Supplemental informations

For

New Scandium Based Catalyst for the Green Synthesis of Polyols-Polyesters Starting from Waste Raw Materials

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(21 pages including the cover)

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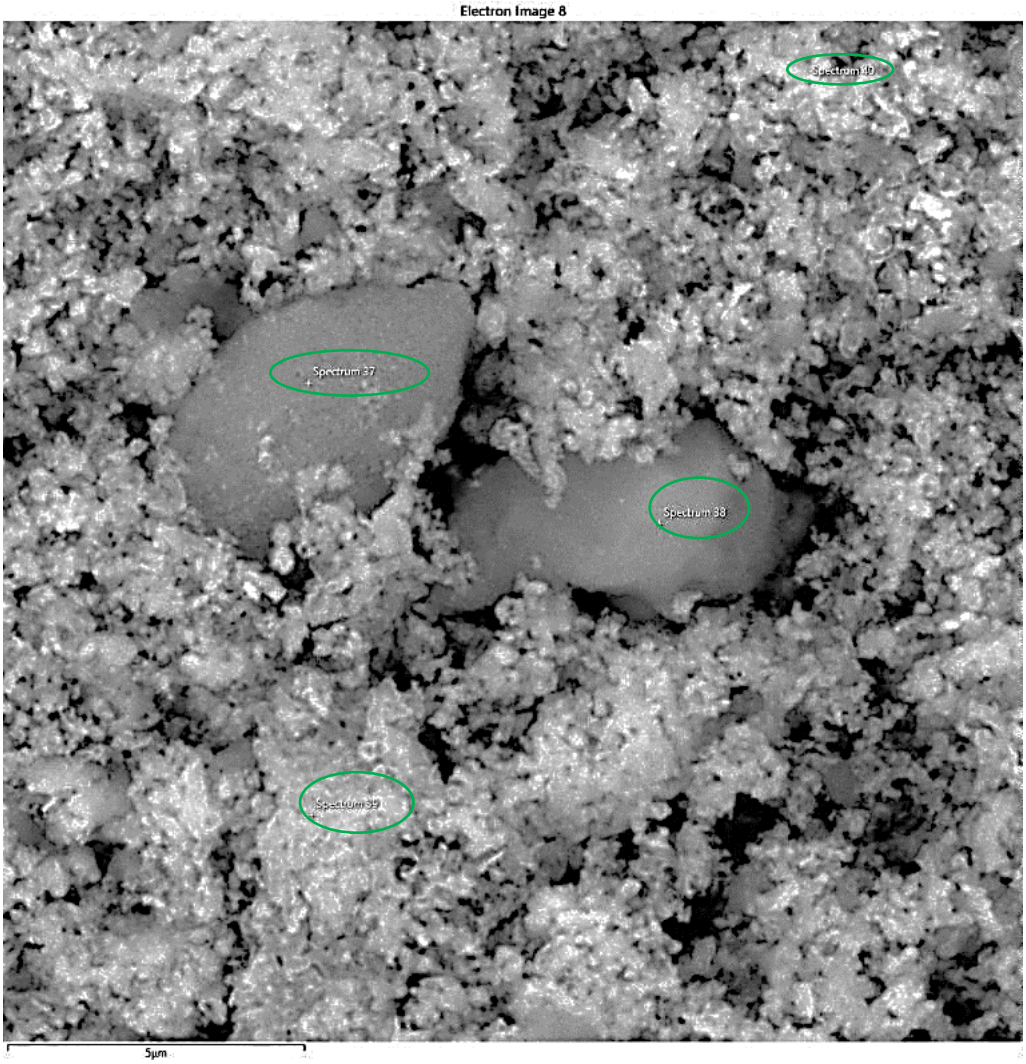
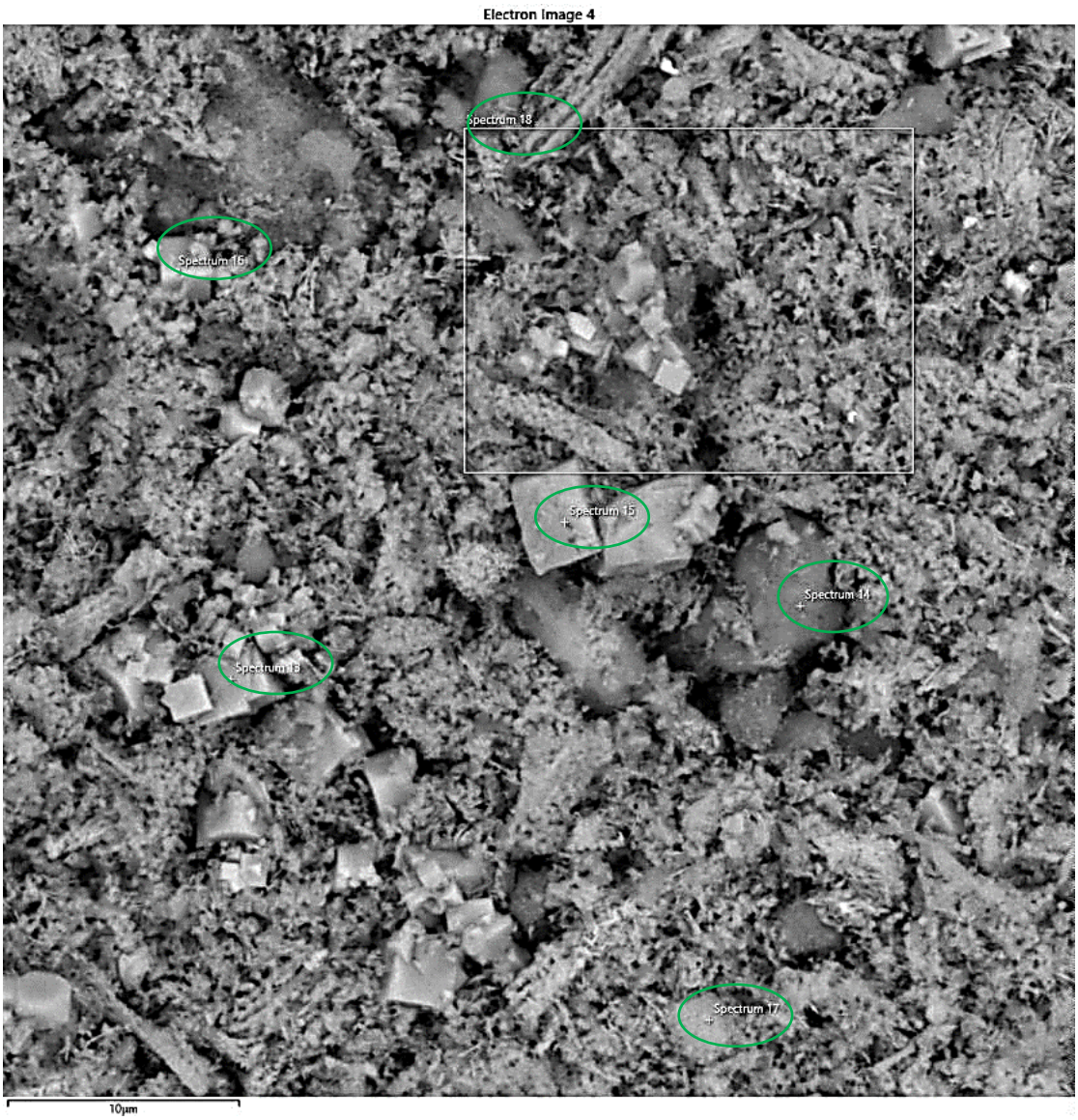
List of abbreviations: GSX-XX (Samples obtained from Glycerol and succinic acid), GSA-XX (Samples obtained from Glycerol and Succinic acid with **Sc-A.T.** catalyst), GSB-XX (Samples obtained from Glycerol and Succinic acid with **Sc(III)O-KIT-6**), **GSN-XX** (Samples obtained from Glycerol and Succinic acid with no catalyst), **GSA-03N** (sample obtained in Nitrogen atmosphere), **GSA-03V** (sample obtained in vacuum), **GSA-03D** (sample obtained with glycerol 70% purity), **GSA-03Sc, GSR-XX** (Samples obtained from Glycerol and Succinic acid using commercial Sc_2O_3 and $Sc(OTf)_3$ as catalyst).



