Phosphate Functionalized Nonisocyanate Polyurethanes with Bio-origin, Water Solubility and Biodegradability

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Supporting Information

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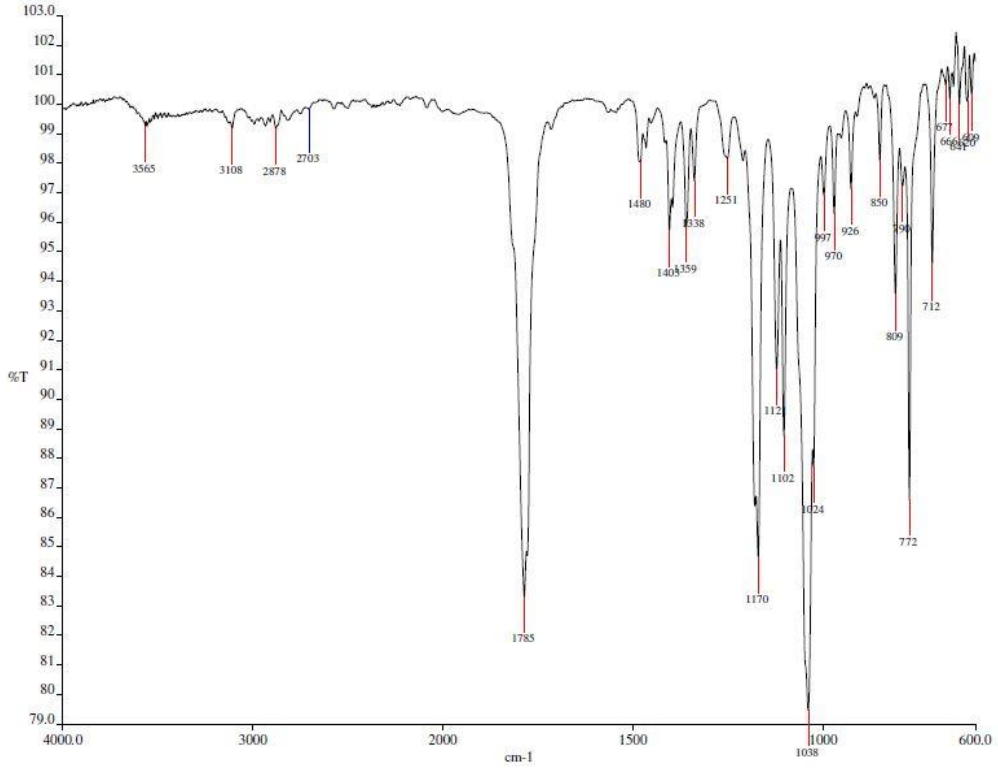


Figure S1: FTIR spectrum of FuBCC monomer

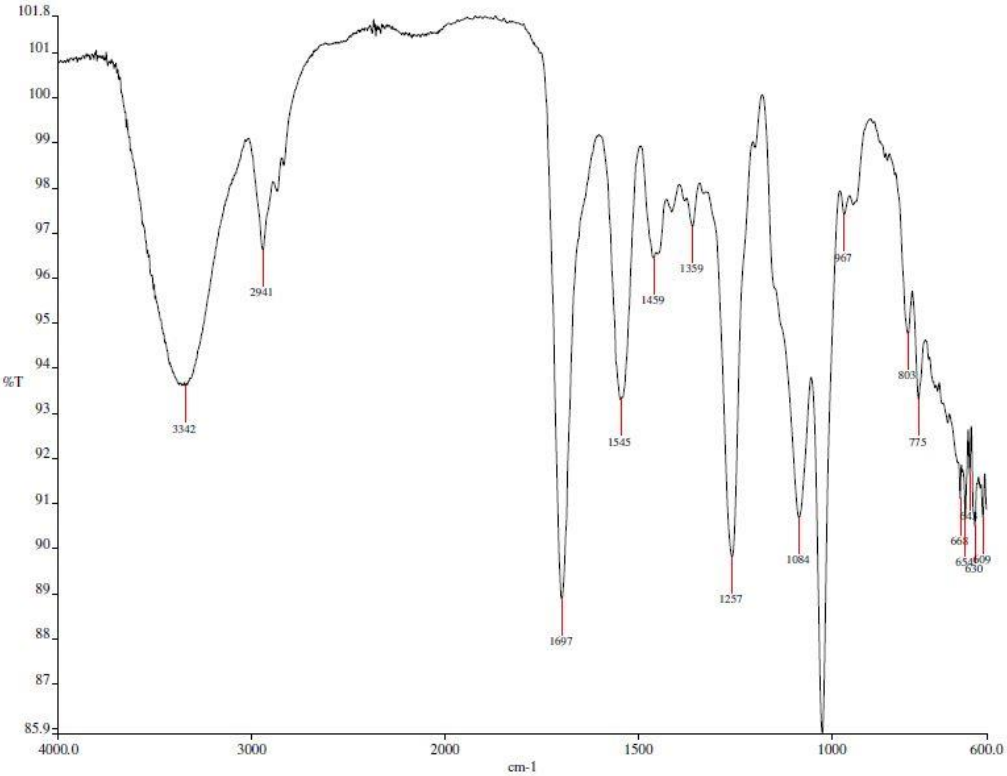


Figure S2: FTIR spectrum of Poly(FuCa)

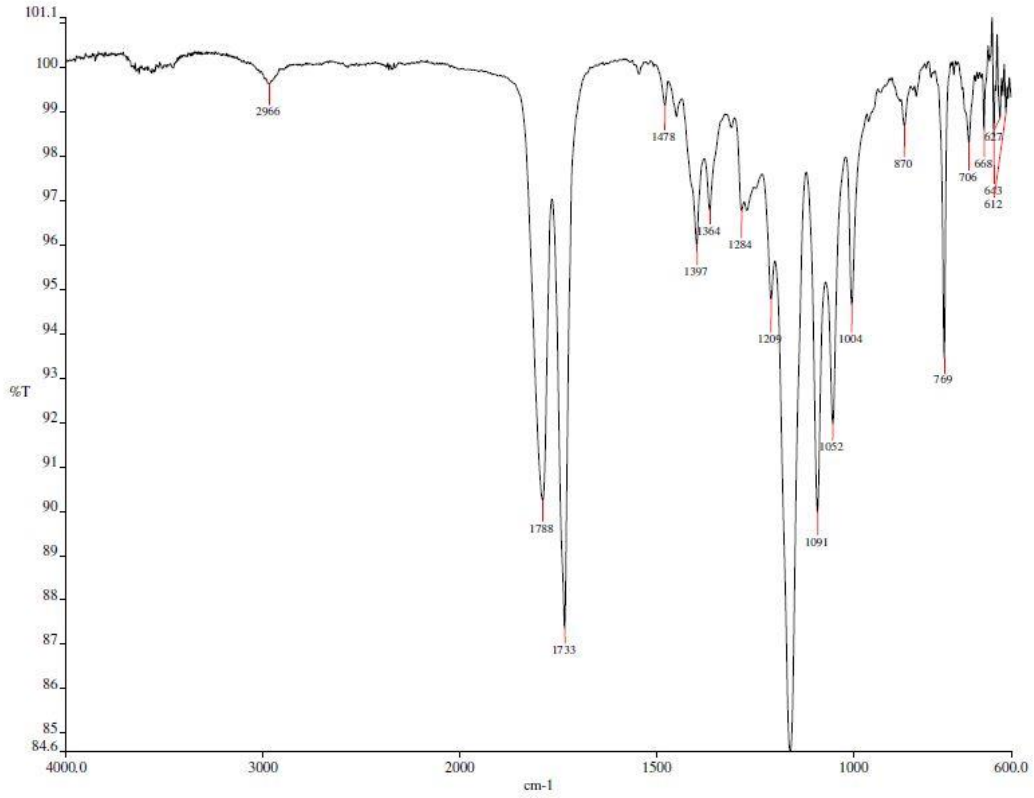


Figure S3: FTIR spectrum of SuBCC monomer

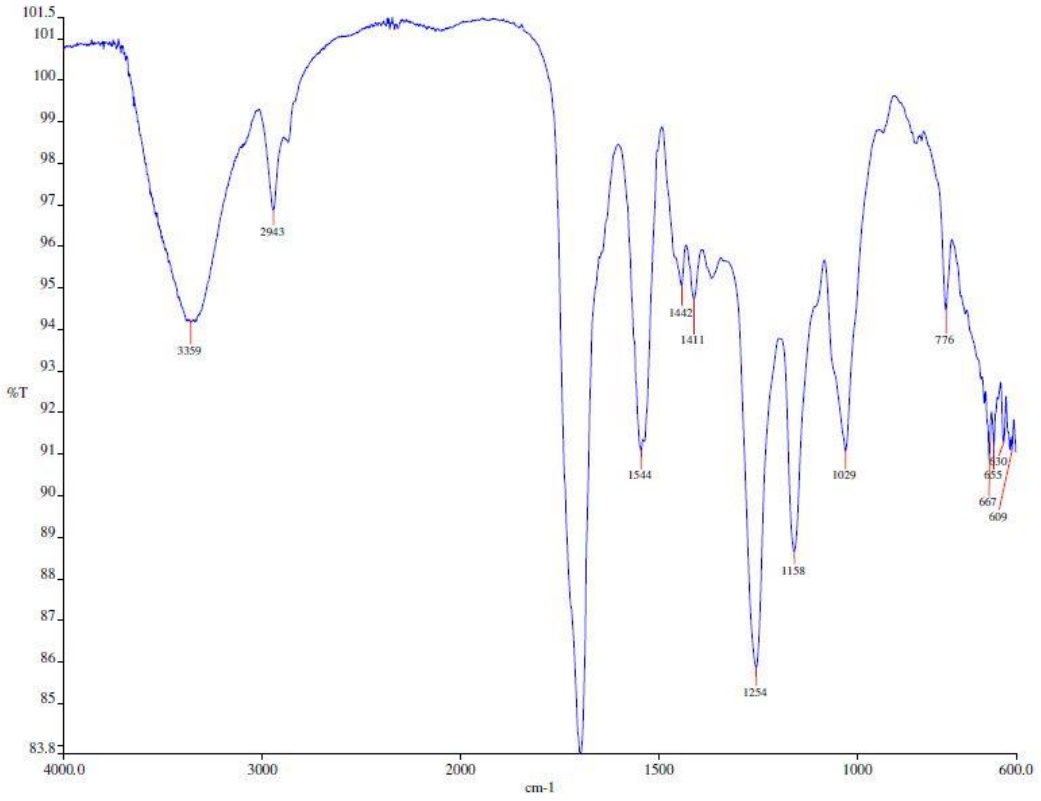


Figure S4: FTIR spectrum of Poly(SuCa)

