Electronic Supplementary Material (ESI) for RSC Advances.

Post Polymer Modification of Polyethylenimine with Citrate Esters: Selectivity and Hydrophobicity

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Table S1. Reactivity of amines with citrate esters.[a]

Citrate ester	Amine	Type of amine	Abs_{amide}/Abs_{ester} [b]
TEC	*n*-Butyl amine	Primary	1.75
TBC	*n*-Butyl amine	Primary	2.02
TEC	Oleyl amine	Primary	0.56
TBC	Oleyl amine	Primary	0.62
TEC	Allyl amine	Primary	1.00
TBC	Allyl amine	Primary	0.88
TEC	Benzyl amine	Primary	0.64
TBC	Benzyl amine	Primary	0.61
TEC	Diethyl amine	Secondary	0.016
TBC	Diethyl amine	Secondary	0.021
TEC	Di-*n*-butyl amine	Secondary	0.032
TBC	Di-*n*-butyl amine	Secondary	0.019
TEC	Diisopropyl amine	Secondary	0.019
TBC	Diisopropyl amine	Secondary	0.022
TEC	Hexamethyleneimine	Secondary	0.026
TBC	Hexamethyleneimine	Secondary	0.040
TEC	Morpholine	Secondary	0.017
TBC	Morpholine	Secondary	0.064
TEC	Diisopropylethyl amine	Tertiary	0.0096
TBC	Diisopropylethyl amine	Tertiary	0.019
TEC	*n*-Tripropyl amine	Tertiary	0.015
TBC	*n*-Tripropyl amine	Tertiary	0.026
TEC	N,N,N-trimethylethylene diamine	Secondary/Tertiary	0.049
TBC	N,N,N-trimethylethylene diamine	Secondary/Tertiary	0.071

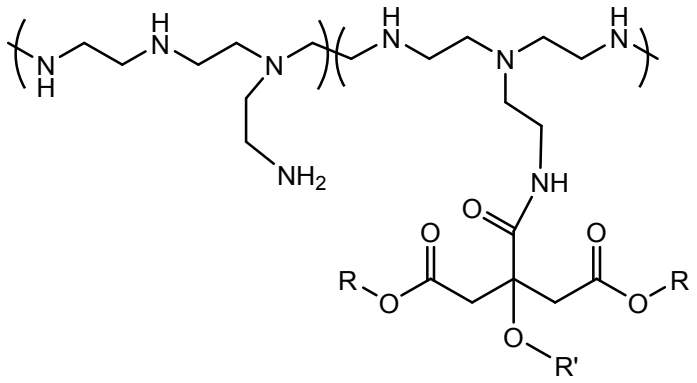
[a]Reaction conditions: Amine (0.3 mL) and citrate ester (0.2 mL) reacted for 2 h at 80 °C in capped vials. [b]Using FTIR spectroscopy, reactivity determined by heights of amide and ester (1734 cm^{-1}) absorbances.

Table S2. Octanol-water partition coefficients ($LogP_{oct}$) and surface area data for molecular models shown in Scheme S1 using Chem3D.

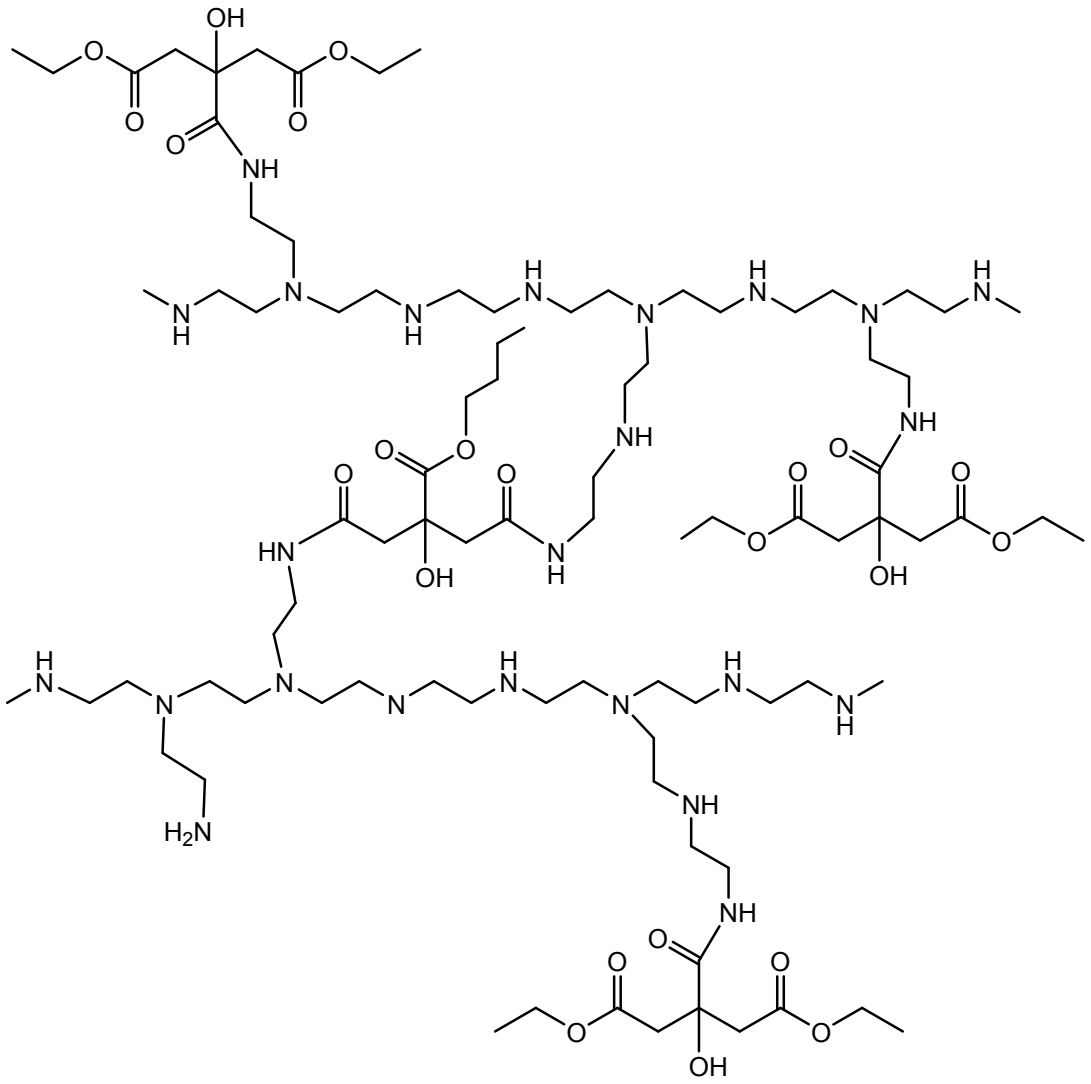
Citrate Ester	[1° NH_2]/[esters]	$LogP_{oct}$	Connelly Surface Area ($Å^2$)	$LogP_{oct}$/SA
TEC	1	-1.87	427.14	-0.0044
TEC	2	-3.51	617.22	-0.0057
TEC	3	-5.15	769.59	-0.0067
TBC	1	-0.087	485.12	-0.00018
TBC	2	-1.73	638.05	-0.0027
TBC	3	-3.37	795.19	-0.0042
TBC-OAc	1	0.65	523.95	0.0012
TBC-OAc	2	-0.99	704.09	-0.0014
TBC-OAc	3	-2.63	866.22	-0.0030

Table S3. Octanol-water partition coefficients (ALogP) and surface area (SA) data for molecular models shown in Scheme S1 using Materials Studio.