Label	O	Al	Si	S	K	Sc	Fe	Total W%
Spectrum 37	21.08		22.10	0.95	0.31	54.93	0.63	100.00
Spectrum 38	36.24		39.06	0.49	0.22	24.00		100.00
Spectrum 39	29.32		21.67	0.82	0.26	47.92		100.00
Spectrum 40	31.12	0.25	16.97	0.68	0.20	50.36	0.42	100.00

Figure S1. EDS analysis and composition **Sc(III)O-KIT-6** catalyst before NaOH treatment



Label	O	Al	Si	S	K	Ca	Sc	Total W%
Spectrum 13	10.69	0.41	0.89				88.01	100.00
Spectrum 14	20.20		28.05	0.44	5.66	2.53	43.12	100.00
Spectrum 15	6.95	0.46	0.59				91.83	100.00
Spectrum 16	23.51	0.33	2.54		0.22		73.40	100.00
Spectrum 17	22.13		10.05	0.45	0.32		67.05	100.00
Spectrum 18	16.81	0.27	11.76	0.45	0.38		69.92	100.00

Figure S2. EDS analysis and composition **Sc. A.T.** after NaOH treatment.

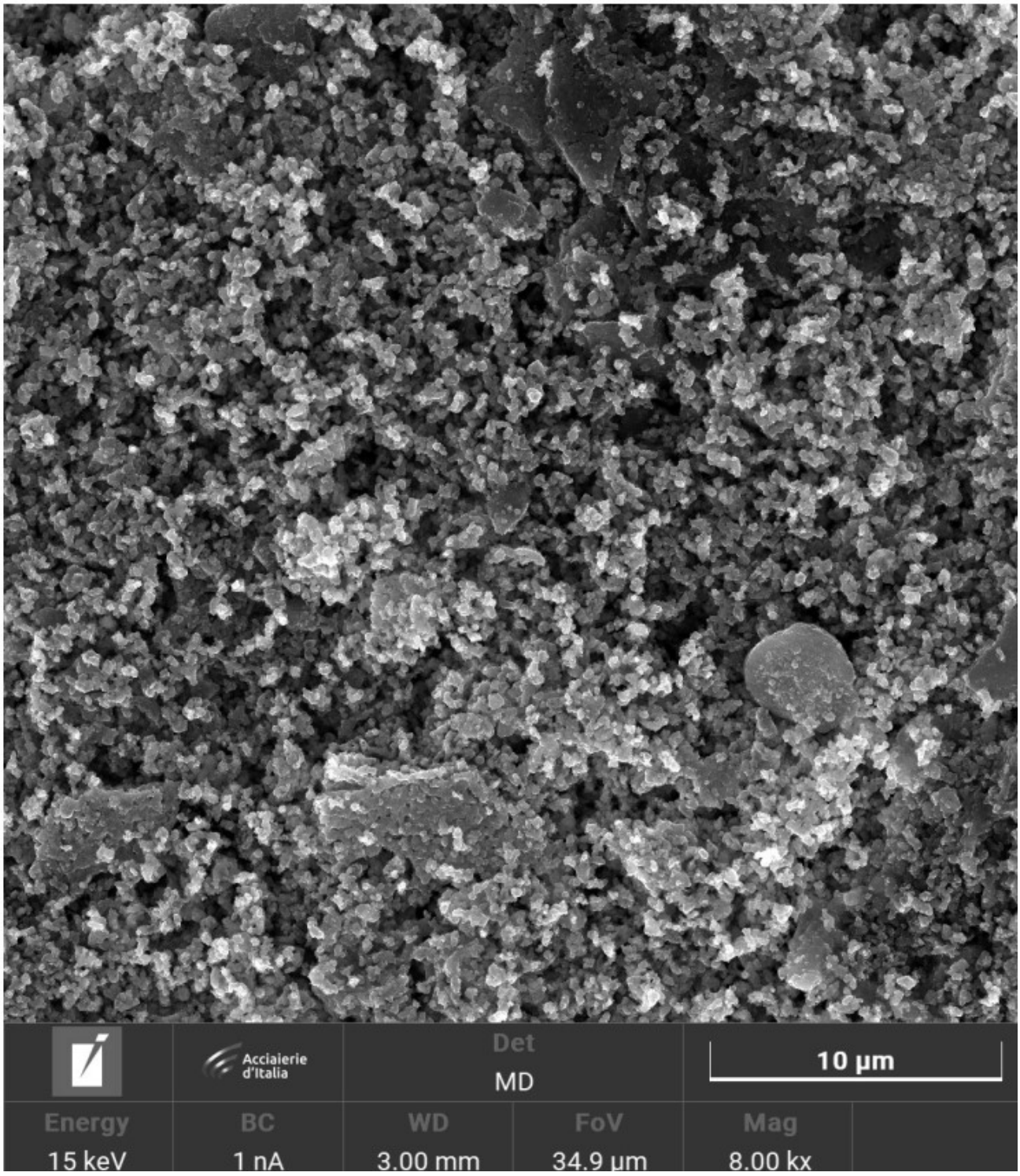


Figure S3. Magnification of SEM image at 10 µm Sc(III)O-KIT-6 before NaOH treatment

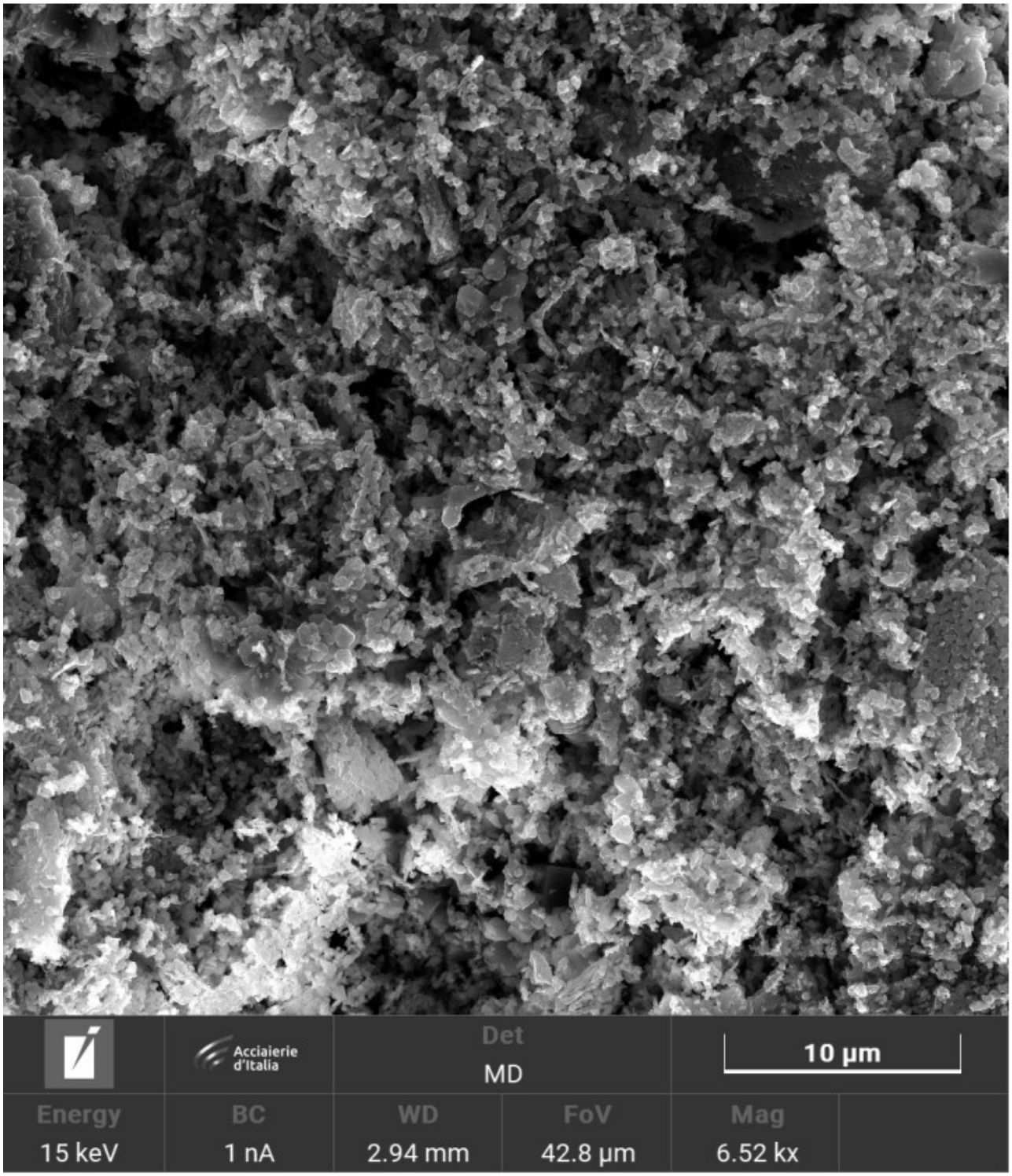


Figure S4. Magnification of SEM image at 10 µm of the Sc. A.T. after NaOH treatment.

