Electronic supplementary information for

Physically cross-linked polyethylene via reactive extrusion

Arkadiusz Zych, Alice Verdelli, Maria Solimant, Roberta Pinalli, Jerome Vachon and Enrico Dalcanale

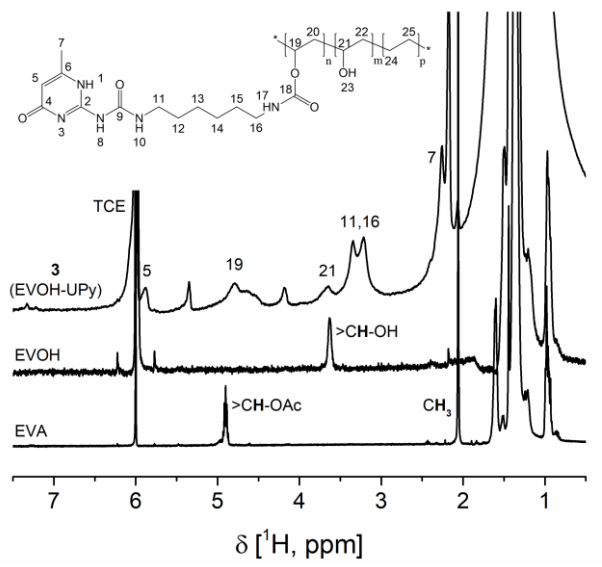

Figure S1. ^{1}H NMR spectra overlay of EVA, EVOH and polymer **3** (EVOH-UPy) recorded at 120 °C in deuterated TCE.

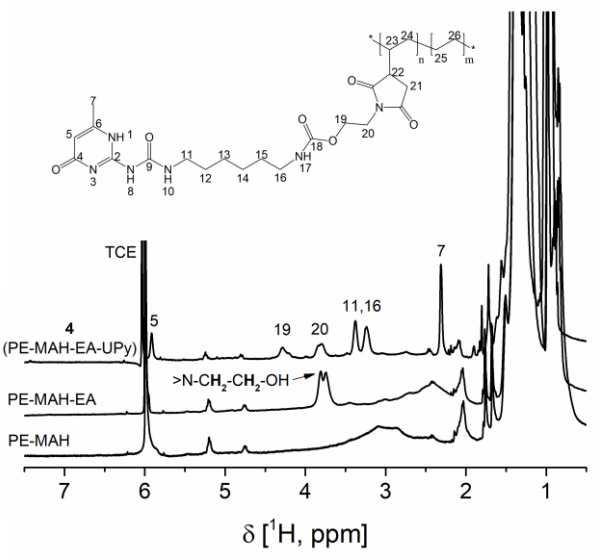

Figure S2. ^{1}H NMR spectra overlay of PE-MAH, PE-MAH-EA and polymer **4** (PE-MAH-EA-UPy) recorded at 120 °C in deuterated TCE.

Table S1. Functional group content, melting temperatures (T_m), β transition temperatures (T_β) degrees of crystallinity (X_{cr}) as well as molecular weights (M_n, M_w) and molecular weight distributions ($Đ_M$) of the starting polyolefins.

Polymer	Functional group content [mol%] [a]	T_m [b] [°C]	T_β [c] [°C]	X_{cr} [d] [%]	M_n [e] [g/mol]	M_w [e] [g/mol]	$Đ_M$ [e]
EVA	3.0	99.1	-9.5 [f] 59.8 [f]	11.7	13 500	69 100	5.1
PE-MAH	0.4	99.2	-16.4	9.3	2 500	5 900	2.4

[a] Functional group content was calculated from ^{1}H-NMR (400 MHz, 120 °C, TCE d_2); PE-MAH with higher functional group content is not commercially available. [b] Melting temperatures (T_m) were determined by DSC from the second heating scan. [c] β transition temperatures (T_β) were determined by DMTA from the maximum of tan □□ [d] Degrees of crystallinity (X_{cr}) were calculated dividing the melting enthalpy of 100% crystalline PE (286.2 J/g, B. Wunderlich, C. M. Cormier, Heat of fusion of polyethylene. *Journal of Polymer Science Part A-2: Polymer Physics* **1967,** *5* (5), 987-988.) by melting enthalpy of a polymer determined by DSC from the second heating scan. [e] Molecular weight and polydispersity were determined by SEC in *o*DCB at 150 °C with respect to polyethylene standards. [f] two β transition temperatures were observed.