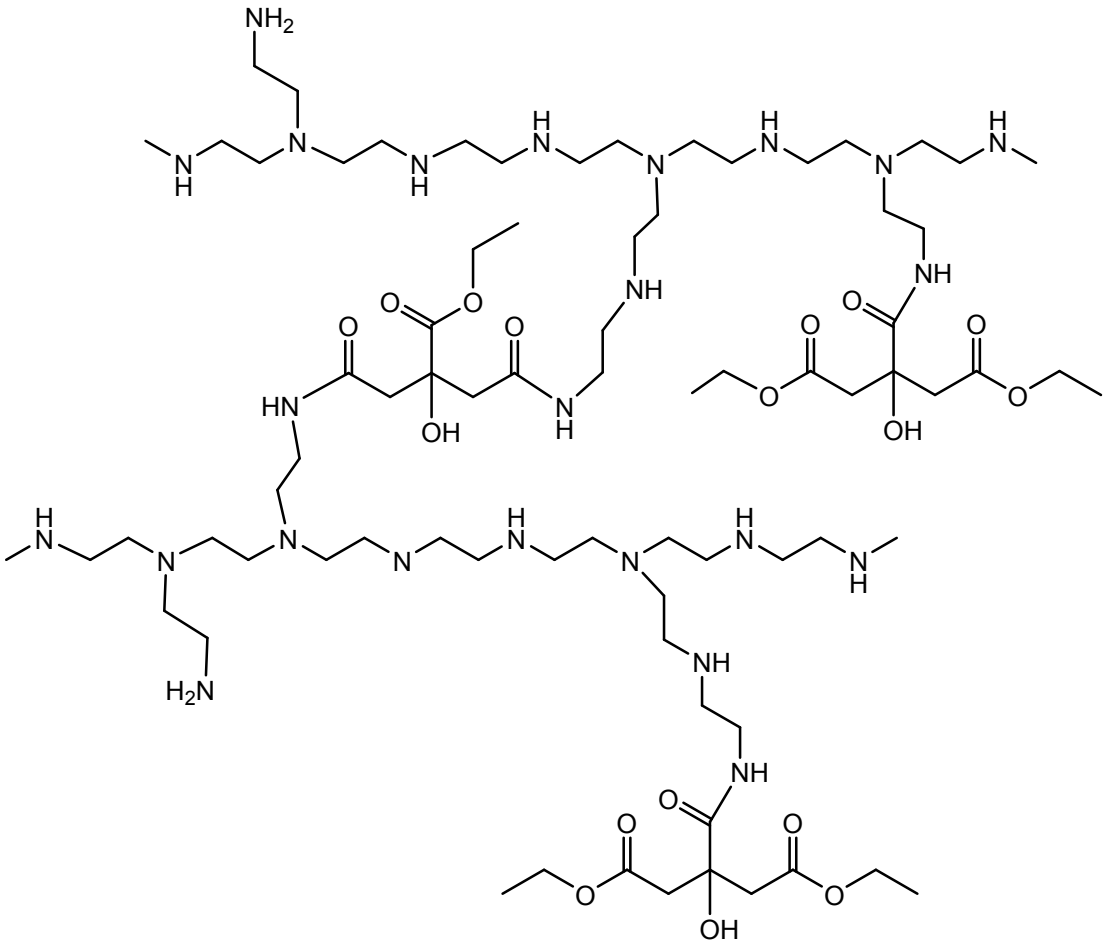
Citrate Ester	[1° NH_2]/[esters]	ALogP	Connelly Surface Area ($Å^2$)	ALogP/SA
TEC	1	-1.88	458.1	-0.0043
TEC	2	-3.45	658.4	-0.0055
TEC	3	-5.03	867.5	-0.0061
TBC	1	-0.148	558.0	-0.00030
TBC	2	-1.72	802.8	-0.0024
TBC	3	-3.30	932.6	-0.0036
TBC-OAc	1	-0.0187	584.9	-0.000036
TBC-OAc	2	-1.595	768.4	-0.0022
TBC-OAc	3	-3.17	1046.98	-0.0033



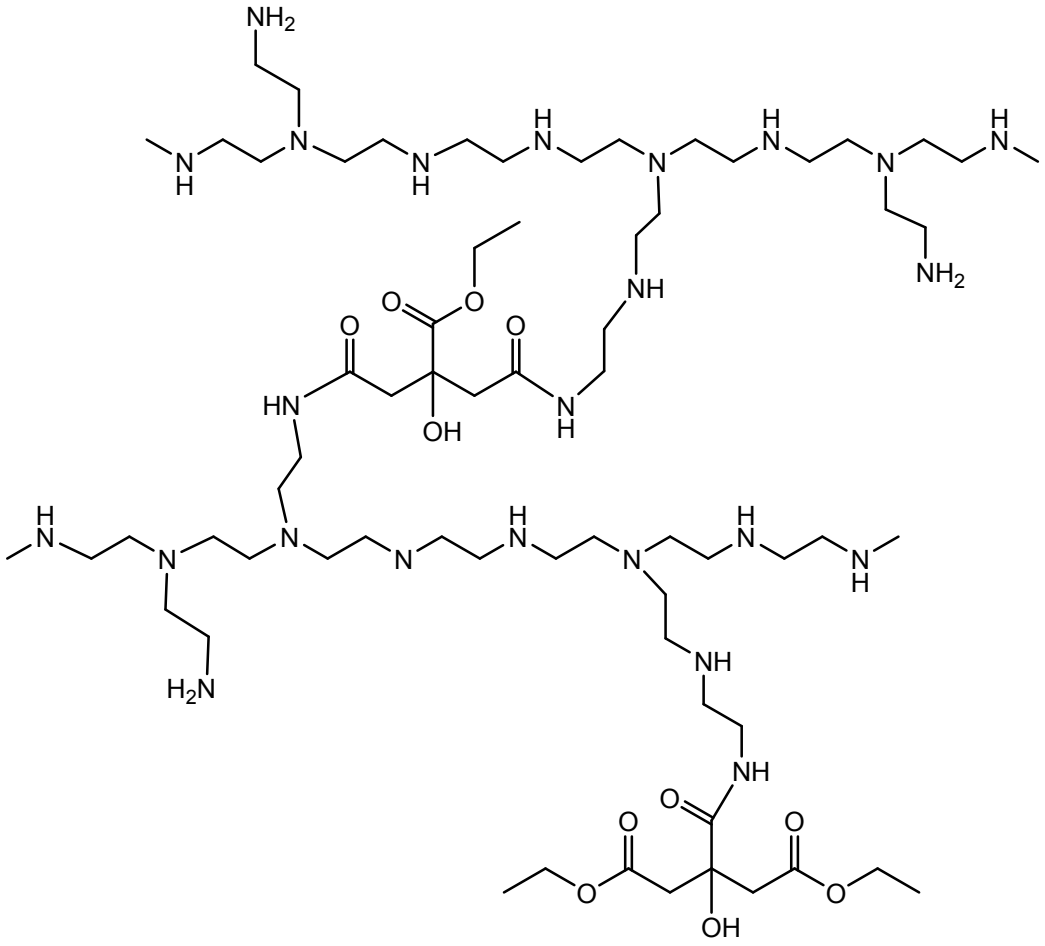
Scheme S1. Molecular model of PEI thermosets for $LogP_{oct}$ calculations without crosslinks. The model used a 1:2:1 ratio for primary:secondary:tertiary amines. The [primary NH_2]:[citrate ester] ratio ranged from 1-3 in order to resemble experimental conditions.