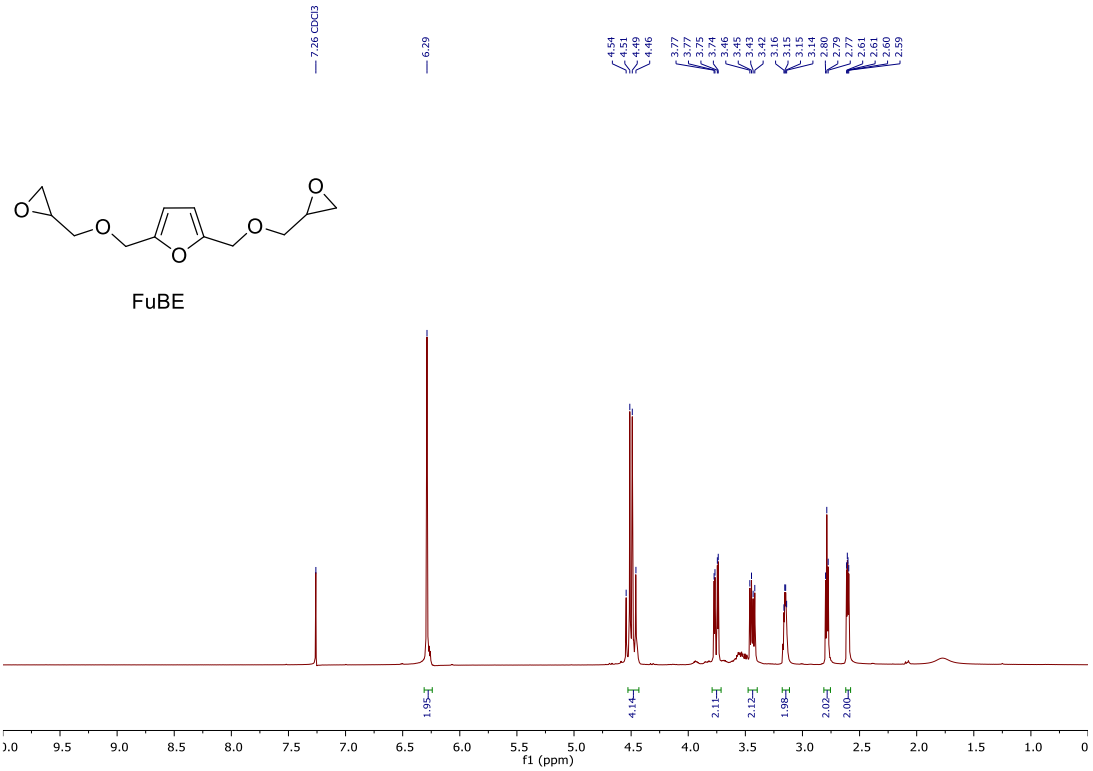


Figure S5: ^{1}H NMR spectrum of FuBE in $CDCl_3$

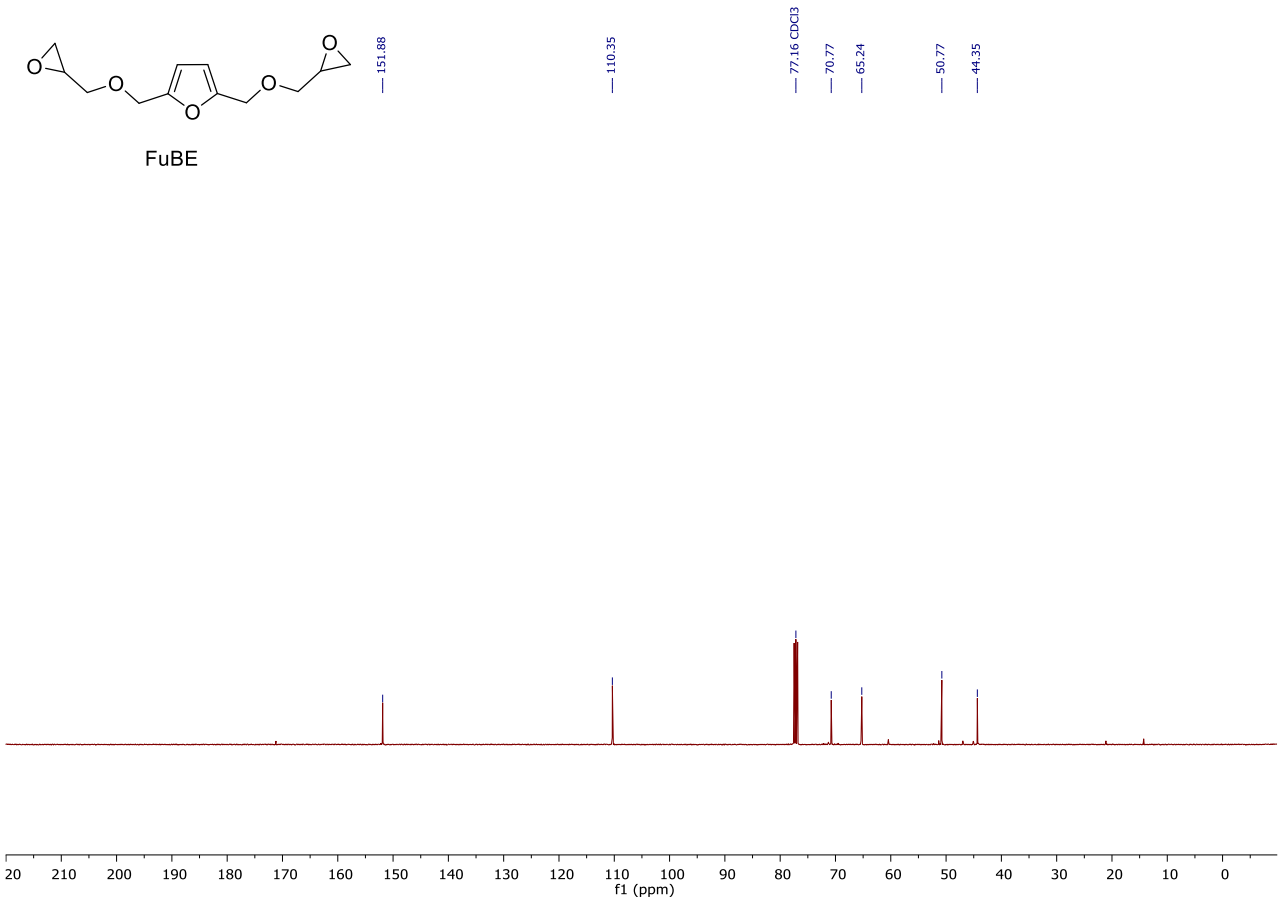


Figure S6: ^{13}C NMR spectrum of FuBE in $CDCl_3$

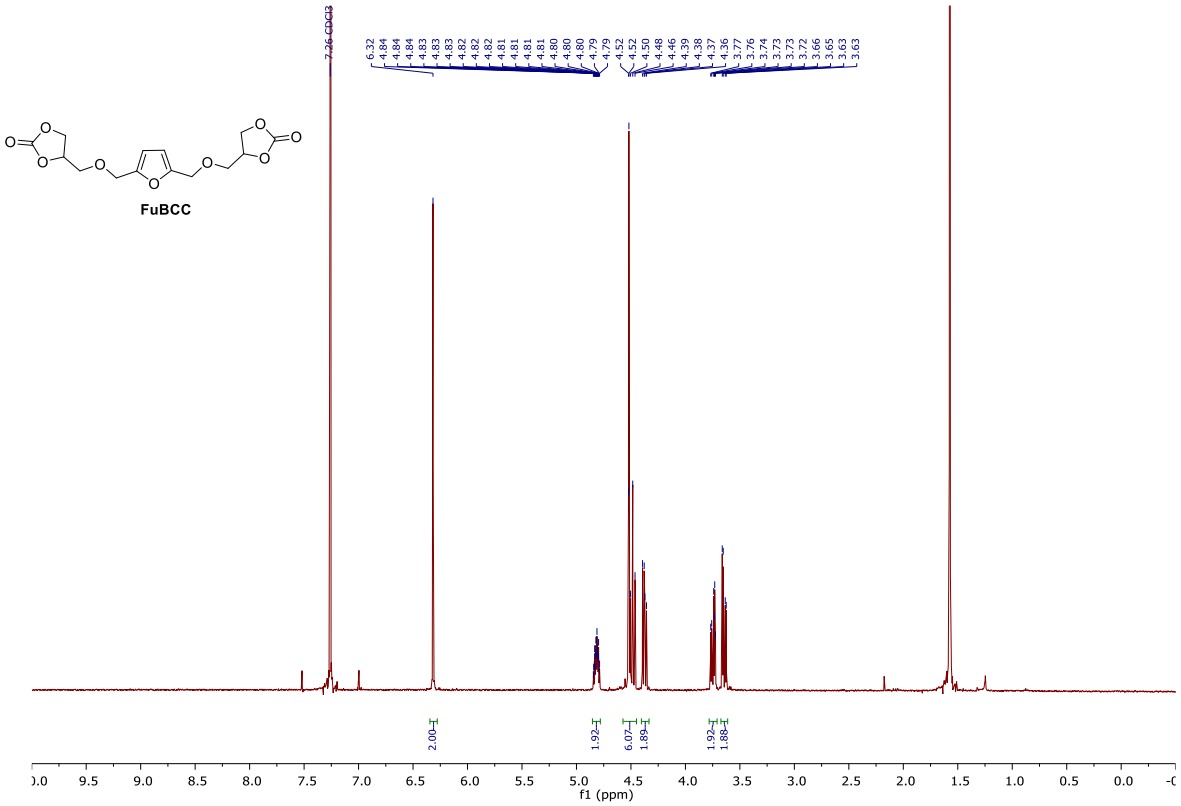


Figure S7: 1H NMR spectrum of FuBCC monomer in CDCl3

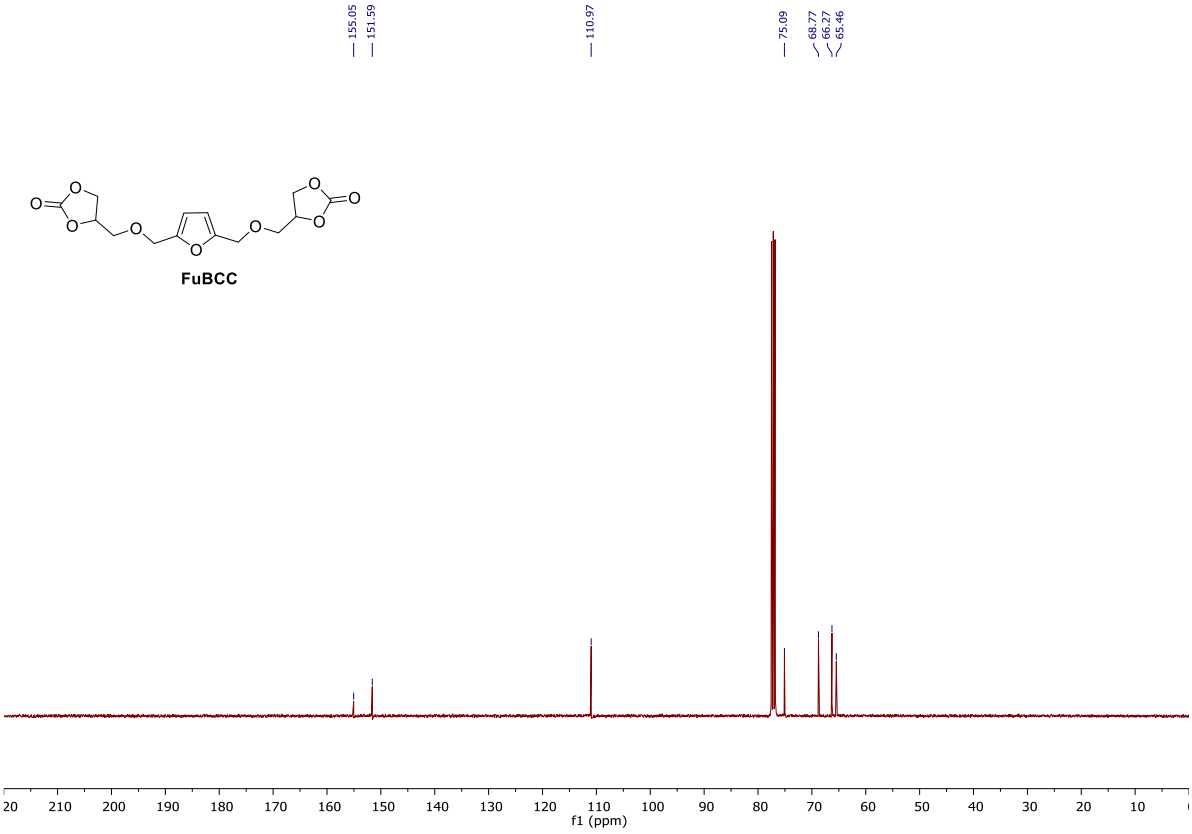