Table S1. Parameters of XRD characterization for the catalysts

	Literature data	Catalysts			
Parameters	**Ref XX in paper**	**Sc2O3**	**Sc(III)-KIT 6**	**SC A T**	**SC A T m**
Sc2O3					
Unit Cell Parameters					
a (Å)	9,81	9.8462(6)	9.849(1)	9.8419(4)	9.859(2)
Volume (Å³)	930,704	954.57(17)	955.38(29)	953.32(12)	958.29(58)
Bond Distances (Å)					
Sc1-O (x6)	2,12	2,130	2,131	2,129	2,133
Sc2-O (x2)	2,16	2,087	2,088	2,086	2,090
Sc2-O' (x2)	2,08	2,100	2,101	2,093	2,103
Sc2-O'' (x2)	2,09	2,171	2,171	2,170	2,173
<Sc2-O>	2,11	2,119	2,120	2,116	2,122
$Sc_2Si_2O_7$					
Unit Cell Parameters					
a (Å)	6,56		6.516(1)	6.5046(4)	6.49(1)
b ((Å)	8,58		8.512(1)	8.5087(6)	8.58(2)
c (Å)	4,74		4.6950(8)	4.6902(4)	4.693(8)
β (°)	103,83		102.78(1)	102.737(4)	103.1(1)
Volume (Å³)	259,52		253.95(7)	253.19(3)	254.53(84)
Bond Distances (Å)					
Sc-O2	2.162(1)		2,140	2,139	2,147
Sc-O3	2.124(2)		2,088	2,086	2,086
Sc-O3'	2.234(2)		2,212	2,208	2,210
<Sc-O>	2,173		2,146	2,144	2,148
Si-O1	1.608(1)		1,583	1,580	1,580
Si-O2	1.624(2)		1,606	1,605	1,589
Si-O3 (x2)	1.631(2)		1,619	1,628	1,628
<Si-O>	1,623		1,607	1,610	1,606

Table S2. Catalyst scope in the polymerization of glycerol and succinic acid under solvent free conditions.[a]

Entry	***Catalyst*** *(mg)**	***T*** *(°C)*	***Time*** *(h)*	***Polyester Label***	M_{w1} *(Da)/* Selectivity (%)[d]	$P.D._1$	M_{w2}	$P.D._2$	M_{w3}	$P.D._3$
1	none	180	2	**GS-N01**[b]	**----**[c]	**----------**				
2	none	150	2	**GS-N02**	15,592 / 8	1.13	805 / 92			
3	La-B.T. (120)	150	2	**GS-B01**	1,458 / 92[e]	1.37				
4	Sc-B.T. (120)	150	2	**GSB02**	18,389/10	1.008	5,345/77	1.09	642/12	1.007
5	Sc-B.T. (120)	120	2	**no reaction**	**---**	**----------**				
6	Sc-A.T. (120)	120	2	**GS-A01**	27,643 / 65[e]	2.2				
7	$Sc(OTf)_3$ (25)	120	2	**GS-R01**	2,408 / 56	1.06	448 / 43	1.03		
+8	Sc_2O_3	120	2	**GS-R02**	1,655 / 90[e]	4.06				

[a] Ratio Succinic acid/Glycerol (w/w) 2:1, [b]Valerio et al., 2015, [c]Determinated using the GPC analysis, , [d]Polyethers tetramer of glycerol Mw 315 ($Mw\text{-}H^+$)

