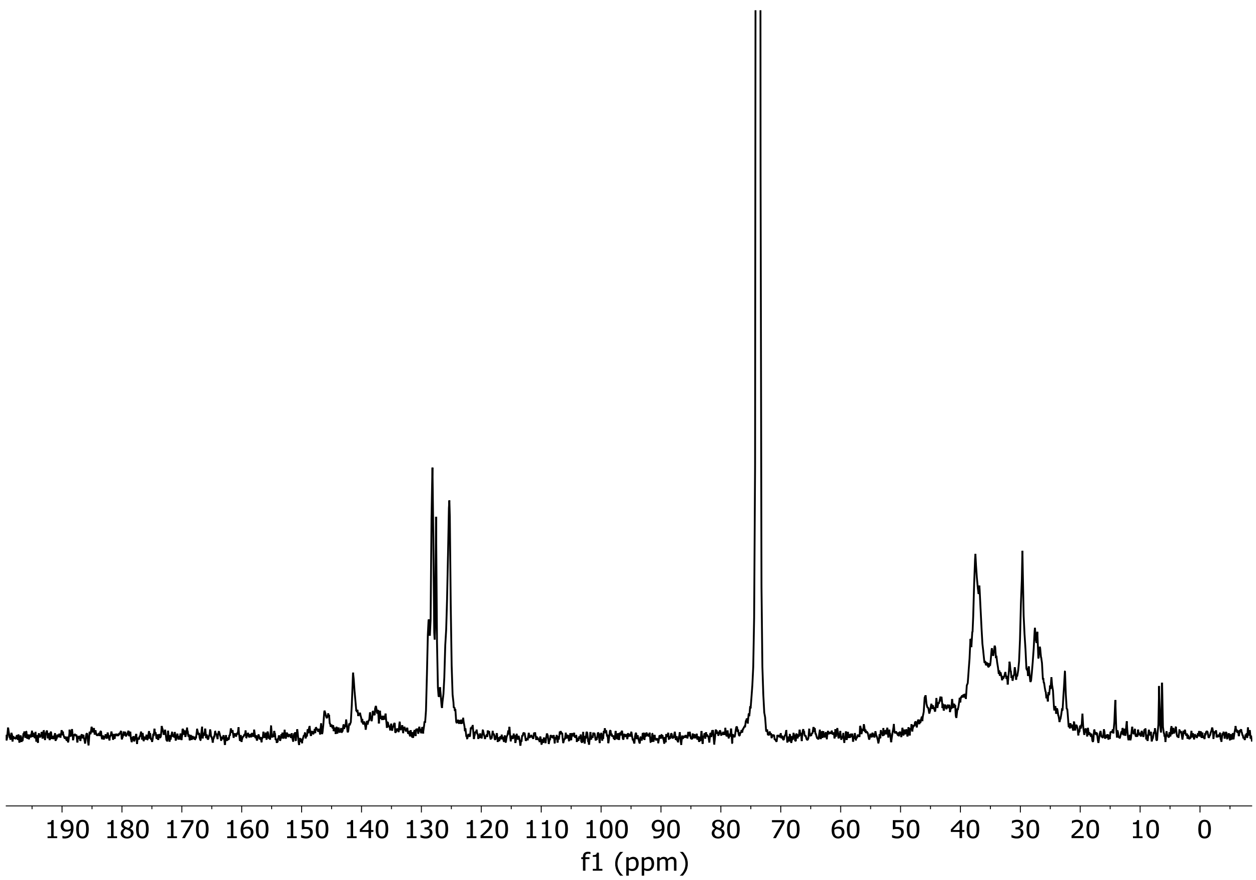

Fig. S12 $^{13}C\{^{1}H\}$ NMR spectrum, in tetrachloroethane-d_2, of product isolated from tandem hydrodechlorination/Friedel-Crafts alkylation of painted PVC toys.

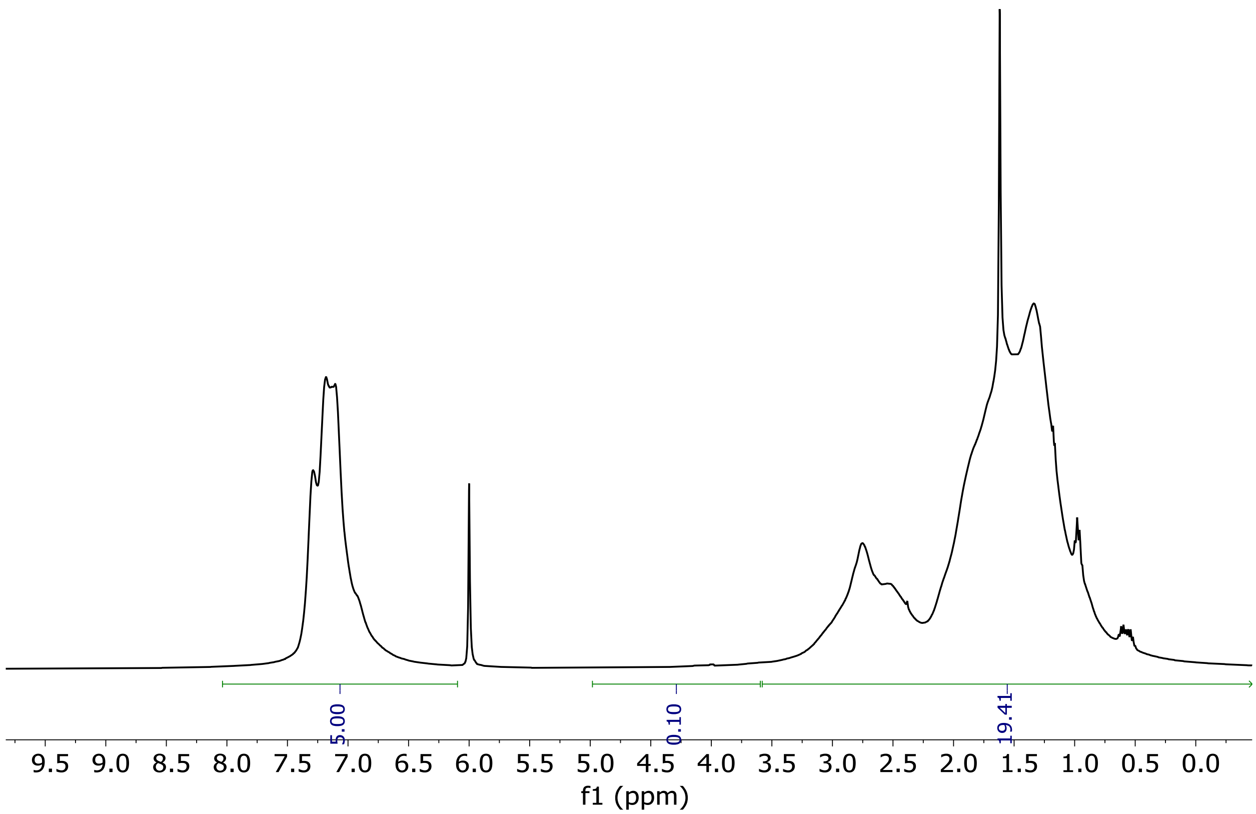

Fig. S13 ^{1}H NMR spectrum, in tetrachloroethane-d_2, of poly(ethylene-*co*-styrene) prepared under bench conditions.

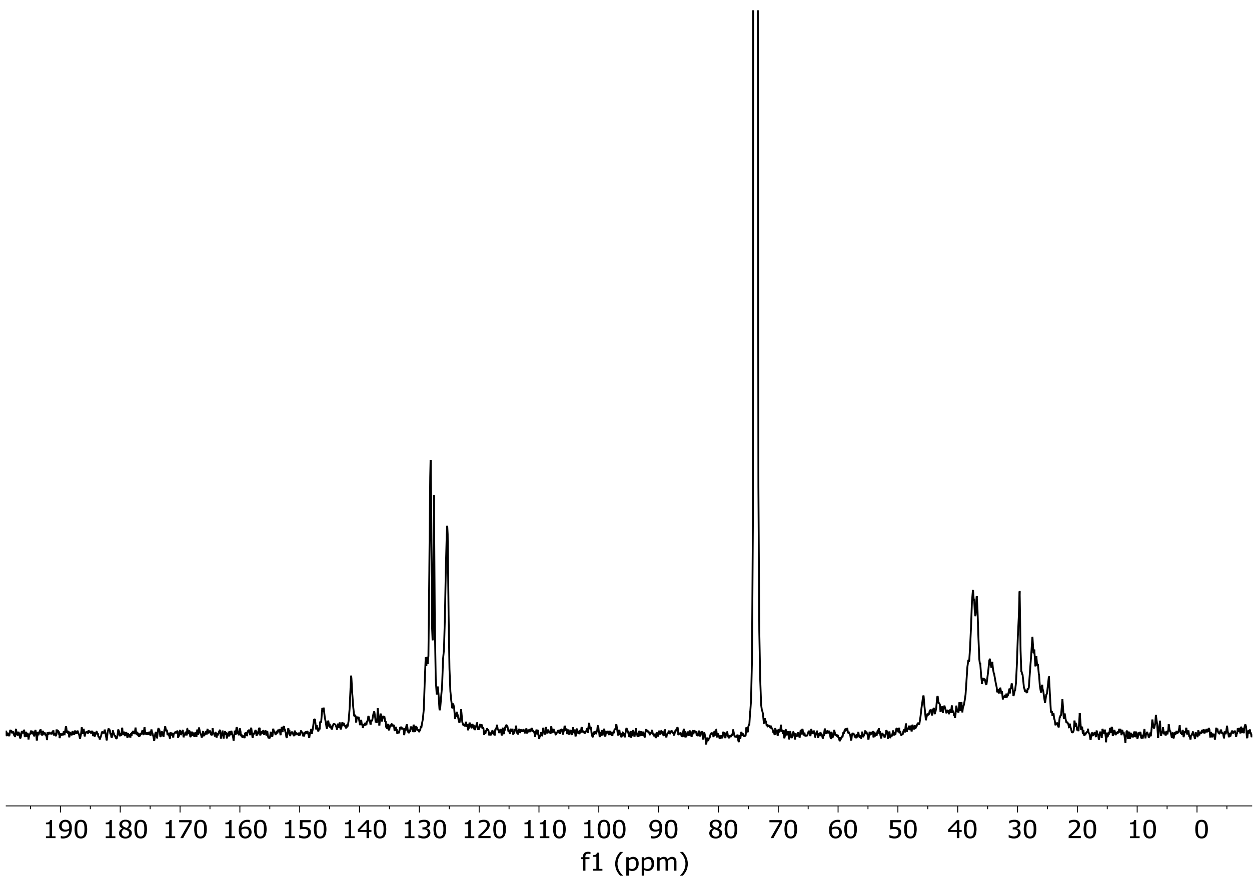

Fig. S14 $^{13}C\{^{1}H\}$ NMR spectrum, in tetrachloroethane-d_2, of poly(ethylene-*co*-styrene) prepared under bench conditions.

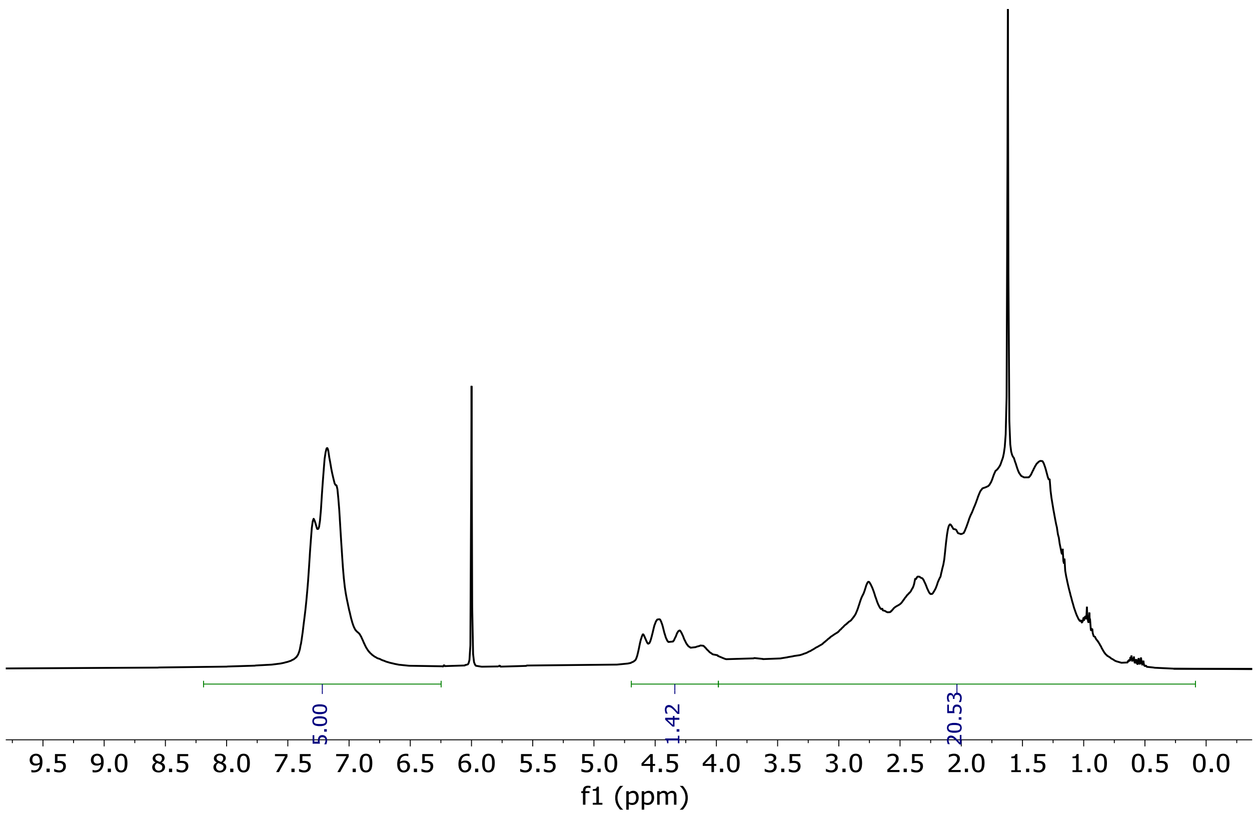

Fig. S15 ^{1}H NMR spectrum, in tetrachloroethane-d_2, of poly(vinyl chloride-*co*-ethylene-*co*-styrene) with a 23:61:16 respective monomer ratio.