Figure S8: ^{13}C NMR spectrum of FuBCC monomer in CDCl3

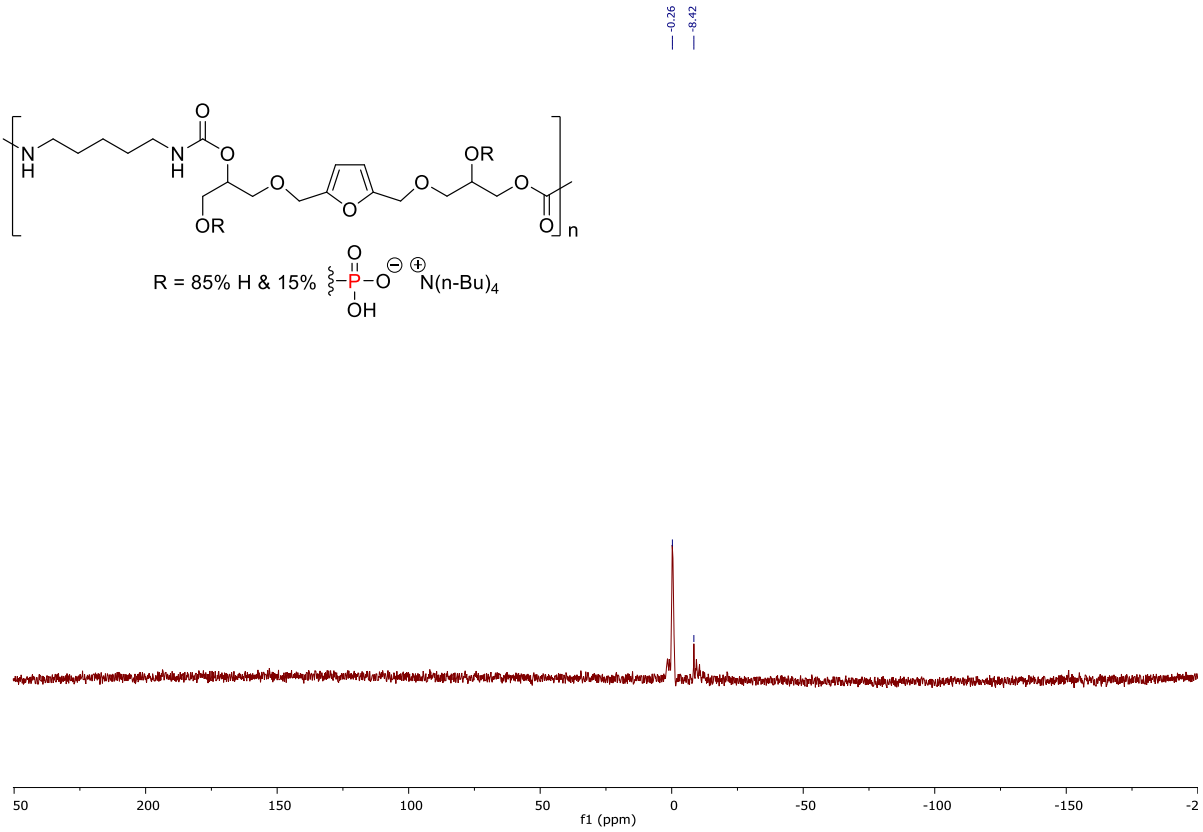


Figure S9: ^{31}P NMR spectrum of Poly(FuCa)-P15 in DMSO d_6

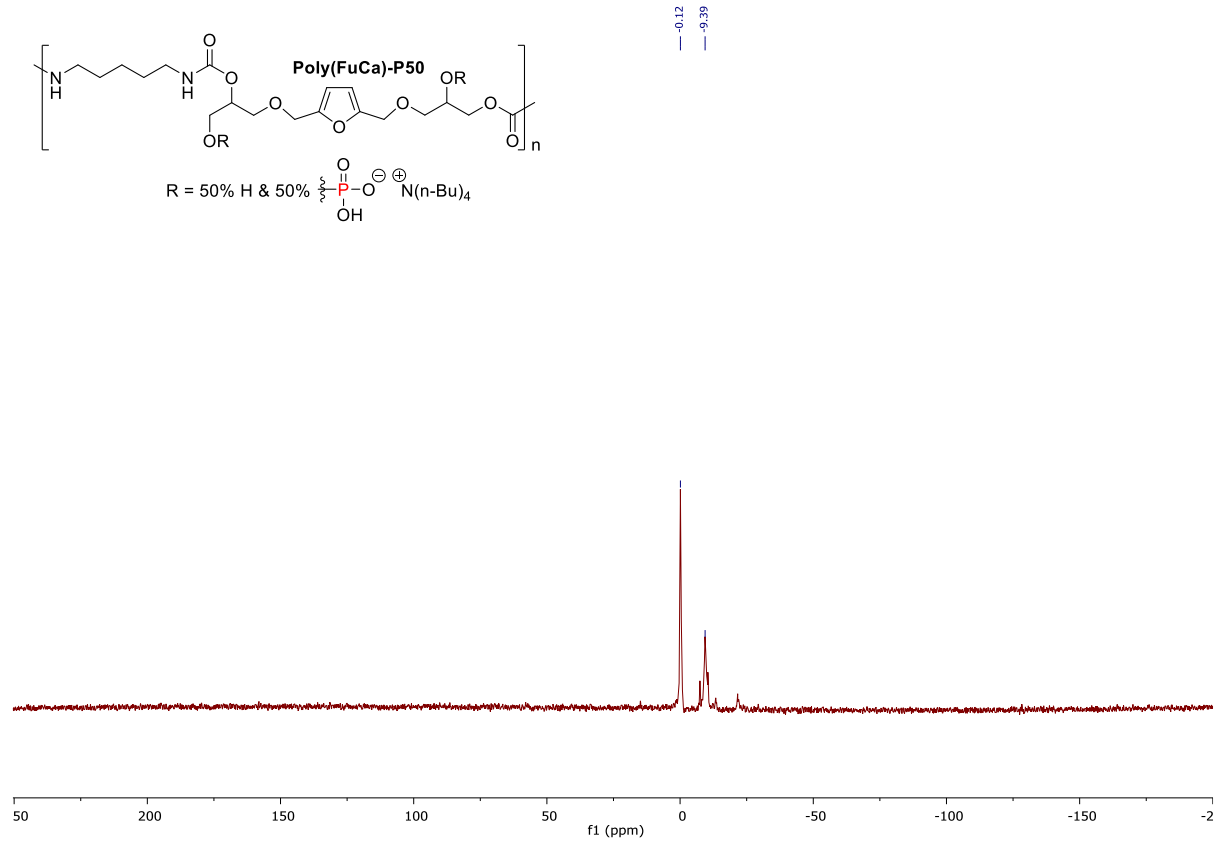


Figure S10: ^{31}P NMR spectrum of Poly(FuCa)-P50 in DMSO-d_6

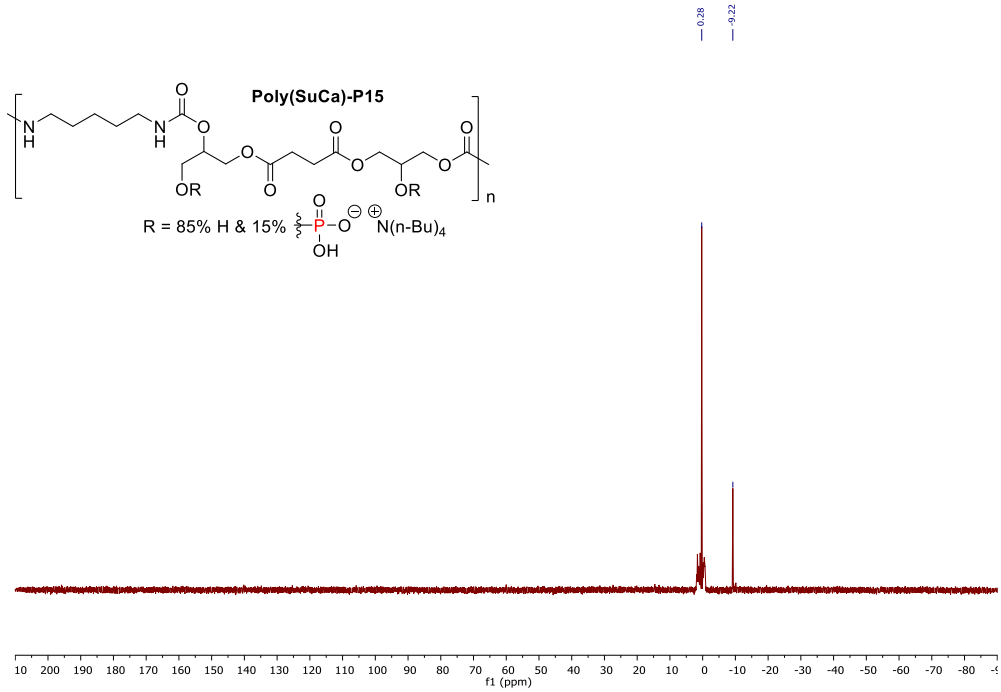