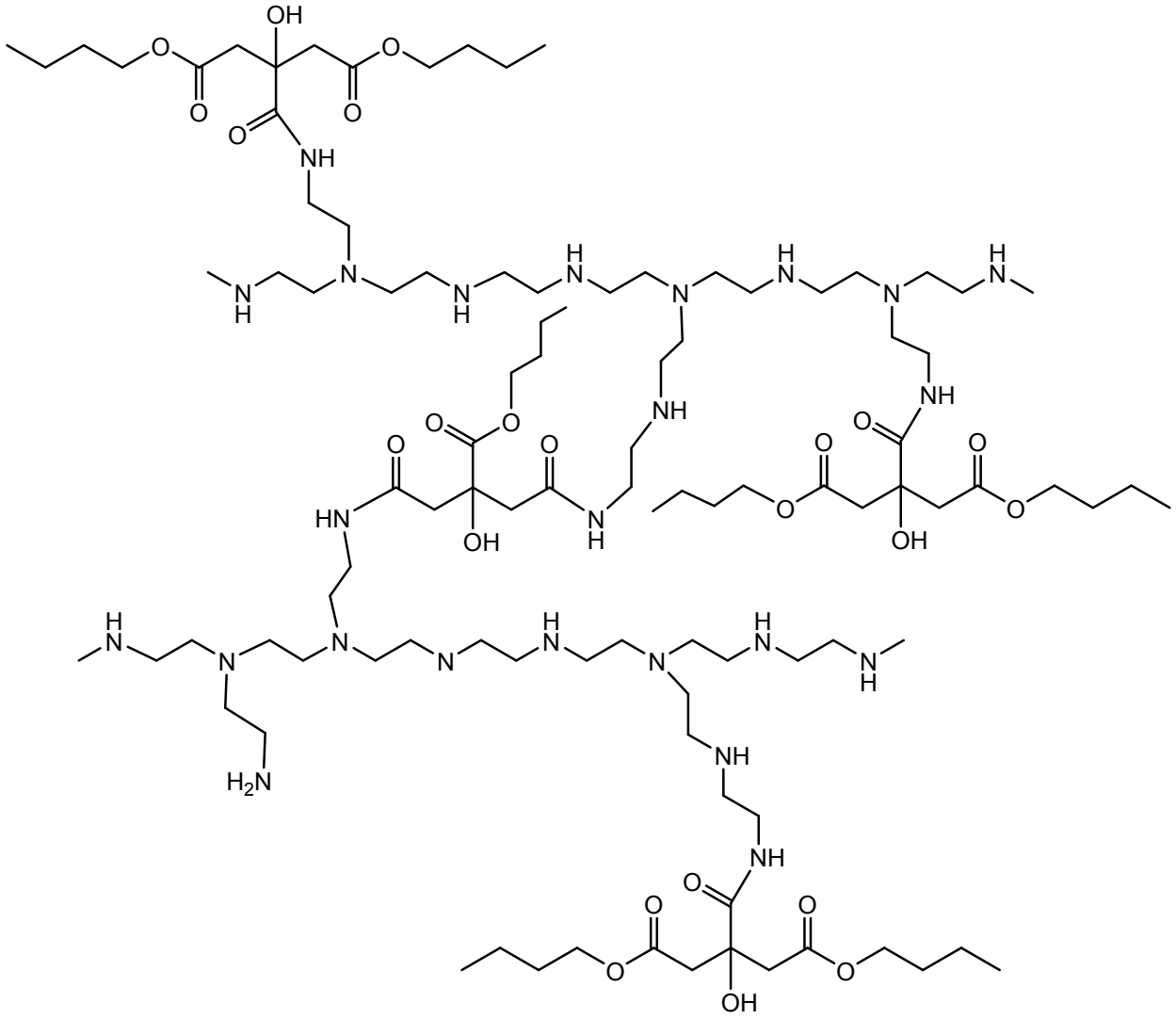
Scheme S2. Molecular model of PEI thermosets for $LogP_{oct}$ calculations with one crosslink and three terminal TEC groups. The model used a 1:2:1 ratio for primary:secondary:tertiary amines. The [primary NH_2]:[citrate ester] ratio of 1.5 resembled experimental conditions. Methyl groups on nitrogen atoms represent a connection to other PEI chains.



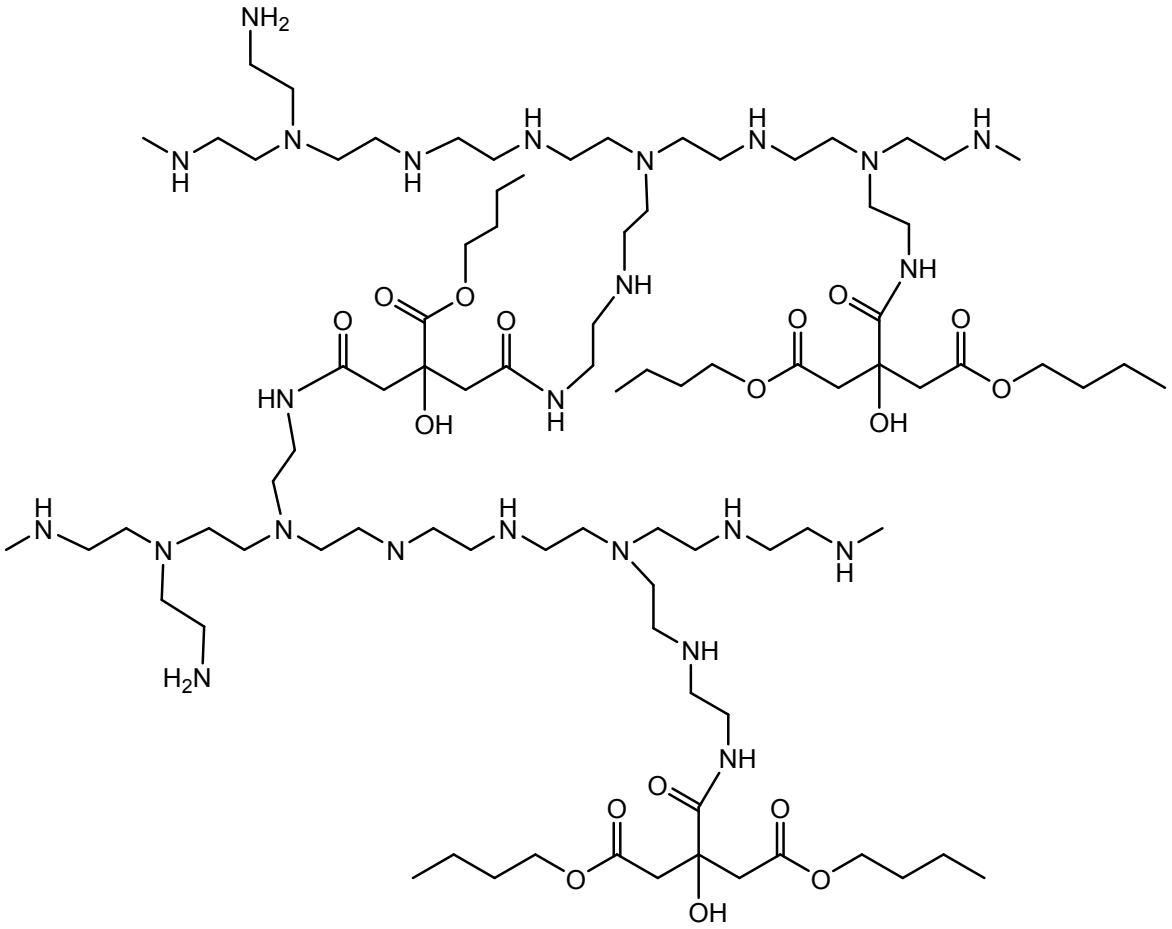
Scheme S3. Molecular model of PEI thermosets for $LogP_{oct}$ calculations with one crosslink and two terminal TEC groups. The model used a 1:2:1 ratio for primary:secondary:tertiary amines. The [primary NH_2]:[citrate ester] ratio of 2 resembled experimental conditions. Methyl groups on nitrogen atoms represent a connection to other PEI chains.