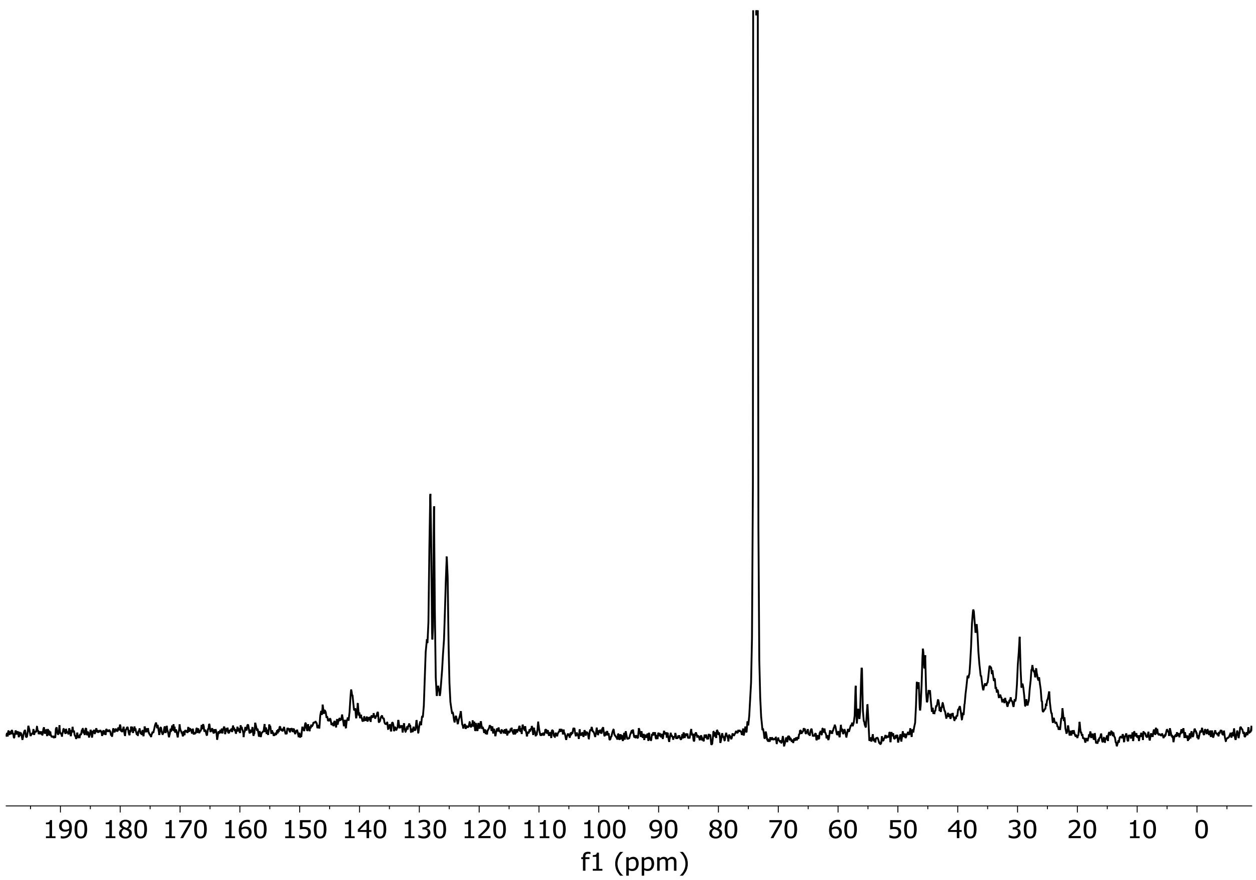

Fig. S16 $^{13}C\{^1H\}$ NMR spectrum, in tetrachloroethane-d_2, of poly(vinyl chloride-*co*-ethylene-*co*-styrene) with a 23:61:16 respective monomer ratio.

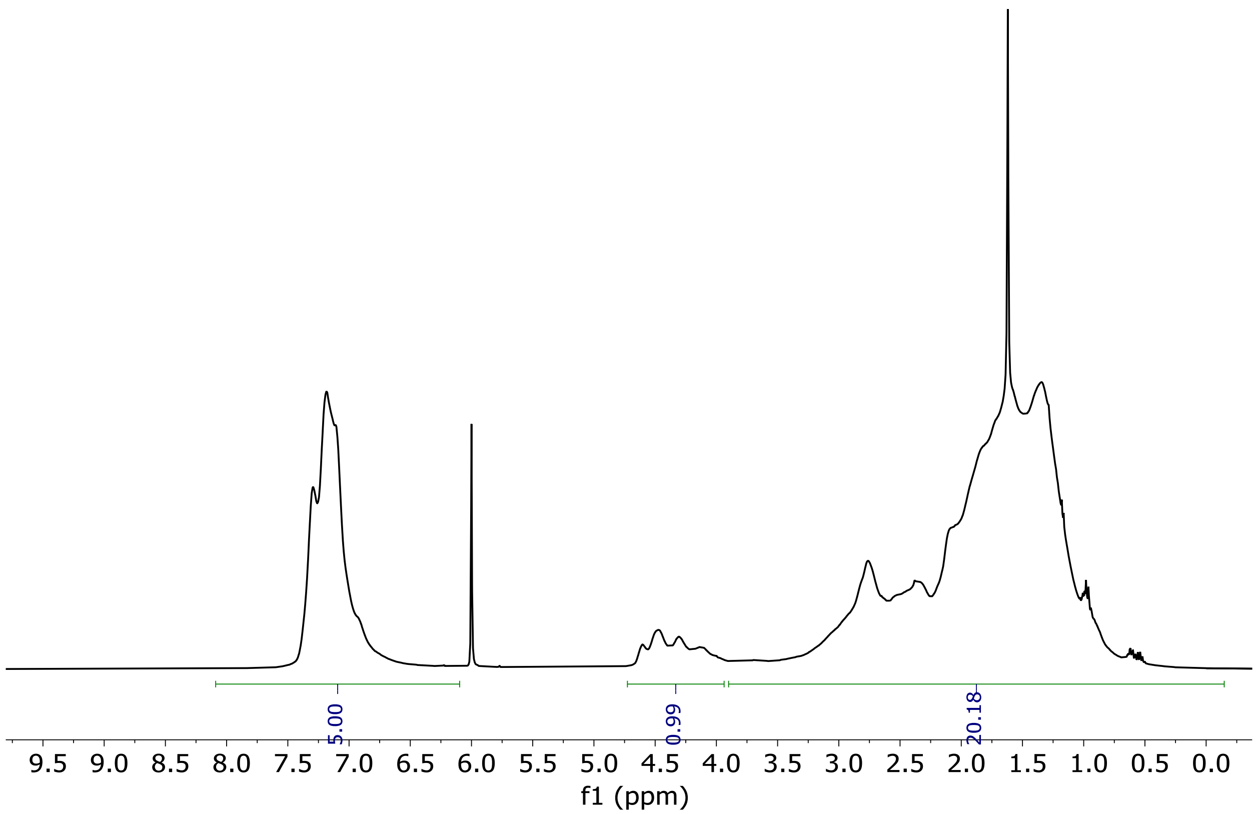

Fig. S17 ^{1}H NMR spectrum, in tetrachloroethane-d_2, of poly(vinyl chloride-*co*-ethylene-*co*-styrene) with a 17:66:17 respective monomer ratio.

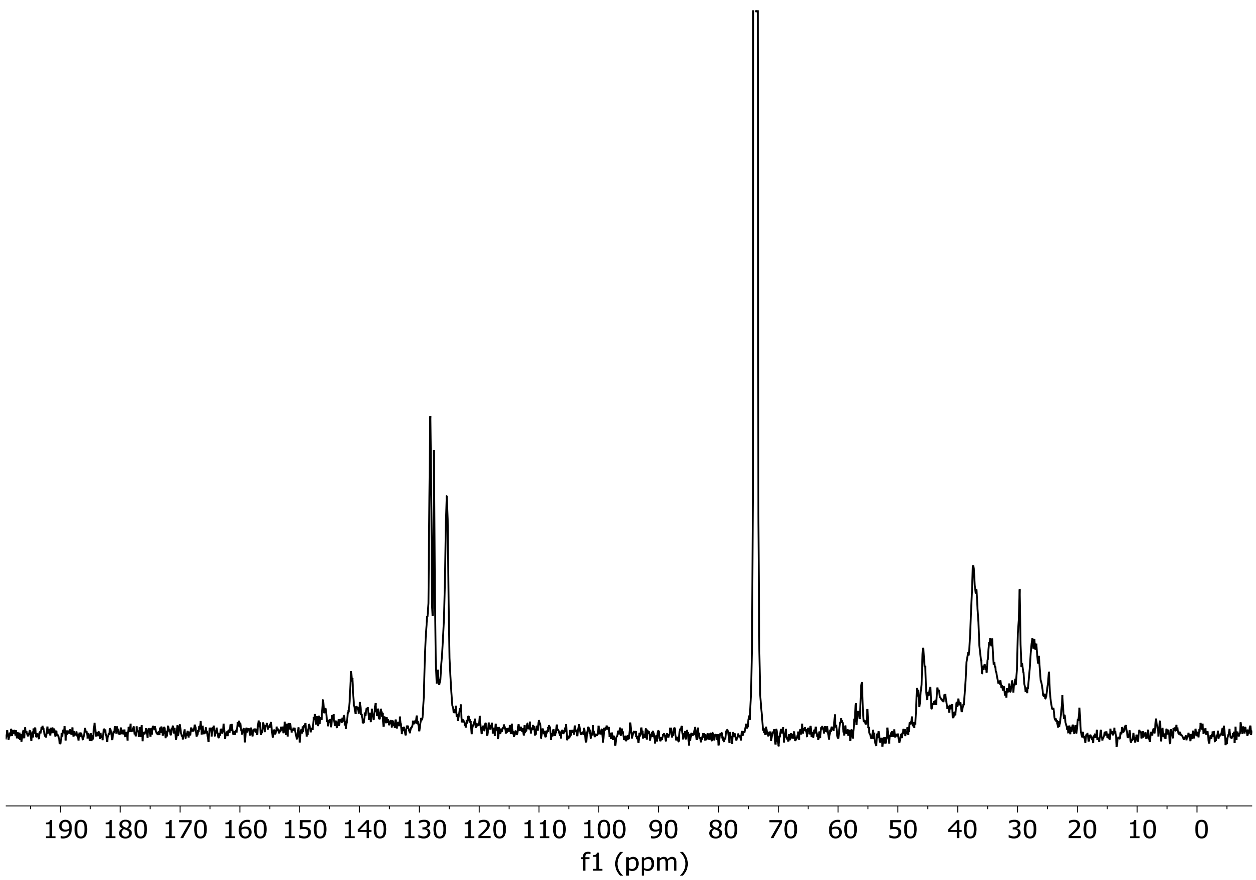

Fig. S18 $^{13}C\{^1H\}$ NMR spectrum, in tetrachloroethane-d_2, of poly(vinyl chloride-*co*-ethylene-*co*-styrene) with a 17:66:17 respective monomer ratio.

4. Differential Scanning Calorimetry

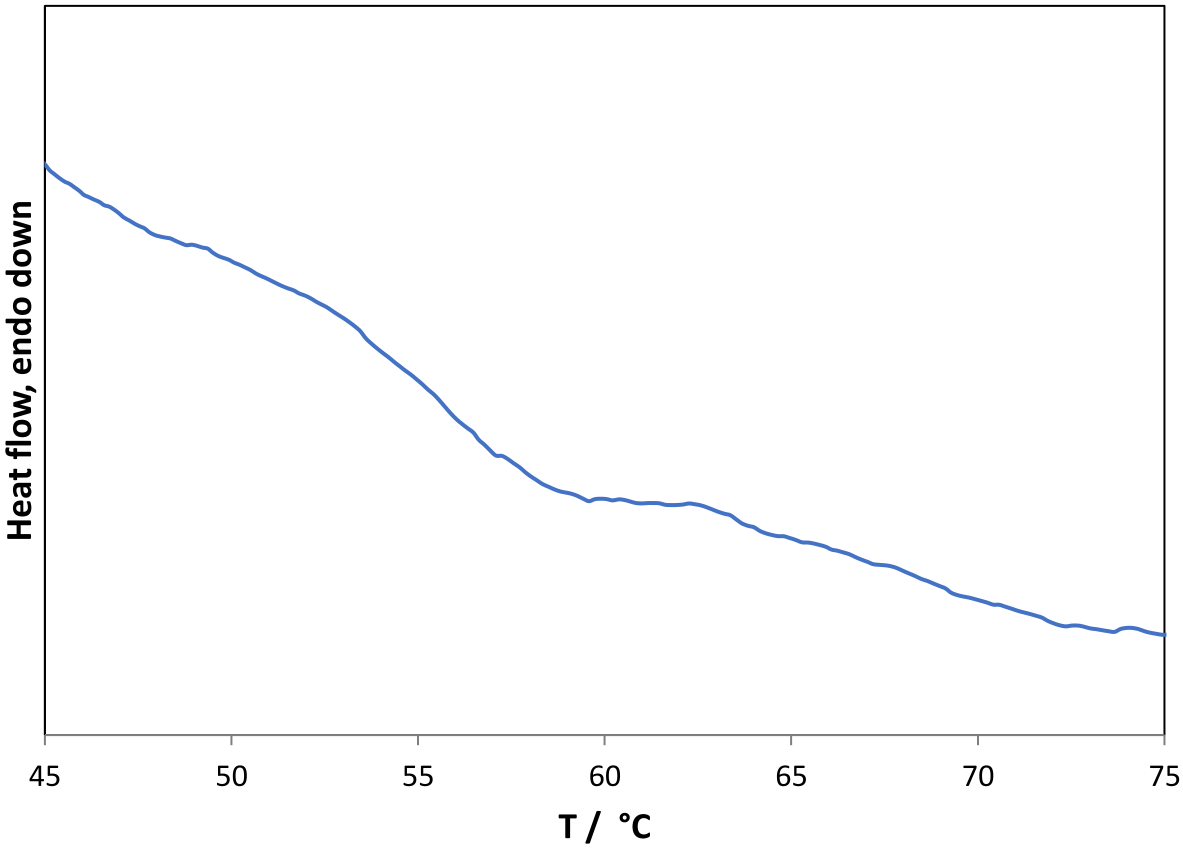

Fig. S19 DSC curve of product isolated from tandem hydrodechlorination/Friedel-Crafts alkylation of painted PVC toys.