Figure S11: ^{31}P NMR spectrum of Poly(SuCa)-P15 in DMSO-d_6

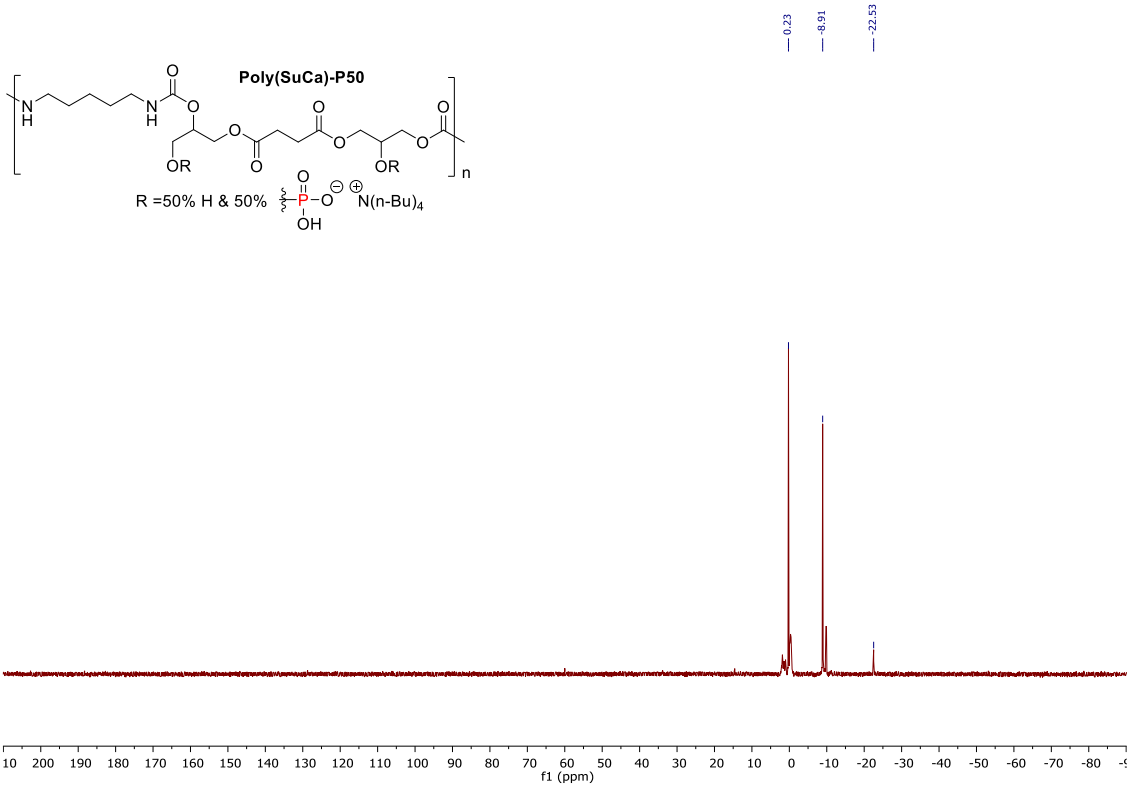


Figure S12: ^{31}P NMR spectrum of Poly(SuCa)-P50 in DMSO-d_6

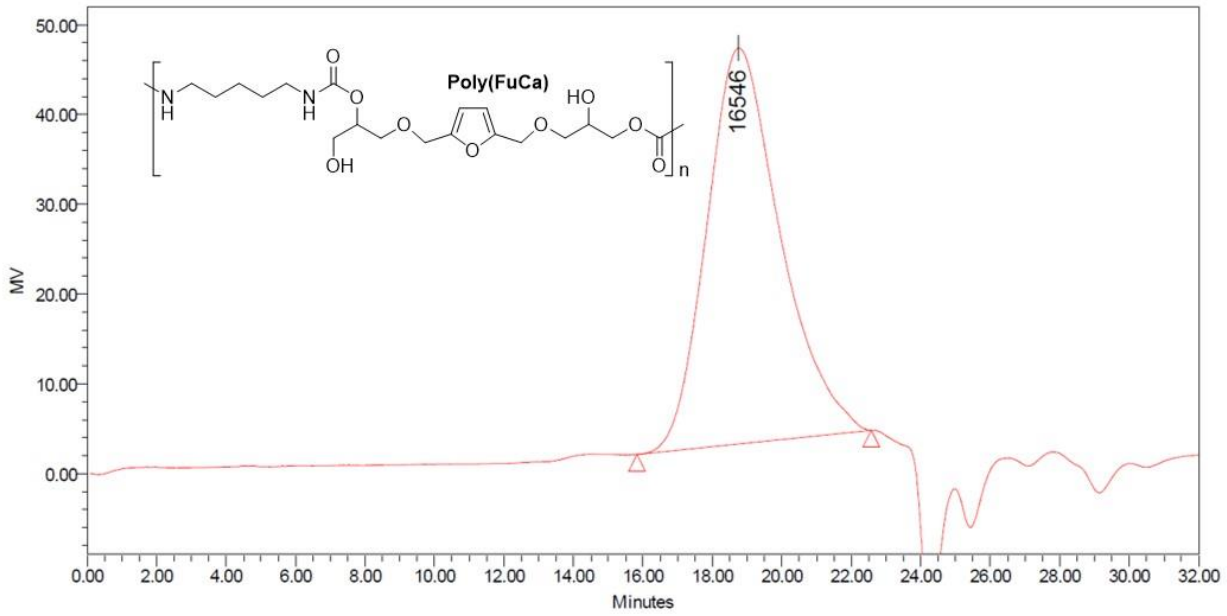


Figure S13: GPC chromatogram of Poly(FuCa)

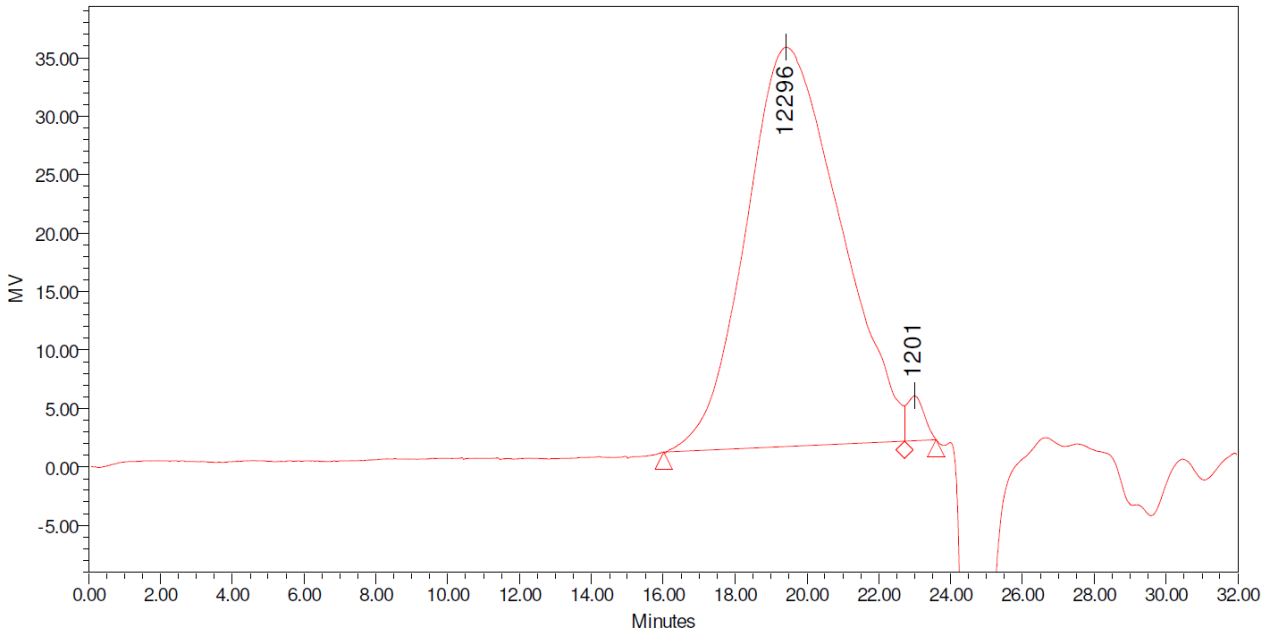


Figure S14: GPC chromatogram of Poly(SuCa)

