Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Muconic acid esters as bio-based acrylate mimics

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A Nuclear Magnetic Resonance (NMR)

For all monomers and polymers synthesized within this research, ^{1}H and ^{13}C NMR were measured and displayed below. All peaks are defined by corresponding colored dots on the structure and NMR spectra.

A.1 Monomer synthesis

A.1.1 Diethyl muconate (DEM)

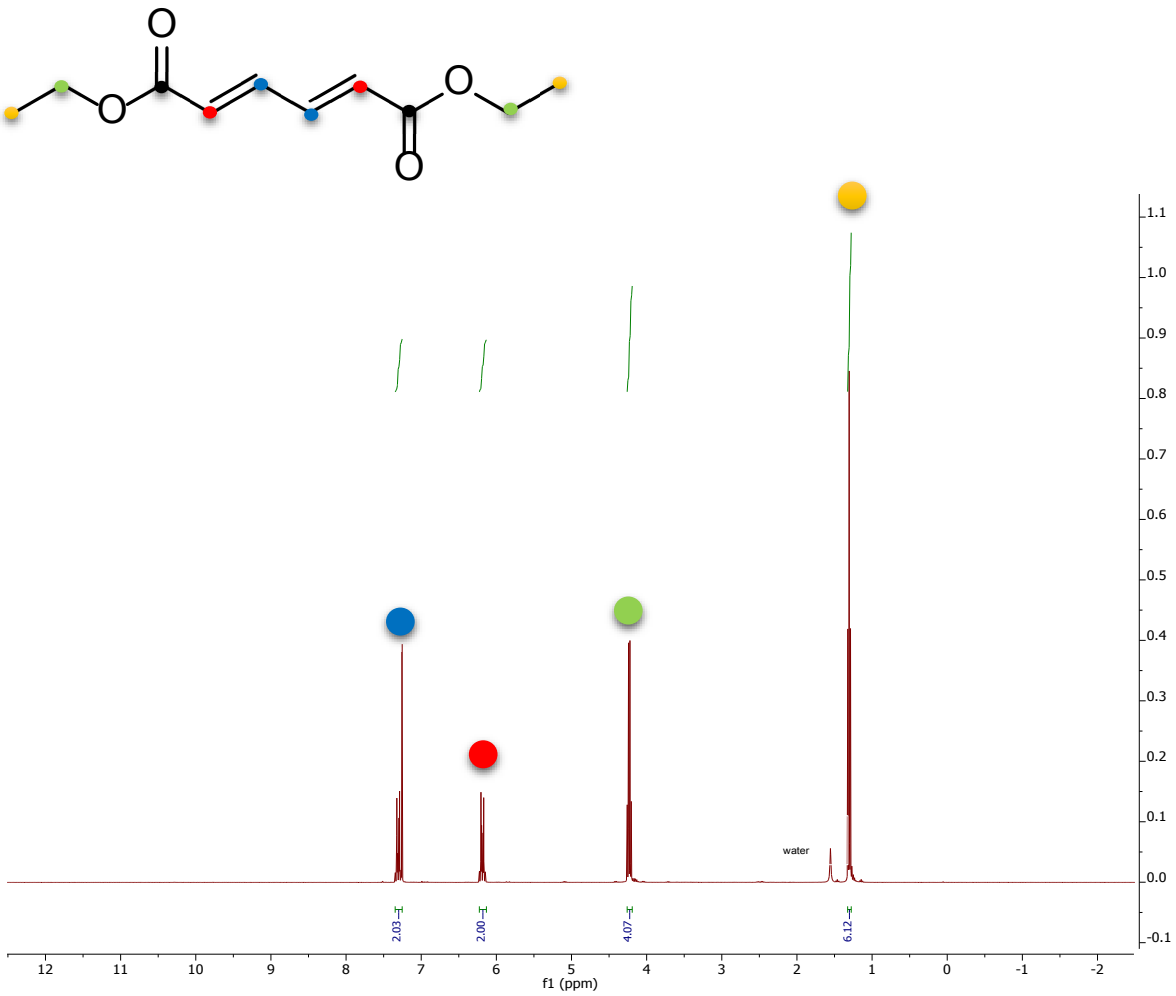


Figure S 1 ^{1}H NMR of diethyl muconate (DEM)

Supporting information

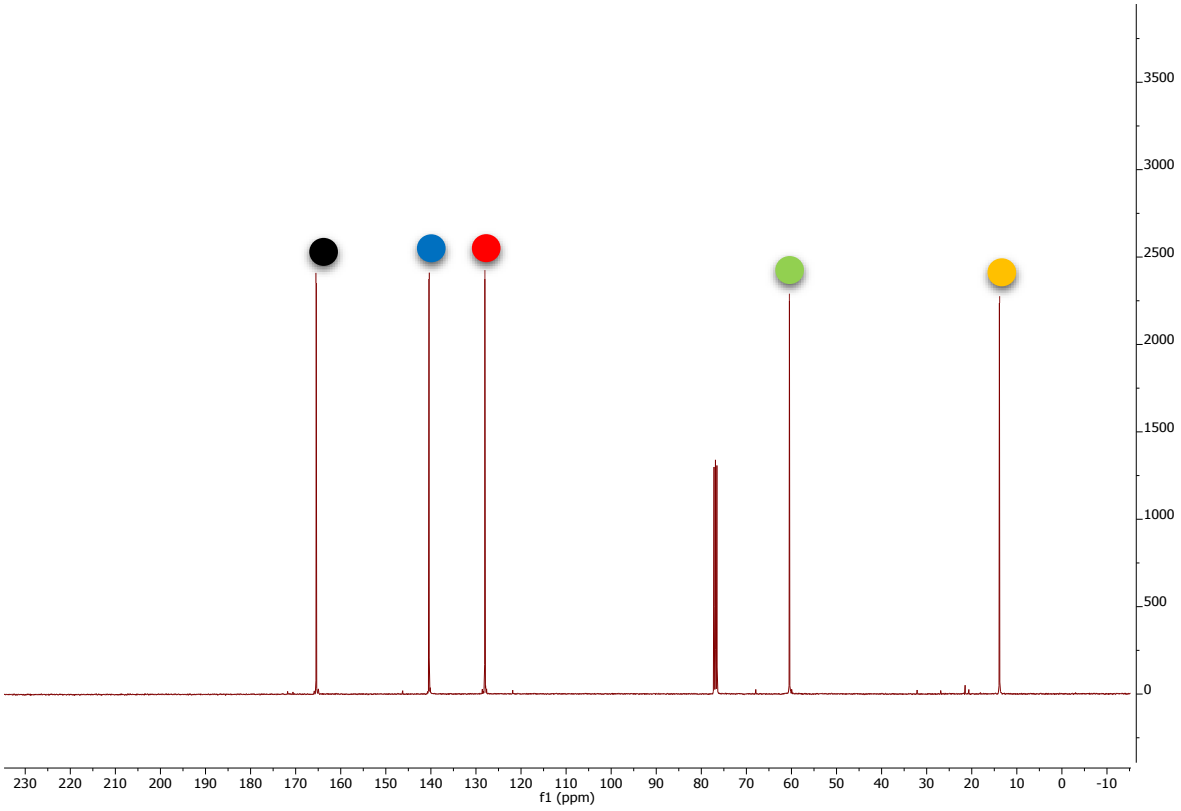
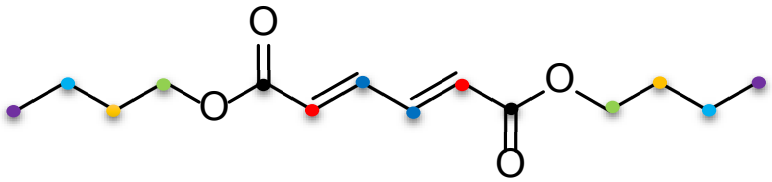