5. Thermogravimetric Analysis

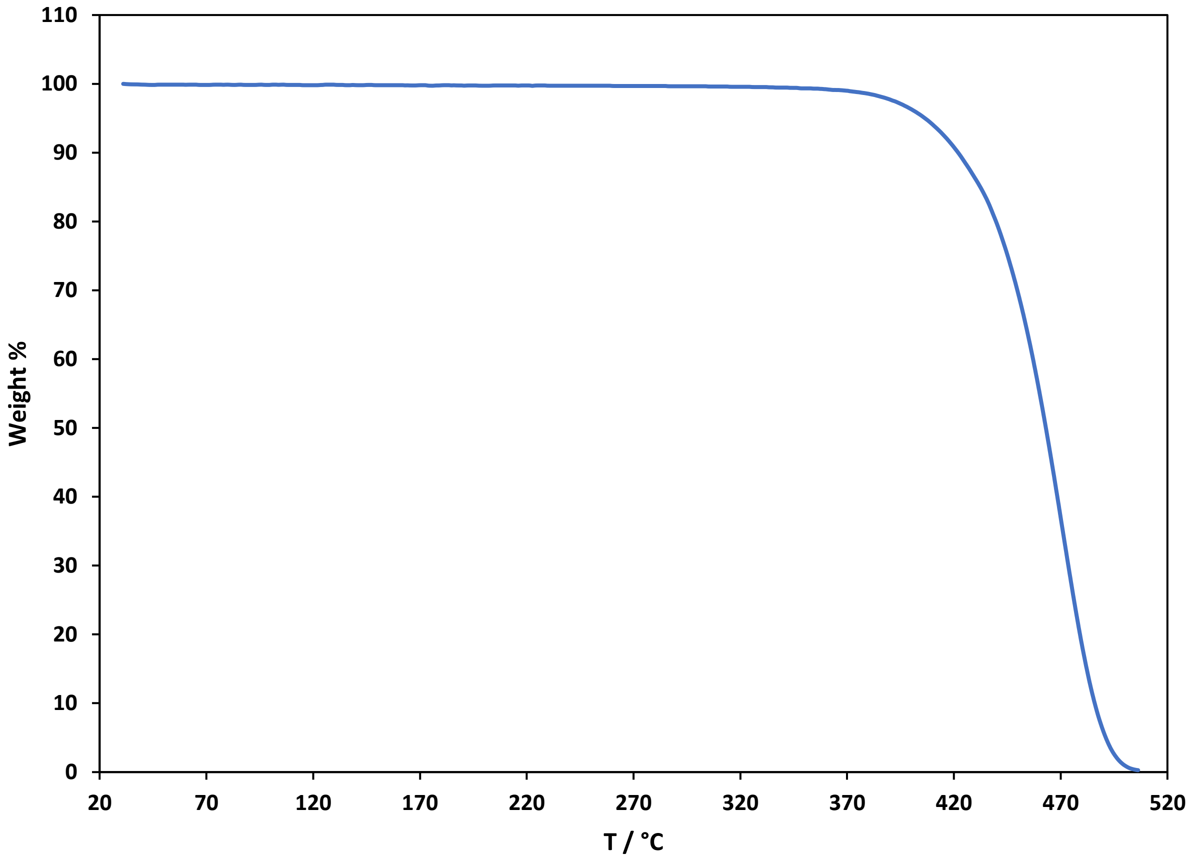

Fig. S20 TGA curve of poly(ethylene-*co*-styrene).

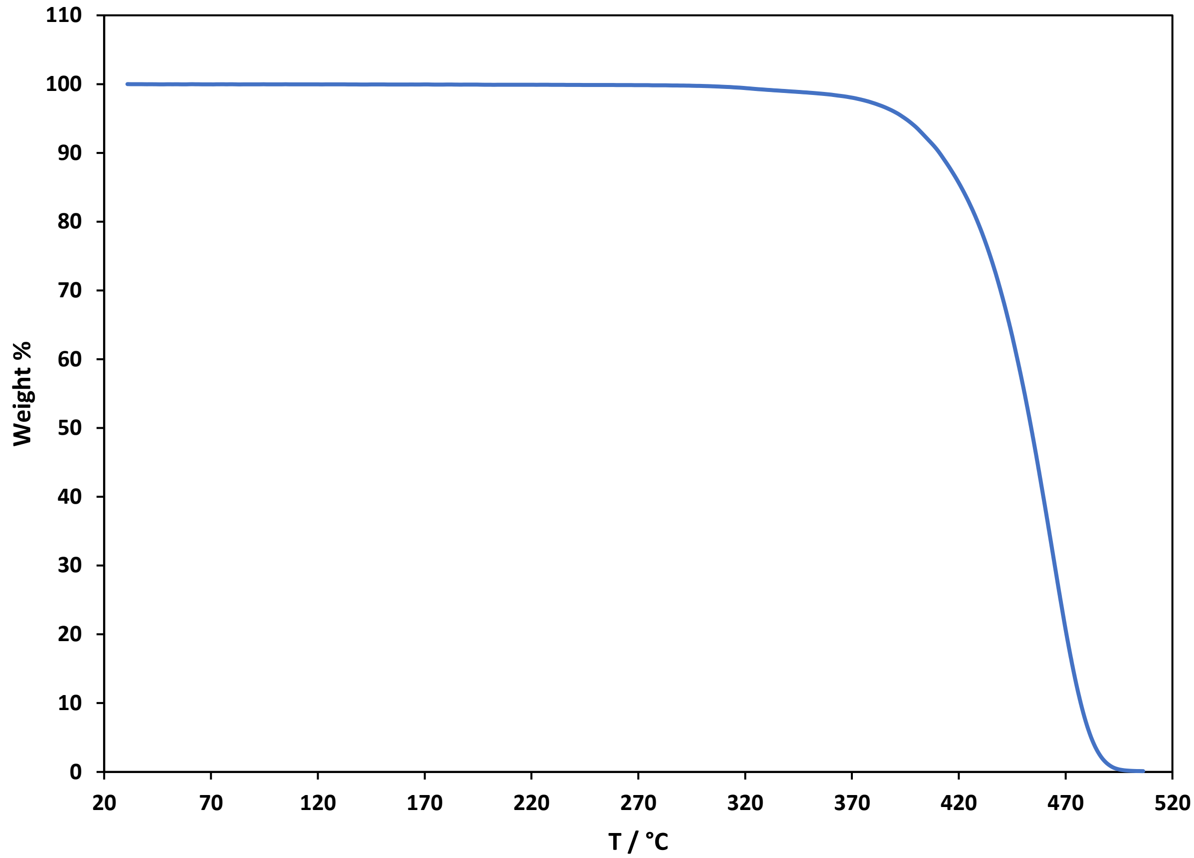

Fig. S21 TGA curve of poly(ethylene-*co*-toluene).

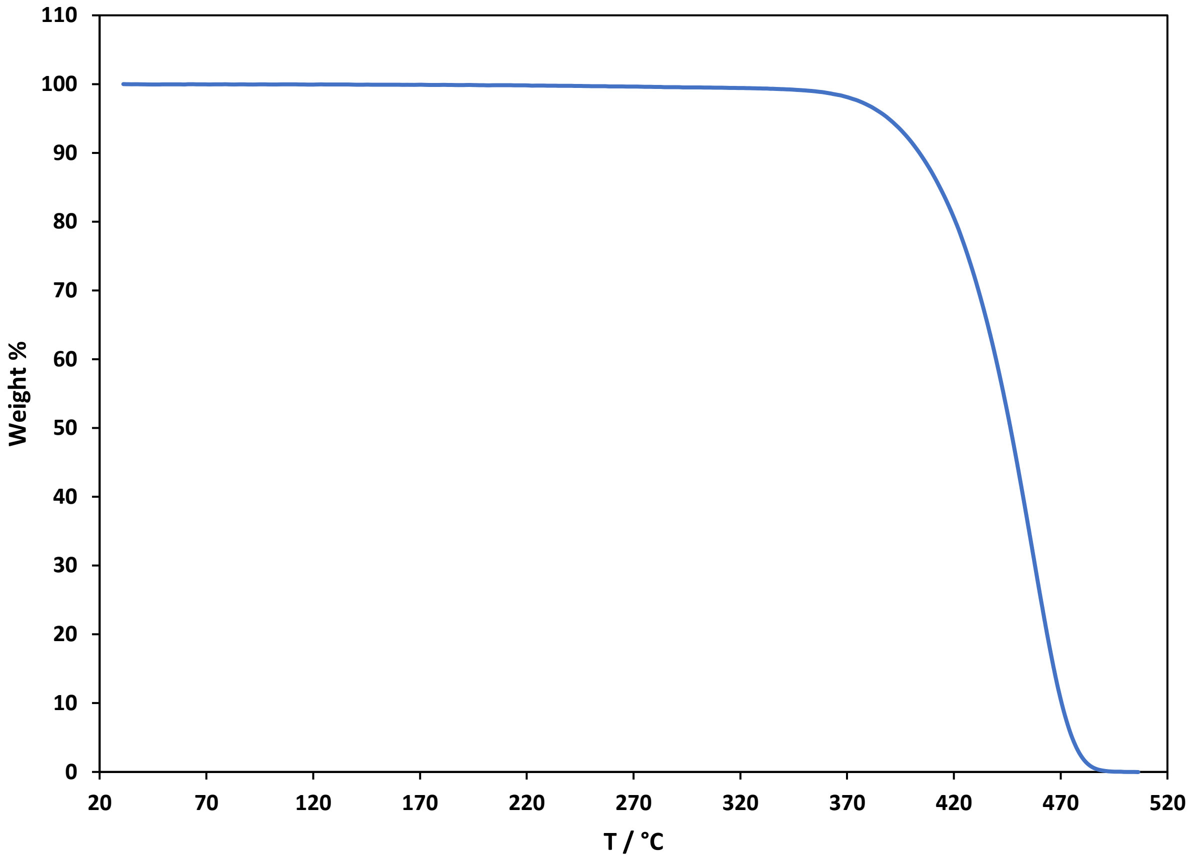

Fig. S22 TGA curve of poly(ethylene-*co*-*o*-xylene).

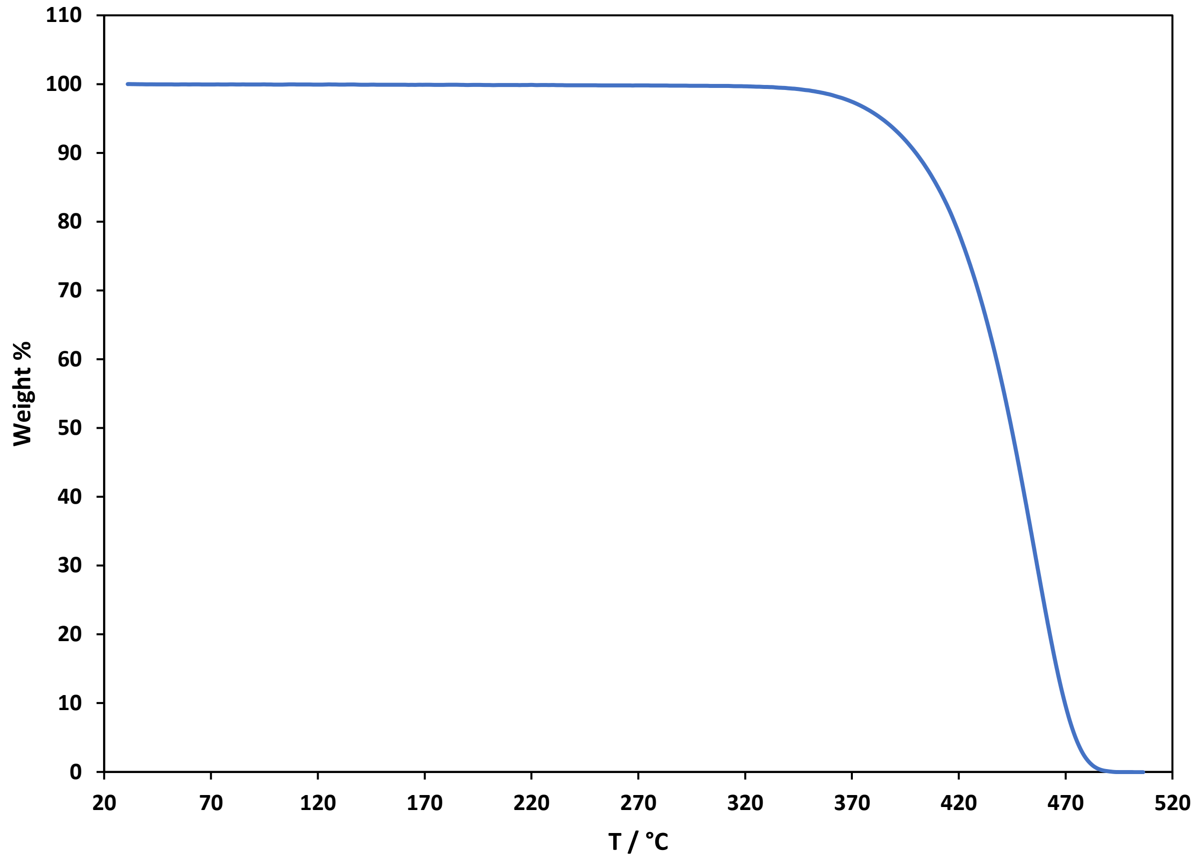

Fig. S23 TGA curve of poly(ethylene-*co*-*m*-xylene).