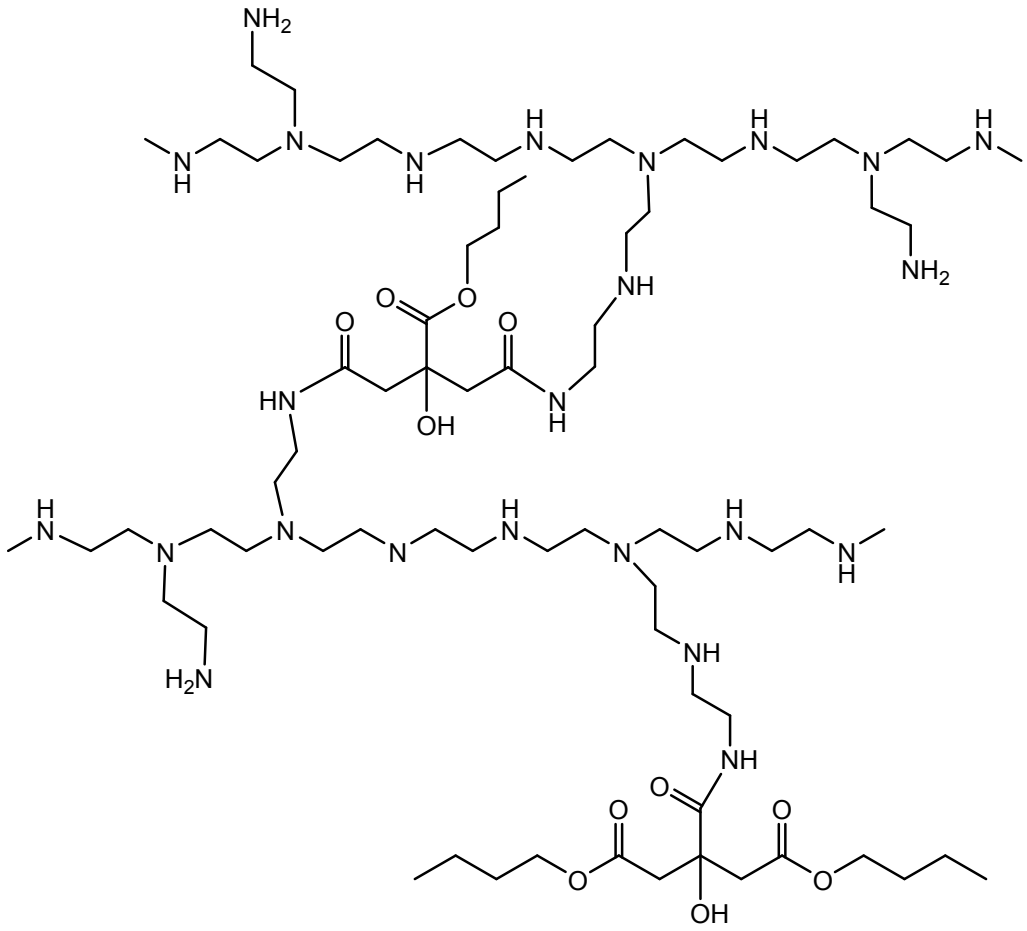
Scheme S4. Molecular model of PEI thermosets for $LogP_{oct}$ calculations with one crosslink and one terminal TEC group. The model used a 1:2:1 ratio for primary:secondary:tertiary amines. The [primary NH_2]:[citrate ester] ratio of 3 resembled experimental conditions. Methyl groups on nitrogen atoms represent a connection to other PEI chains.



Scheme S5. Molecular model of PEI thermosets for $LogP_{oct}$ calculations with one crosslink and three terminal TBC groups. The model used a 1:2:1 ratio for primary:secondary:tertiary amines. The [primary NH_2]:[citrate ester] ratio of 1.5 resembled experimental conditions. Methyl groups on nitrogen atoms represent a connection to other PEI chains.



Scheme S6. Molecular model of PEI thermosets for $LogP_{oct}$ calculations with one crosslink and two terminal TBC groups. The model used a 1:2:1 ratio for primary:secondary:tertiary amines. The [primary NH_2]:[citrate ester] ratio of 2 resembled experimental conditions. Methyl groups on nitrogen atoms represent a connection to other PEI chains.



Scheme S7. Molecular model of PEI thermosets for $LogP_{oct}$ calculations with one crosslink and one terminal TBC groups. The model used a 1:2:1 ratio for primary:secondary:tertiary amines. The [primary NH_2]:[citrate ester] ratio of 3 resembled experimental conditions. Methyl groups on nitrogen atoms represent a connection to other PEI chains.

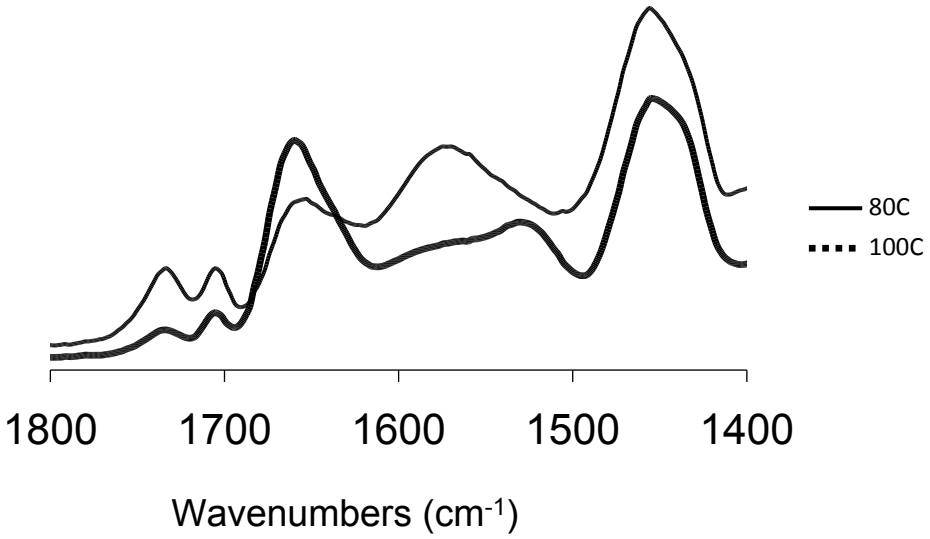


Figure S1. Overlay of FTIR spectra for polymerization of PEI (M_n ~ 10,000 g/mol) and triethyl citrate (TEC) after 2 h at 80 °C (solid line) and 100 °C (dashed line). The amount of PEI (2.0 g) and TEC (0.400 g) gave a molar ratio of [primary NH_2 groups]/[TEC] = 8. Compared to the starting materials, the polymerization caused a decrease in the ester absorbance (1734 cm^{-1}) and created a new amide absorbance (1662 cm^{-1}).