Figure S 2 ^{13}C NMR of diethyl muconate (DBM)

Supporting information

A.1.2 Dibutyl muconate (DBM)



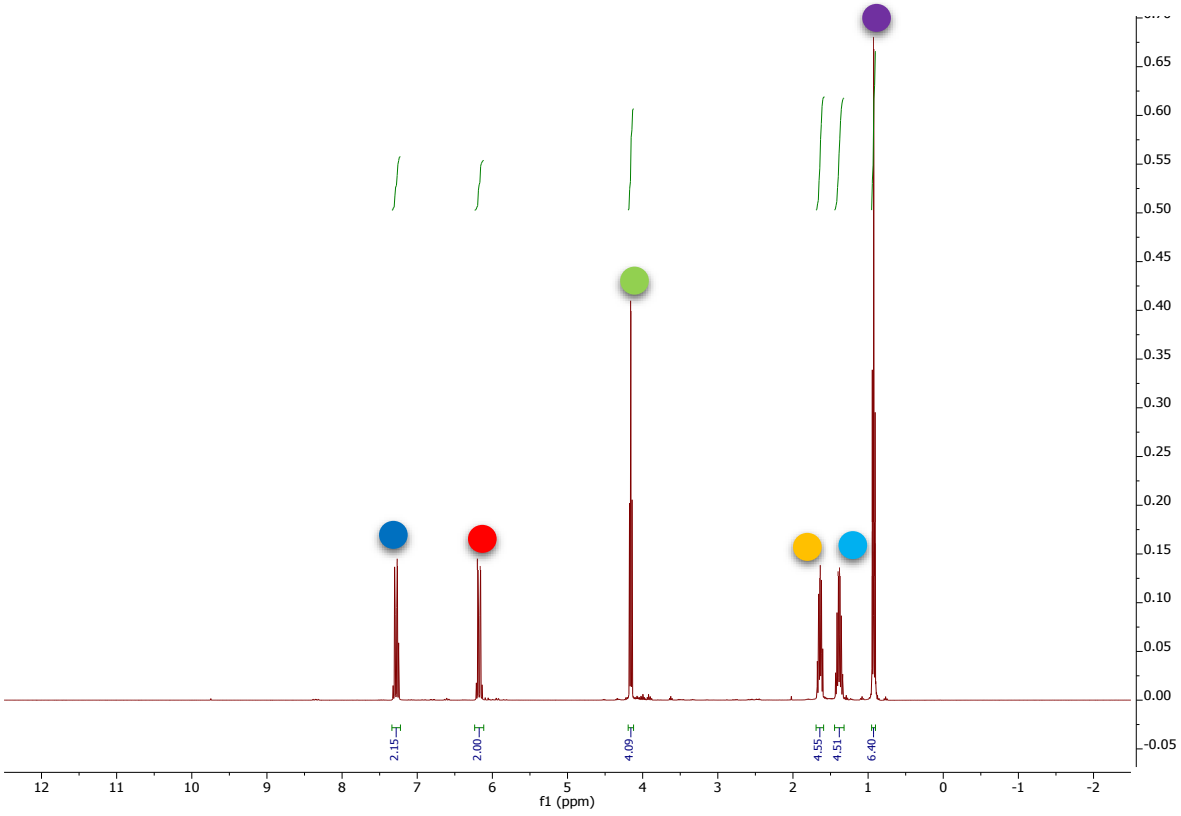


Figure S 3 ^{1}H NMR of dibutyl muconate (DBM)

Supporting information

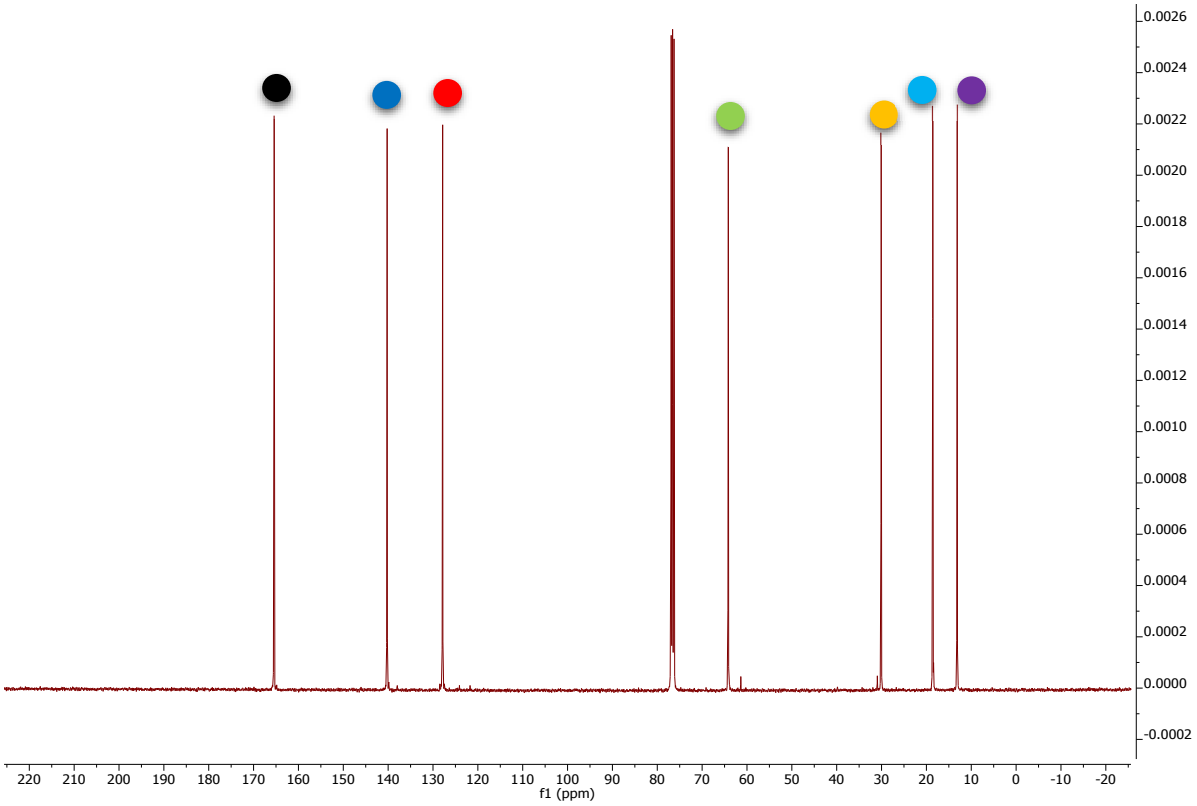


Figure S 4 ^{13}C NMR of dibutyl muconate (DBM)

Supporting information

A.1.3 Di-(2-ethylhexyl) muconate (DEHM)