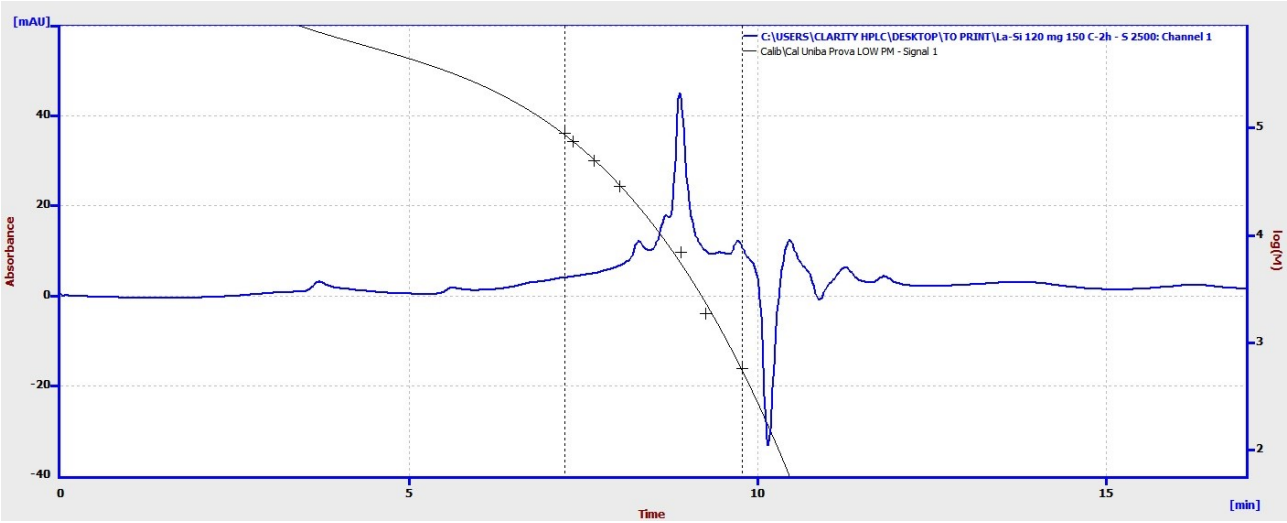


Figure S5. GPC analysis of sample **GSB-01**

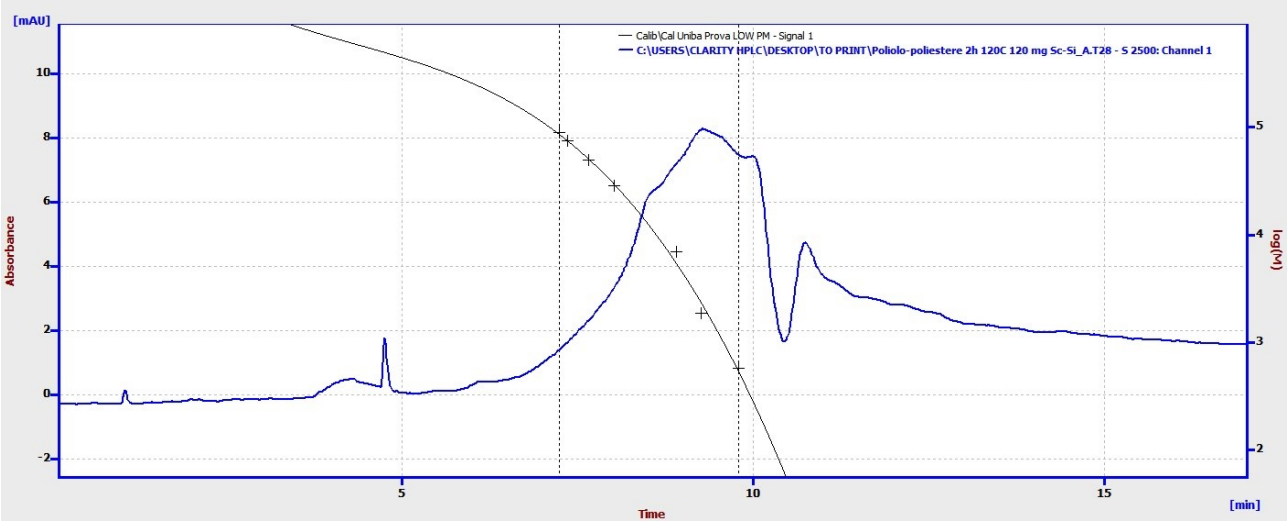


Figure S6. GPC analysis of sample **GSA-01**

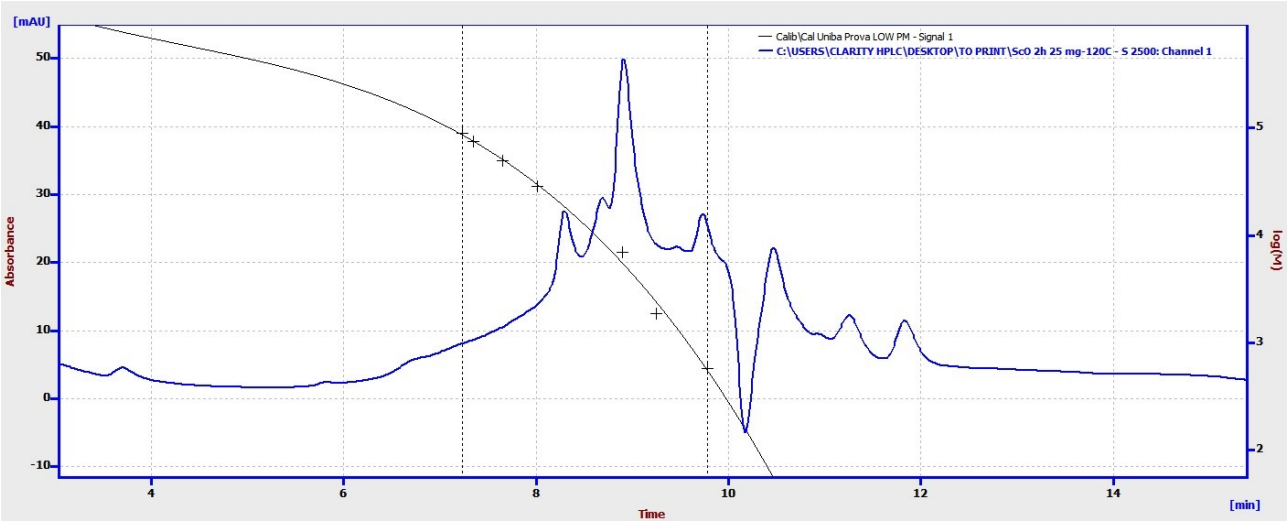


Figure S7. GPC analysis of sample **GSA-03**

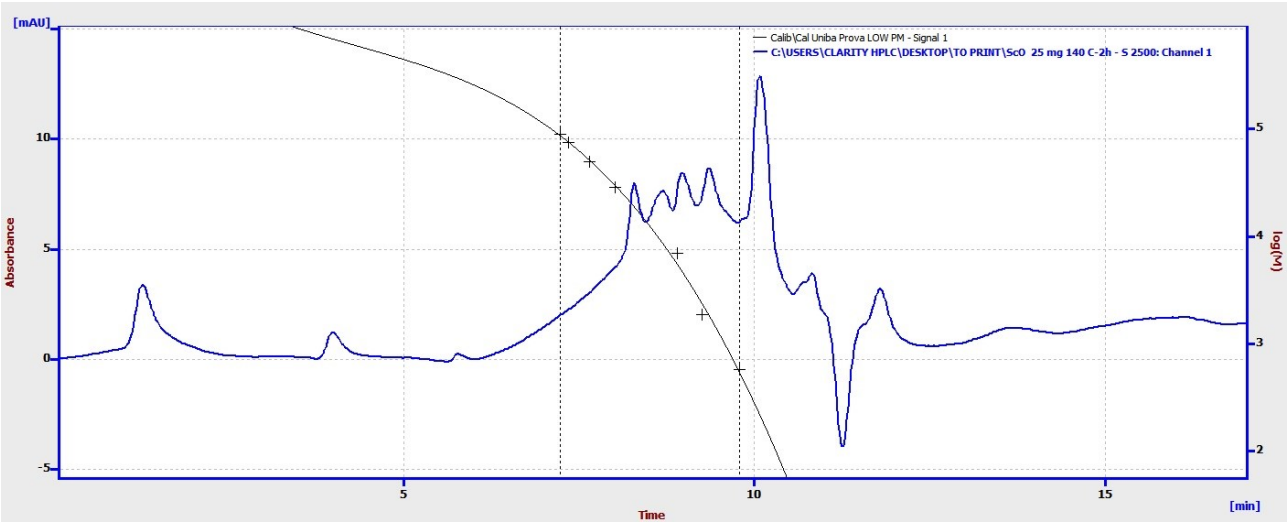
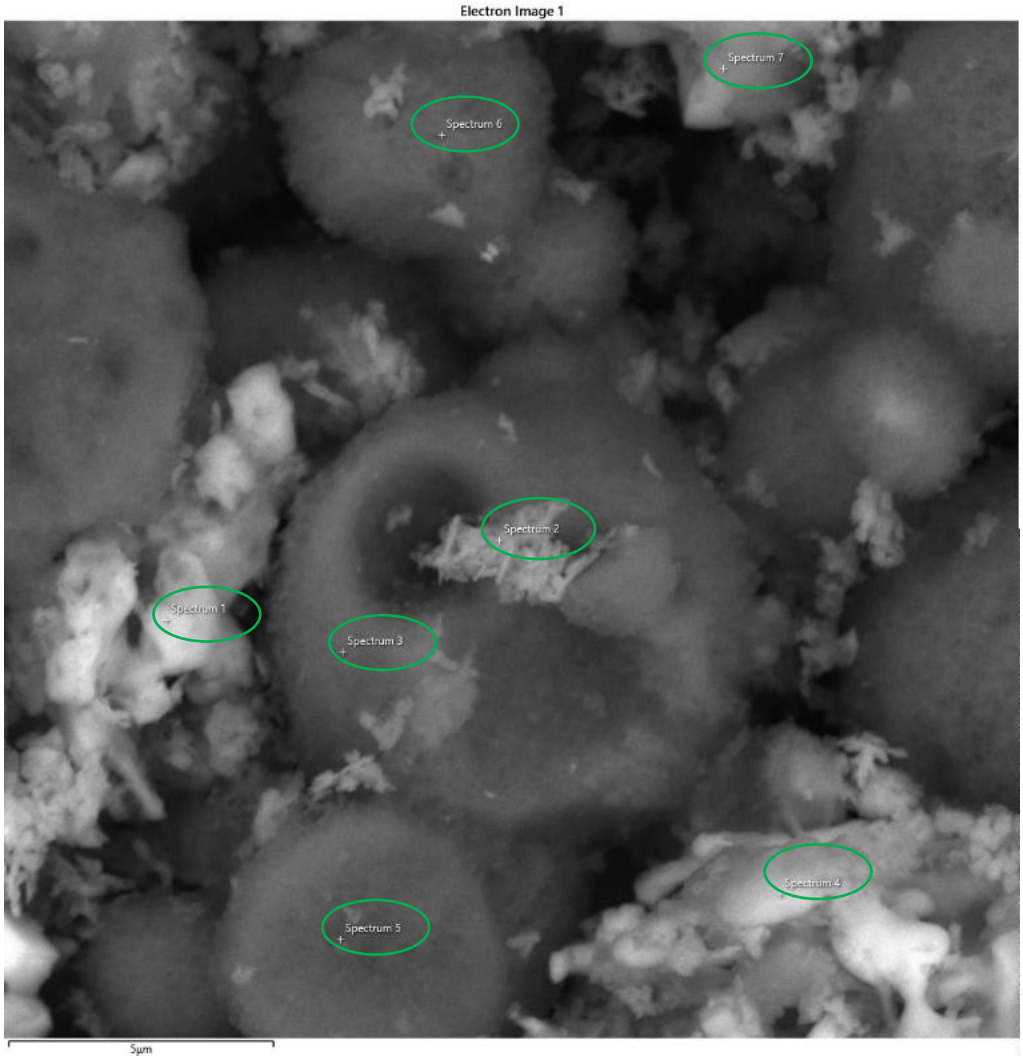


Figure S8. GPC analysis of sample **GSA-05**



Label	O	Na	Al	Si	S	K	Ca	Sc	Fe	Total W%
Spectrum 1	32.57	2.14	1.33	18.52	0.78			44.23	0.42	100.00
Spectrum 2	32.89	20.05		1.58			0.42	45.06		100.00
Spectrum 3	30.33	51.83	0.53	4.66			0.66	12.00		100.00
Spectrum 4	34.06	2.38	2.64	16.36		0.21		43.67	0.68	100.00
Spectrum 5	34.84	48.68		2.31			0.59	13.59		100.00
Spectrum 6	27.06	55.69		2.60			1.23	13.42		100.00
Spectrum 7	6.77	3.05	0.19	1.71	0.31			86.71	1.26	100.00

