

Supporting information for

## Chiral Anion Triggered *Helical* Poly(Ionic Liquids)

Nellepalli Pothanagandhi, Akella Sivaramakrishna, Kari Vijayakrishna\*

Department of Chemistry, School of Advanced Sciences, VIT University, Vellore 632014, Tamil Nadu, India

### Spectral data for the synthesized PILs:

**Poly-1-vinyl-3-ethylimidazolium bromide:** White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta_{\text{H}}$ : 1.40 (3H, bs,  $\text{N-CH}_2\text{CH}_3$ ), 2.42 (2H, bs,  $\text{N-CHCH}_2$ ), 4.07 (3H, bs,  $\text{N-CH}_2\text{CH}_3$ ,  $\text{N-CHCH}_2$ ), 7.45 (3H, bs,  $\text{CHCH-N-CH-N}$ ).

**Poly-1-vinyl-3-ethylimidazolium hydroxide:** Brownish solid.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta_{\text{H}}$ : 1.31 (3H, bs,  $\text{N-CH}_2\text{CH}_3$ ), 2.39 (2H, bs,  $\text{N-CHCH}_2$ ), 4.08 (3H, bs,  $\text{N-CH}_2\text{CH}_3$ ,  $\text{N-CHCH}_2$ ).

**Poly-1-vinyl-3-ethylimidazolium-L-proline:** Brownish solid.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta_{\text{H}}$ : 1.34 (3H, bs,  $\text{N-CH}_2\text{CH}_3$ ), 1.77 (4H, m,  $\text{CH}_2\text{CH}_2\text{H}$ ), 2.42 (2H, bs,  $\text{N-CHCH}_2$ ), 2.91 (1H, m,  $\text{CHH}$ ), 3.13 (1H, m,  $\text{CHNH}$ ), 3.68 (1H, m,  $\text{CH-COO}$ ), 4.06 (3H, bs,  $\text{N-CH}_2\text{CH}_3$ ,  $\text{N-CHCH}_2$ ), 7.43 (3H, bs,  $\text{CHCH-N-CH-N}$ ).

**Poly-1-vinyl-3-ethylimidazolium-D-proline:** Brownish solid.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta_{\text{H}}$ : 1.35 (3H, bs,  $\text{N-CH}_2\text{CH}_3$ ), 1.82 (4H, m,  $\text{CH}_2\text{CH}_2\text{H}$ ), 2.41 (2H, bs,  $\text{N-CHCH}_2$ ), 3.04 (1H, m,  $\text{CHH}$ ), 3.19 (1H, m,  $\text{CHNH}$ ), 3.80 (1H, m,  $\text{CH-COO}$ ), 4.06 (3H, bs,  $\text{N-CH}_2\text{CH}_3$ ,  $\text{N-CHCH}_2$ ), 7.43 (3H, bs,  $\text{CHCH-N-CH-N}$ ).

**Poly-1-vinyl-3-ethylimidazolium-L-histidine:** Brownish solid.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta_{\text{H}}$ : 1.38 (3H, bs,  $\text{N-CH}_2\text{CH}_3$ ), 2.57 (2H,  $\text{N-CHCH}_2$ ), 2.80 (1H, s,  $\text{CHHC}$ ), 2.95 (1H, s,  $\text{CHHC}$ ), 3.47 (1H, s,  $\text{CHNH}_2$ ), 4.13 (3H, bs,  $\text{N-CH}_2\text{CH}_3$ ,  $\text{N-CHCH}_2$ ), 6.89 (1H, s,  $\text{C=CH}$ ), 7.48 (3H, bs,  $\text{CHCH-N-CH-N}$ ), 8.43 (1H, s,  $\text{N-CH-N}$ ).

**Poly-1-vinyl-3-ethylimidazolium-D-histidine:** Brownish solid.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta_{\text{H}}$ : 1.40 (3H, bs,  $\text{N-CH}_2\text{CH}_3$ ), 2.57 (2H,  $\text{N-CHCH}_2$ ), 2.78 (1H, s,  $\text{CHHC}$ ), 2.91 (1H, s,  $\text{CHHC}$ ), 3.46 (1H, s,  $\text{CHNH}_2$ ), 4.12 (3H, bs,  $\text{N-CH}_2\text{CH}_3$ ,  $\text{N-CHCH}_2$ ), 6.88 (1H, s,  $\text{C=CH}$ ), 7.48 (3H, bs,  $\text{CHCH-N-CH-N}$ ), 8.42 (1H, s,  $\text{N-CH-N}$ ).

**Polydiallyldimethylammonium hydroxide:** White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta_{\text{H}}$ : 1.18 (2H, bd,  $\text{CHCH}_2$ ), 1.41 (2H, bd,  $\text{CHCH}_2$ ), 2.58 (2H, bs,  $\text{CHCH}_2$ ), 3.01 (2H, bs,  $\text{N-CH}_2$ ), 3.07 (6H, m,  $\text{N-(CH}_3)_2$ ), 3.69 (2H, bs,  $\text{N-CH}_2$ ).

**Polydiallyldimethylammonium-L-proline:** White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta_{\text{H}}$ : 1.28 (4H, bd,  $\text{CHCH}_2$ ), 1.67 (3H, bs,  $\text{CH}_2\text{CHH}$ ), 2.05 (1H, bs,  $\text{CH}_2\text{CHH}$ ), 2.70 (2H, bs,  $\text{CHCH}_2$ ), 2.96 (1H, bs,  $\text{CHNH}$ ), 3.18 (6H, m,  $\text{N-(CH}_3)_2$ ), 3.41 (1H, bs,  $\text{CH-COO}$ ) 3.80 (4H, bs,  $\text{N-CH}_2$ ).

**Polydiallyldimethylammonium-D-proline:** White solid.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta_{\text{H}}$ : 1.28 (4H, bd,  $\text{CHCH}_2$ ), 1.50 (3H, bs,  $\text{CH}_2\text{CHH}$ ), 2.05 (1H, bs,  $\text{CH}_2\text{CHH}$ ), 2.71 (2H, bs,  $\text{CHCH}_2$ ), 2.97 (1H, bs,  $\text{CHNH}$ ), 3.17 (6H, m,  $\text{N-(CH}_3)_2$ ), 3.40 (1H, bs,  $\text{CH-COO}$ ) 3.79 (4H, bs,  $\text{N-CH}_2$ ).

**3-[Hydroxy-(4-nitro-phenyl)-methyl]-but-3-en-2-one:** Pale yellow solid, m.p. 79-81 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 2.34 (3H, t,  $\text{CH}_3$ ), 3.28 (1H, bs,  $-\text{OH}$ ), 5.66 (1H, s,  $\text{HO-CH}$ ), 6.01 (1H, s,  $\text{C-CHH}$ ), 6.24 (1H, s,  $\text{C-CHH}$ ), 7.54 (2H, dd, aromatic ring  $\text{CH}$ ), 8.19 (2H, dd, aromatic ring  $\text{CH}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 200.1, 149.0, 148.9, 147.3, 127.7, 127.2, 123.6, 72.2, 26.3; GC-MS,  $m/z$  221.30 ( $\text{M}^+$ ). Enantiomers of products were separated by chiral HPLC employing a Chiralpak IC column (Diacel). Conditions: 92.5:7.5 hexanes: isopropanol; Flow rate 0.3 mL/min; 270 nm, For reaction catalyzed with Poly(ViEm)-L-pr; 61.2 min (major), 66.4 min (minor), For reaction catalyzed with Poly(ViEm)-D-pr; 61.4 min (minor), 66.8 min (major).