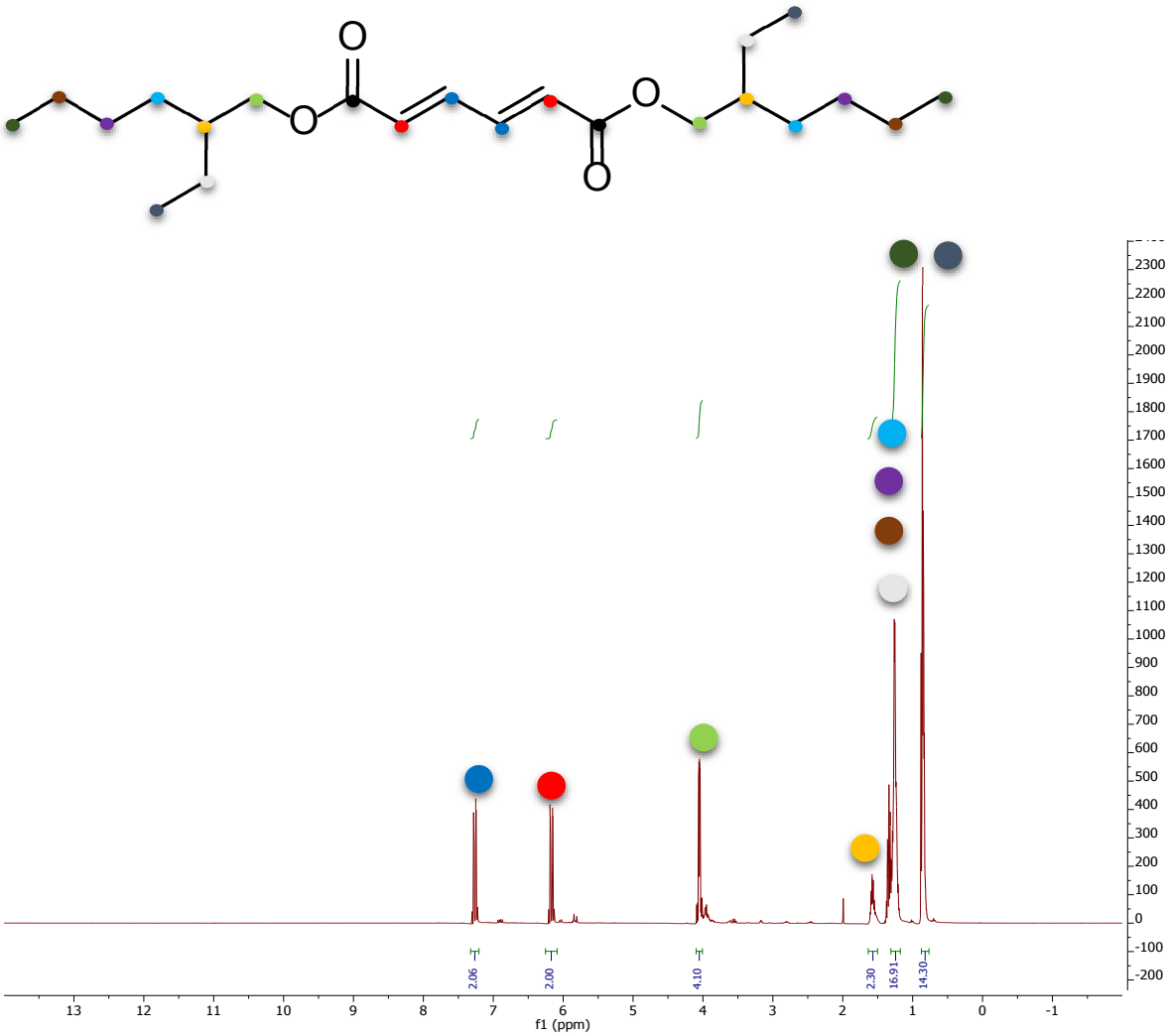


Figure S 5 ^{1}H NMR of di-(2-ethylhexyl) muconate (DEHM)

Supporting information

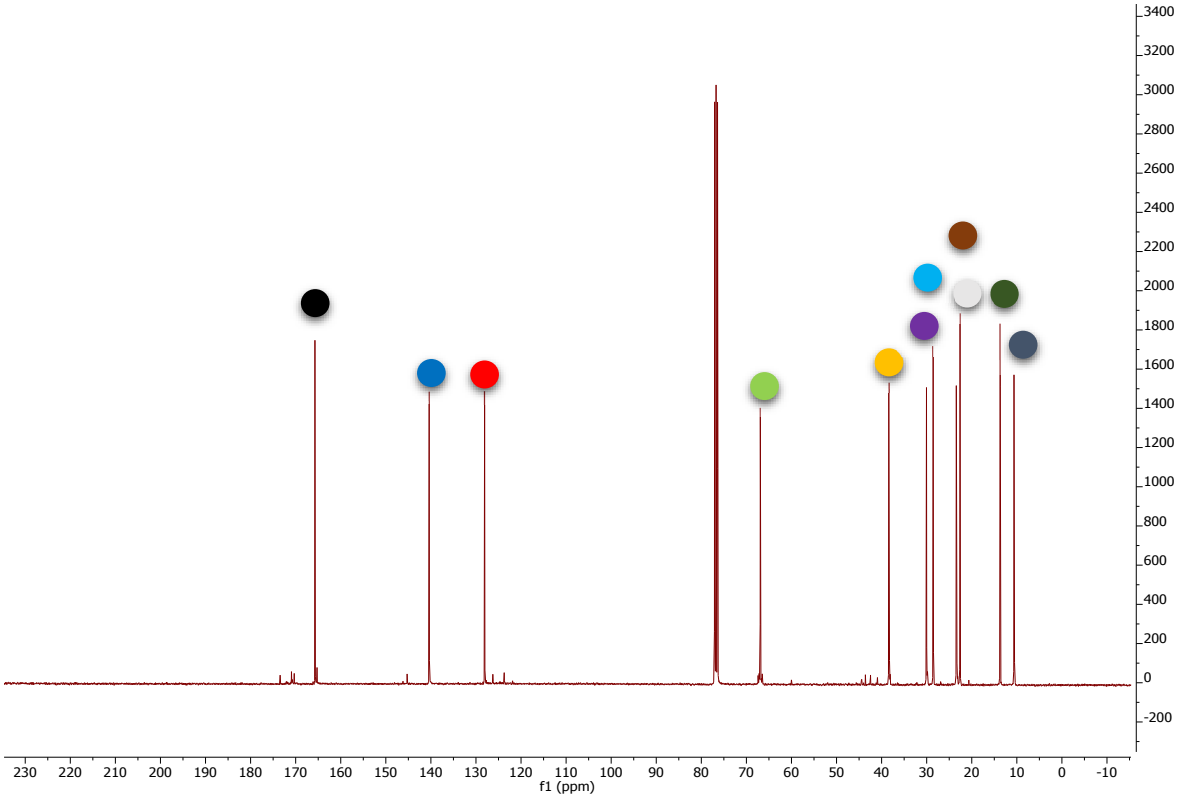
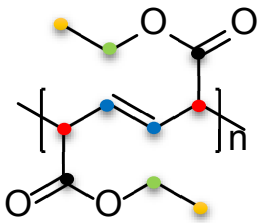


Figure S 6 ^{13}C NMR of di-(2-ethylhexyl) muconate (DEHM)