Figure S9. EDS analysis and composition **Sc. A.T.** after III cycles

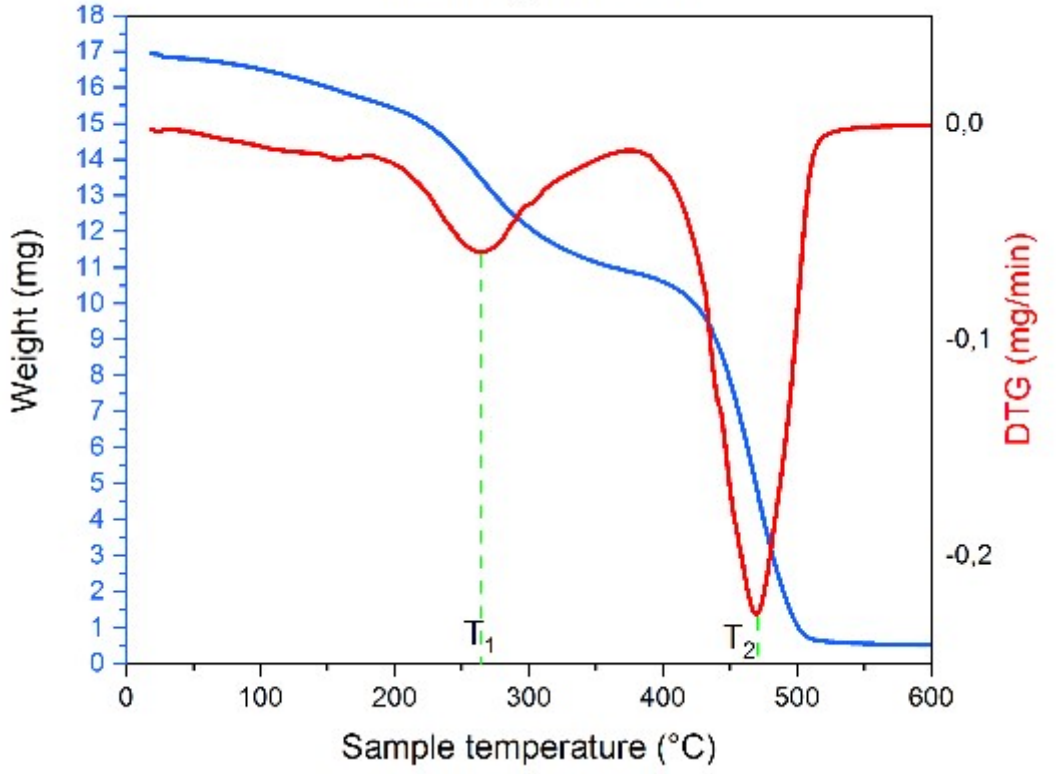


Figure S10. TGA and DTG of **GSA-02** polymer.

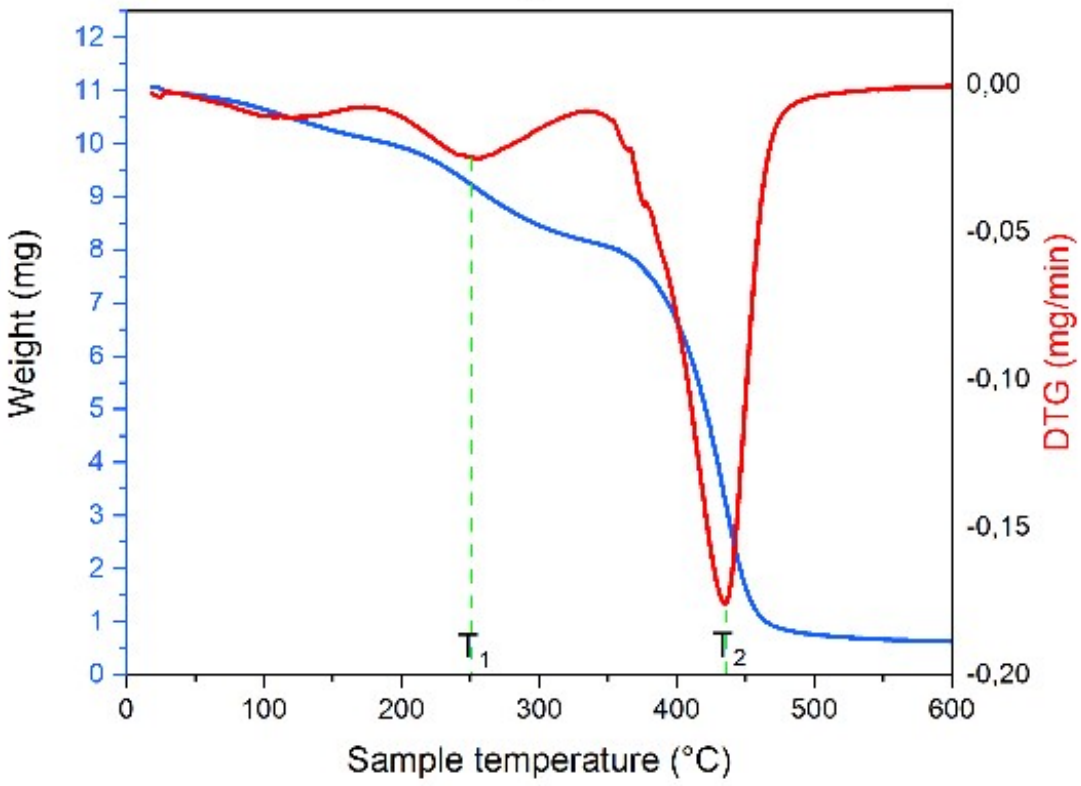


Figure S11. TGA and DTG of **GSA-03** polymer.

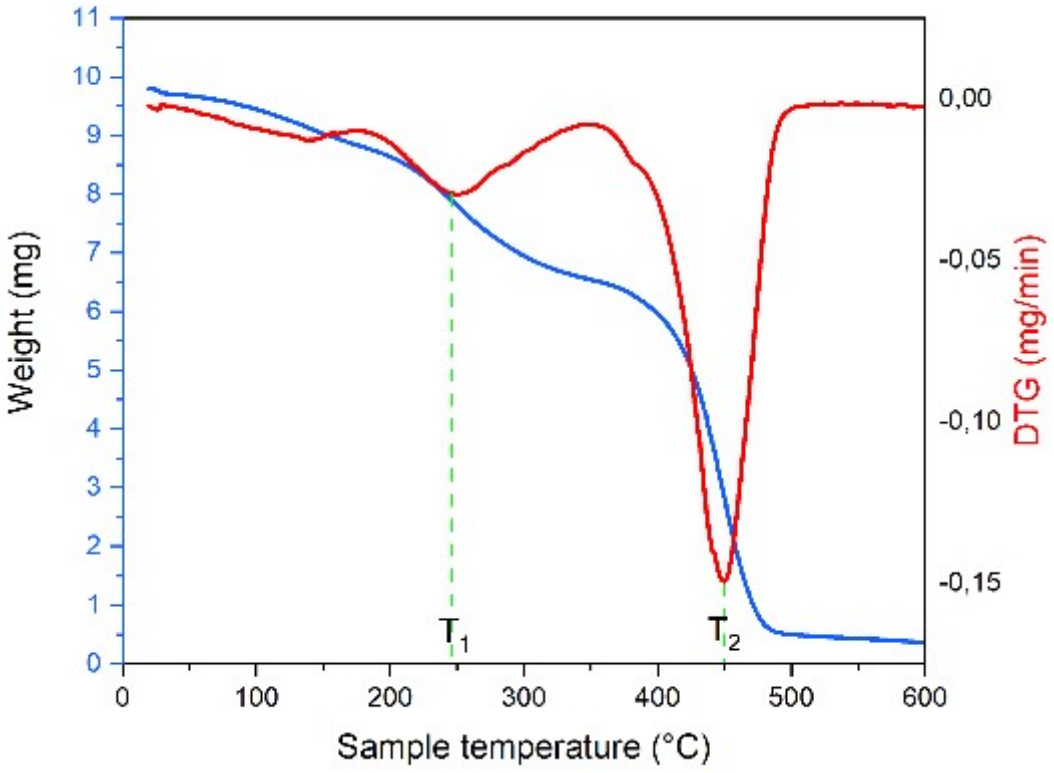


Figure S12. TGA and DTG of **GSA-04** polymer.

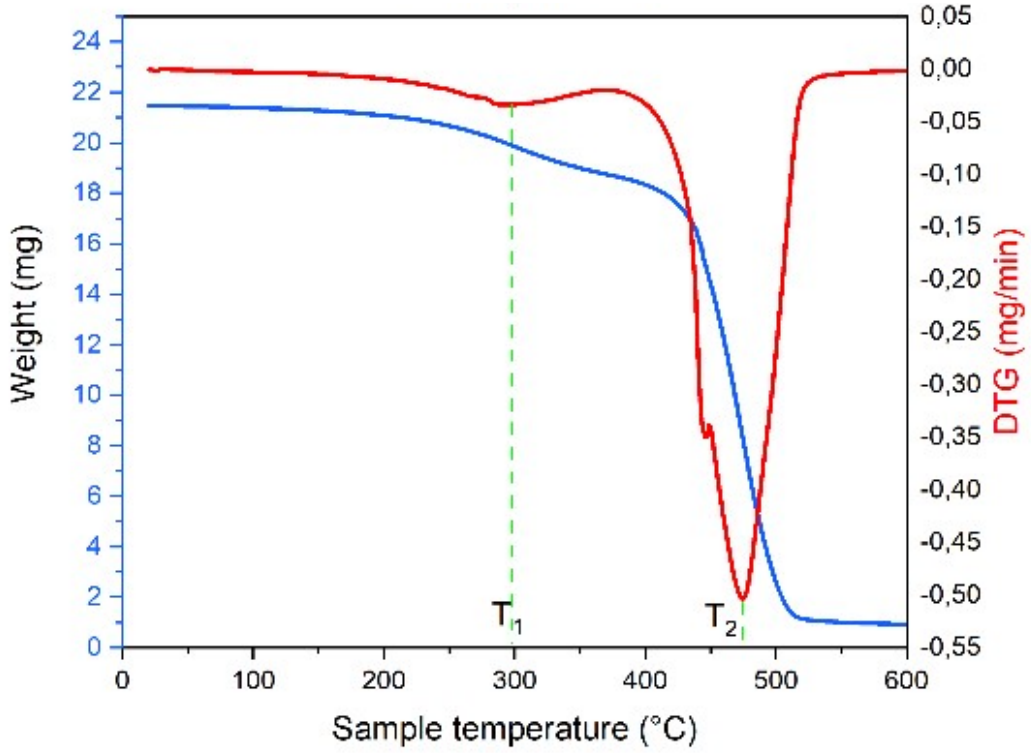


Figure S13. TGA and DTG of **GSA-05** polymer.