Sample: PVIEm Br  
Size: 7.8100 mg  
Method: mehPIL

DSC

File: C:\Users\dhrusya\Desktop\LPVEIm Br.001

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Instrument: DSC Q2000 V24.10 Build 122

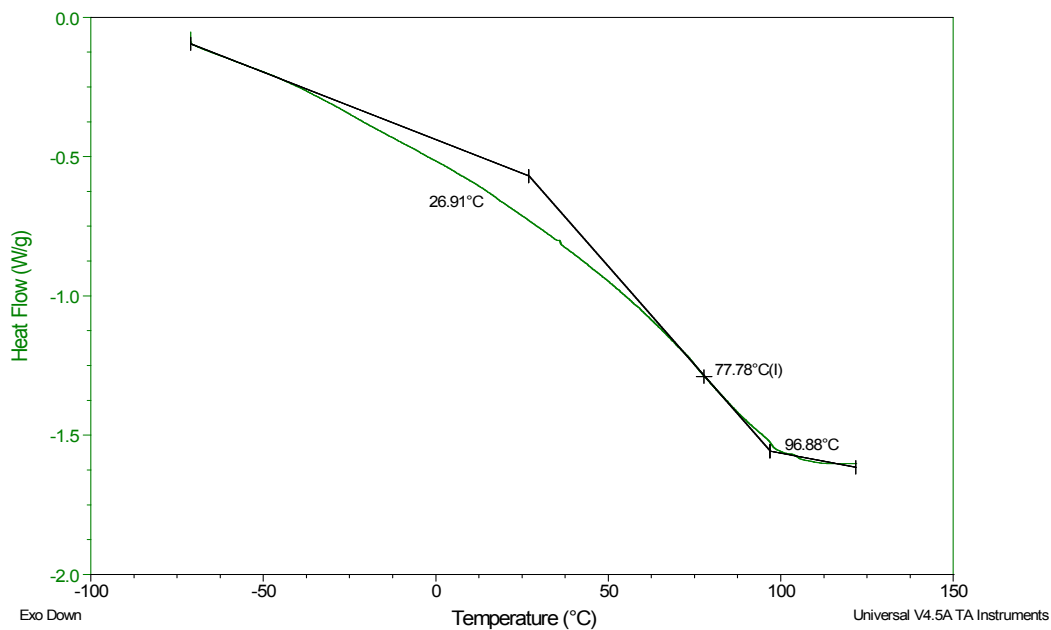


Figure S1. DSC traces of poly(ViEm) Br.

Sample: GROH  
Size: 3.6000 mg  
Method: mehPIL

DSC

File: C:\Users\dhrusya\Desktop\GROH.001

Run Date: 22-Apr-2015 17:36  
Instrument: DSC Q2000 V24.10 Build 122

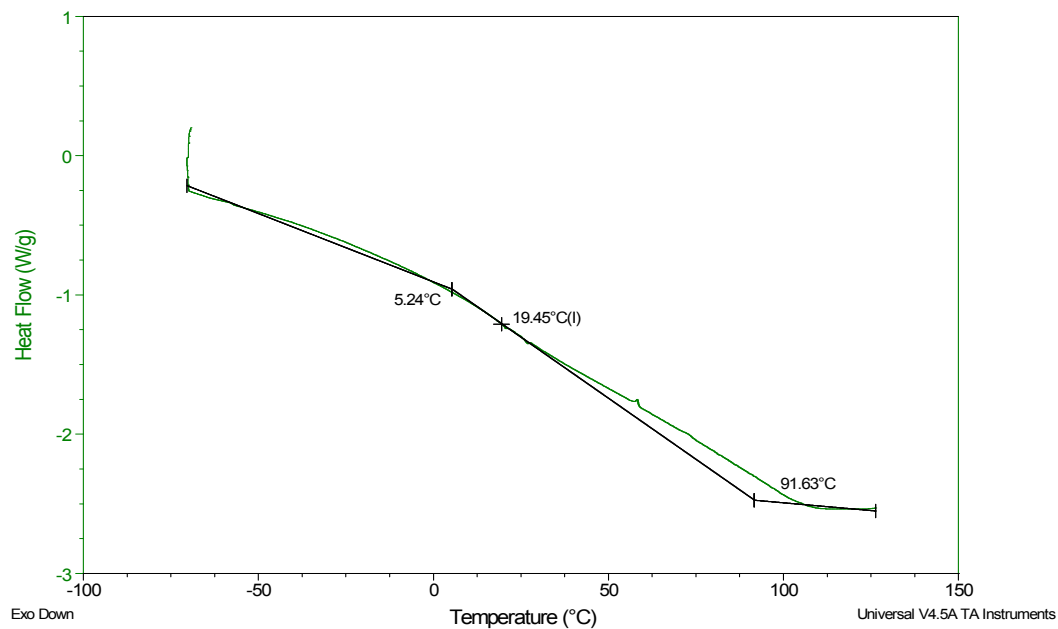


Figure S2. DSC traces of poly(ViEm) OH.

Sample: GRLP  
Size: 4.4000 mg  
Method: mehPIL

DSC

File: C:\Users\dhrusya\Desktop\GRLP.001

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Instrument: DSC Q2000 V24.10 Build 122

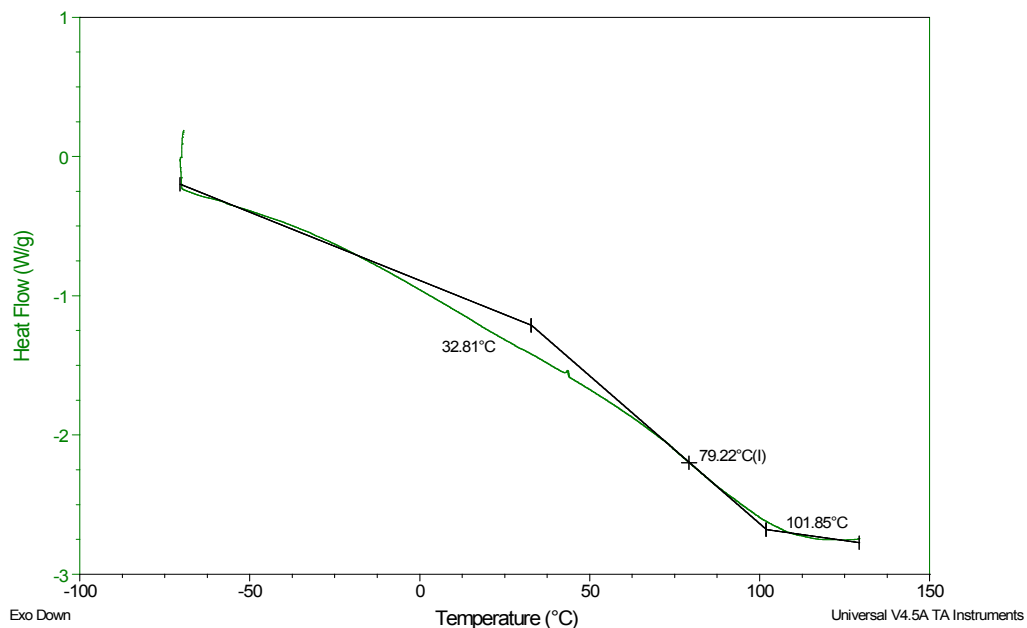


Figure S3. DSC traces of poly(ViEm)-L-pr.