A.2 Polymerization

A.2.1 PDEM



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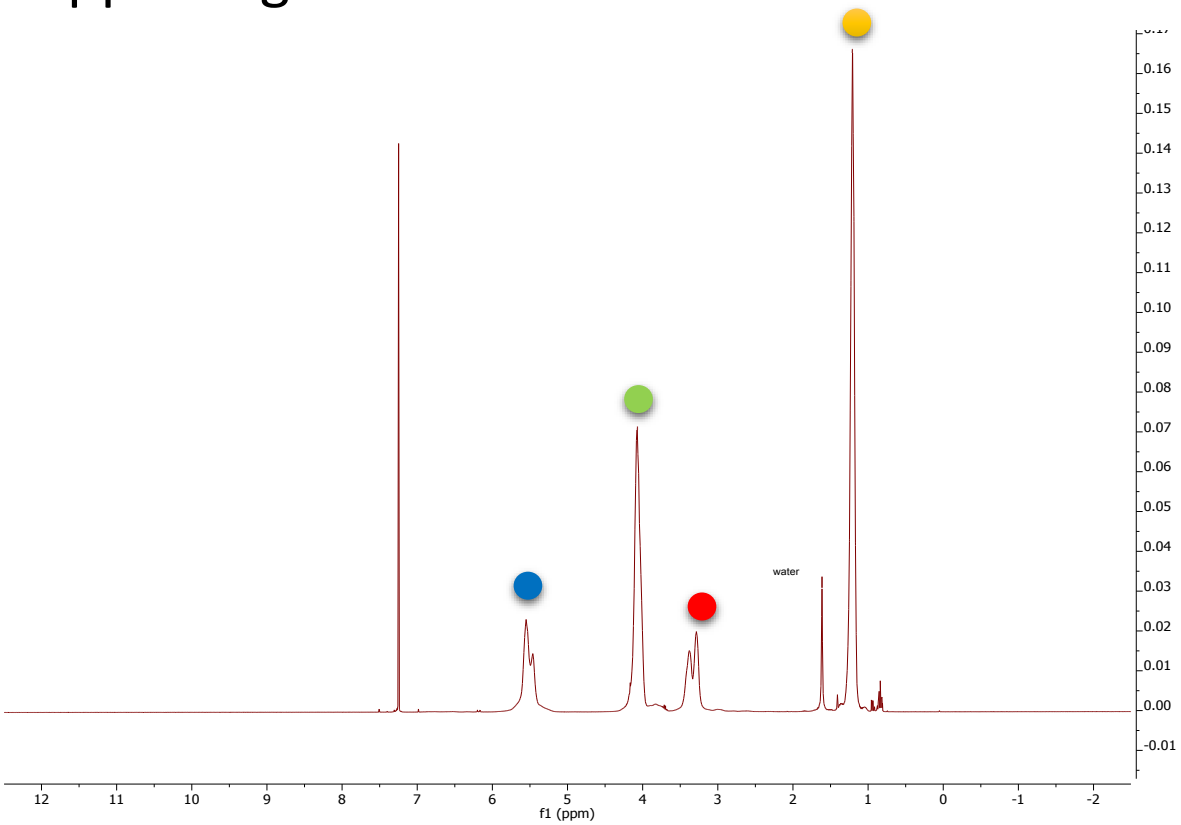


Figure S 7 ^{1}H NMR of poly(diethyl muconate) (PDEM)

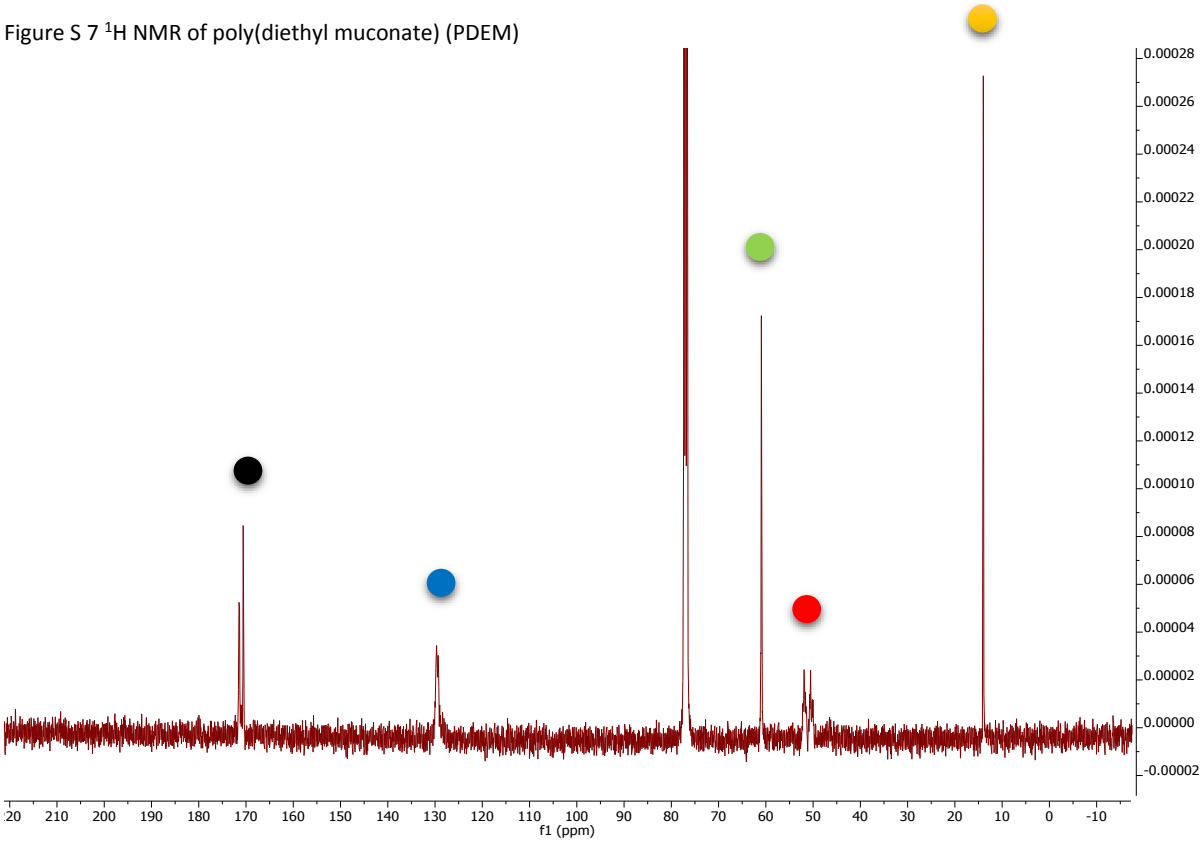


Figure S 8 ^{13}C NMR of poly(diethyl muconate) (PDEM)