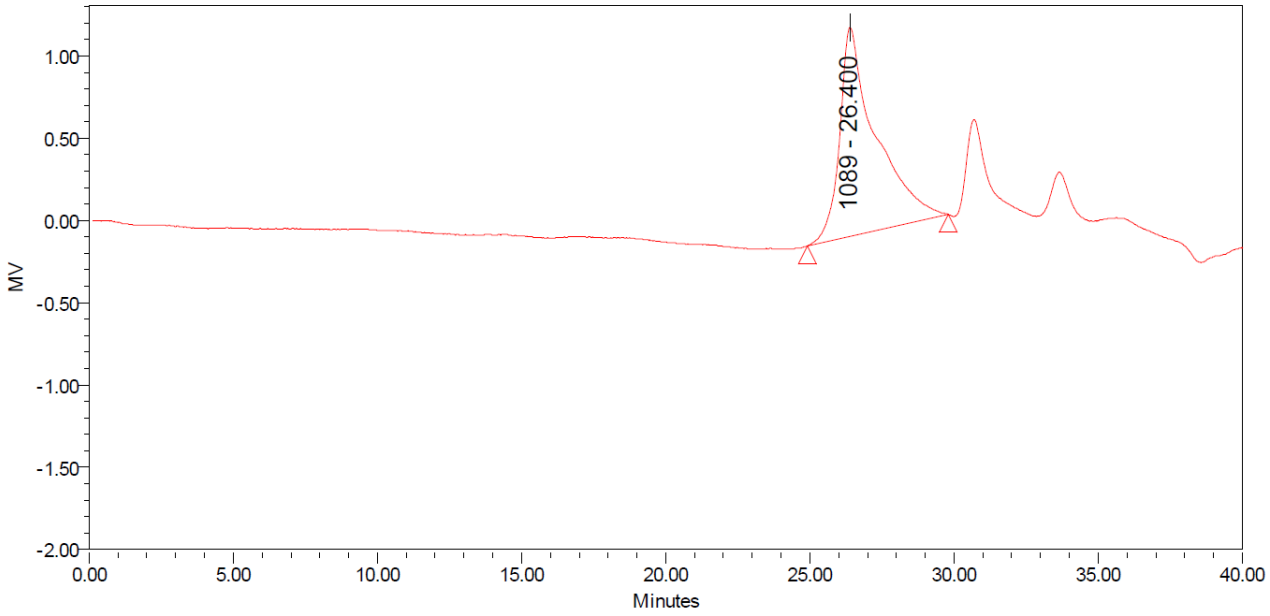


Figure S15: GPC chromatogram of Poly(FuCa)-P15

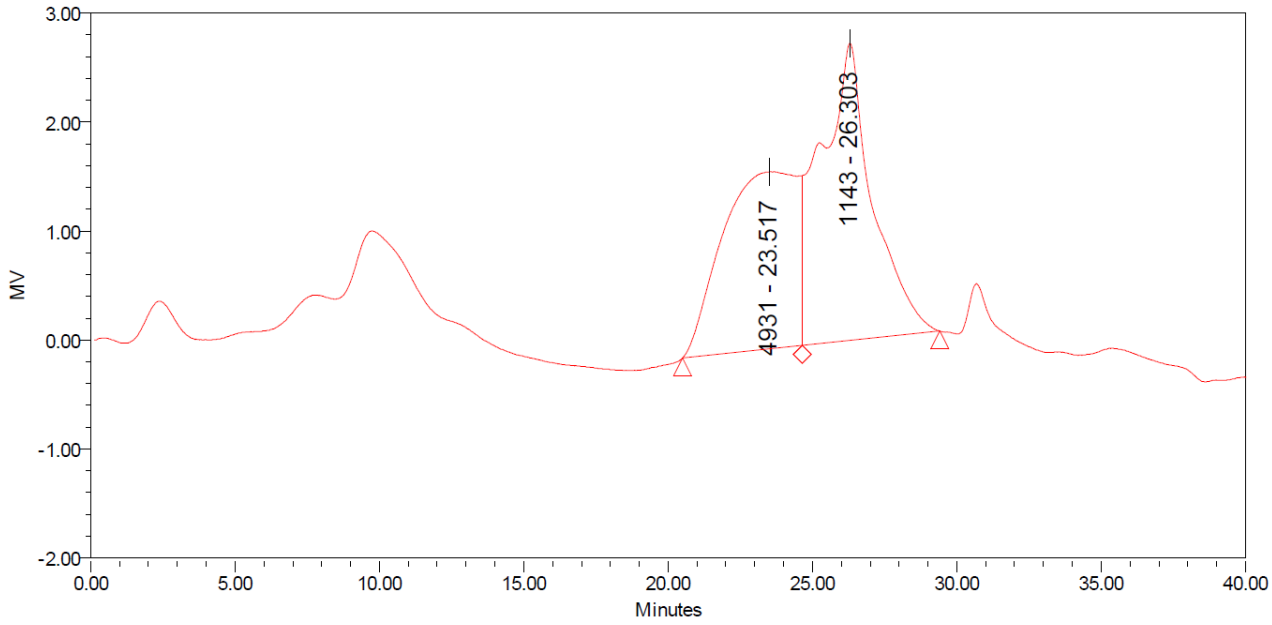


Figure S16: GPC spectrum of Poly(FuCa)-P50

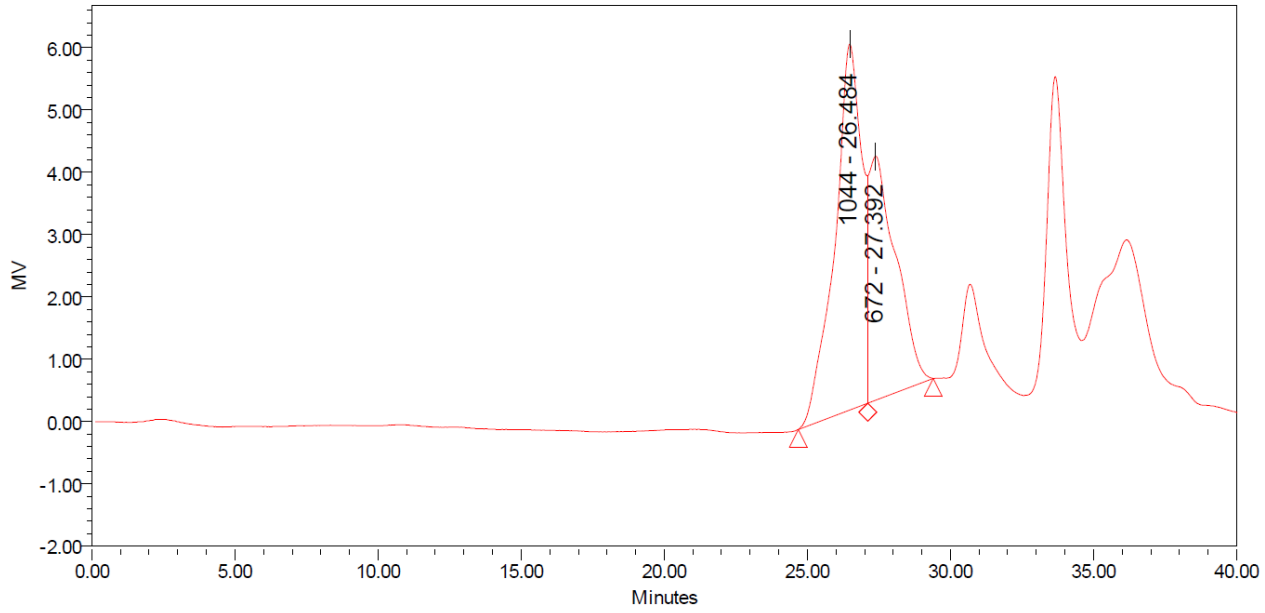


Figure S17: GPC spectrum of Poly(SuCa)-P15