Sample: GRDP  
Size: 3.3000 mg  
Method: mehPIL

DSC

File: C:\Users\dhrusya\Desktop\GRDP.001

Run Date: 22-Apr-2015 15:01

Instrument: DSC Q2000 V24.10 Build 122

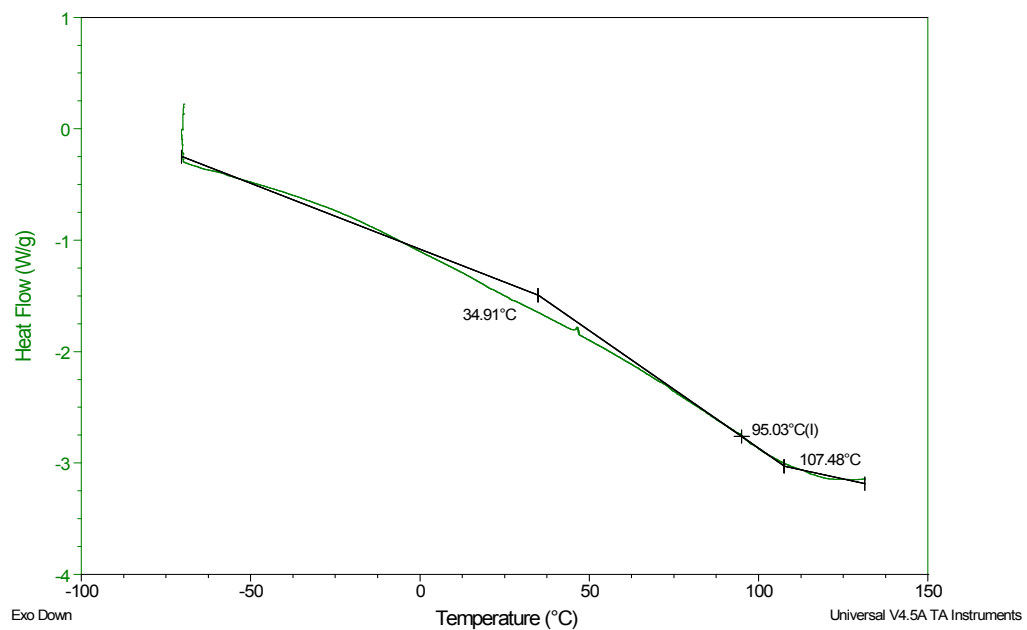


Figure S4. DSC traces of poly(ViEm)-D-pr.

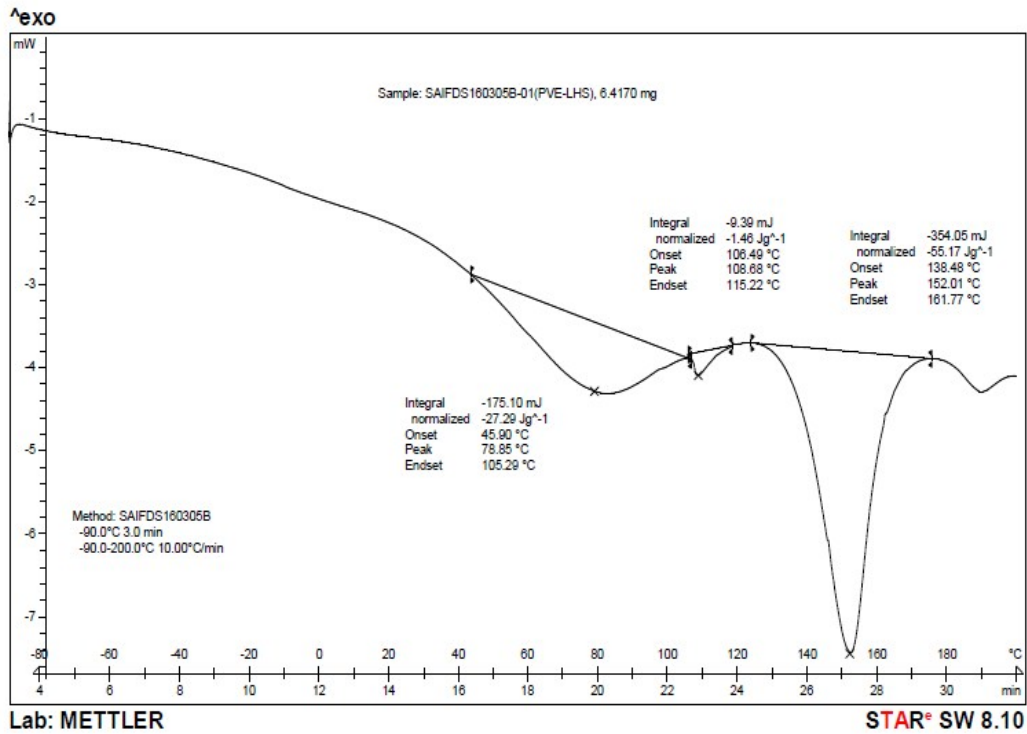


Figure S5. DSC traces of poly(ViElm)-L-his.