Supporting information

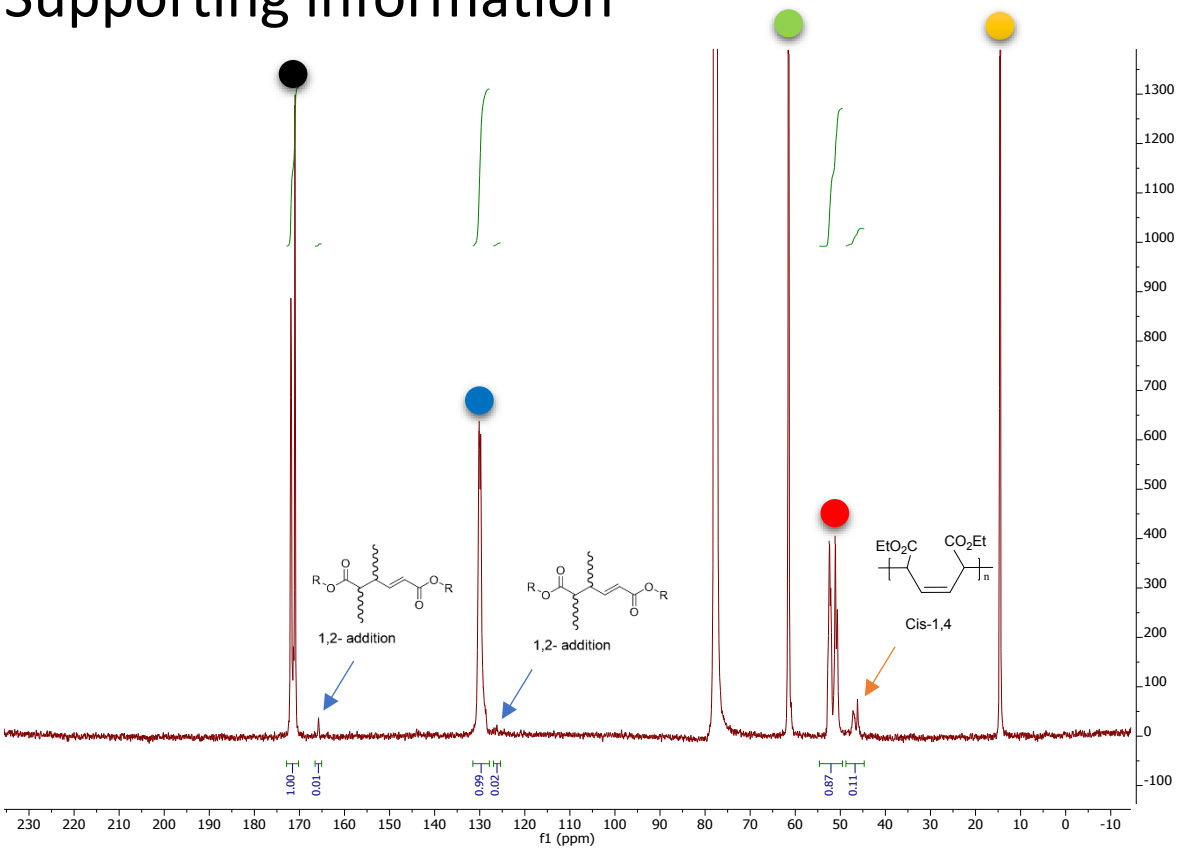
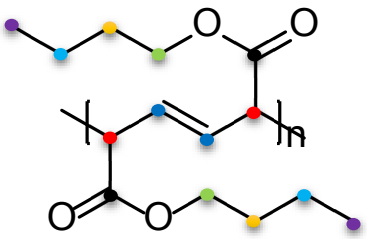


Figure S 9 Quantitative ^{13}C NMR of poly(diethyl muconate) (PDEM)

A.2.2 PDBM



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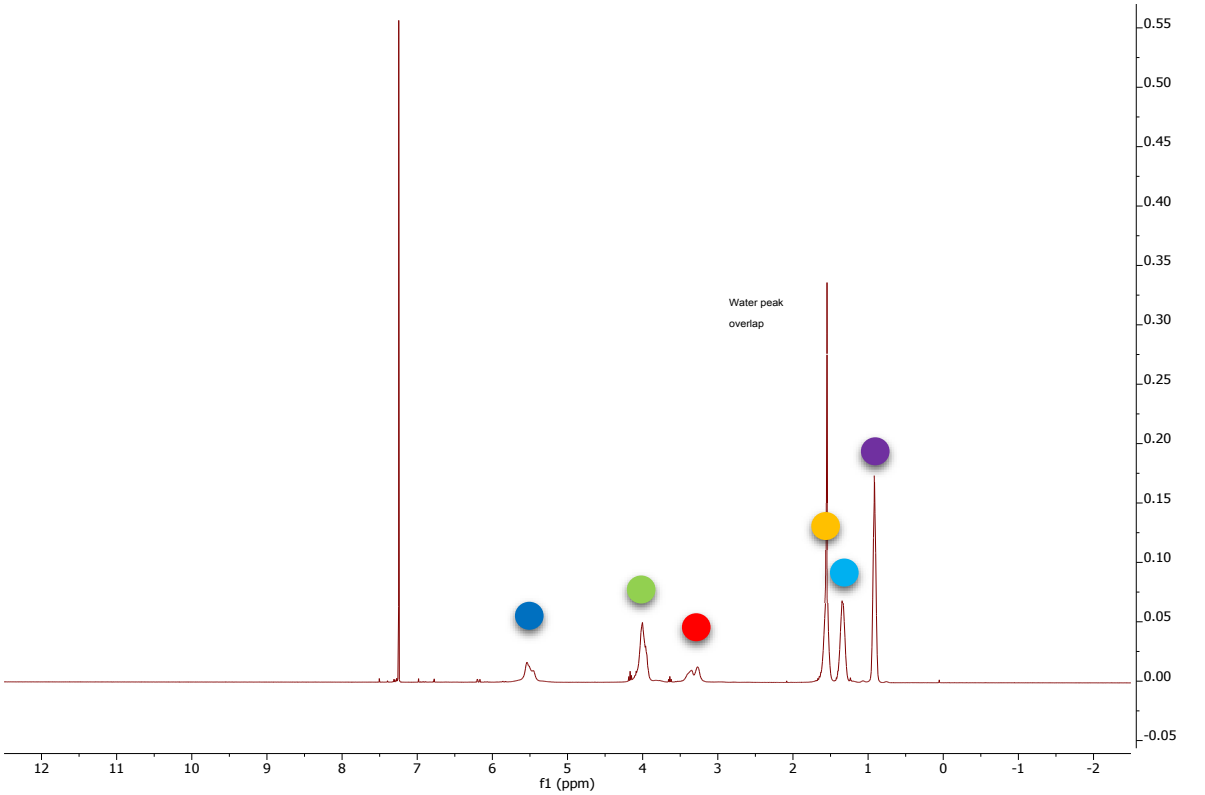


Figure S 10 ^{1}H NMR of poly(dibutyl muconate) (PDBM)