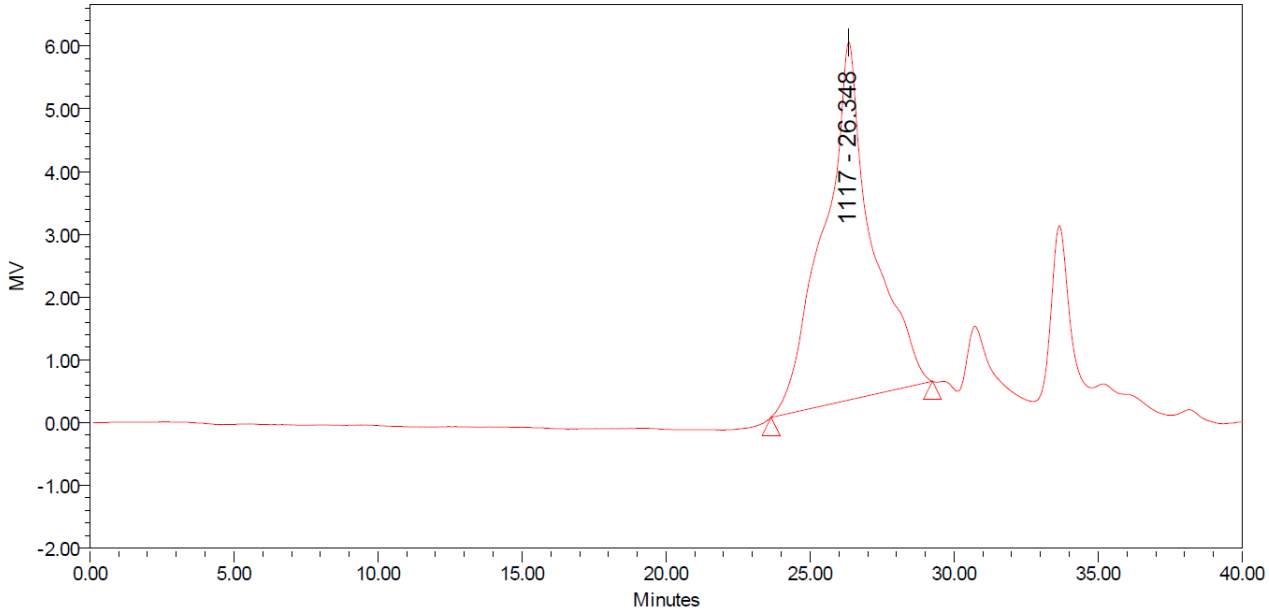


Figure S18: GPC spectrum of Poly(SuCa)-P50

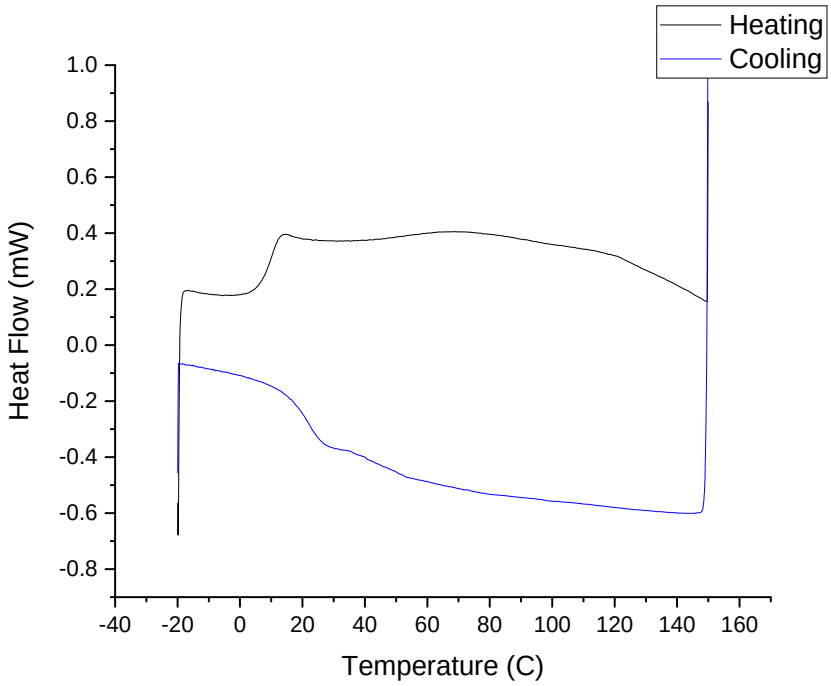


Figure S19: DSC thermogram of Poly(FuCa)

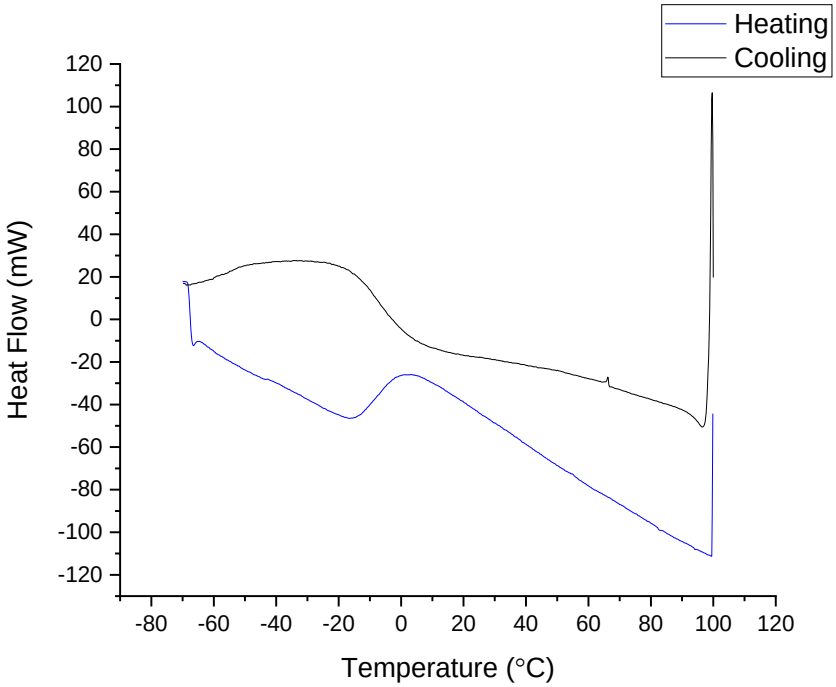


Figure S20: DSC thermogram of Poly(SuCa)