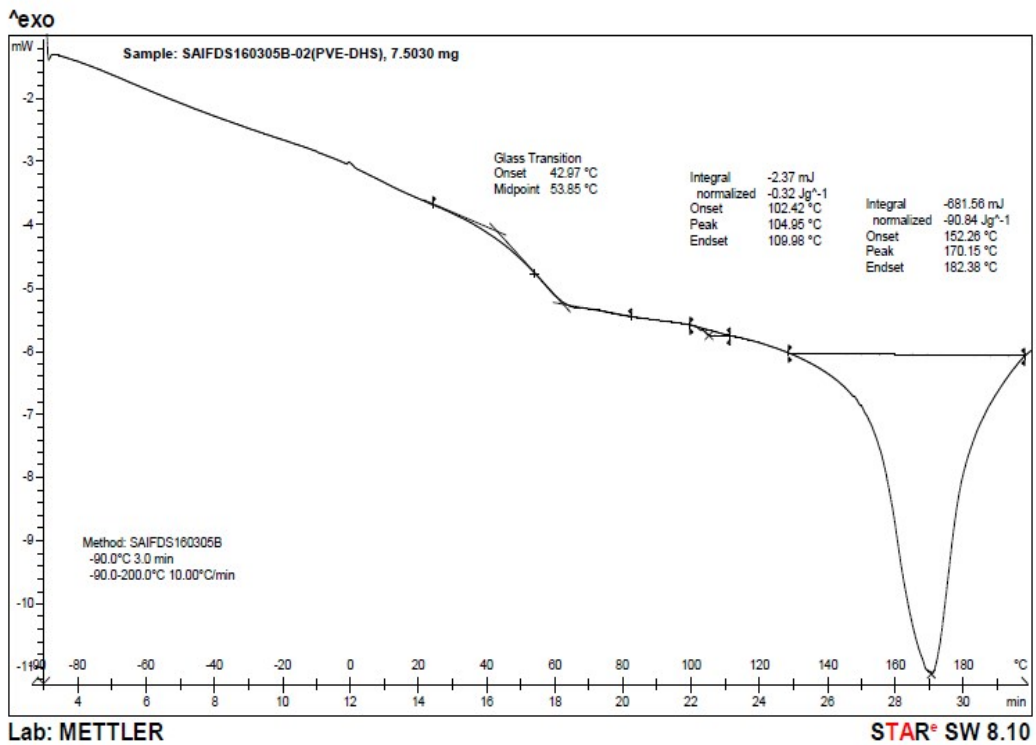


Figure S6. DSC traces of poly(ViElm)-D-his.

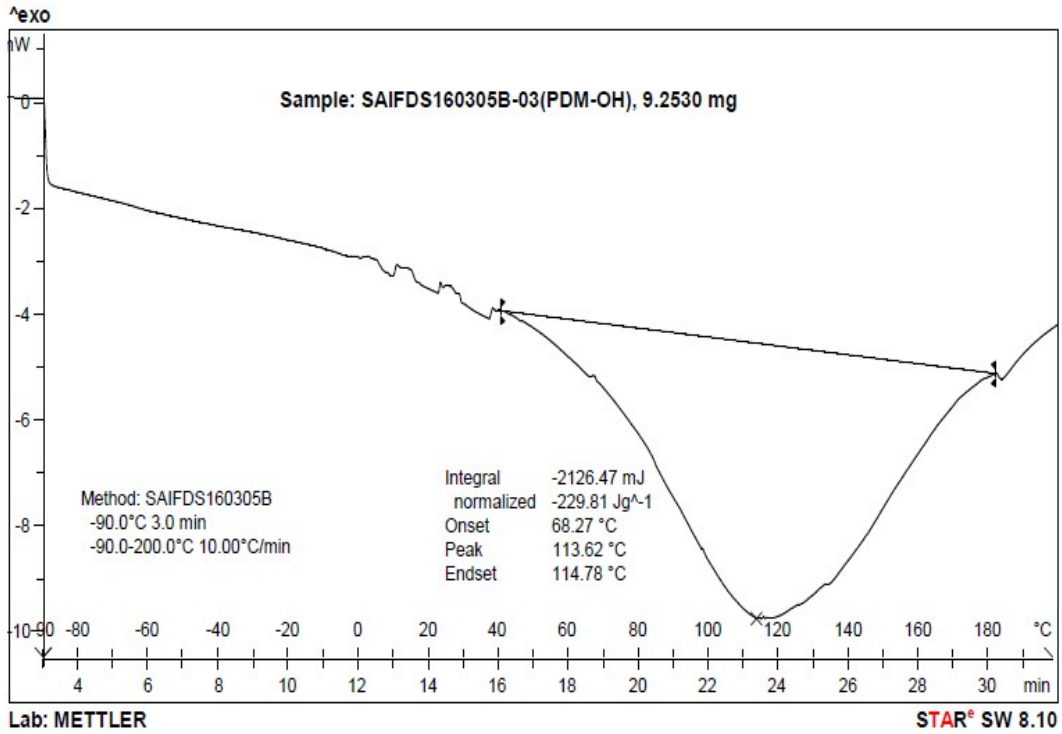


Figure S7. DSC traces of poly(dadma) OH.

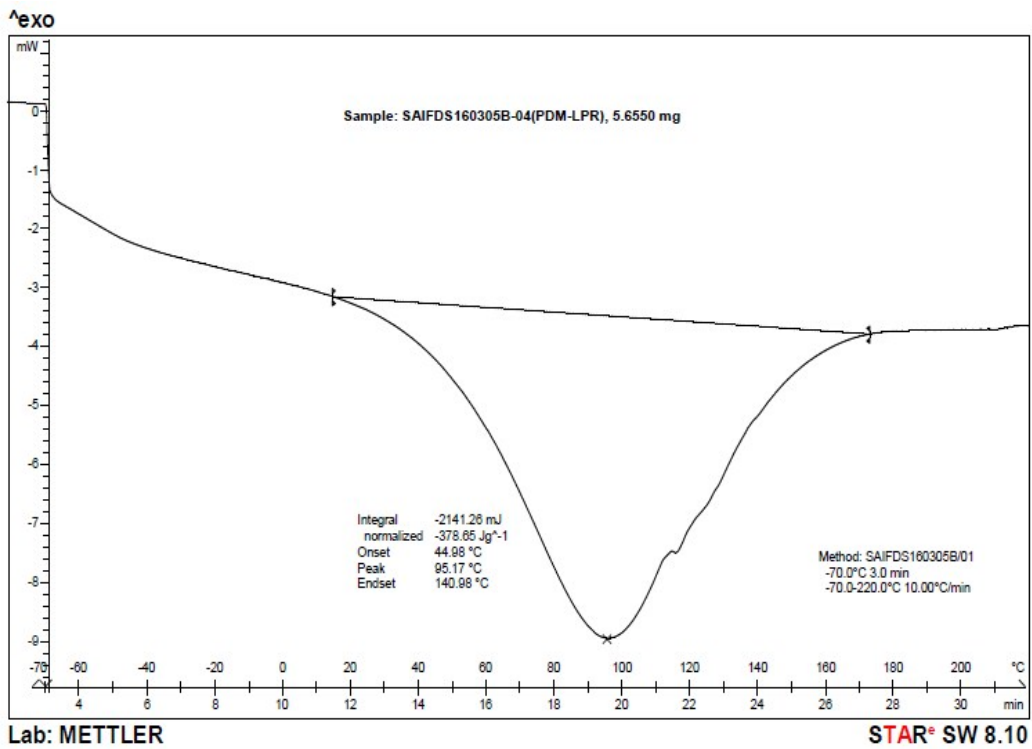


Figure S8. DSC traces of poly(dadma)-L-pr.