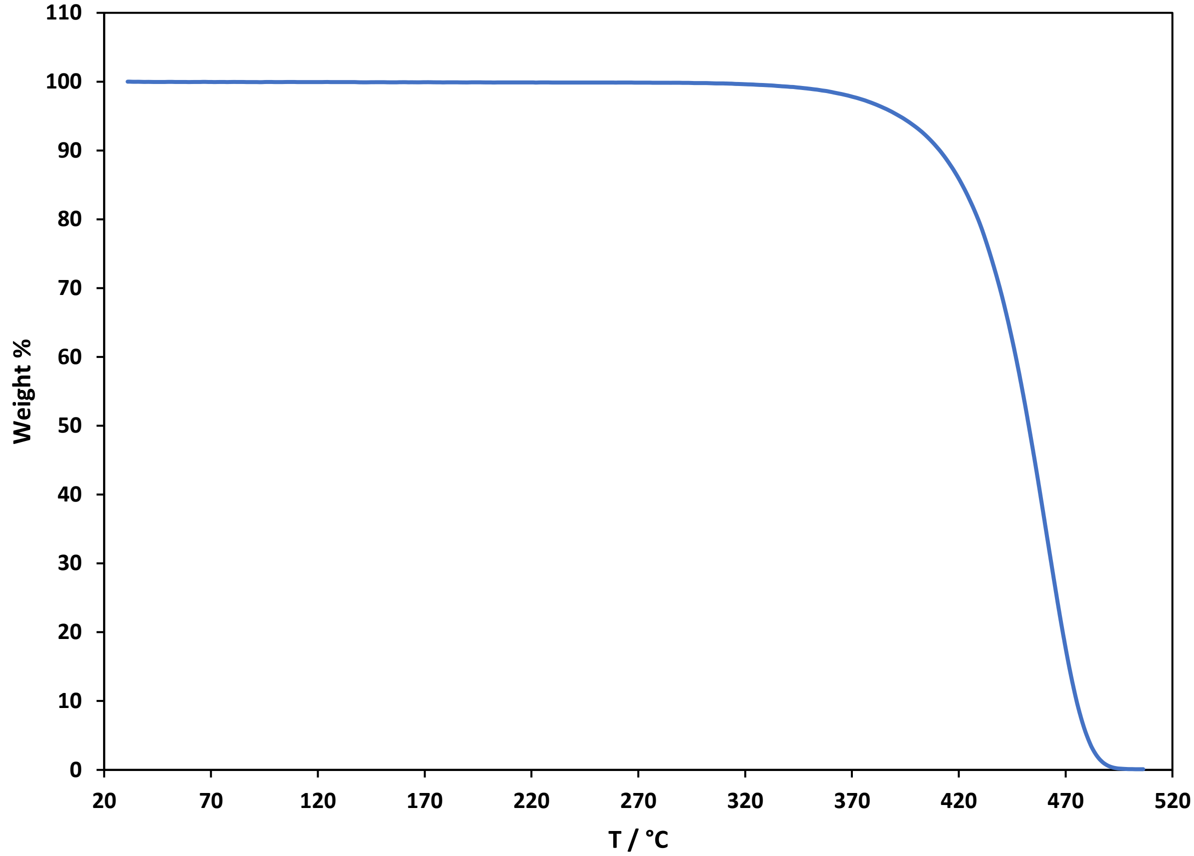

Fig. S24 TGA curve of poly(ethylene-*co*-*p*-xylene).

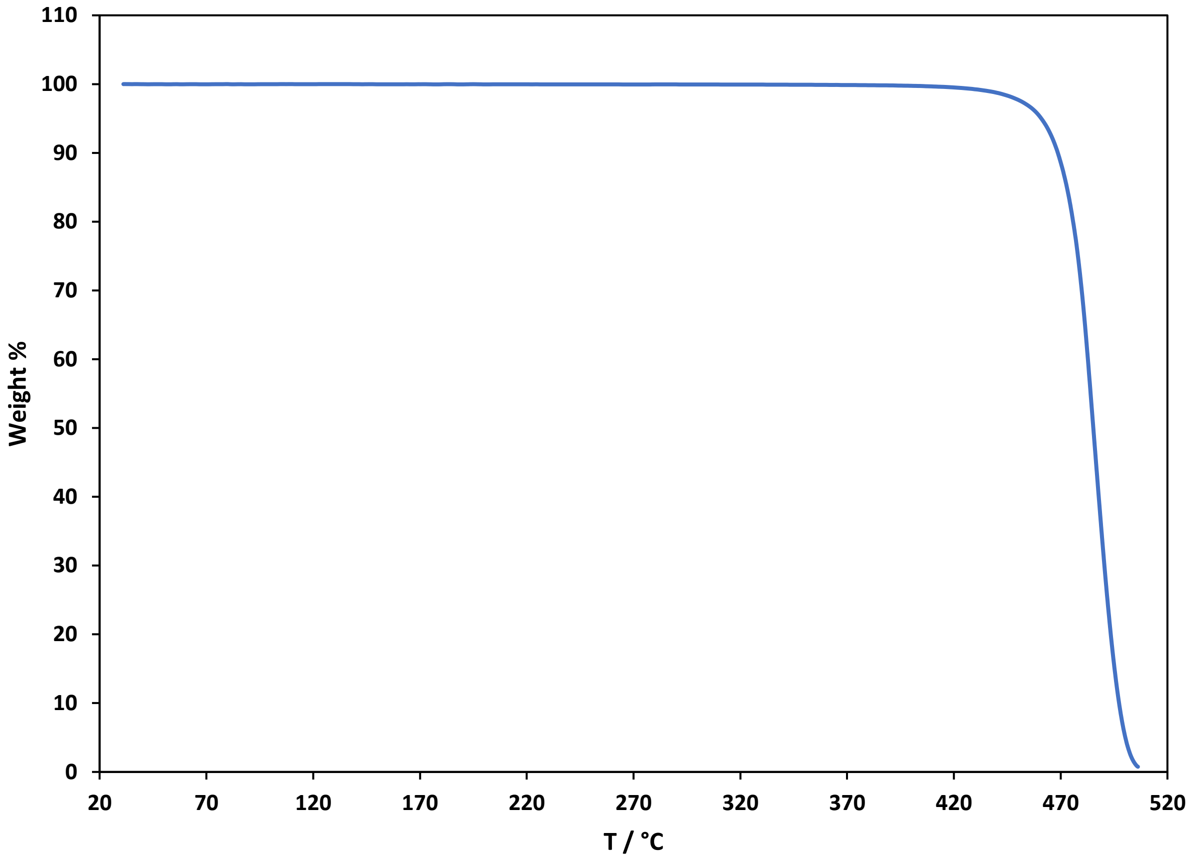

Fig. S25 TGA curve of PE.

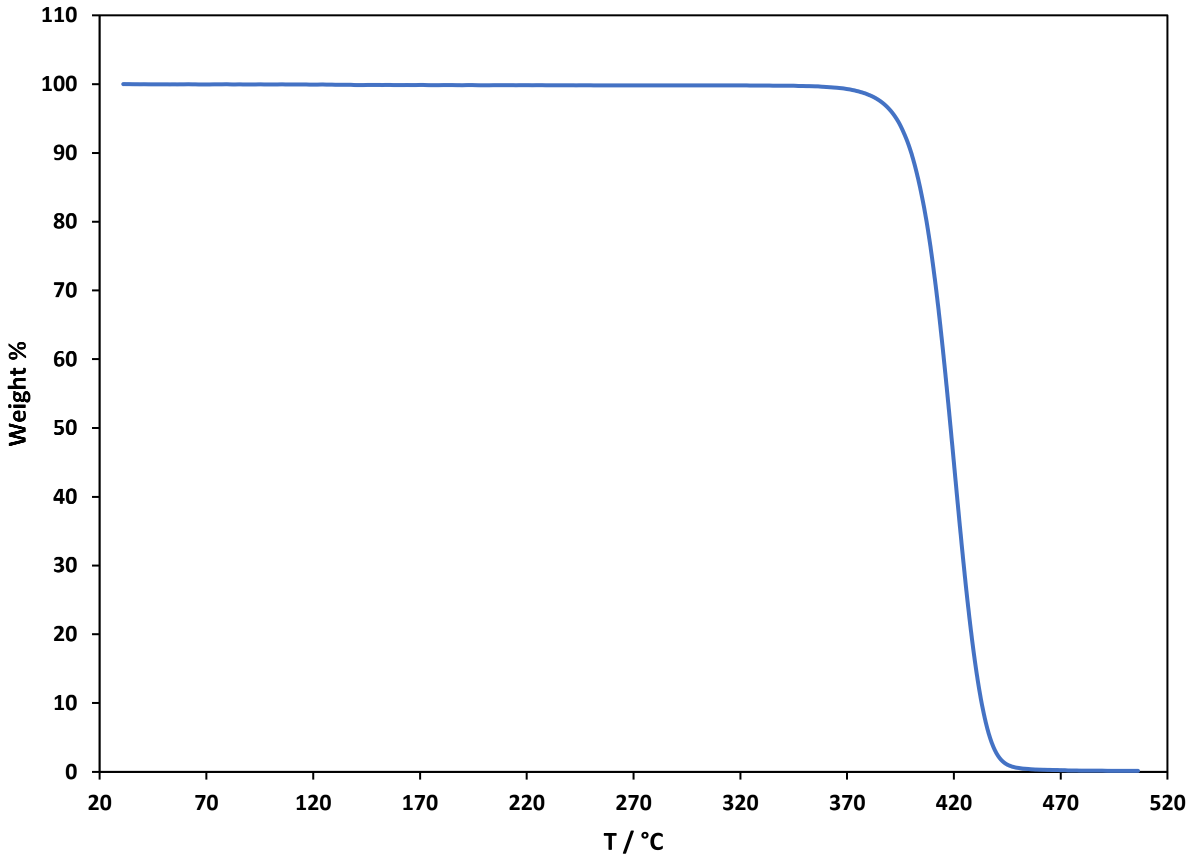

Fig. S26 TGA curve of PS.

6. ATR-IR Spectroscopy

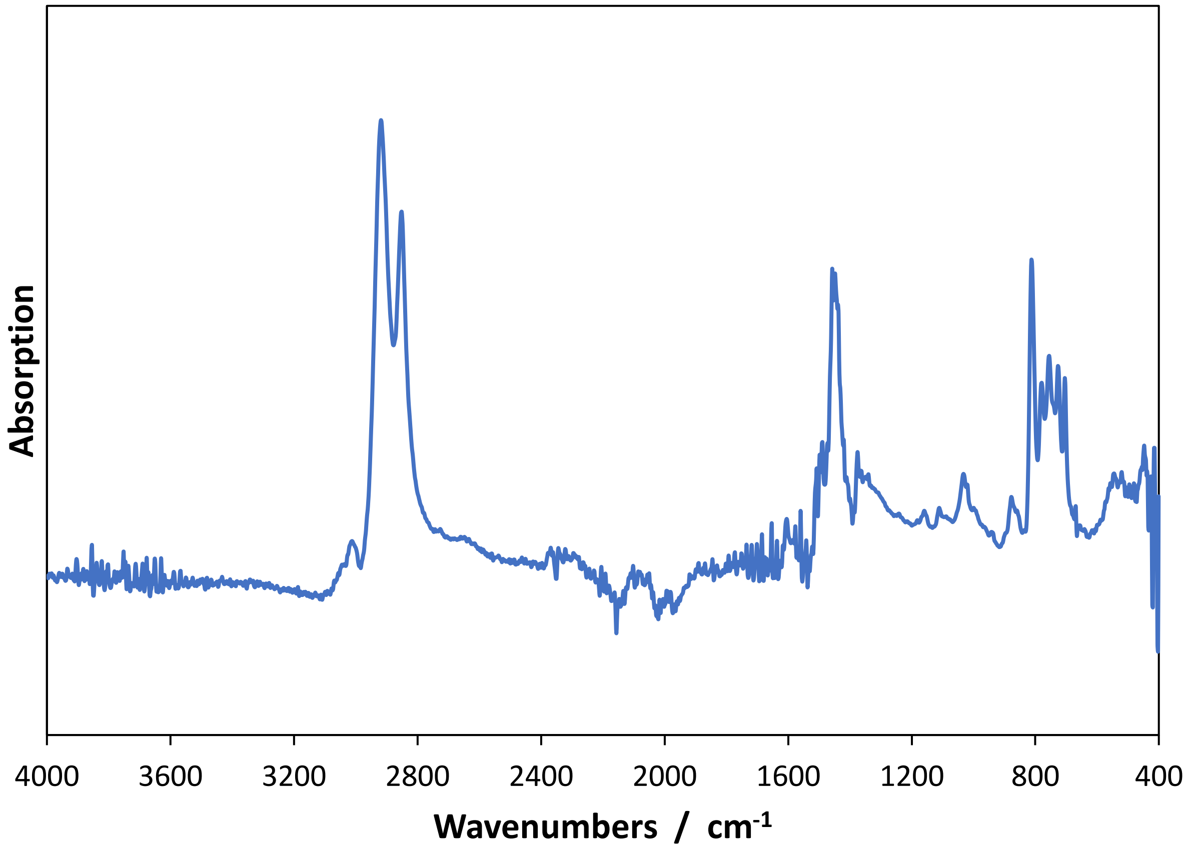

Fig. S27 ATR IR spectrum of poly(ethylene-*co*-toluene).