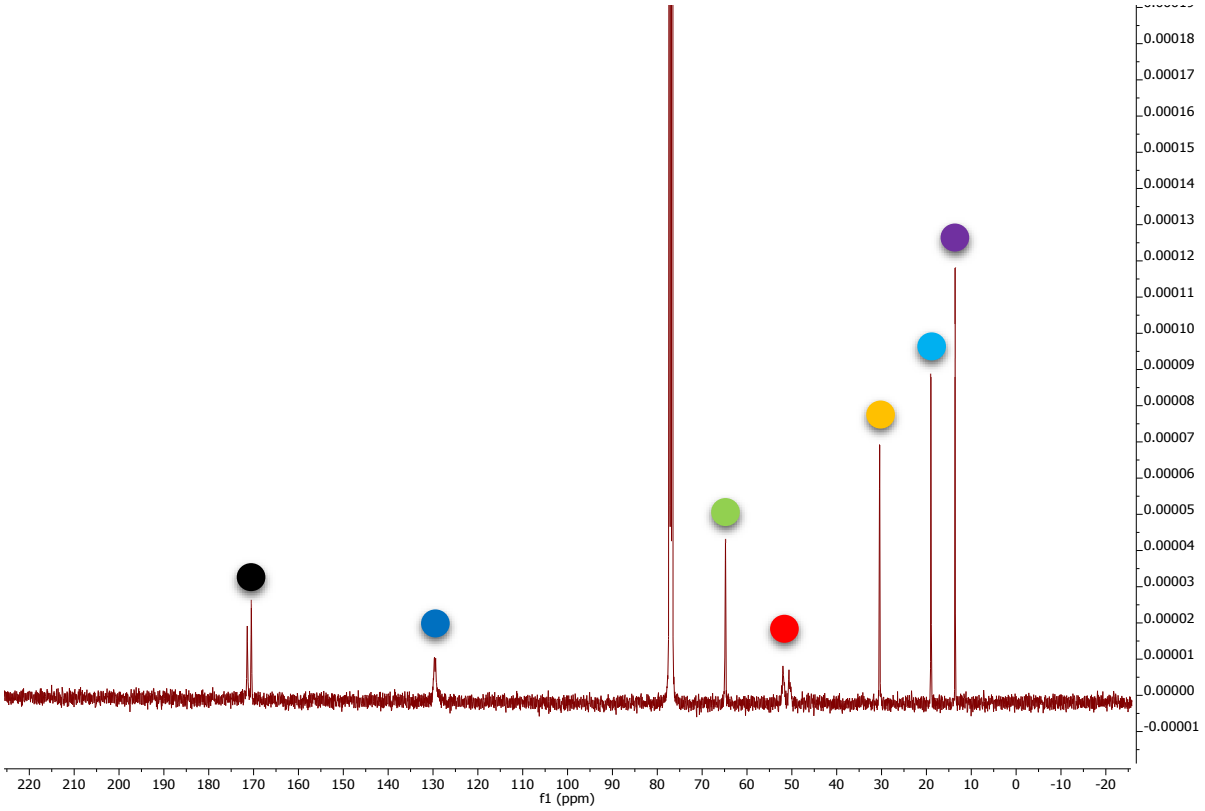
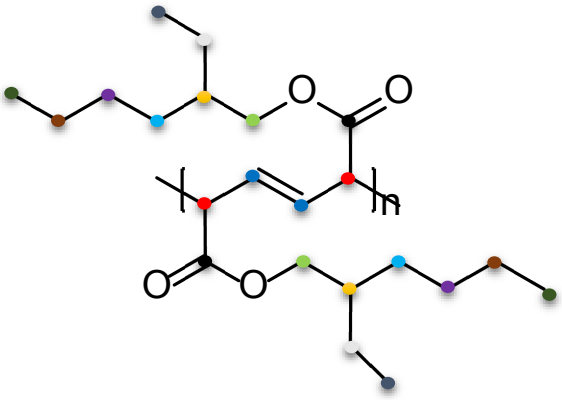


Figure S 11 ^{13}C NMR of poly(dibutyl muconate) (PDBM)

Supporting information

A.2.3 PDEHM



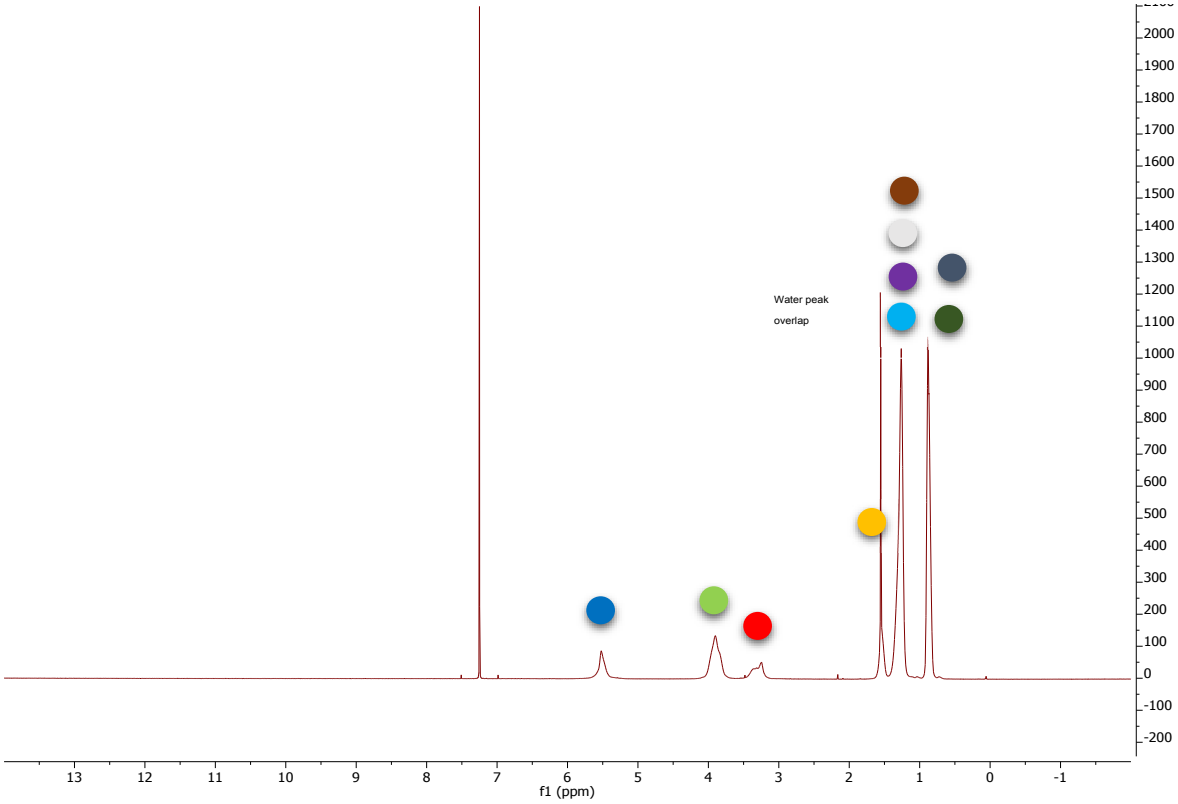


Figure S 12 ^{1}H NMR of poly(di-(2-ethylhexyl) muconate) (PDEHM)