Sample: 3T2A  
Size: 2.2160 mg  
Method: Alba

### TGA

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Instrument: TGA Q500 V20.13 Build 39

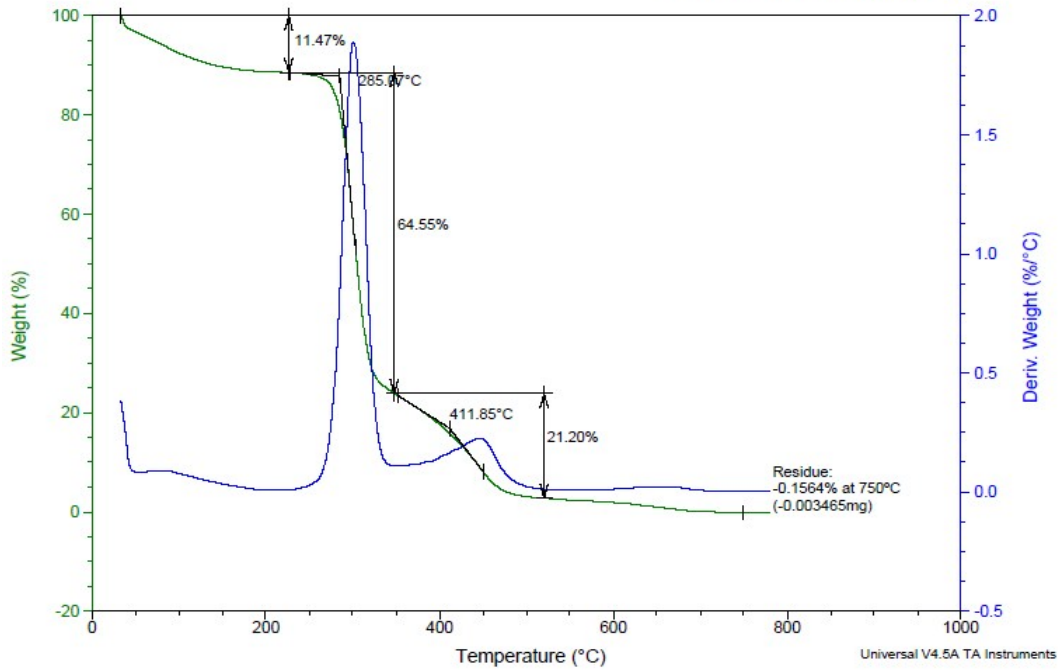


Figure S9. TGA spectrum of poly(ViIm) Br.

Sample: 3T2B  
Size: 2.6870 mg  
Method: Alba

### TGA

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Instrument: TGA Q500 V20.13 Build 39

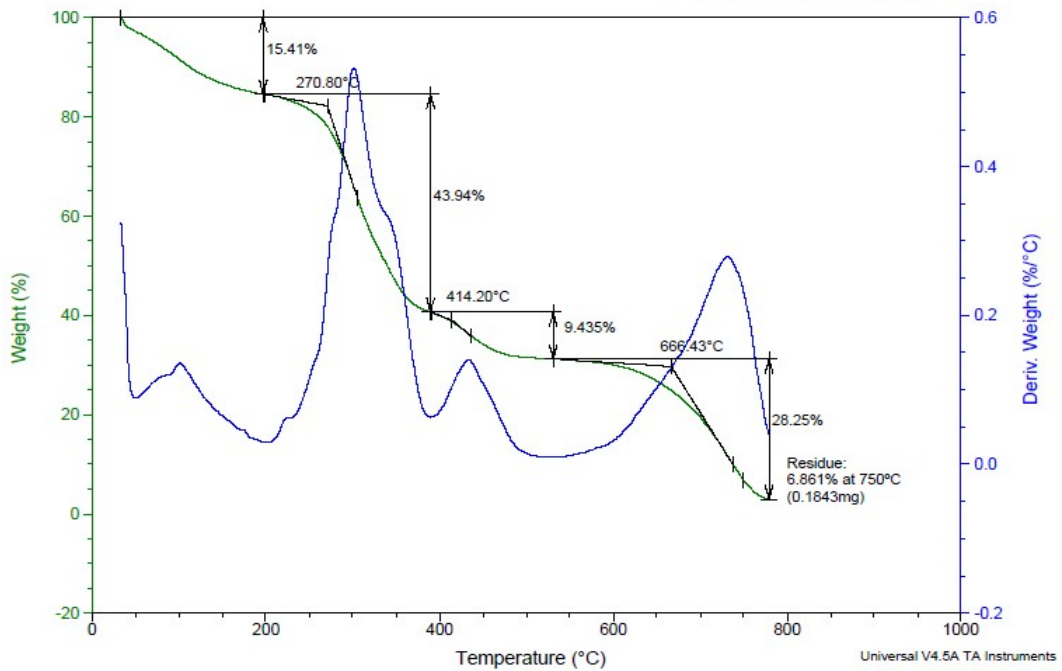


Figure S10. TGA spectrum of poly(ViIm) OH.

Sample: 3T2C  
Size: 2.8970 mg  
Method: Alba

TGA

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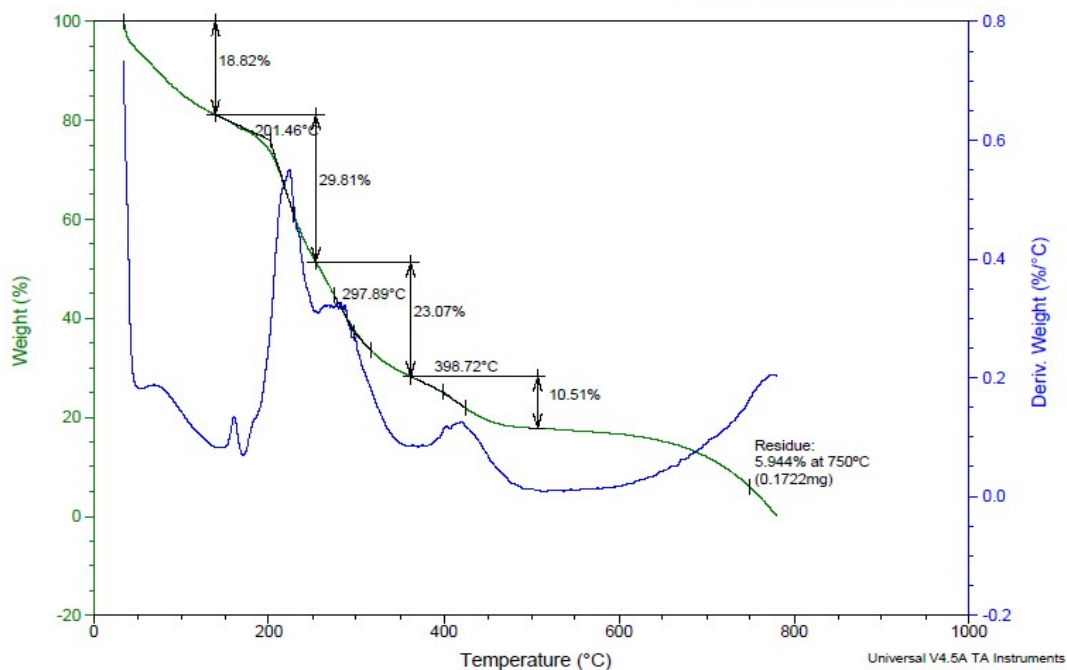


Figure S11. TGA spectrum of poly(ViElm)-L-pr.