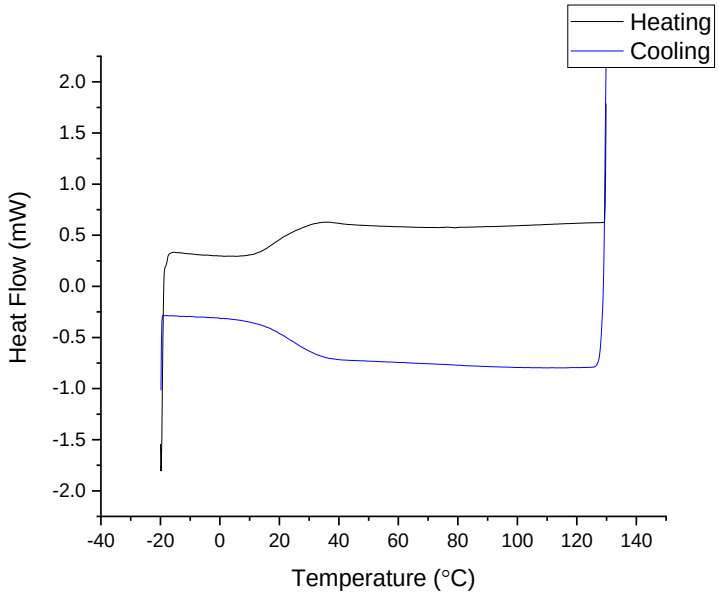


Figure S21: DSC thermogram of Poly(FuCa)-P15

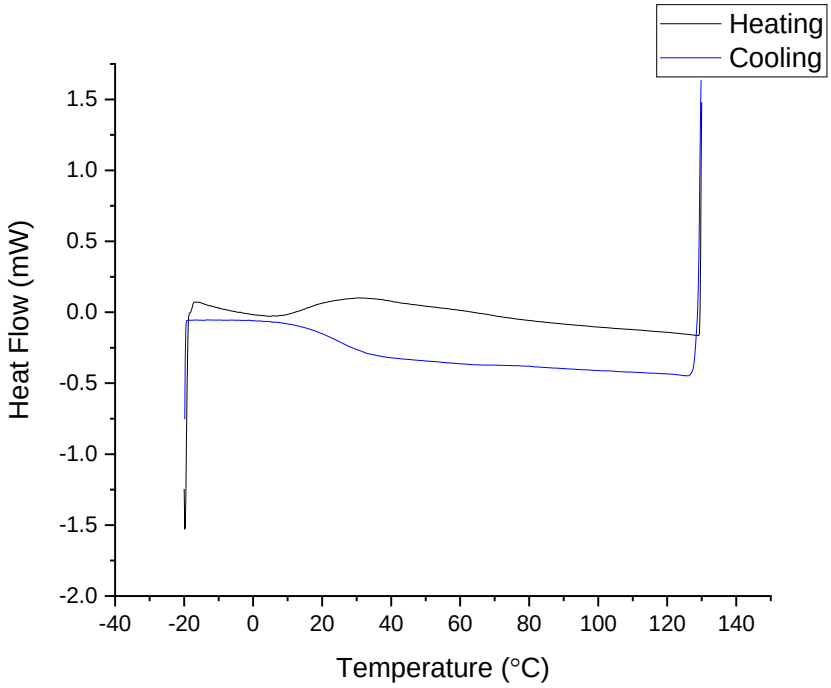


Figure S22: DSC thermogram of Poly(FuCa)-P50

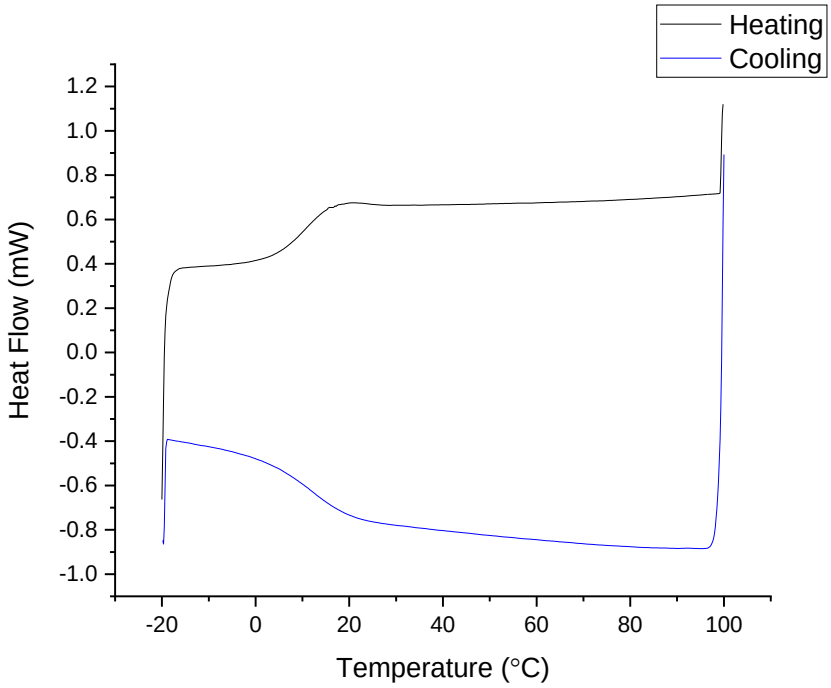


Figure S23: DSC thermogram of Poly(SuCa)-P15

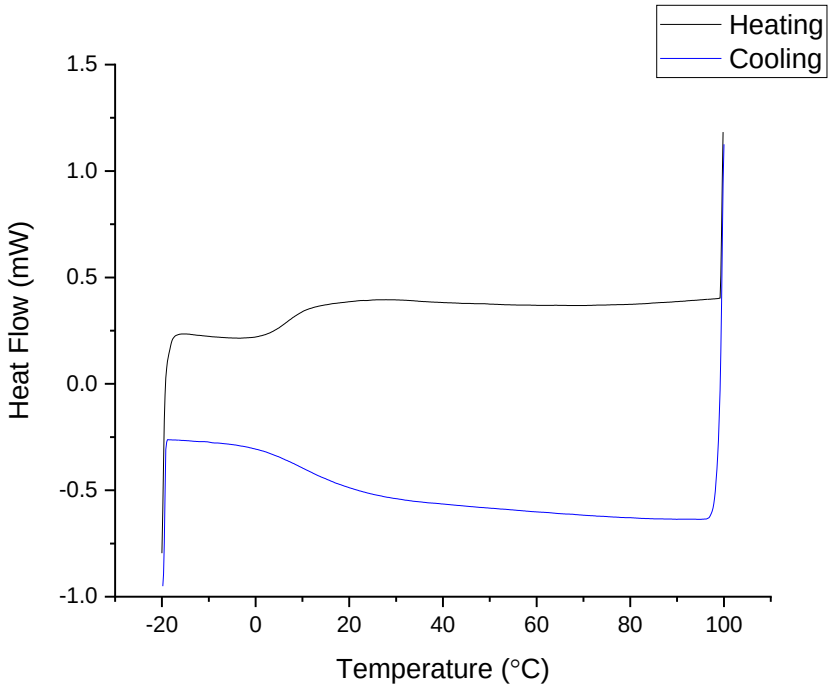


Figure S24: DSC thermogram of Poly(SuCa)-P50

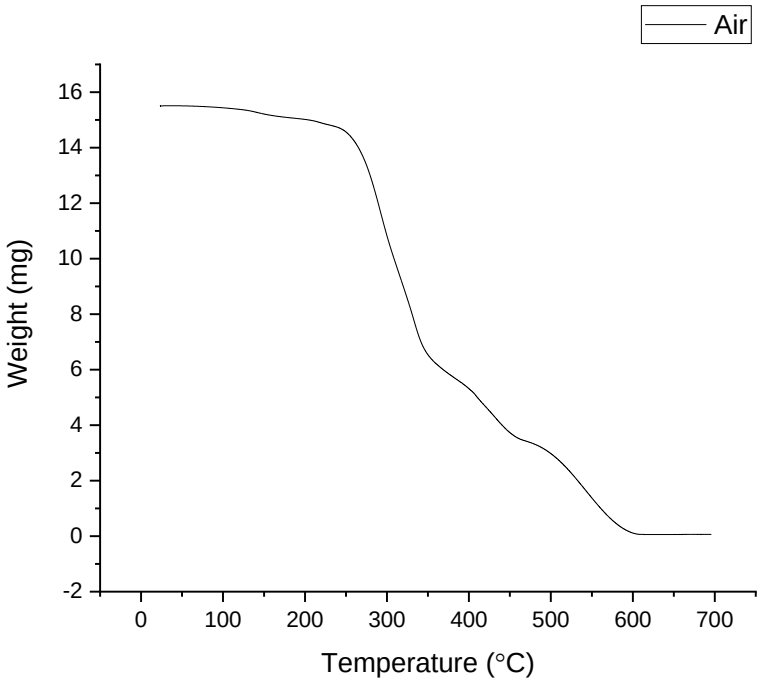


Figure S25: TGA in Air trace of Poly(FuCa)

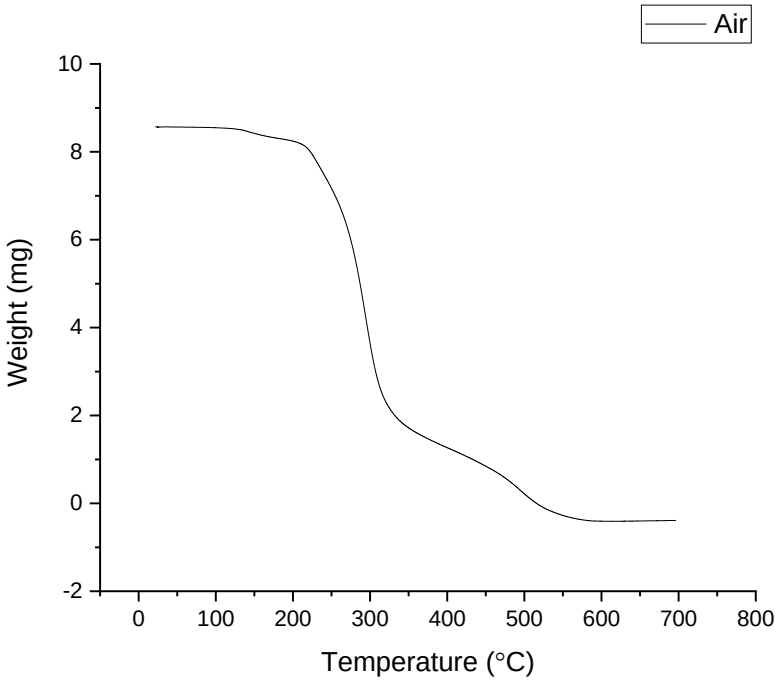


Figure S26: TGA in Air trace of Poly(SuCa)