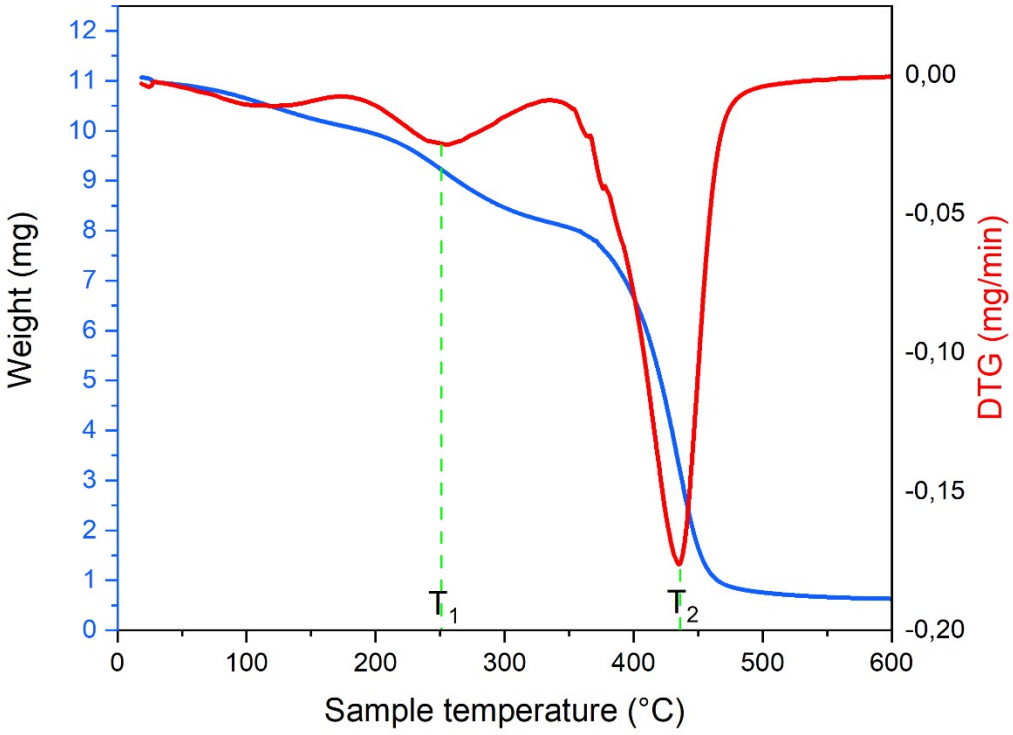


Figure S14. TGA and DTG of **GSA-06** polymer.

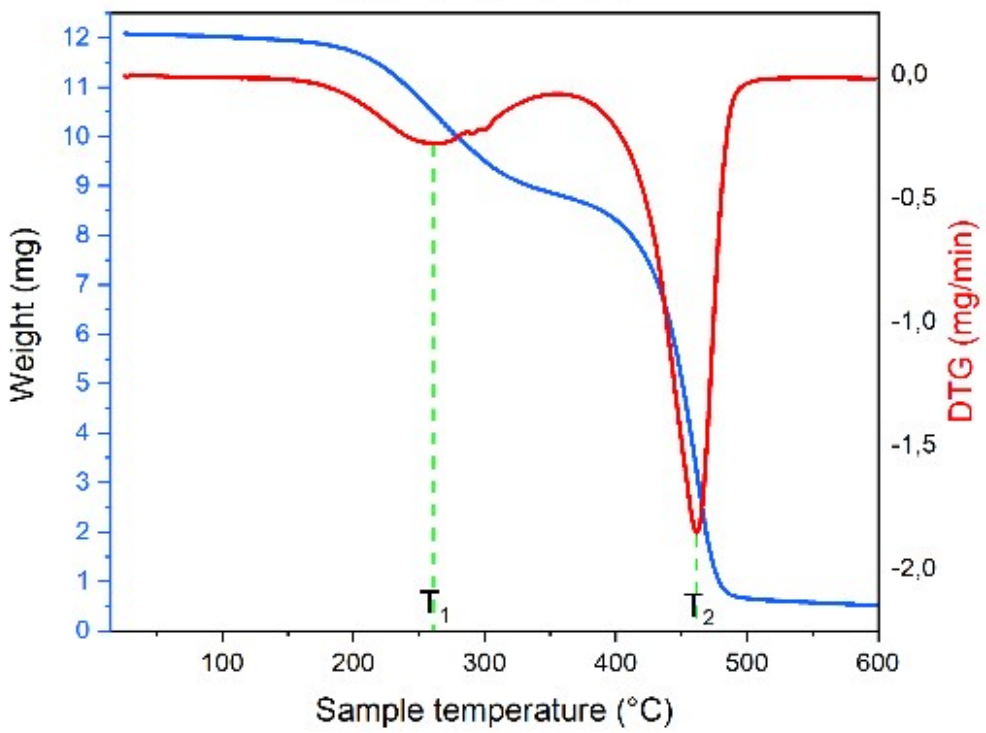


Figure S15. TGA and DTG of **GSA-07** polymer.