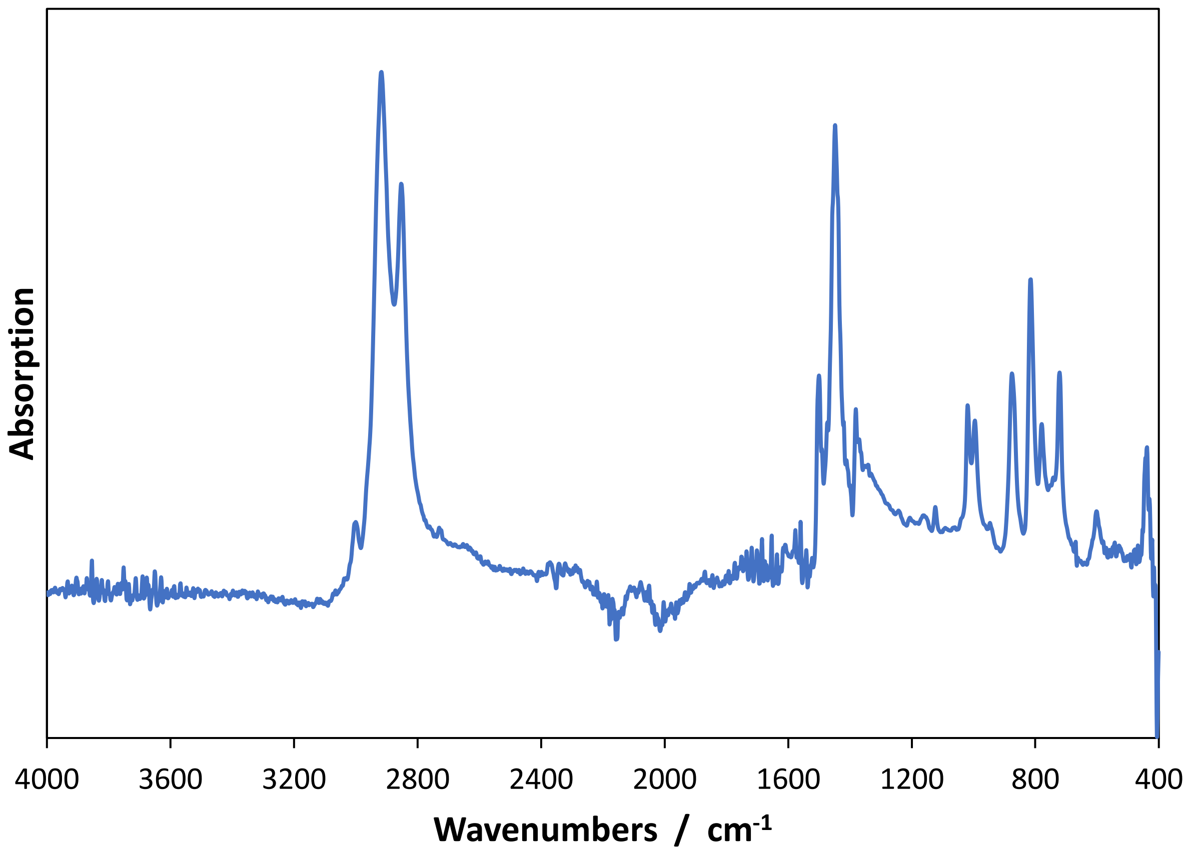

Fig. S28 ATR IR spectrum of poly(ethylene-*co*-*o*-xylene).

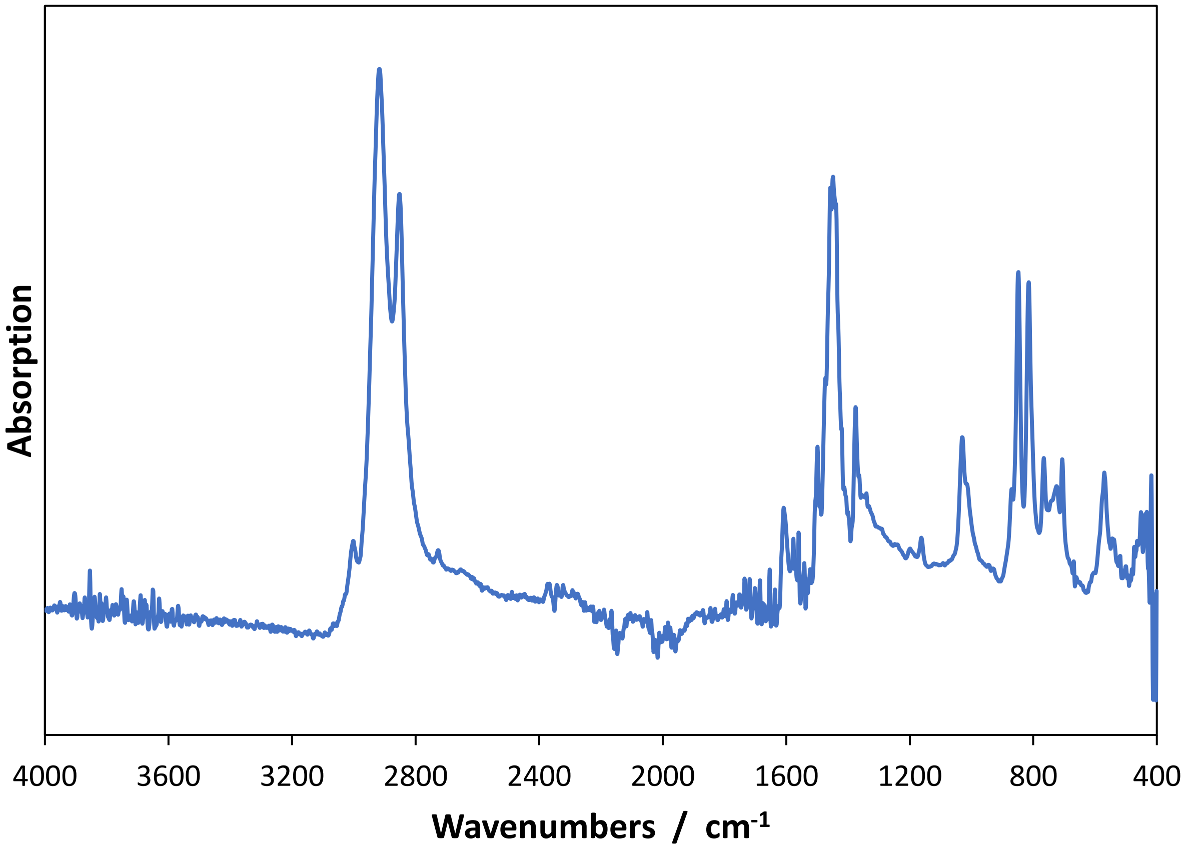

Fig. S29 ATR IR spectrum of poly(ethylene-*co*-*m*-xylene).

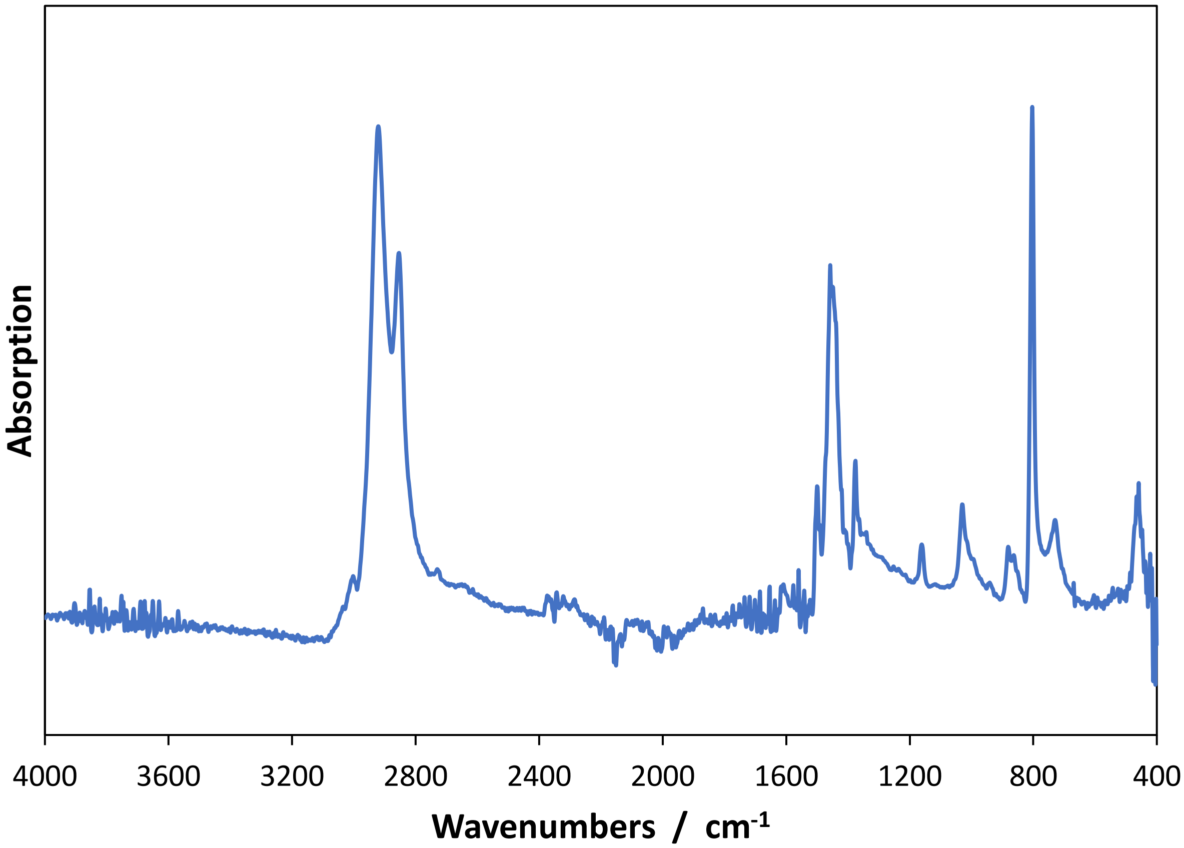

Fig. S30 ATR IR spectrum of poly(ethylene-*co*-*p*-xylene).

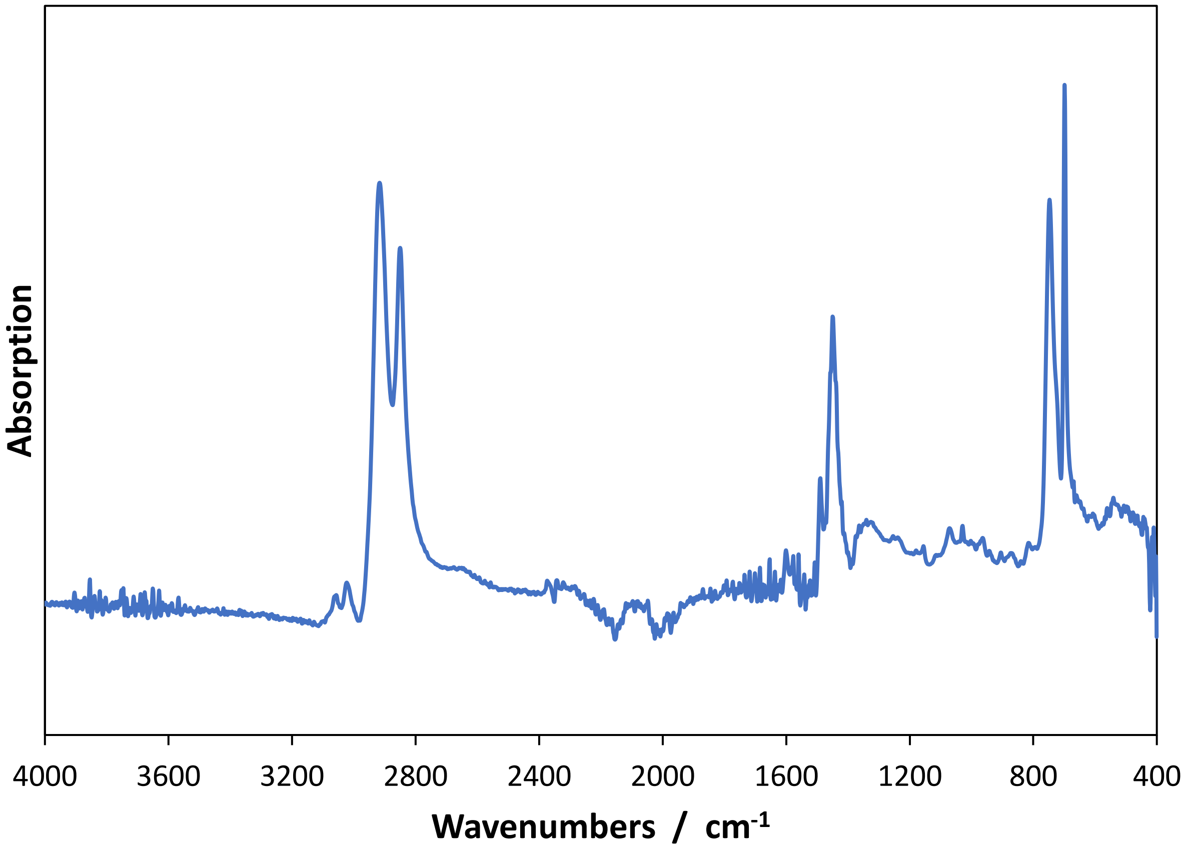

Fig. S31 ATR IR spectrum of product isolated from tandem hydrodechlorination/Friedel-Crafts alkylation of painted PVC toys.