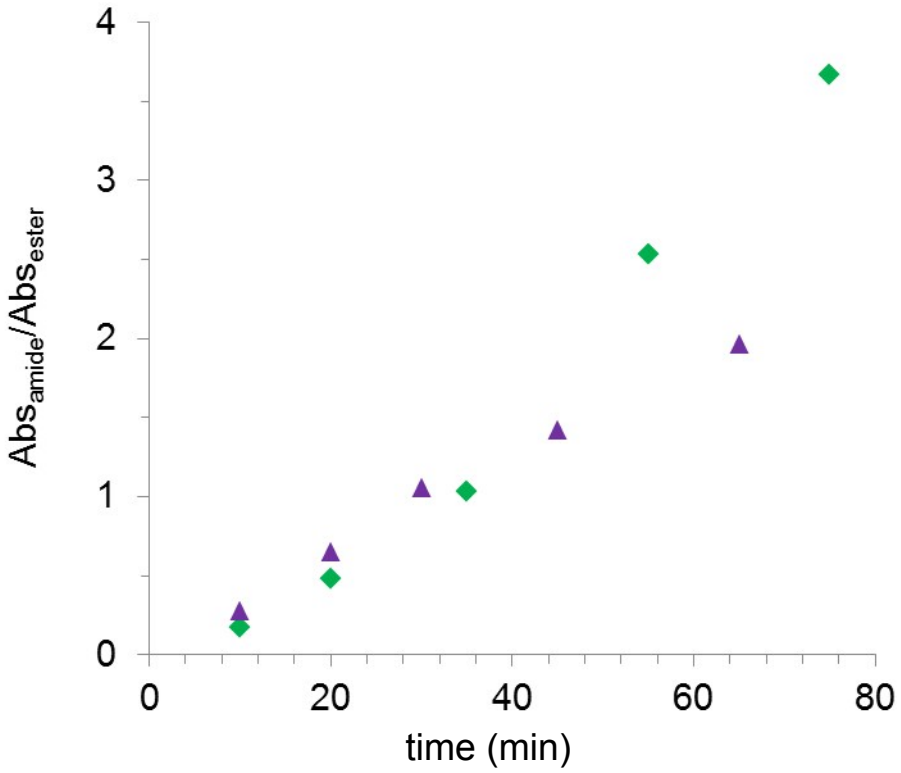
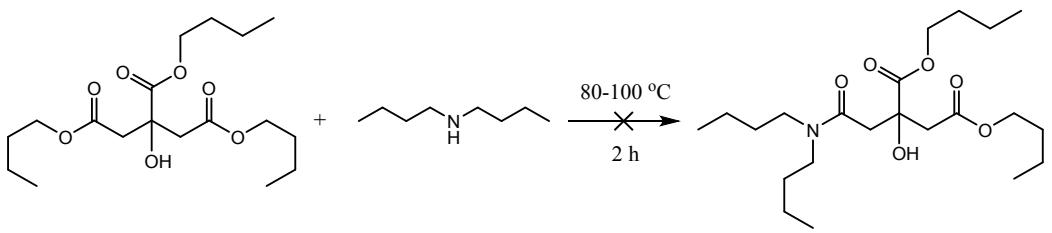


Figure S2. FTIR spectroscopy data for reaction of PEI (M_n ~ 10,000 g/mol) with triethyl citrate (TEC) (♦) and tributyl citrate (TBC) (▲) at 100 °C. Abs_{amide}/Abs_{ester} ratio calculated from height of amide (1662 cm^{-1}) and ester (1734 cm^{-1}) absorbances.



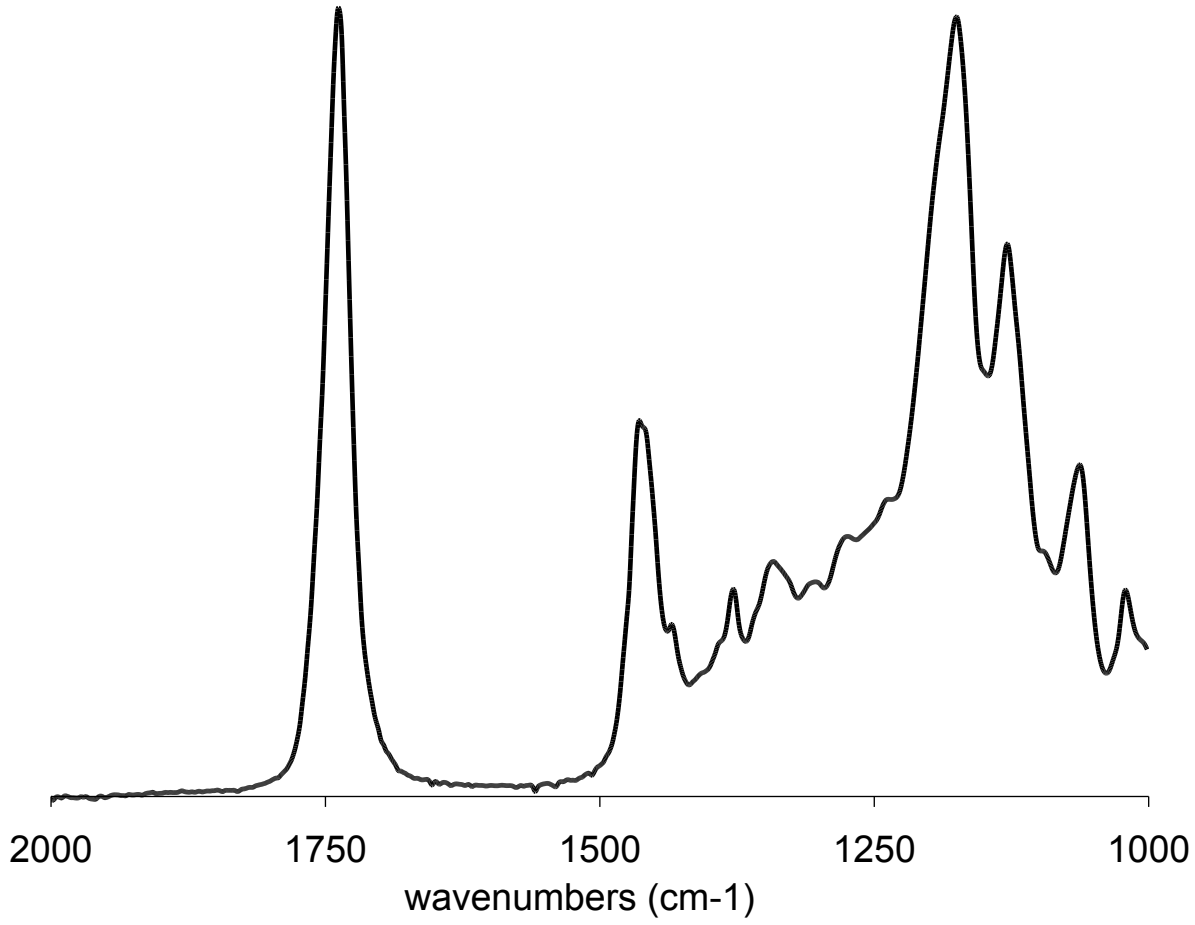


Figure S3. FTIR spectrum after heating tributyl citrate (TBC) and di-*n*-butyl amine for 2 h at 100 °C. The reaction was run without any solvent using [amine]/[TBC]=3. The formation of amide (1654 cm^{-1}) bonds or decreases in the ester absorbance at 1738 cm^{-1} were not detectable by FTIR after 120 min at 100 °C. Similar results were obtained at 80 °C.