Supporting information

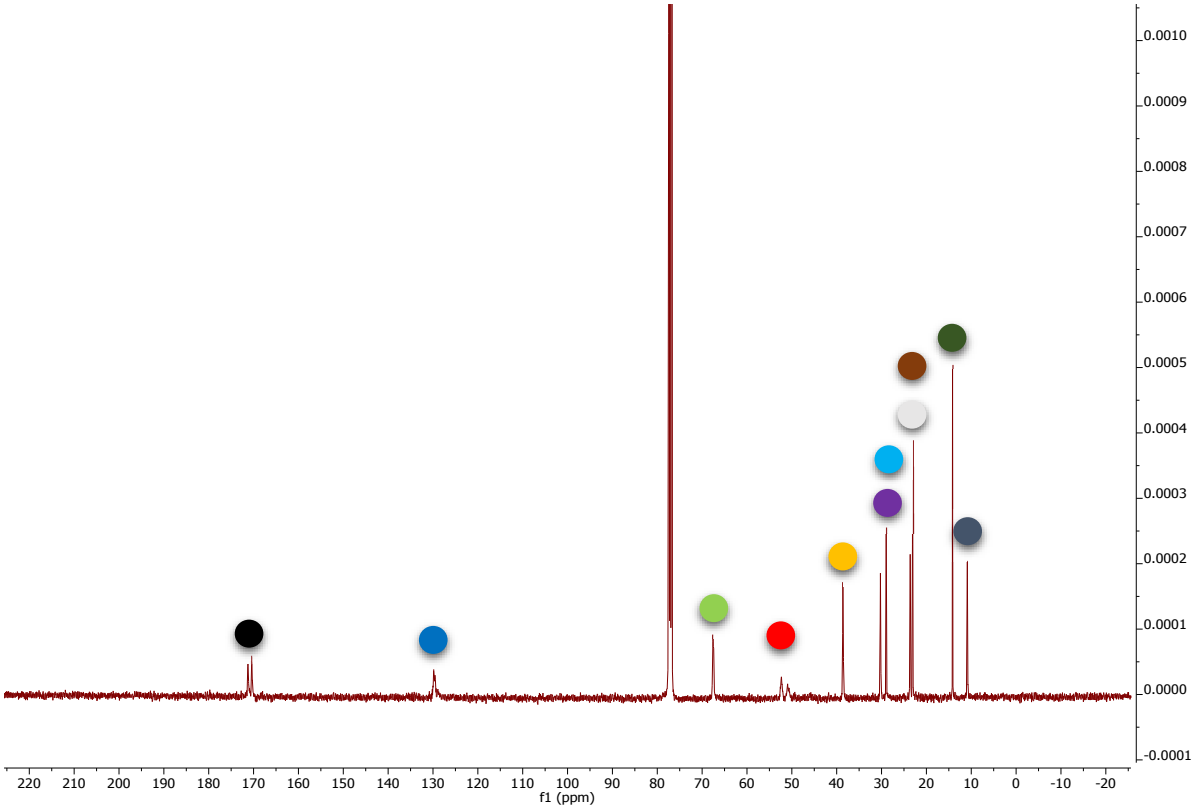


Figure S 13 ^{13}C NMR of poly(di-(2-ethylhexyl) muconate) (PDEHM)

B Size Exclusion Chromatography (SEC)

B.1 Free Radical Polymerization (FRP)

B.1.1 PDEM

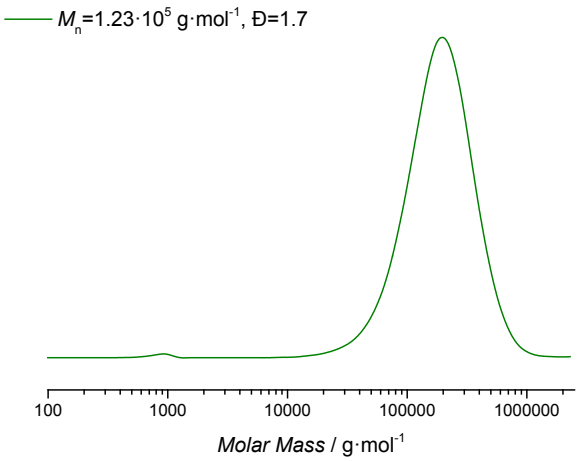


Figure S 14 Molecular weight distribution of PDEM after purification via precipitation.

Supporting information

B.1.2 PDBM

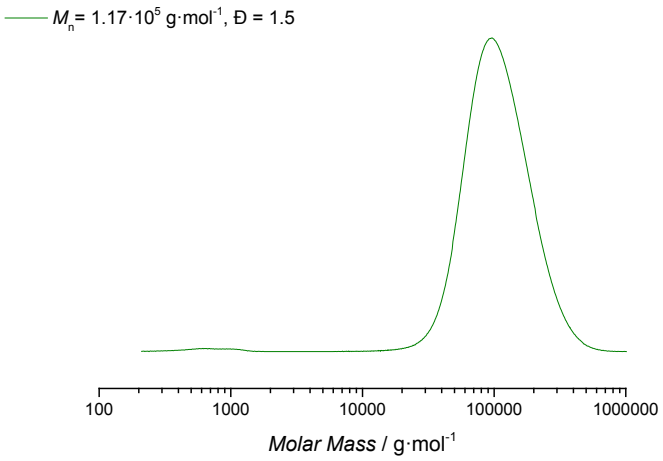


Figure S 15 Molecular weight distribution of PDBM after purification via precipitation.

B.1.3 PDEHM

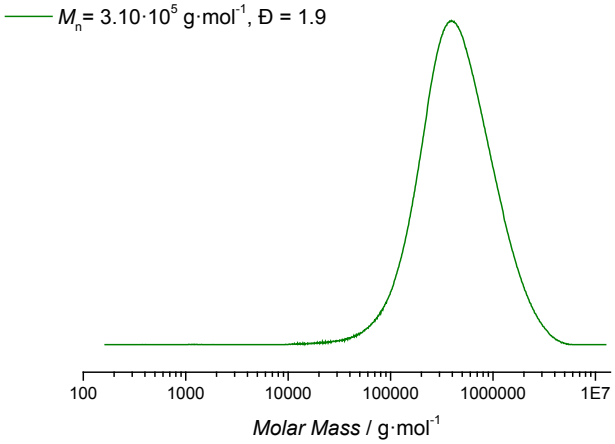


Figure S 16 Molecular weight distribution of PDEHM after purification via precipitation.

Supporting information

B.2 Mark-Houwink parameters

Mark-Houwink coefficients of PDEHM, PDEM and PDBM (α and K) were determined via SEC-MALS using a Tosoh EcoSEC coupled to a Dawn Heleos II multi angle light scattering detector and an Optilab TrEX refractive index detector from Wyatt Technology. Tetrahydrofuran (THF) is used as eluent at 40°C with a flowrate of 1 mL·min^{-1}. The dn/dc values of the polymers were determined via 100% mass recovery. The intrinsic viscosities ([η]) of the analytes for every measured molecular weight (MW) datapoint was then determined via universal calibration with narrow polystyrene standards from Polymer Standards Service (PSS) by using the Mark-Houwink equation:

$$[\eta]_{analyte} \cdot MW_{analyte} = [\eta]_{polystyrene} \cdot MW_{polystyrene}$$

$$[\eta]_{analyte} = \frac{[\eta]_{polystyrene} \cdot MW_{polystyrene}}{MW_{analyte}}$$

Mark-Houwink plots were then constructed by plotting the measured molecular weight versus the calculated intrinsic viscosities on logarithmic scales. A linear fit was then performed of which the slope and intercept respectively equal α and log(K). The calculated variables for the various analytes are given in Table S 1.

Table S 1: Experimentally determined dn/dc and calculated Mark-Houwink values of PDEHM, PDEM and PDBM.

analyte	dn/dc (mL·mg^{-1})	α	K	MW range (g·mol^{-1})
PDEHM	0.065	0.81	1.8 x 10^{-3}	10^5-10^6
PDEM	0.066	0.88	1.3 x 10^{-3}	10^3-10^6
PDBM	0.063	0.86	1.6 x 10^{-3}	10^3-10^6

Strictly speaking, the parameters given above are only valid in the MW range covered in the MALLS experiments (see table).