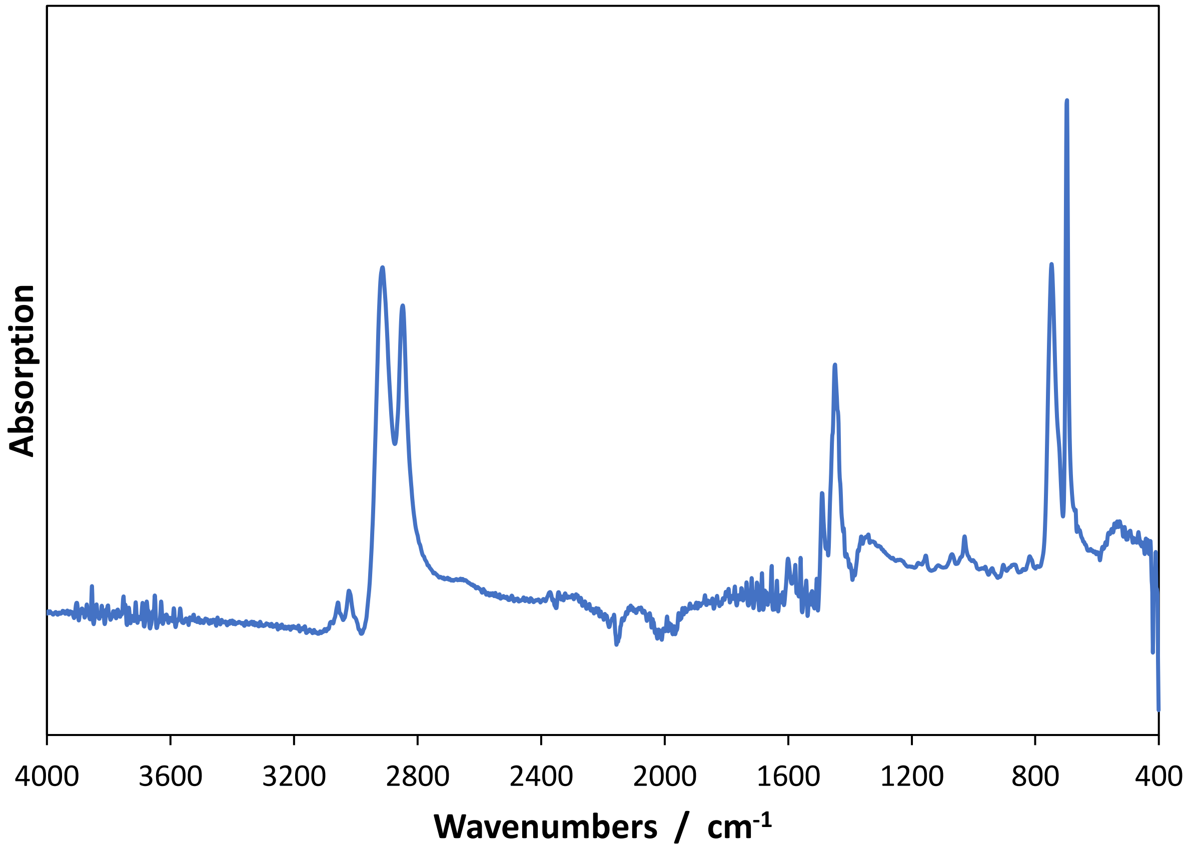

Fig. S32 ATR IR spectrum of poly(ethylene-*co*-styrene) prepared under bench conditions.

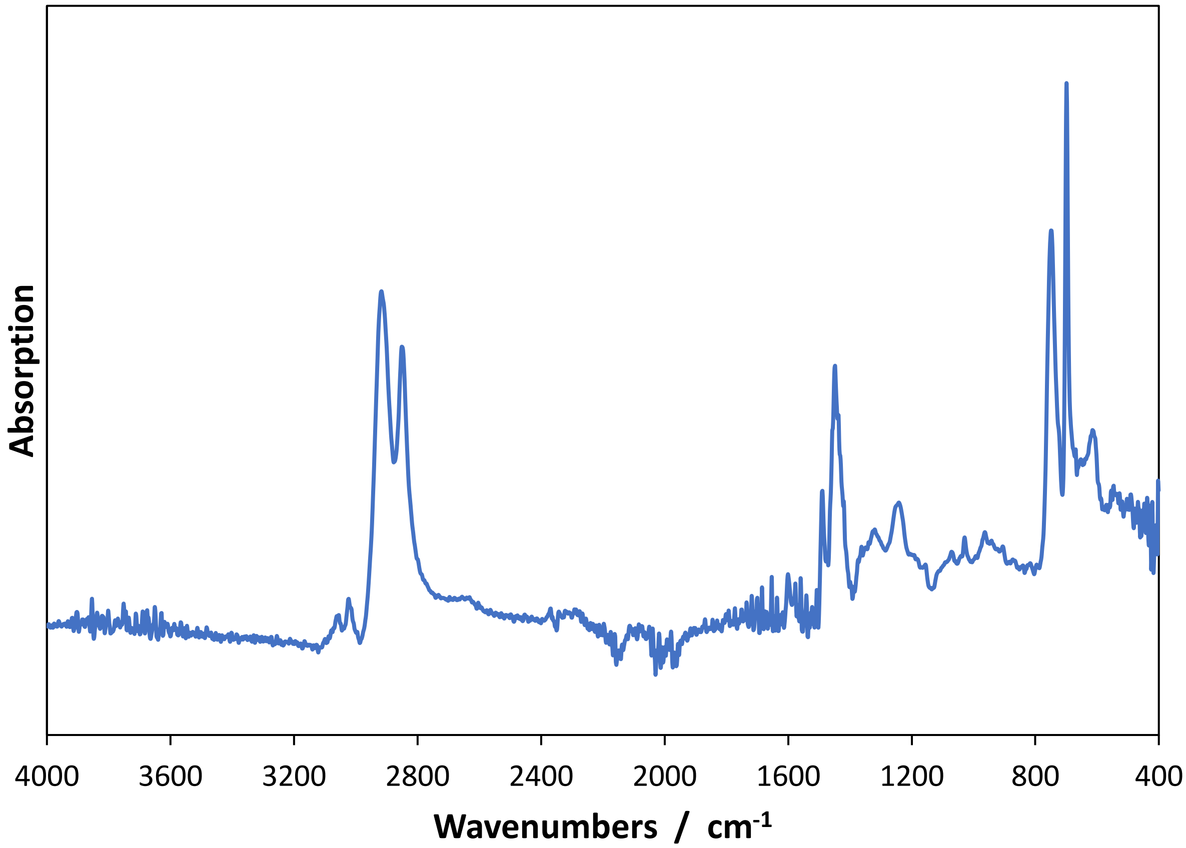

Fig. S33 ATR IR spectrum of poly(vinyl chloride-*co*-ethylene-*co*-styrene) with a 23:61:16 respective monomer ratio.

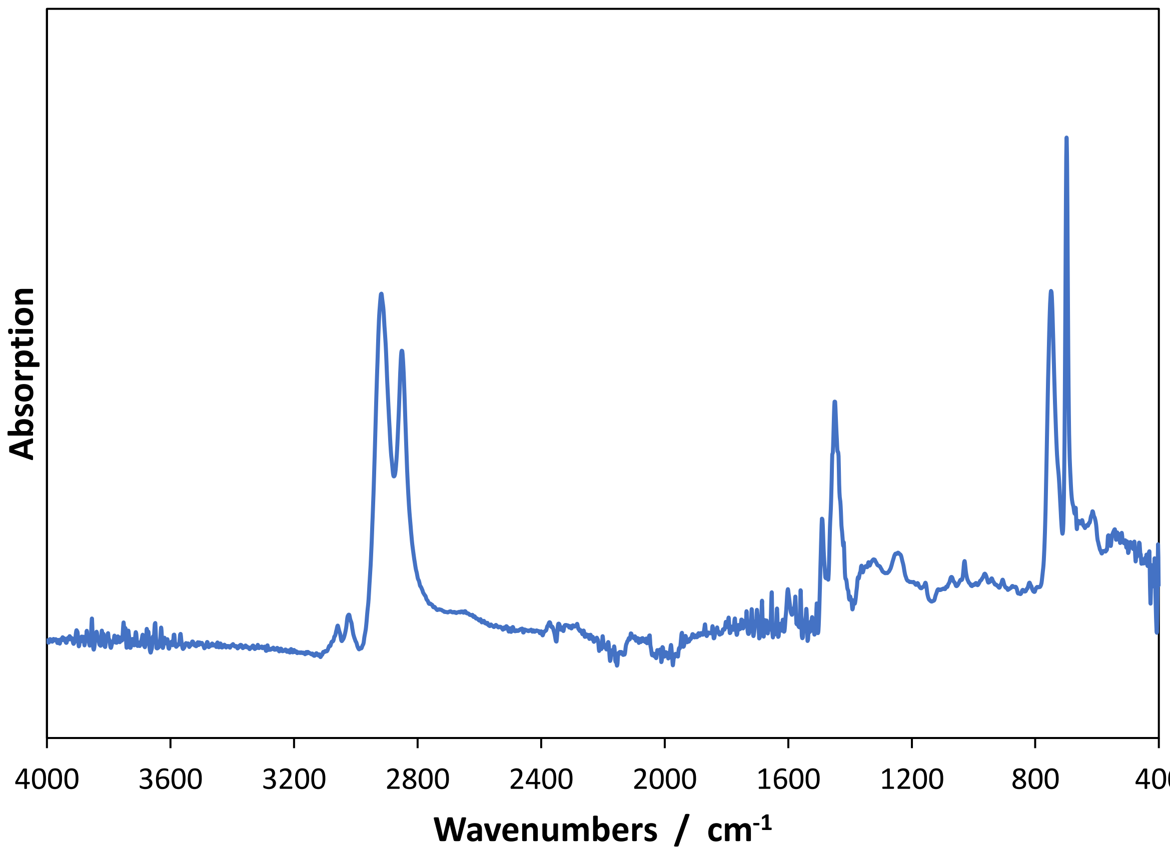

Fig. S34 ATR IR spectrum of poly(vinyl chloride-*co*-ethylene-*co*-styrene) with a 17:66:17 respective monomer ratio.

7. Energy-Dispersive X-ray Spectroscopy

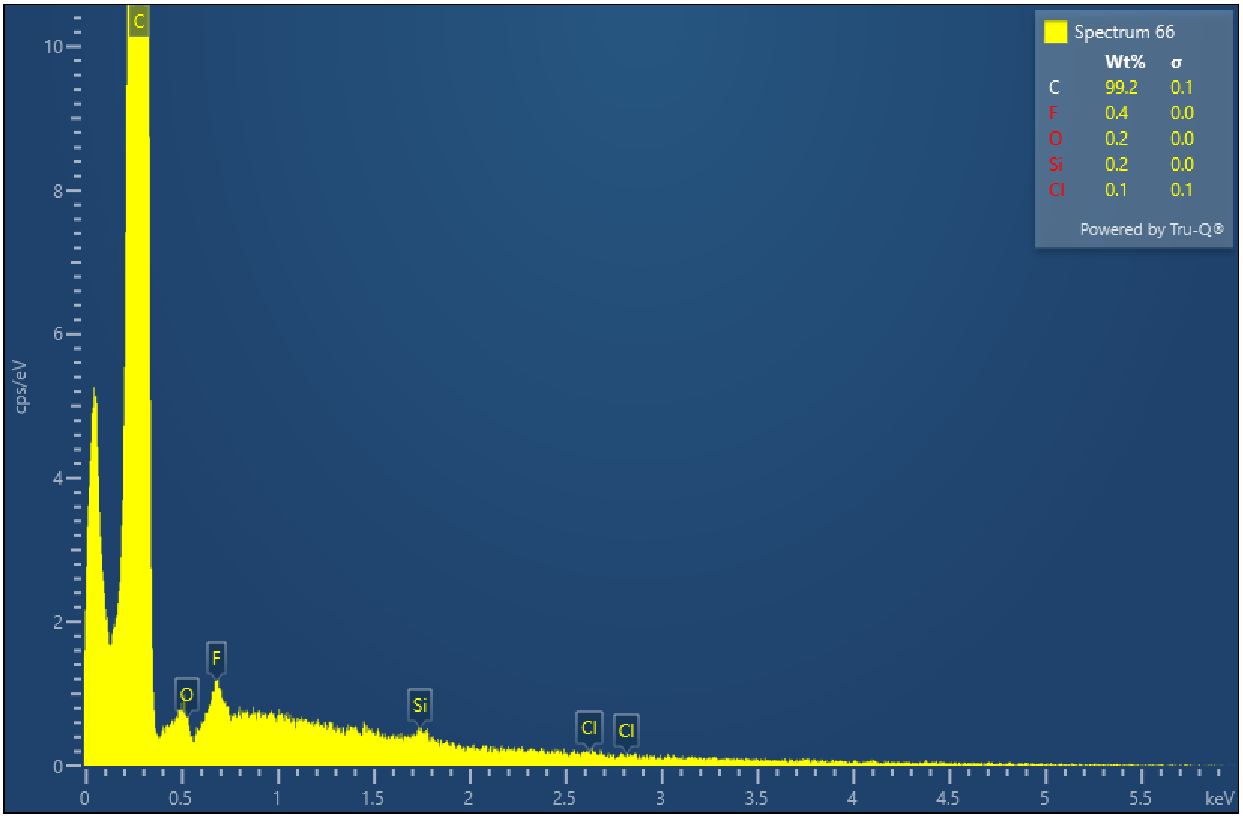

Fig. S35 Energy-dispersive X-ray spectrum of poly(ethylene-*co*-styrene).