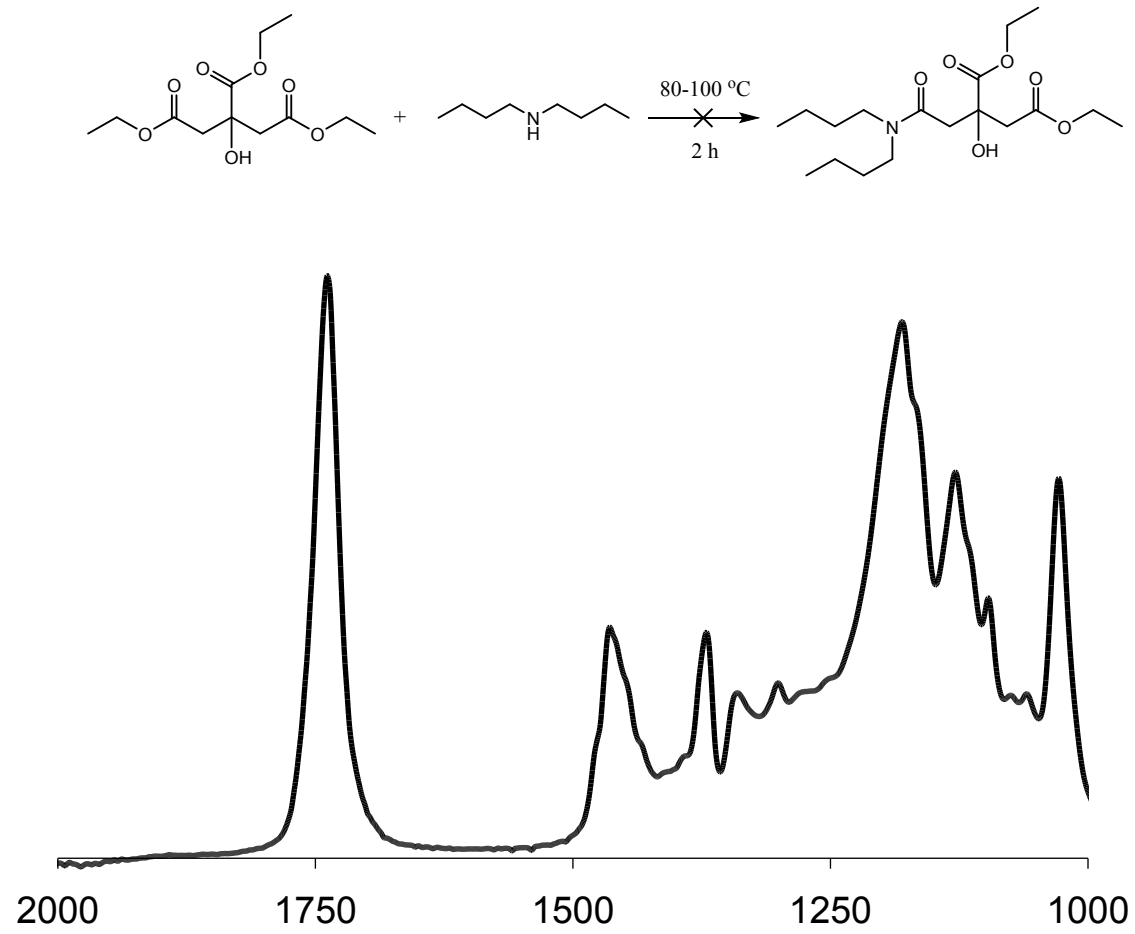


Figure S4. FTIR spectrum after heating triethyl citrate (TEC) and di-*n*-butyl amine for 2 h at 100 °C. The reaction was run without any solvent using [amine]/[TBC]=3. The formation of amide (1654 cm^{-1}) bonds or decreases in the ester absorbance at 1738 cm^{-1} were not detectable by FTIR after 120 min at 100 °C.

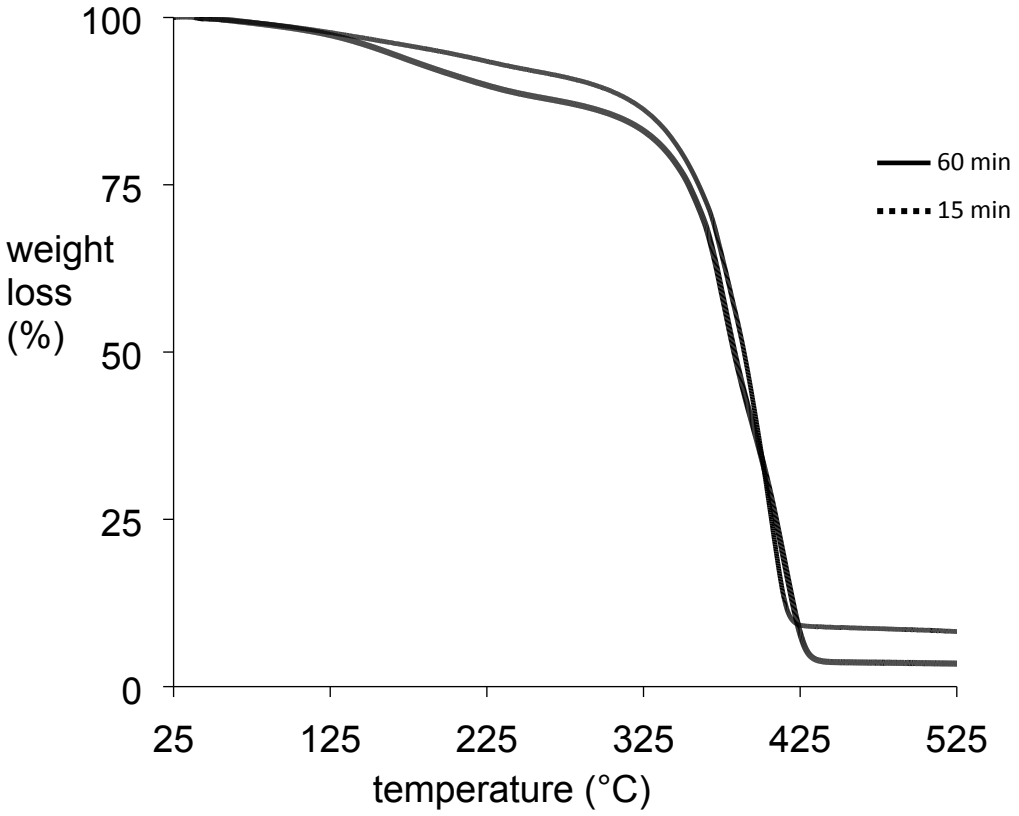


Figure S5. TGA data for polymerization of PEI (M_n ~ 10,000 g/mol) and TEC after 15 min (dashed line) and 60 min (solid line) at 100 °C. The amount of PEI (2.0 g) and TEC (0.400 g) gave a molar ratio of [primary NH_2 groups]/[TEC] = 8.