Sample: 3T2D  
Size: 3.3080 mg  
Method: Alba

TGA

File: C:\...Desktop\Maitane\TGA Manoj\3T2D.001

Run Date: 06-Oct-2015 04:43  
Instrument: TGA Q500 V20.13 Build 39

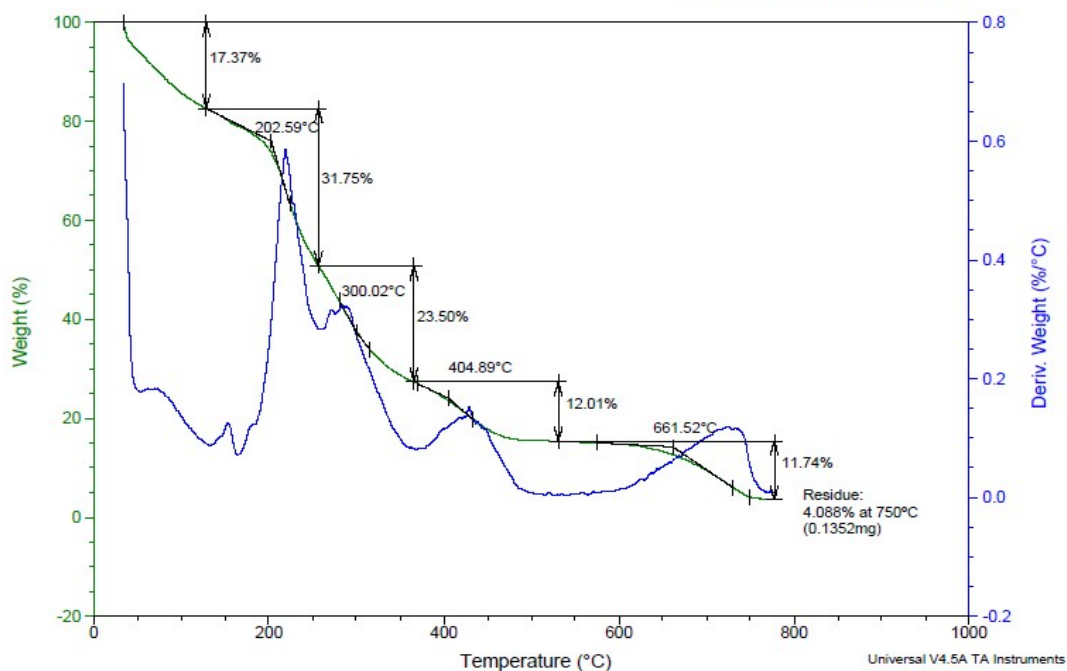


Figure S12. TGA spectrum of poly(ViElm)-D-pr.

Sample: 3T2Gt  
Size: 3.3920 mg  
Method: Alba

TGA

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Run Date: 06-Oct-2015 01:45  
Instrument: TGA Q500 V20.13 Build 39

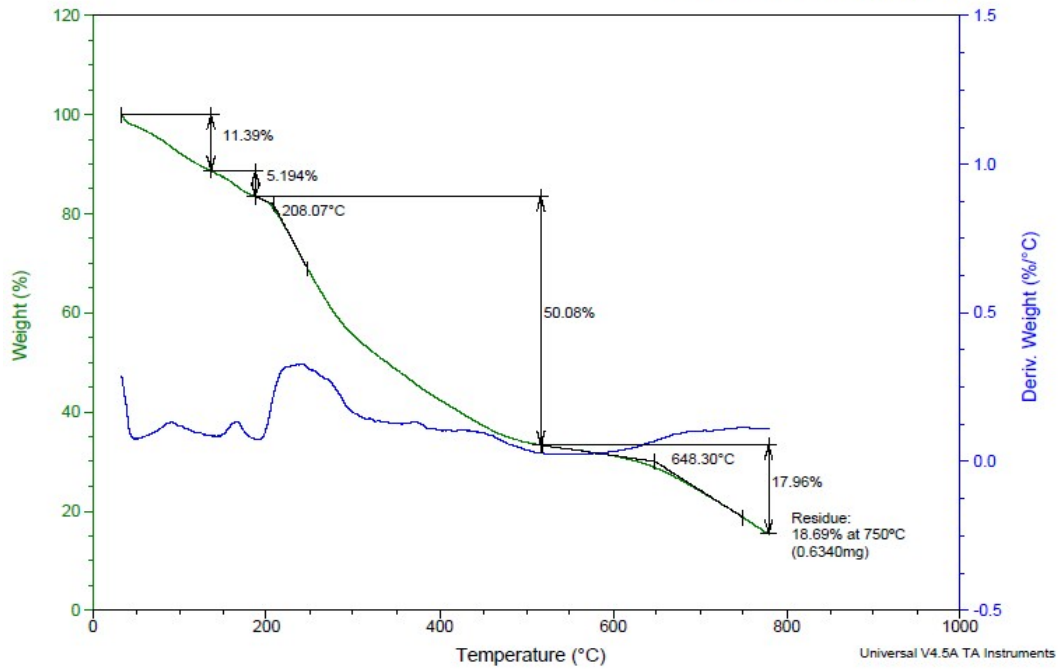


Figure S13. TGA spectrum of poly(ViElm)-L-his.

Sample: 3T2H  
Size: 4.1150 mg  
Method: Alba

TGA

File: C:\...Desktop\Maitane\TGA Manoj\3T2H.001

Run Date: 05-Oct-2015 16:50  
Instrument: TGA Q500 V20.13 Build 39

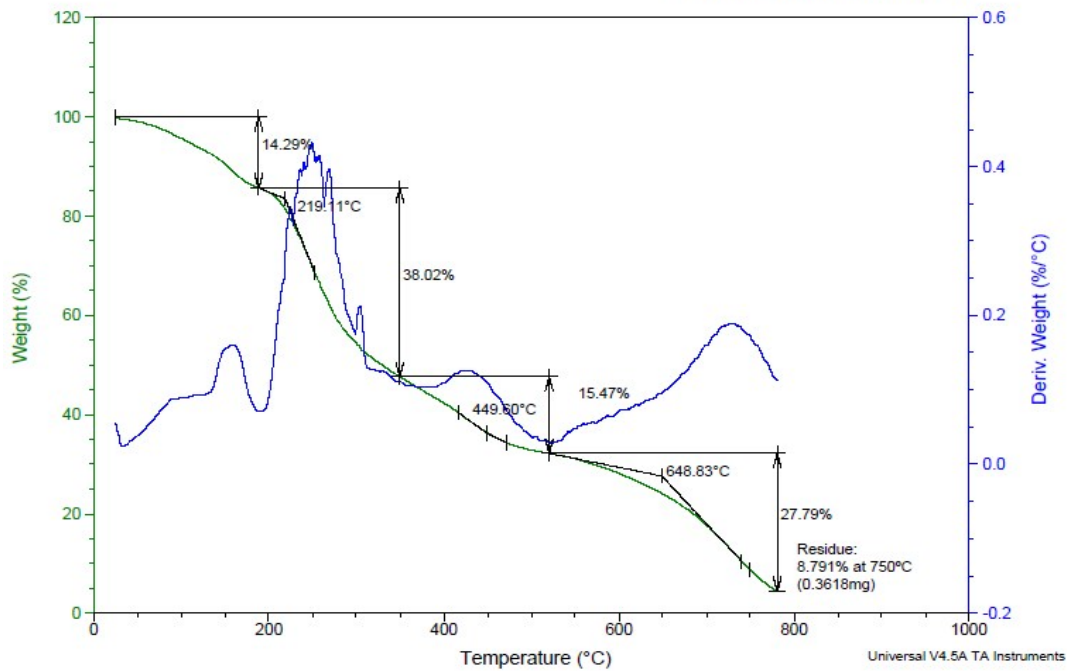


Figure S14. TGA spectrum of poly(ViElm)-D-his.