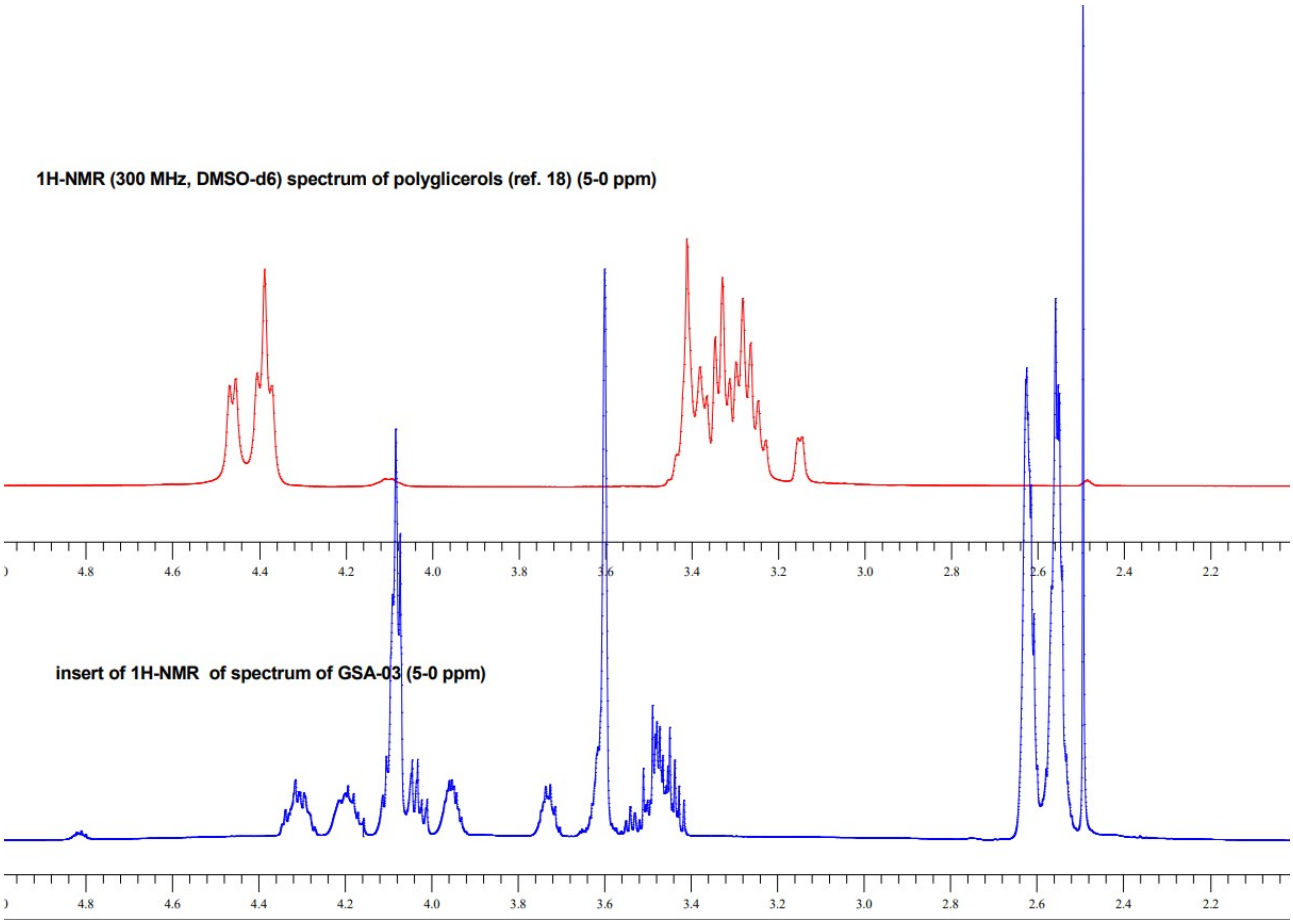


Figure S16. ^{1}H-NMR of GSA-03 (0-5 ppm, blue line) vs polyol-polyether from reference 18

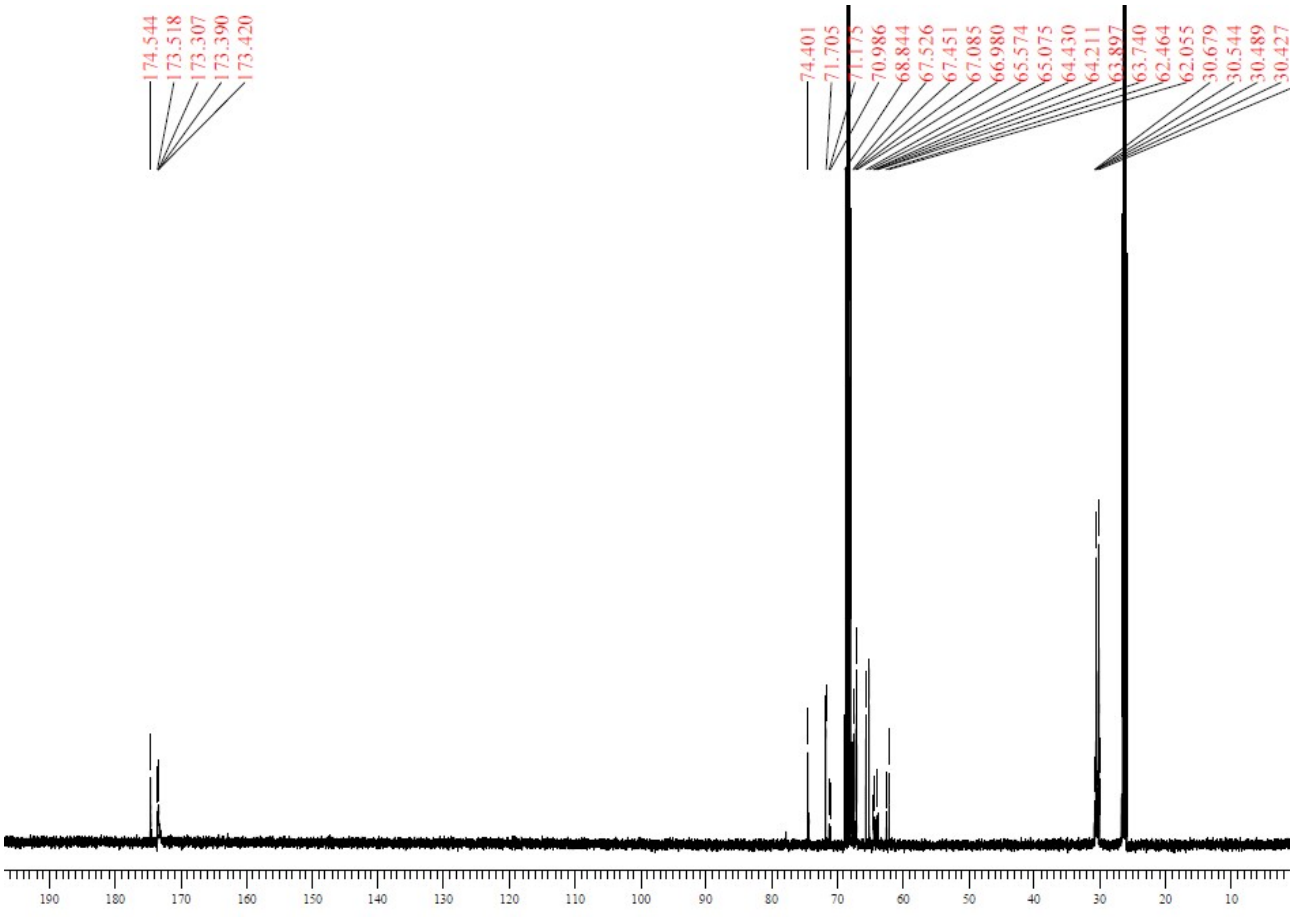


Figure.S17 ^{13}C-NMR analysis of **GSA-03** polymer in Tetrahydrofuran-d_8[1]

Supplementary Studies of Mass structures

The figure *S18* (A-G) shows the experimental mass signals with relative isotopic patterns (blue traces), compared with the theoretical ones (red traces) suggested by the software. It is easy to see high degree of overlap. Moreover, the software provides a possible molecular formula. As expected, the formation of the adduct with the Na^+ cation is preponderant among all oligomers. All measured m/z values have a deviation of less than 15 ppm compared to the theoretical ones and in some cases less than 2 ppm allowing us to have a solid certainty on the attributions of the various signals. A further verification was the analysis of the isotopic patterns, also in this case the software analysis provides to an additional confirmation of the nature of the signals.