Calculation of UPy units per chain

Number of UPy/chain was calculated based on the amount of -OH grafted and M_n of starting material according to the Equaton S1. Functional group content, hydrogen bonding motif content and M_n of the functionalized PE can be found in the Table 1 and Table 2. Repeating unit other then ethylene is treated as a "comonomer" for this calculation even though the polymer might not have beed obtained by copolymerization of this fragment with ethylene.

$$\boldsymbol{UPy\ /\ chain} = \frac{\boldsymbol{M_n}\left[\frac{g}{mol}\right]\cdot \boldsymbol{hydrogen\ bonding\ motif}\ [mol\%]}{\boldsymbol{functional\ group}\ [mol\%]\cdot \boldsymbol{M_{"comonomer"}}\left[\frac{g}{mol}\right]+(100-\boldsymbol{functional\ group}\ [mol\%])\cdot \boldsymbol{M_{ethylene}}\left[\frac{g}{mol}\right]} \quad \textbf{(1)}$$

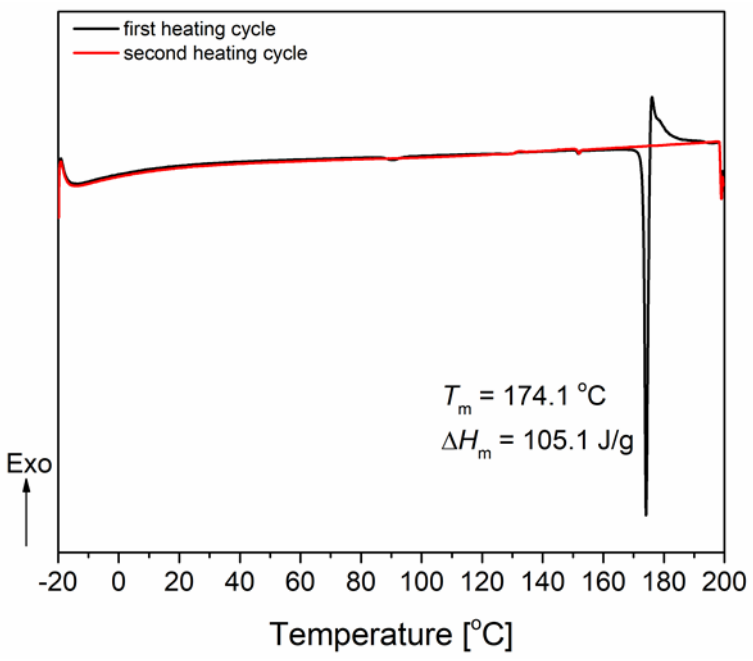

Figure S3. DSC first (black) and second (red) heating curve of UPy.