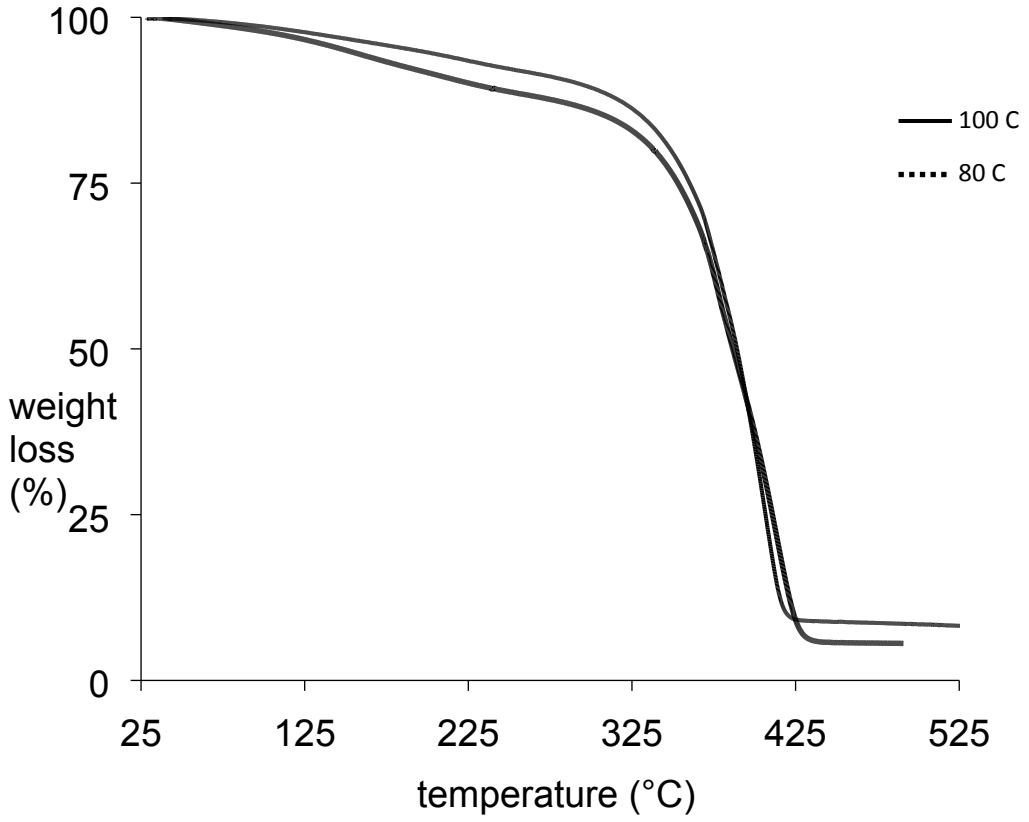


Figure S6. TGA data for polymerization of PEI (M_n ~ 10,000 g/mol) and TEC at 80 °C (dashed line) and 100 °C (solid line) after 1 h. The amount of PEI (2.0 g) and TEC (0.400 g) gave a molar ratio of [primary NH_2 groups]/[TEC] = 8. The onset of decomposition was 353 °C (dashed line) and 366 °C (solid line).

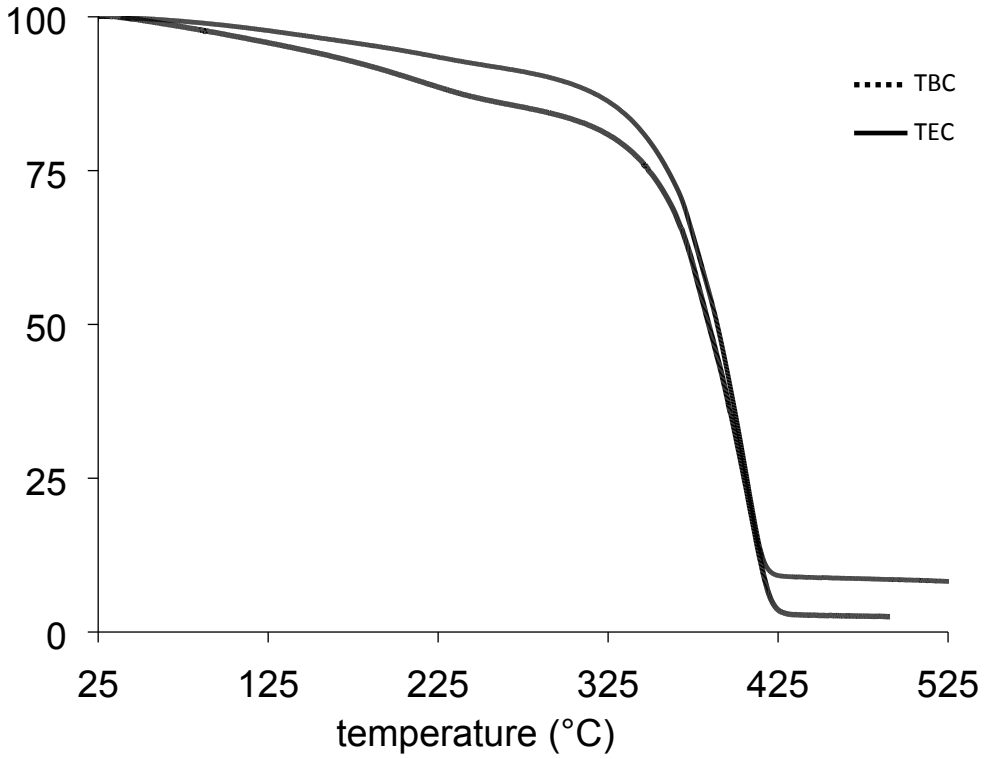


Figure S7. TGA data for polymerization of PEI (M_n ~ 10,000 g/mol) with TBC (dashed line) and TEC (solid line). The amount of PEI and citrate ester gave a molar ratio of [primary NH_2 groups]/[citrate ester] = 8. Polymerization conducted at 100 °C for 1 h.

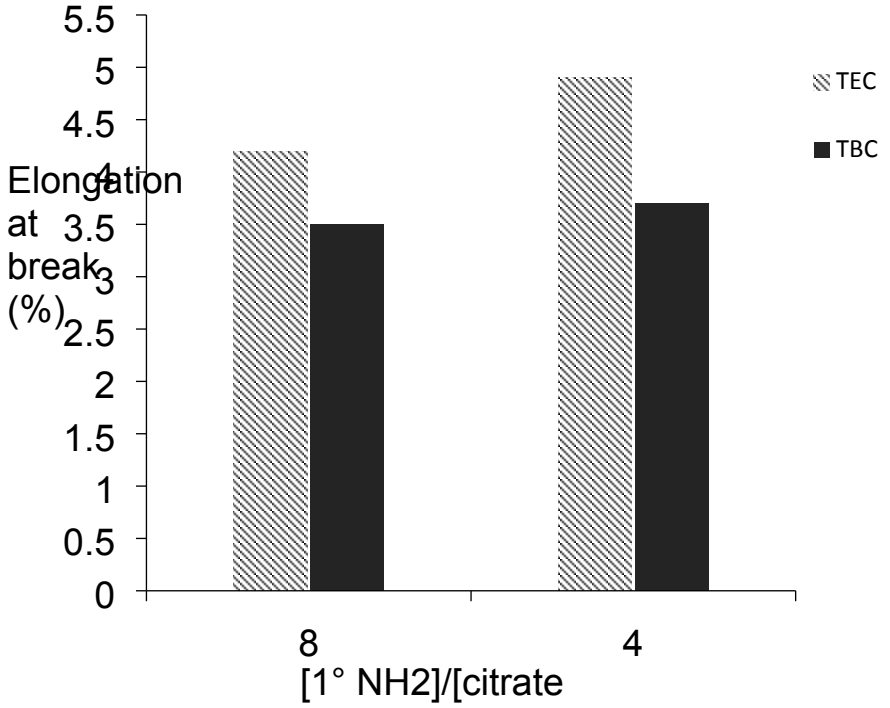


Figure S8. DMA data for polymerization of PEI (M_n ~ 10,000 g/mol) with TBC (solid) and TEC (shaded). Polymerizations were conducted at 100 °C for 2 h. Elongation at break determined from graph of stress versus strain at 1 N/min. The data in Figure S8 was obtained from an average of four samples.