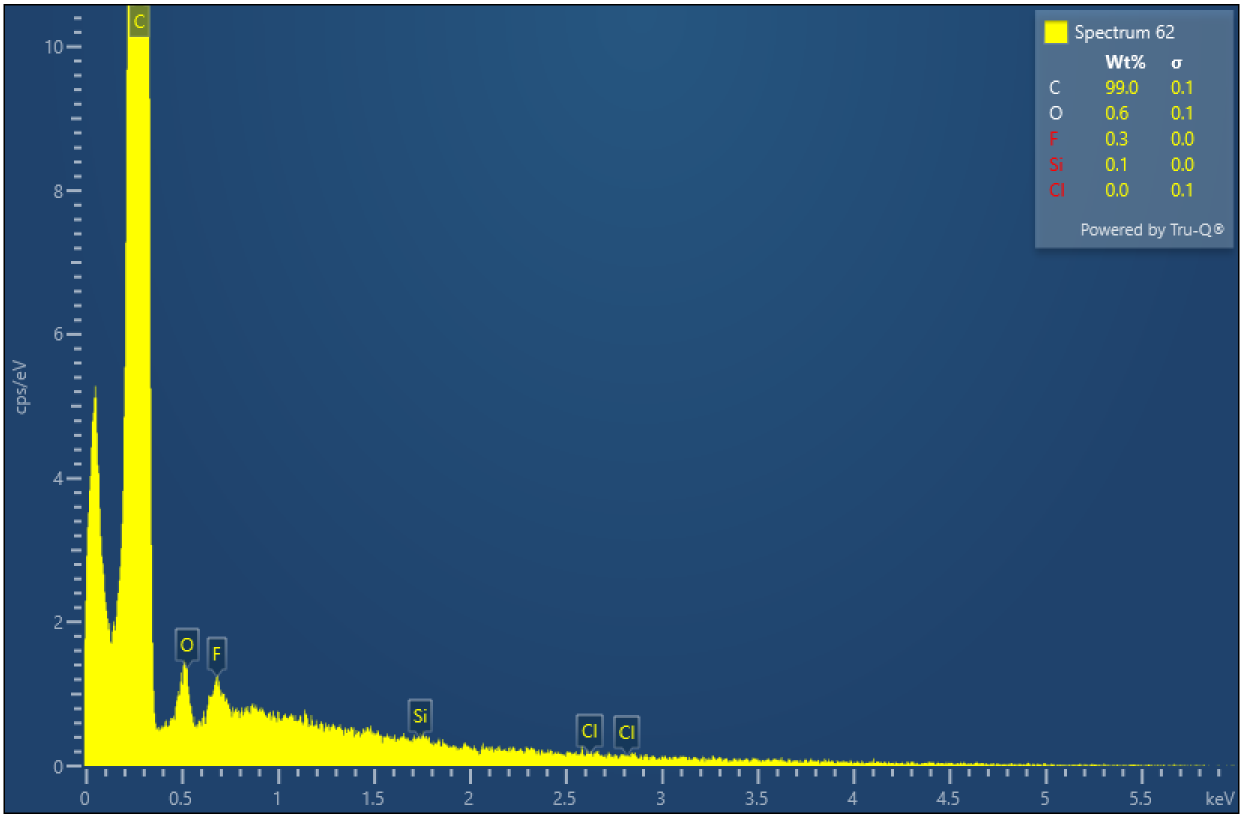

Fig. S36 Energy-dispersive X-ray spectrum of poly(ethylene-*co*-toluene).

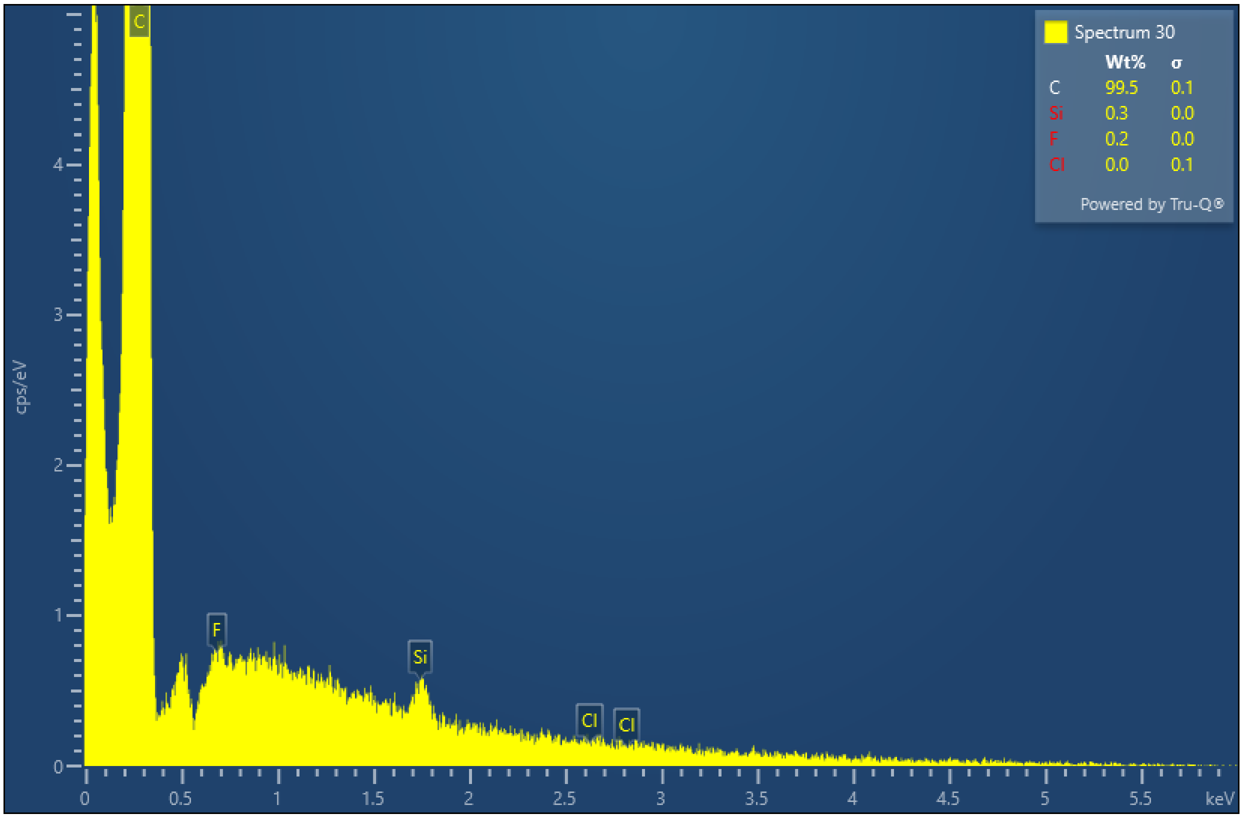

Fig. S37 Energy-dispersive X-ray spectrum of poly(ethylene-*co*-*o*-xylene).

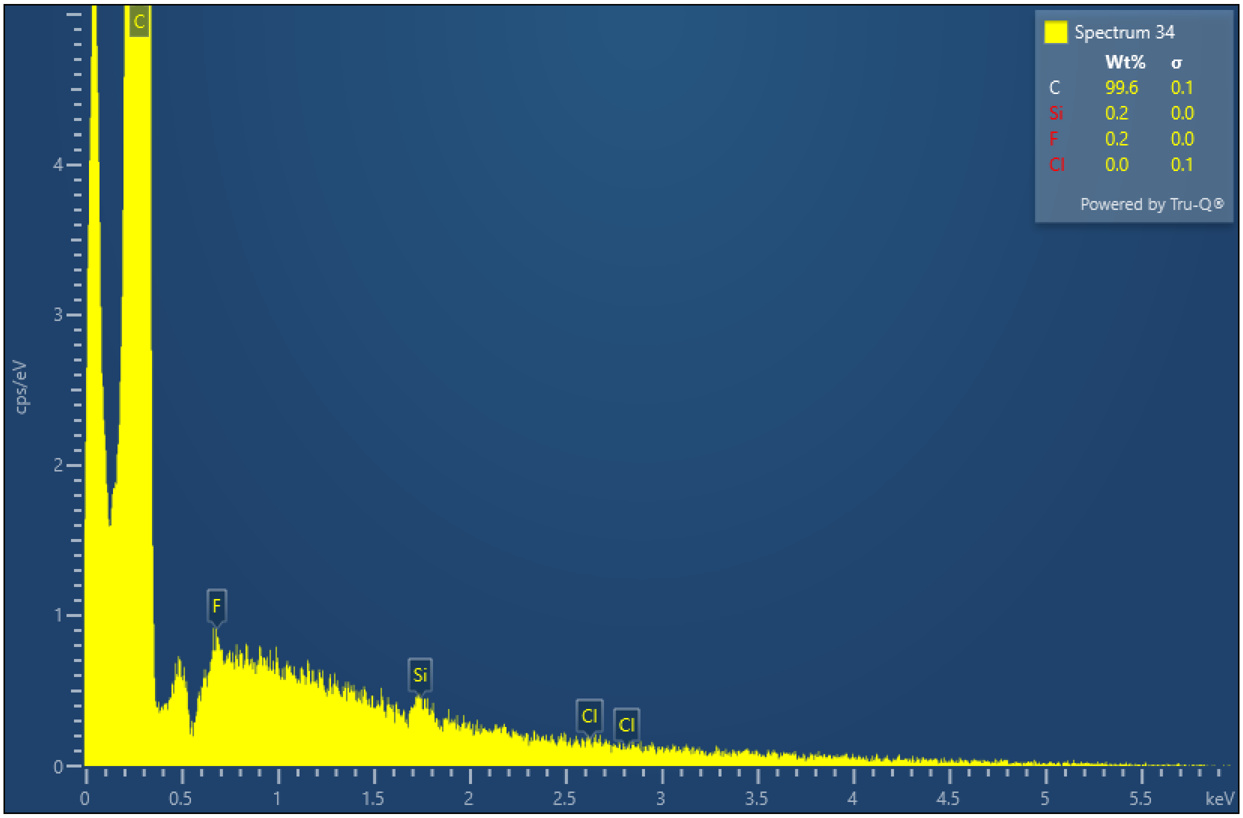

Fig. S38 Energy-dispersive X-ray spectrum of poly(ethylene-*co*-*m*-xylene).

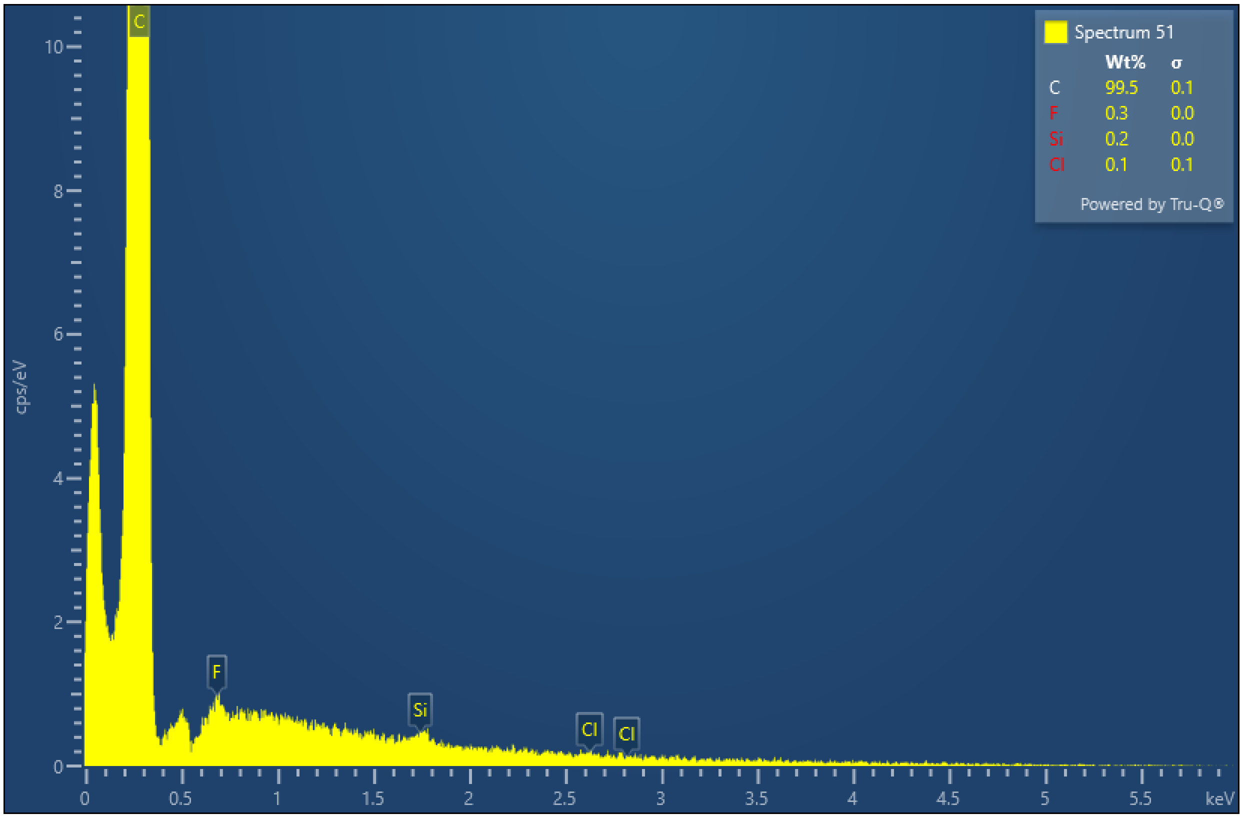

Fig. S39 Energy-dispersive X-ray spectrum of poly(ethylene-*co*-*p*-xylene).