Sample: 3T5B  
Size: 2.8610 mg  
Method: Alba

TGA

File: C:\...Desktop\Maitane\TGA Manoj\3T5B.001

Run Date: 06-Oct-2015 07:42  
Instrument: TGA Q500 V20.13 Build 39

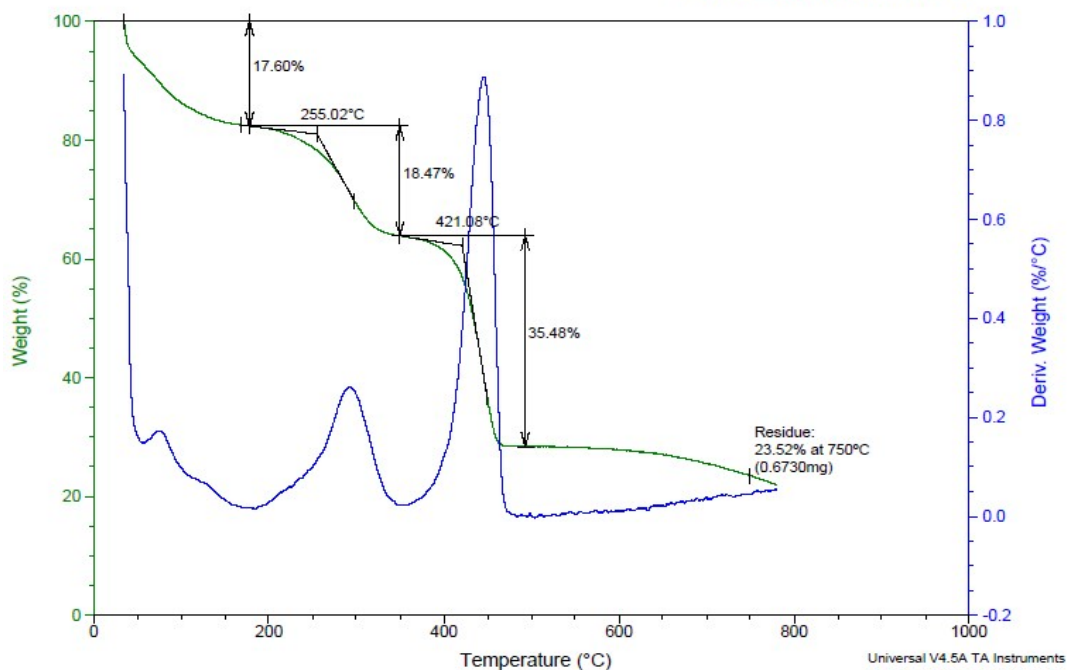


Figure S15. TGA spectrum of poly(dadma) OH.

Sample: PD D-Pr  
Size: 2.2280 mg  
Method: Alba

TGA

File: C:\...Maitane\TGA Manoj\PD D-Pr.001

Run Date: 07-Oct-2015 15:11  
Instrument: TGA Q500 V20.13 Build 39

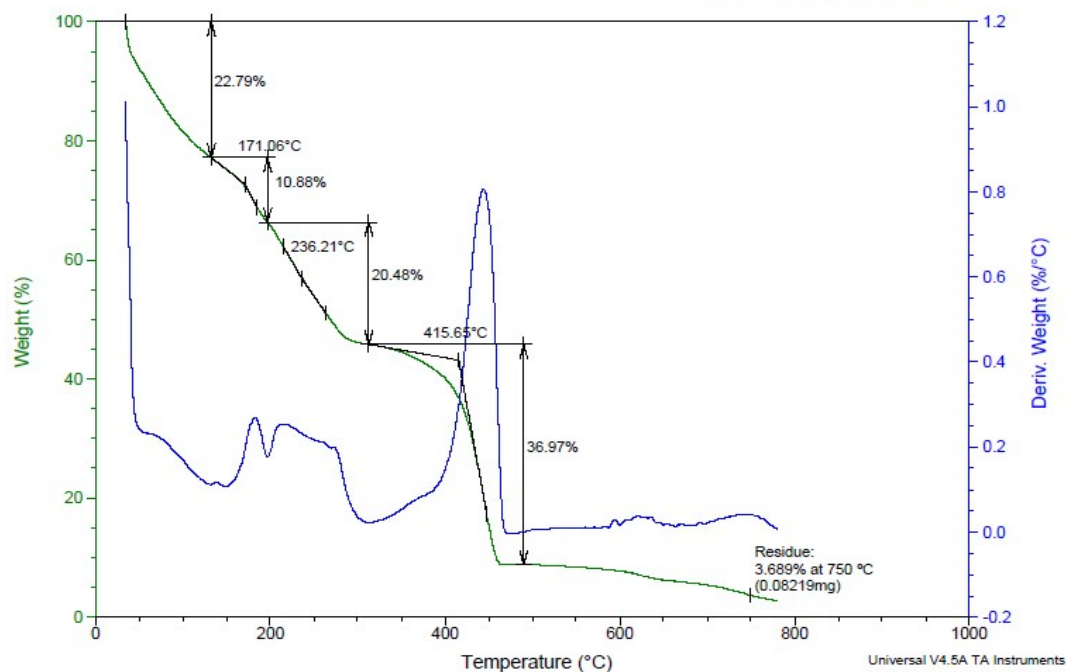


Figure S16. TGA spectrum of poly(dadma)-L-pr.