B.3 Reproducibility FRP

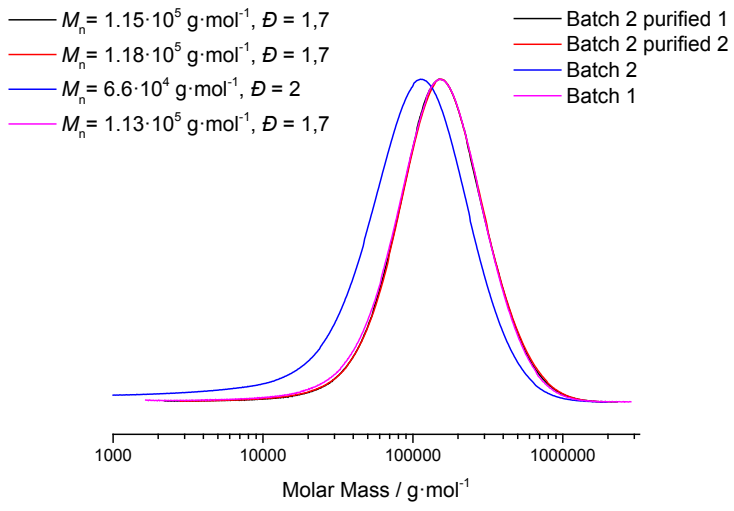


Figure S 17 Reproducibility test using different batches of trans,trans muconic acid.

Supporting information

B.4 Thermal Gravimetrical Analyis (TGA)

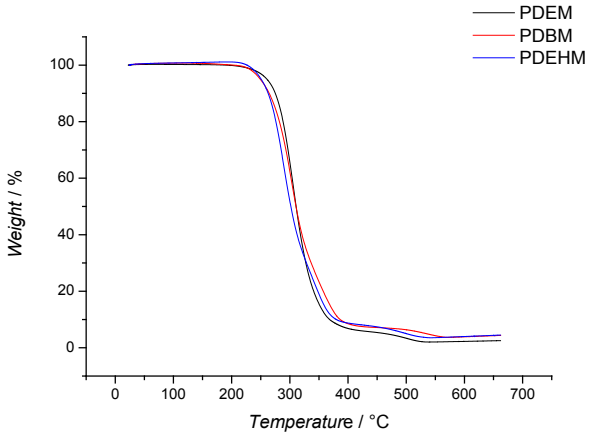
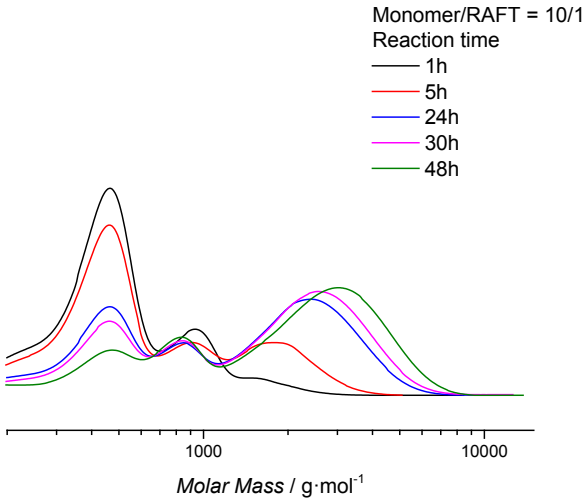


Figure S 18 Combined TGA data of different polymuconates

B.2.4 Reversible Addition-Fragmentation chain Transfer (RAFT)

B.2.4.1 Monomer to RAFT variations



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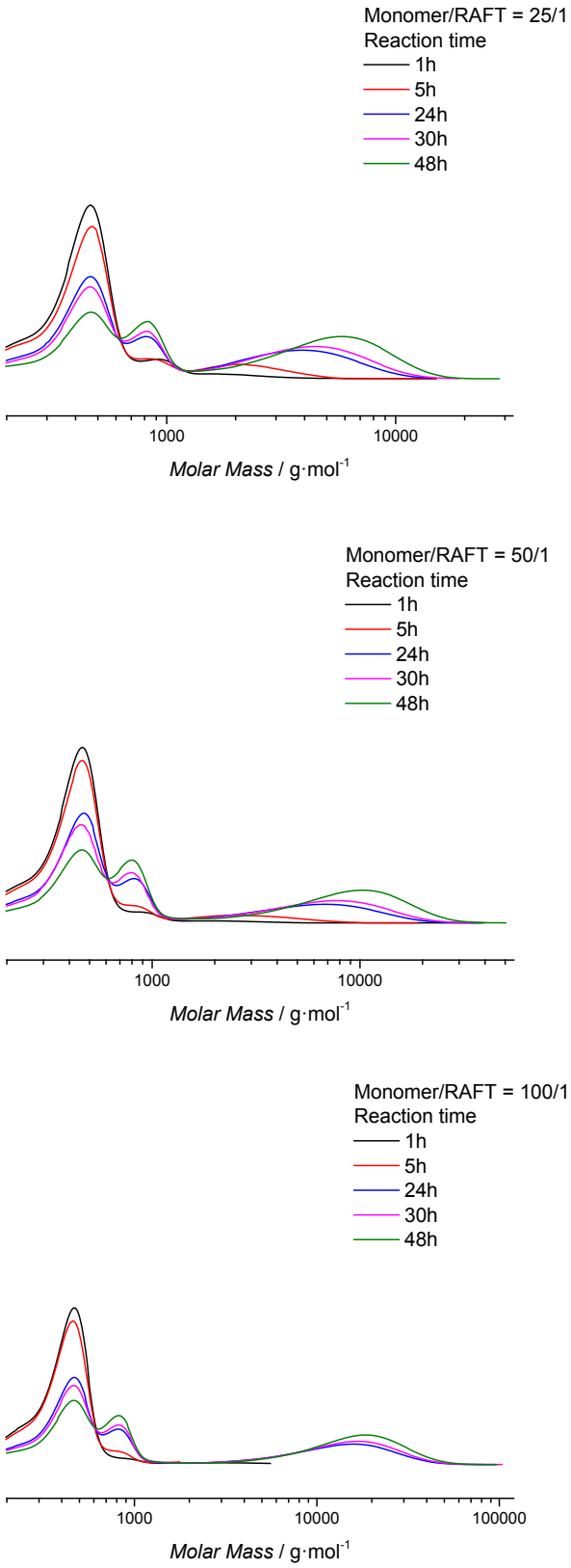

Figure S 19 Overview of monomer to RAFT variations at different reaction times showing the reduction of the monomer peak and the molecular weight distribution of the polymers.

Supporting information

B.2.4.2 Overview of all RAFT polymers after 48 h reaction time

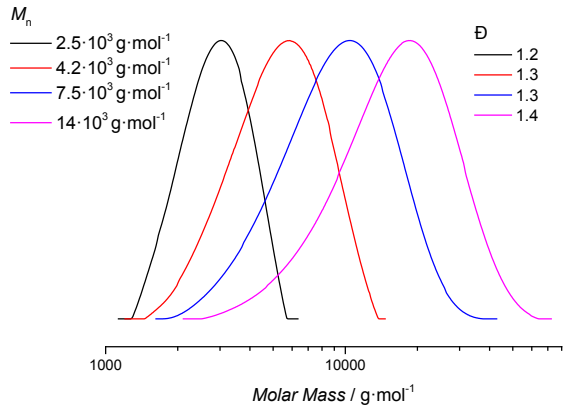

Figure S 20 Molecular weight distributions of the different monomer to RAFT agent ratios after 48 h reaction time.