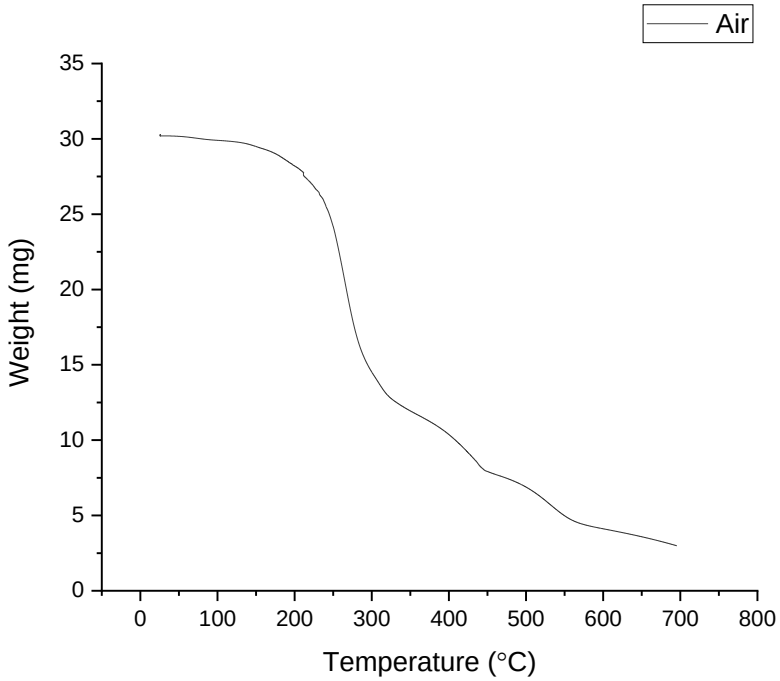


Figure S27: TGA in Air trace of Poly(FuCa)-P15

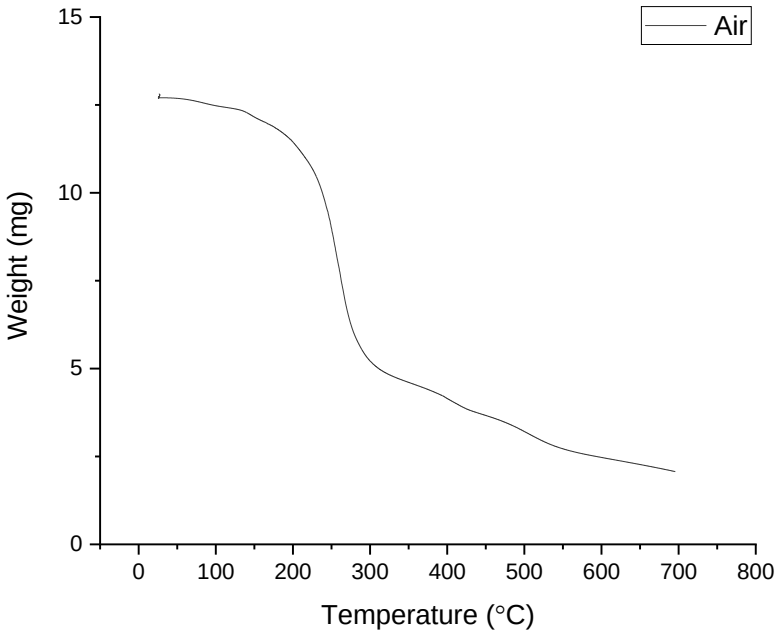


Figure S28: TGA in Air trace of Poly(FuCa)-P50

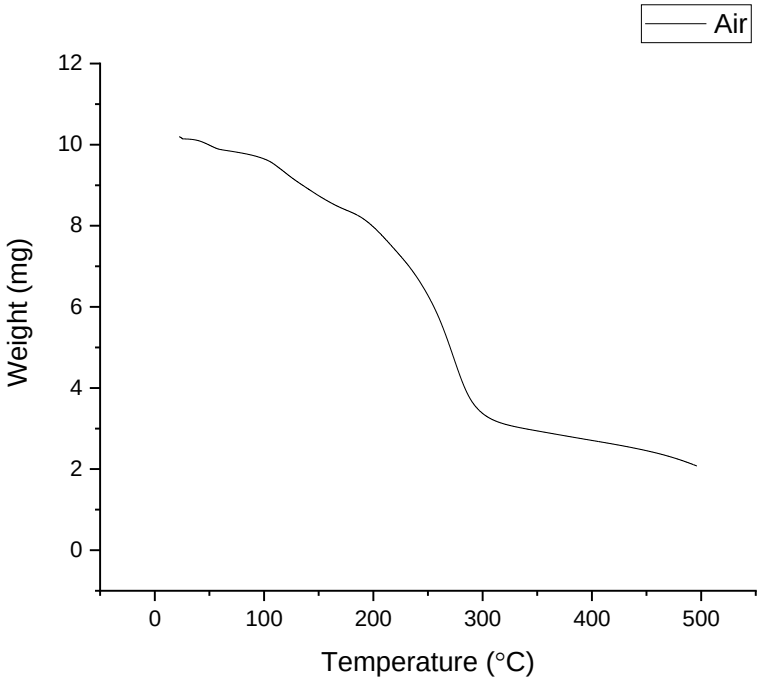


Figure S29: TGA in Air trace of Poly(SuCa)-P15

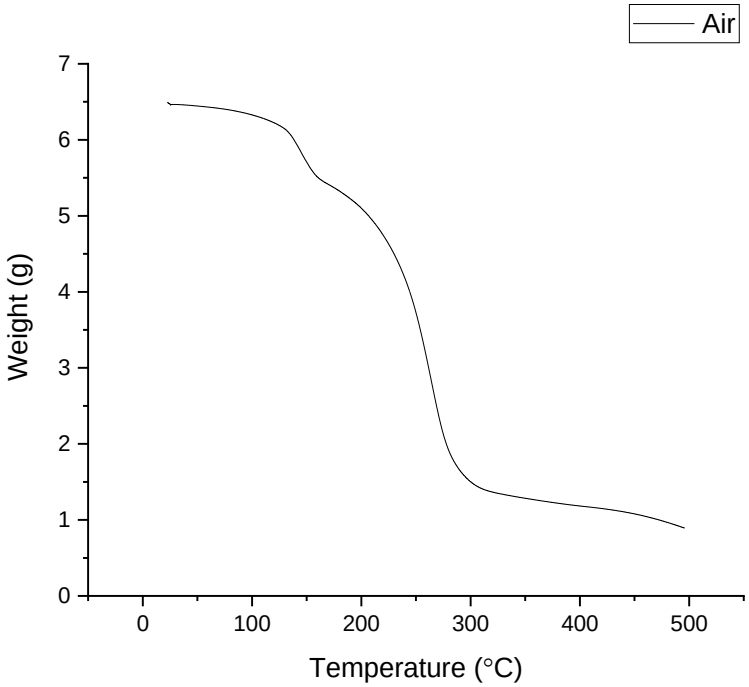
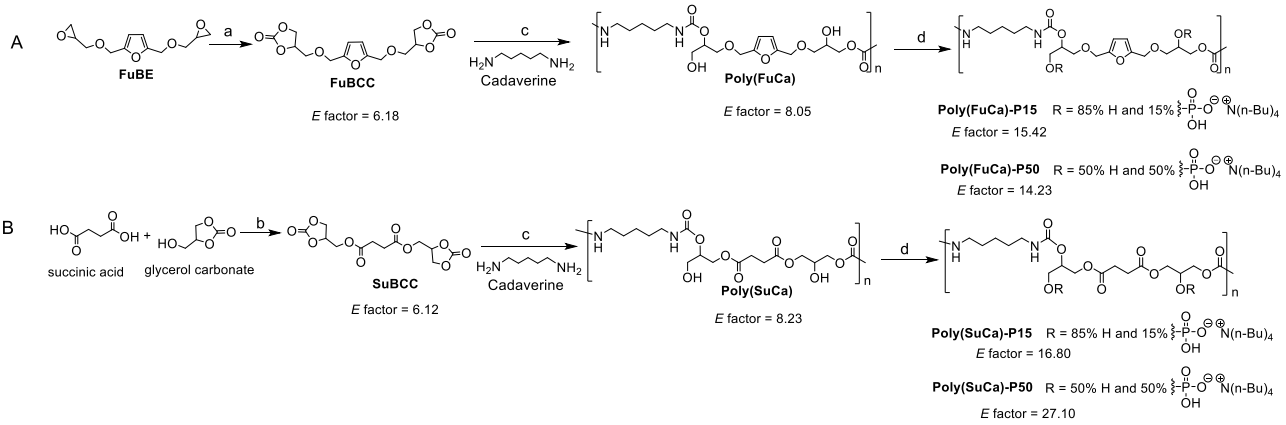


Figure S30: TGA in Air trace of Poly(SuCa)-P50

E factor calculation



Step A-a

Reactants, catalyst and solvent, R	Amount of R, g	Product, P	Amount of P, g
FuBE	10.80	FuBCC	12.7
Catalyst (TBAP)	0.44		
CO2 (approx. based on 20 bar in 160 mL reactor)	6.28		
Ethyl Acetate, 60 mL	54.12		
Pet-ether, 30 mL	19.59		
Σ R (g)	**91.23**	**Σ P (g)**	**12.7**
Waste (g), W = ΣR -Σ P	**78.53**		
E-Factor = W/ΣP	**6.18**		

Step A-c

Reactants, catalyst and solvent, R	Amount of R, g	Product, P	Amount of P, g
FuBCC	10.30	Poly(FuCa)	12.16
Cadaverine	3.22		
Anisole, 30 mL	29.85		
Methanol, 3x10 mL	23.94		
Diethyl ether, 3x20 mL	42.78		
Σ R (g)	**110.09**	**Σ P (g)**	**12.16**
Waste (g), W = ΣR -Σ P	**97.93**		
E-Factor = W/ΣP	**8.05**		

Step A-d-(15%)

Reactants, catalyst and solvent, R	Amount of R, g	Product, P	Amount of P, g
Poly(FuCa)	10.80	Poly(FuCa)-P15	11.047
GVL (solvent), 25 mL	26.25		
TCAN, 1.5 mL	2.16		
TBAP	3.40		
Acetonitrile, 10 mL	7.86		
Methanol, 3x10 mL	23.94		
Diethyl ether, 3x50 mL	106.95		
Σ R (g)	**181.36**	**Σ P (g)**	**11.047**
Waste (g), W = ΣR -Σ P	**170.31**		
E-Factor = W/ΣP	**15.42**		

Step A-d-(50%)

Reactants, catalyst and solvent, R	Amount of R, g	Product, P	Amount of P, g
Poly(FuCa)	10.80	Poly(FuCa)-P50	15.4
GVL (solvent), 25 mL	26.25		
TCAN, 6 mL	8.64		
TBAP	18.70		
Acetonitrile, 50 mL	39.30		
Methanol, 3x10 mL	23.94		
Diethyl ether, 3x0 mL	106.95		
Σ R (g)	**234.58**	**Σ P (g)**	**15.4**
Waste (g), W = ΣR -Σ P	**219.18**		
E-Factor = W/ΣP	**14.23**		

Step B-b

Reactants, catalyst and solvent, R	Amount of R, g	Product, P	Amount of P, g
Succinic acid	98.00	SuBCC	211
Glycerol carbonate	200.00		
Toluene, 750 mL	650.25		
Catalyst (p-TSA)	2.00		
Acetone, 200 mL	156.80		
Ethanol, 500 mL	394.50		
Σ R (g)	**1501.55**	**Σ P (g)**	**211**
Waste (g), W = ΣR -Σ P	**1290.55**		
E-Factor = W/ΣP	**6.12**		

Step B-e

Reactants, catalyst and solvent, R	Amount of R, g	Product, P	Amount of P, g
SuBCC	10.00	Poly(SuCa)	11.89
Cadavarine	3.22		
Anisol, 30 mL	29.85		
Methanol, 3x10 mL	23.94		
Diethyl ether, 3x20 mL	42.78		
Σ R (g)	**109.79**	**Σ P (g)**	**11.89**
Waste (g), W = ΣR -Σ P	**97.9**		
E-Factor = W/ΣP	**8.23**		

Step B-f-(15%)

Reactants, catalyst and solvent, R	Amount of R, g	Product, P	Amount of P, g	
Poly(SuCa)	15.00	Poly(SuCa)-P-15		15.71
GVL-(solvent), 50 mL	52.50			
TCAN, 2.2 mL	3.17			
TBAP	4.75			
Methanol, 3x15 mL	35.91			
Ether, 3x75 mL	160.43			
Acetonitrile, 10 mL	7.86			
Σ R (g)	**279.61**	**Σ P (g)**	**15.71**	
Waste (g), W = ΣR -Σ P	**263.90**			
E-Factor = W/ΣP	**16.80**			

Step B-f-(50%)

Reactants, catalyst and solvent, R	Amount of R, g	Product, P	Amount of P, g
Poly(SuCa)	1.05	Poly(SuCa)-P50	0.9157
GVL-(solvent), 2.5 mL	2.63		
TCAN, 0.6 mL	3.17		
TBAP	1.87		
Methanol, 3x1 mL	2.39		
Ether, 3x5 mL	10.70		
Acetonitrile, 5 mL	3.93		
Σ R (g)	**25.73**	**Σ P (g)**	**0.9157**
Waste (g), W = ΣR -Σ P	**24.82**		
E-Factor = W/ΣP	**27.10**		

Figure S31: Microscopic image of olive oil in water emulsions without the use of any additive taken after leaving the emulsions for 24 h.