Sample: PD L-Pr  
Size: 3.2790 mg  
Method: Alba

### TGA

File: C:\...Maitane\TGA Manoj\PD L-Pr.001

Run Date: 05-Oct-2015 22:47  
Instrument: TGA Q500 V20.13 Build 39

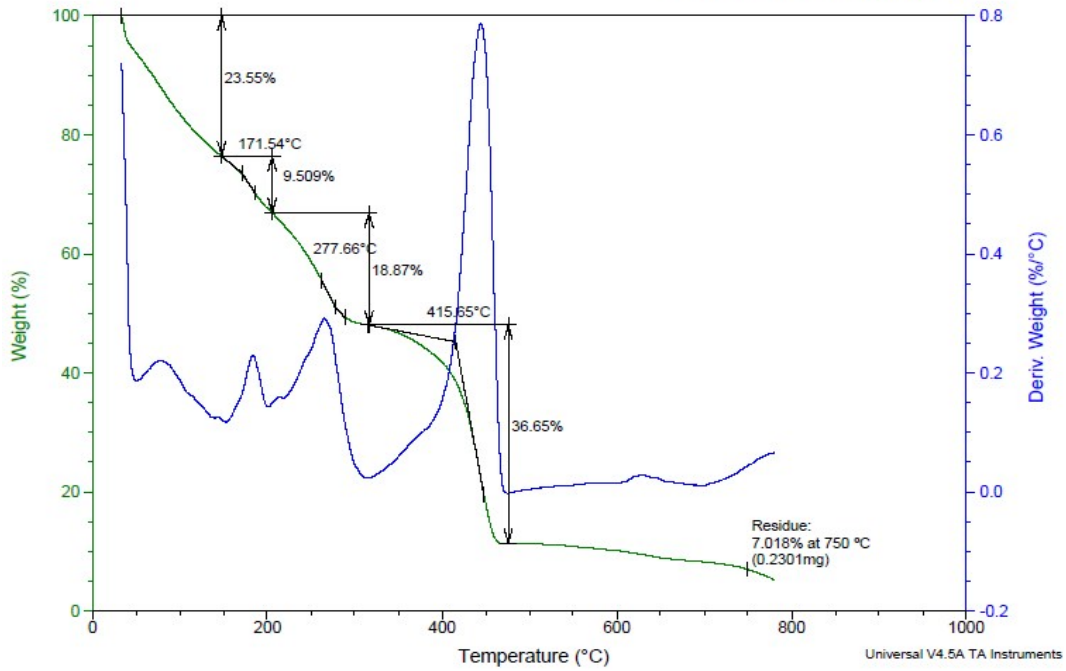


Figure S17. TGA spectrum of poly(dadma)-D-pr.

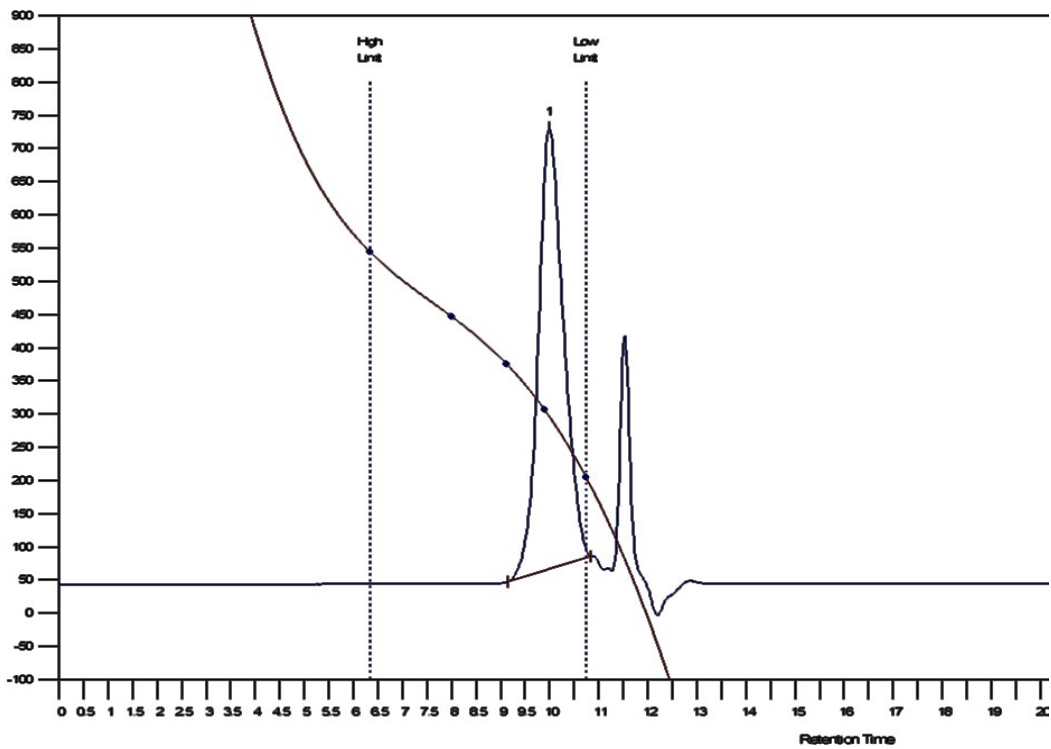
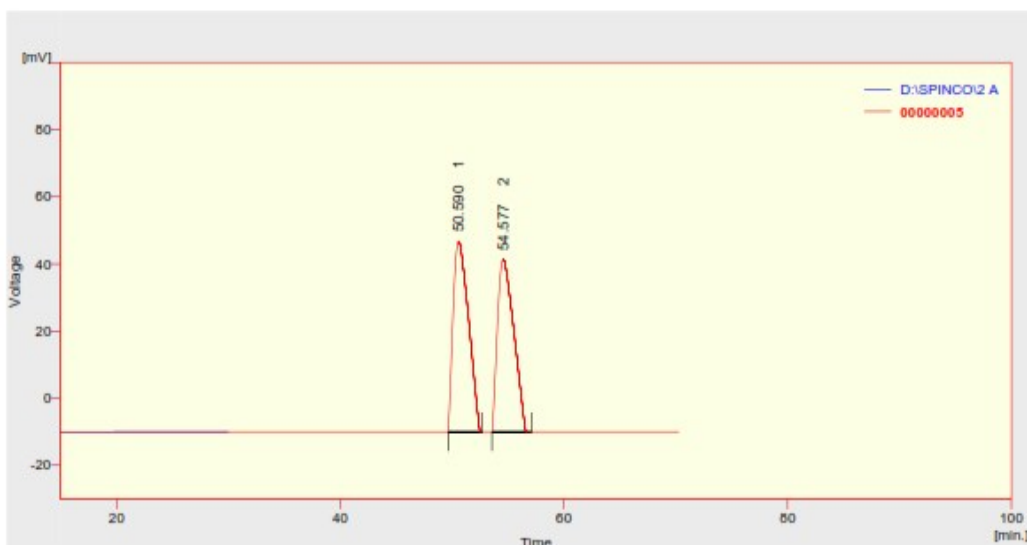


Figure S18. GPC spectrum of poly(ViEm) NTF<sub>2</sub>.



Result Table (Uncaf - 00000005)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	50.590	5414.347	56.801	51.2	52.5	1.02
2	54.577	5163.027	51.392	48.8	47.5	1.71
	Total	10578.174	108.193	100.0	100.0	

**Figure S19.** HPLC spectrum of B-H reaction between MVK and *p*-nitrobenzaldehyde catalyzed by [EMIM]OH/D-proline (Isolated Yield = 29 %, ee < 3)

**Table S1.** Specific rotation values of amino acids and chiral poly(ionic liquids)

Entry	Compound	$[\alpha]_D^a$
1	poly(ViEm)-Br	In active
2	poly(ViEm)-OH	In active
3	poly(dadma)-Cl	In active
4	poly(dadma)-OH	In active
5	L-proline	-80.1
6	poly(ViEm)-L-pr	-30.1
7	D-proline	94.1
8	poly(ViEm)-D-pr	38.1
9	L-histidine	-22.4
10	poly(ViEm)-L-his	-11.3
11	D-histidine	17.0
12	poly(ViEm)-D-his	19.6
13	poly(dadma)-L-pr	-116.5
14	poly(dadma)-D-pr	113.9

<sup>a</sup> All samples were analyzed with 40 mg/ mL in water.