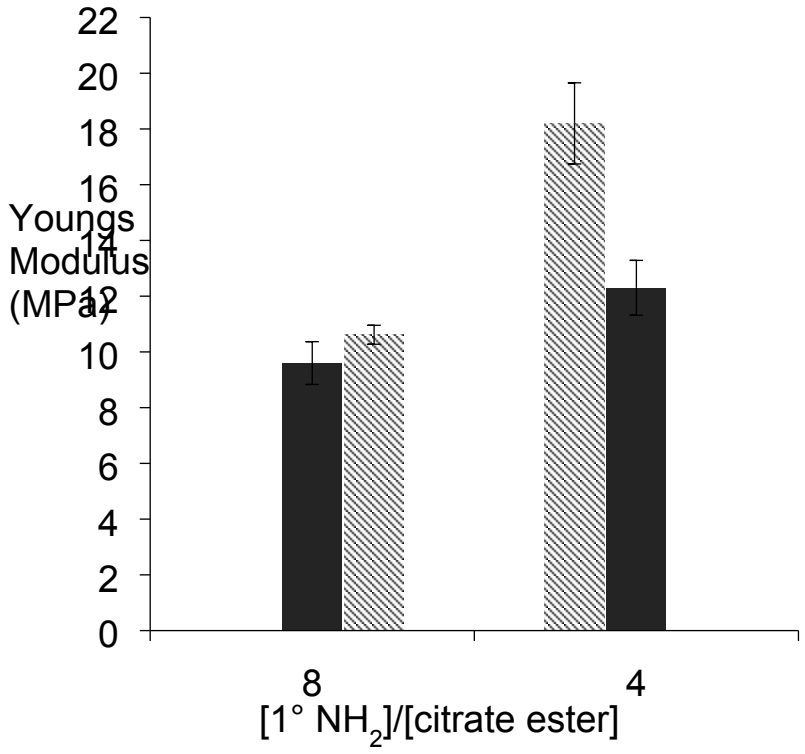


Figure S9. DMA data for polymerization of PEI (M_n ~ 10,000 g/mol) and citrate esters after 2 h at 100 °C. Data and error bars shown for TEC (shaded gray bars) and TBC (solid bars).

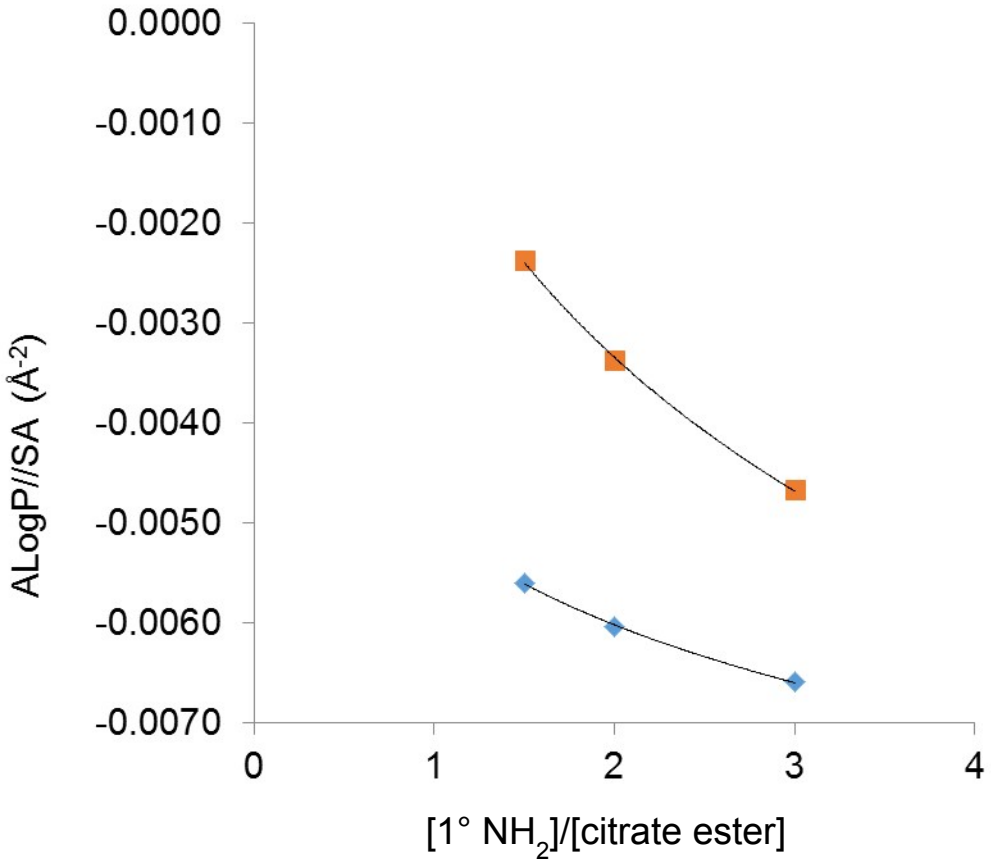


Figure S10. Hydrophobicity calculations of PEI models with one crosslink and terminal TEC (♦) or TBC (■) groups. See Schemes S2-S7 for molecular models. Data calculated with Material Studio using ALogP for the octanol-water partition coefficient. Connolly surface area (SA) calculated using geometry optimization in the Forcite module with a 1.4 Å probe. The solid lines represent logarithmic regression.

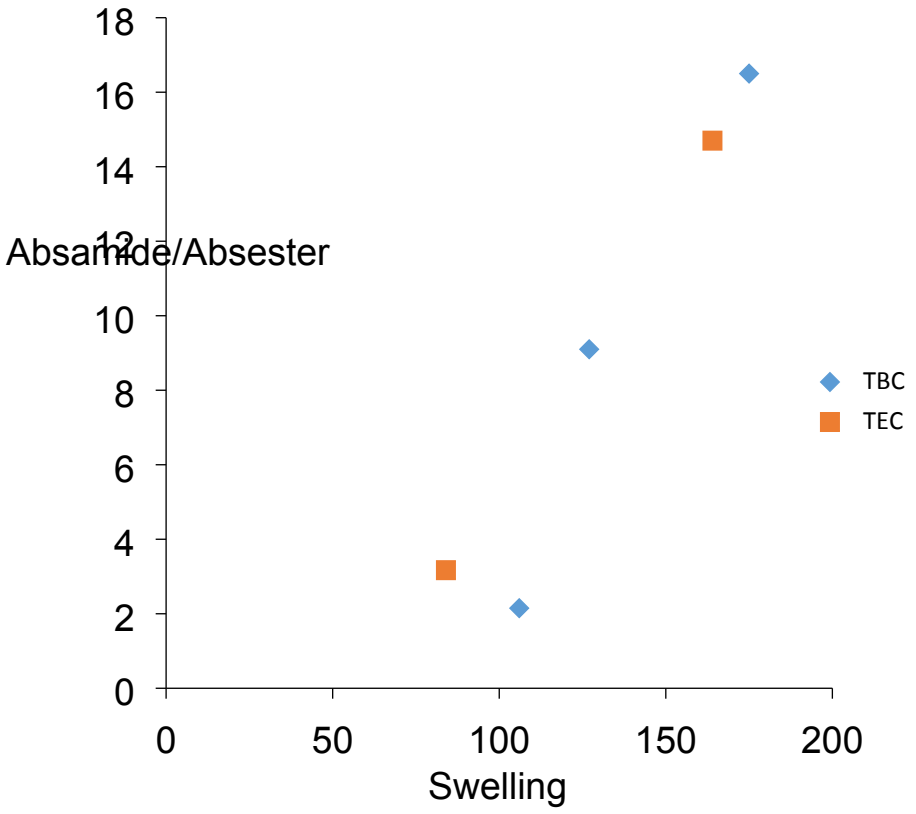


Figure S11. Graph of FTIR data versus swelling ratio (SR) in water. FTIR absorbance ratio based on amide (1654 cm^{-1}) and ester (1738 cm^{-1}) absorbances. Experimentally, all films were made using PEI (M_n ~ 10,000 g/mol) and heated for 2 h at 100 °C.