8. Gel Permeation Chromatography

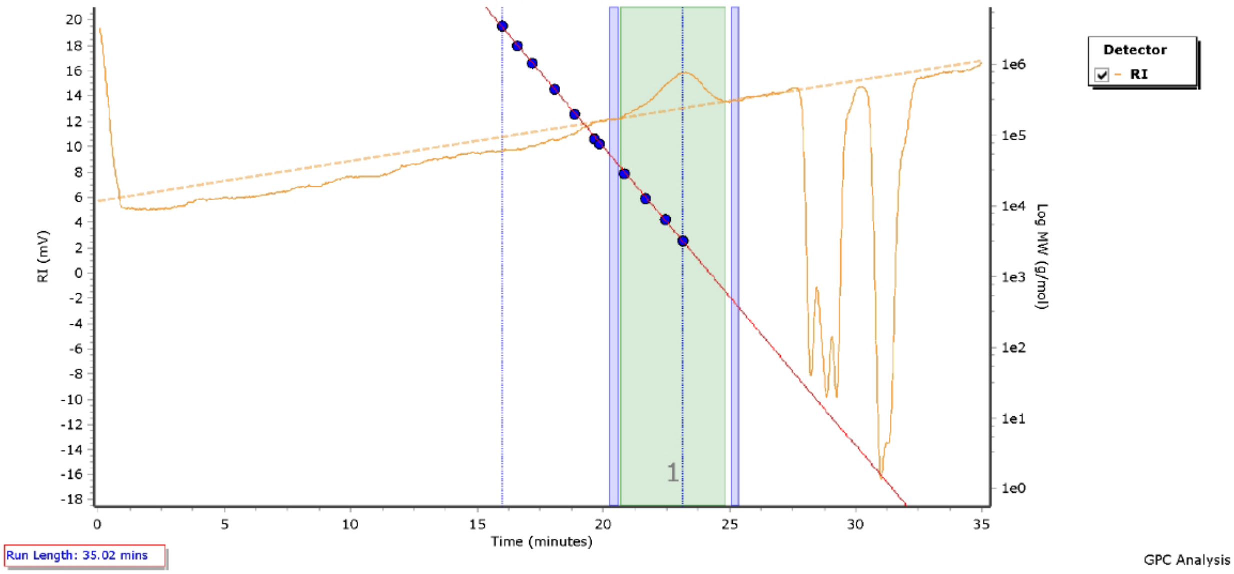

Fig. S40 GPC trace of poly(ethylene-*co*-styrene).

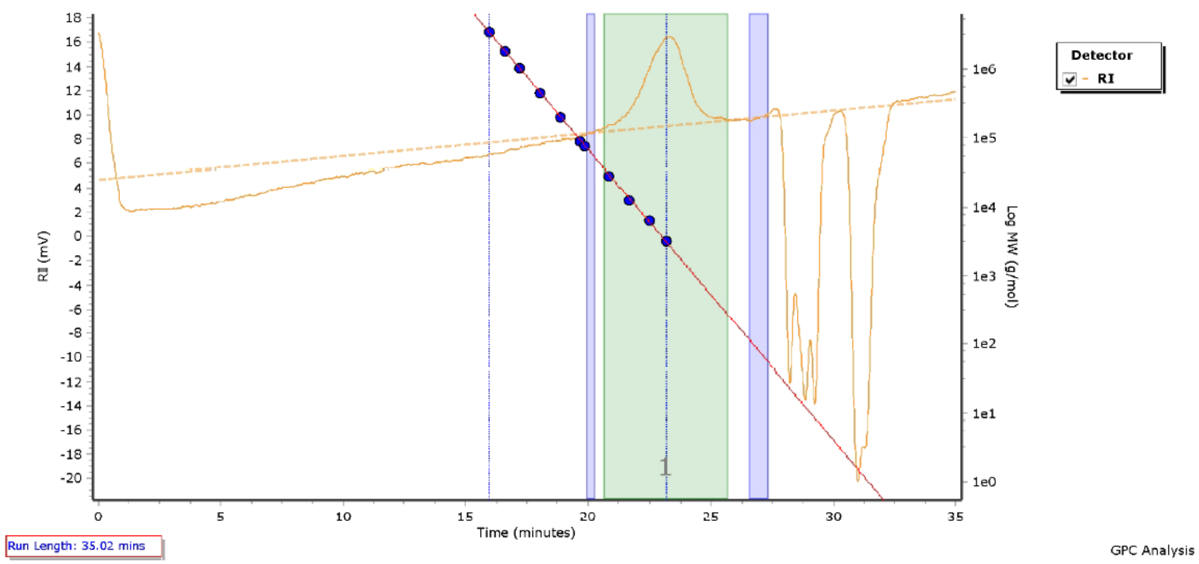

Fig. S41 GPC trace of poly(ethylene-*co*-toluene).

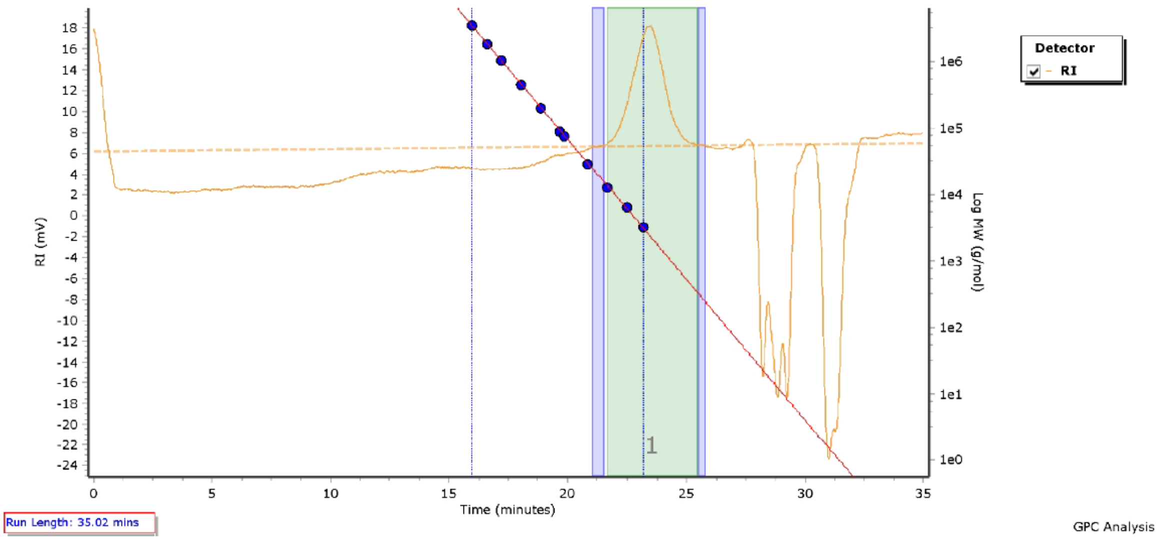

Fig. S42 GPC trace of poly(ethylene-*co*-*o*-xylene).

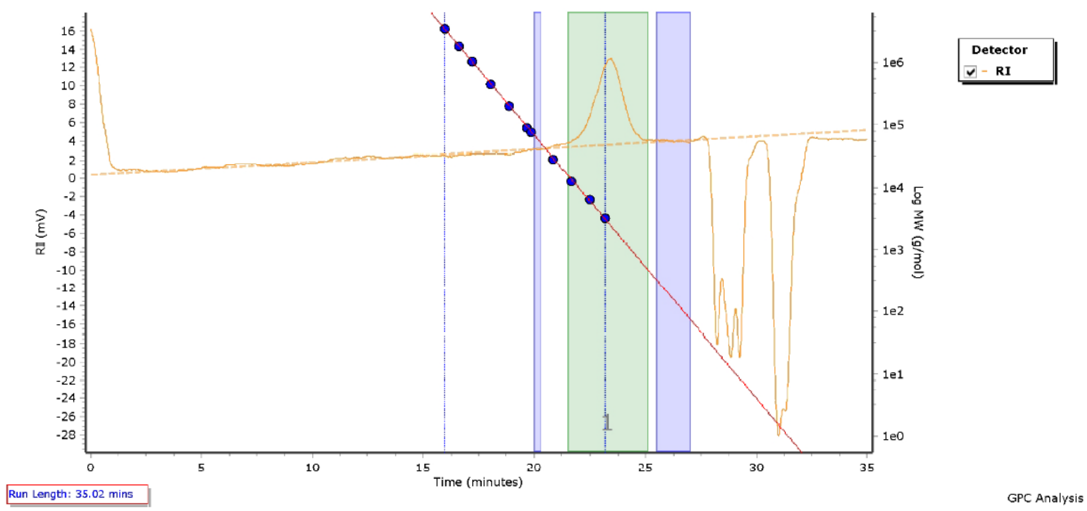

Fig. S43 GPC trace of poly(ethylene-*co*-*m*-xylene).

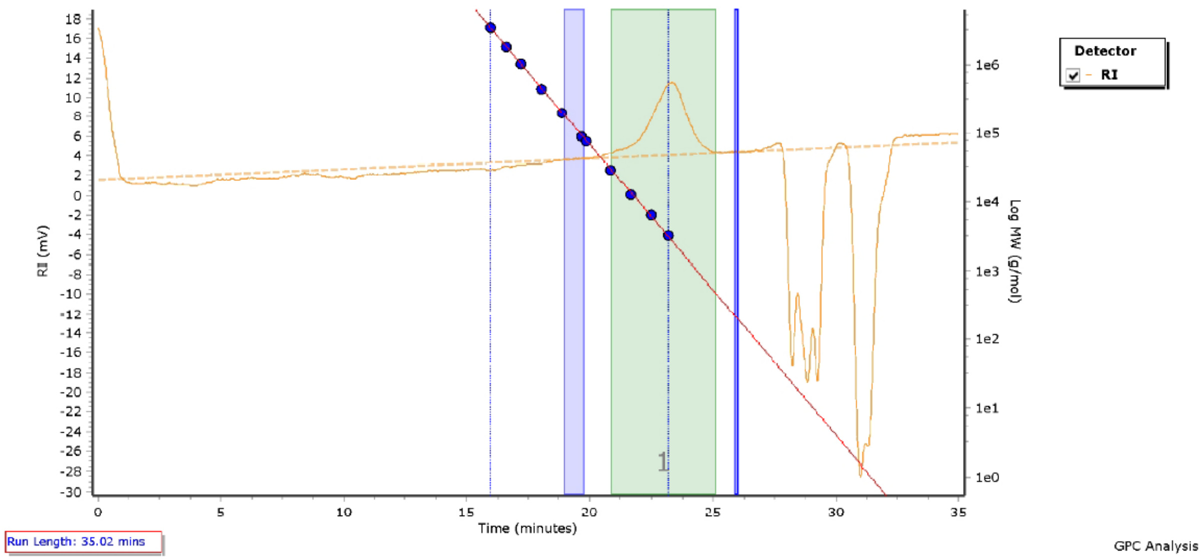

Fig. S44 GPC trace of poly(ethylene-*co*-*p*-xylene).

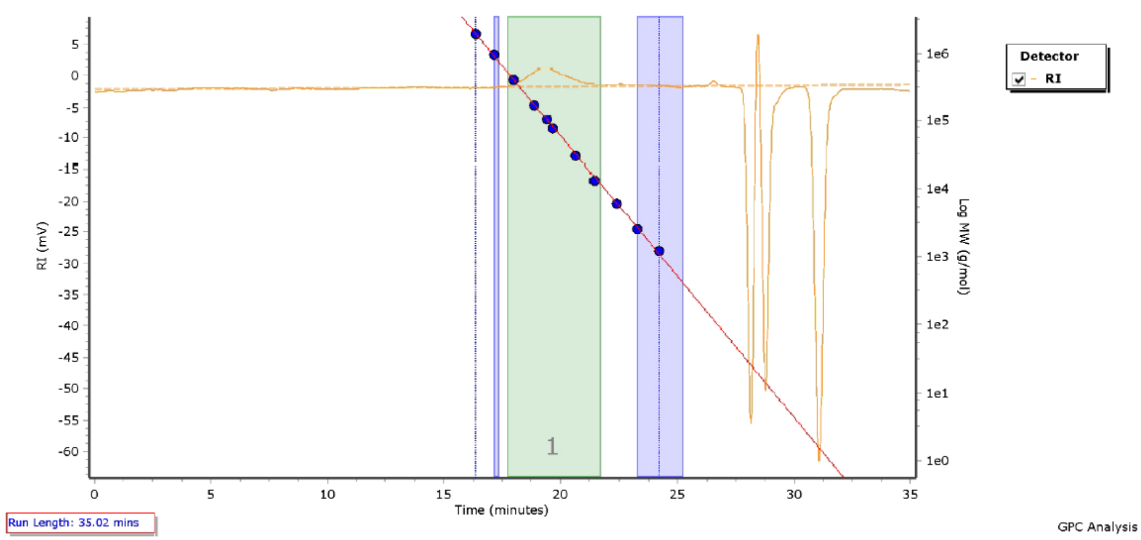

Fig. S45 GPC trace of poly(vinyl chloride) purchased from Aldrich.