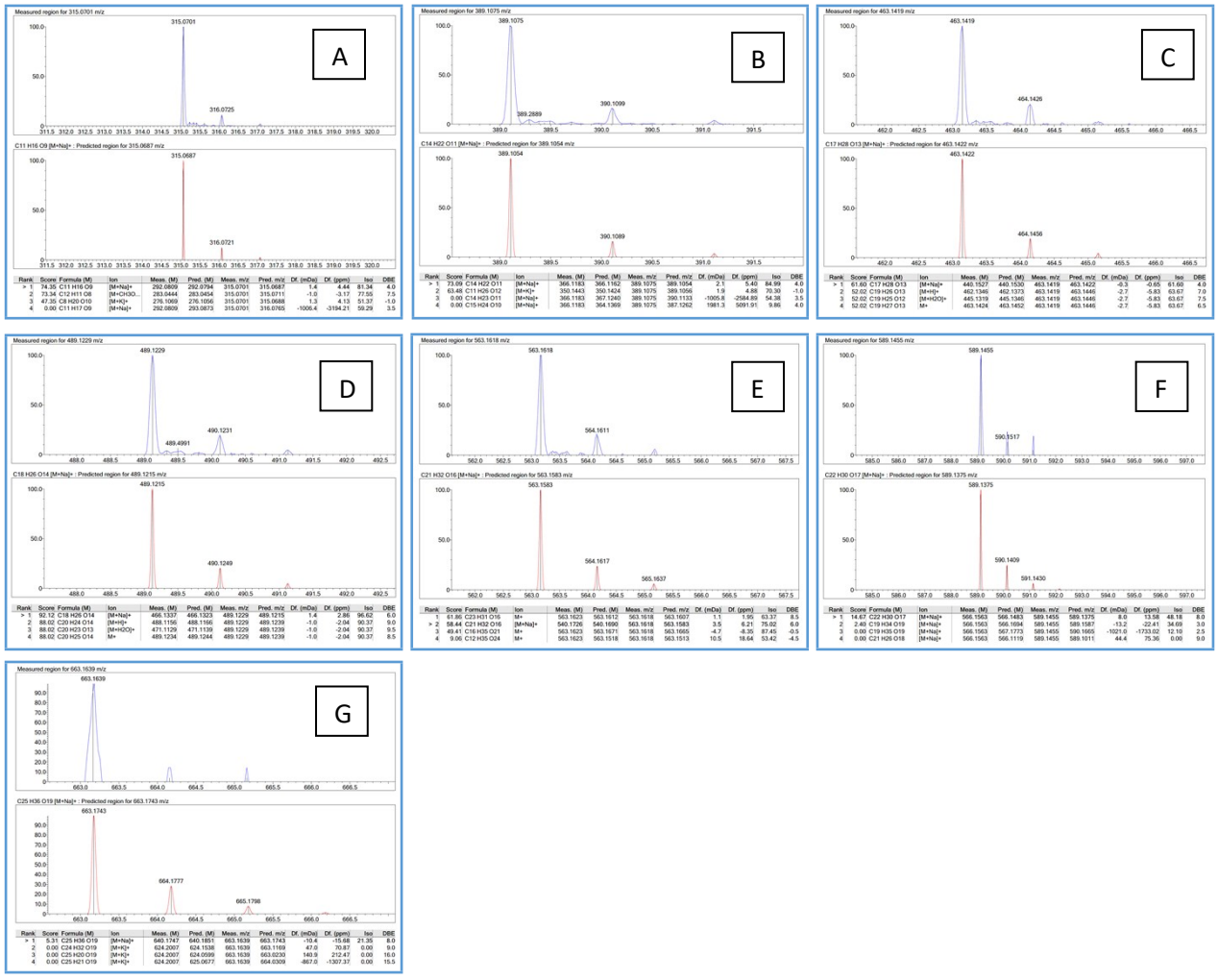


Figure S18*:* Isotopic pattern comparison

Table S3: List of determined oligomers

Oligomers	Molecular formula	Exact Mass (molecular ion)	Predicted Mass (Na adduct)	Measured Mass	Diff ppm
A	$C_{11}H_{16}O_9$	292.0809	315.0687	315.0701	4.44
B	$C_{14}H_{22}O_{11}$	366.1183	389.1054	389.1075	5.40
C	$C_{17}H_{28}O_{13}$	440.1527	463.1422	463.1419	-0.65
D	$C_{18}H_{26}O_{14}$	466.1337	489.1215	489.1229	2.86
E	$C_{21}H_{32}O_{16}$	540.1726	563.1583	563.1618	6.21
F	$C_{22}H_{30}O_{17}$	566.1563	589.1375	589.1455	13.58
G	$C_{25}H_{36}O_{19}$	640.1747	663.1743	663.1639	-15.68

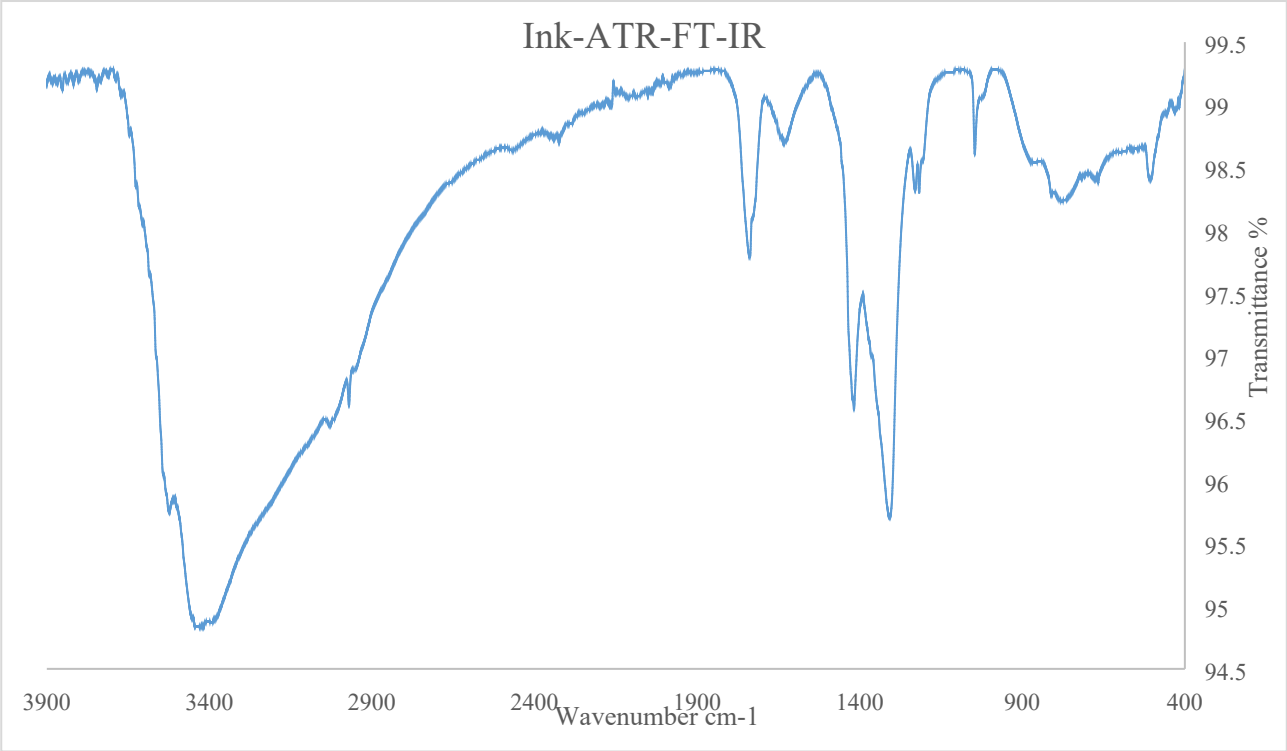


Figure S19. Ink ATR-FT-IR analysis

Greenswitch

DESCRIZIONE	Raw glycerol from FAMES 70
LUOGO DI FABBRICAZIONE	Ferrandina (MT)

Composition	(%weight)
glycerol	65-70
water	15
MONG (organic material No Gly	5
Methanol	1
KCl	5-10

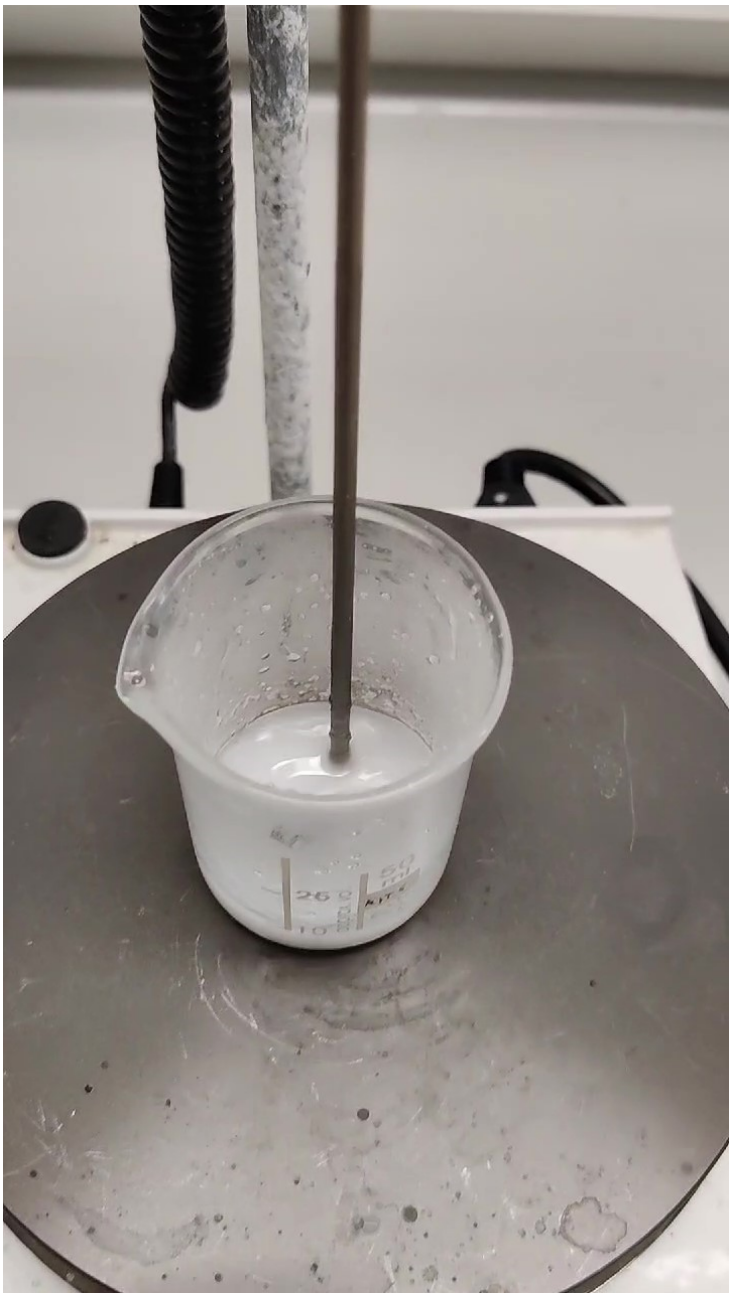


Figure S20. Picture of the reactor

Additional references

M. Agach, S. Delbaere, S. Marinkovic, B. Estrine, V. Nardello-Rataj *Polym. Degrad. Stab.* 2012, **97**, 1956.