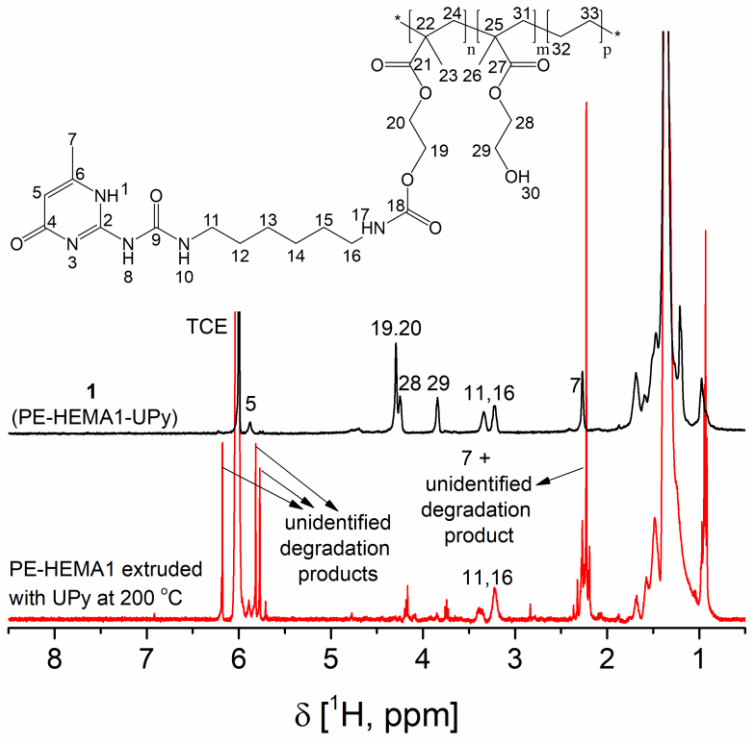

Figure S4. ^{1}H NMR spectra overlay of polymer **1** (PE-HEMA1-UPy, black) and PE-HEMA1 extruded with UPy at 200 °C (red), recorded at 120 °C in deuterated TCE.

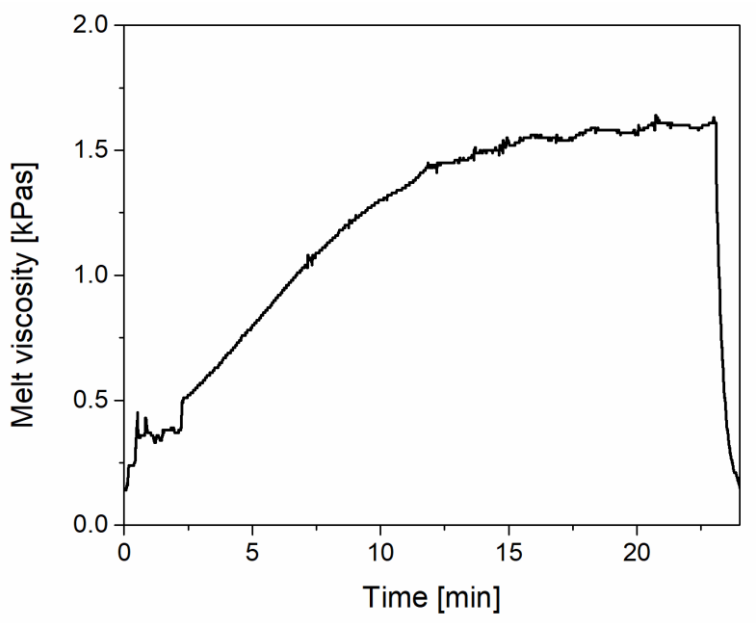

Figure S5. Representative melt viscosity changes recorded during the reactive extrusion of polymer **2** (PE-HEMA2-IPR-UPy)

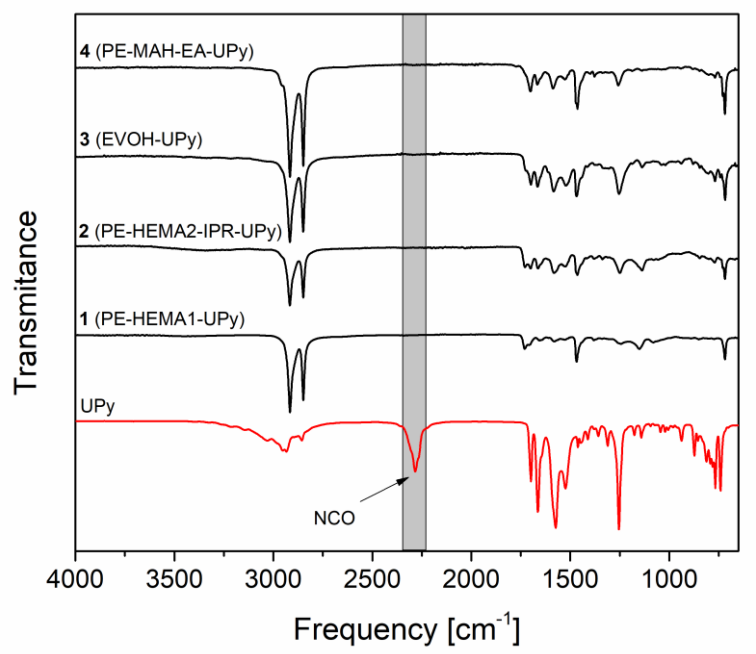

Figure S6. IR spectra overlay of UPy (red line) and functional polyolefins grafted with UPy or IPR-UPy (black lines).

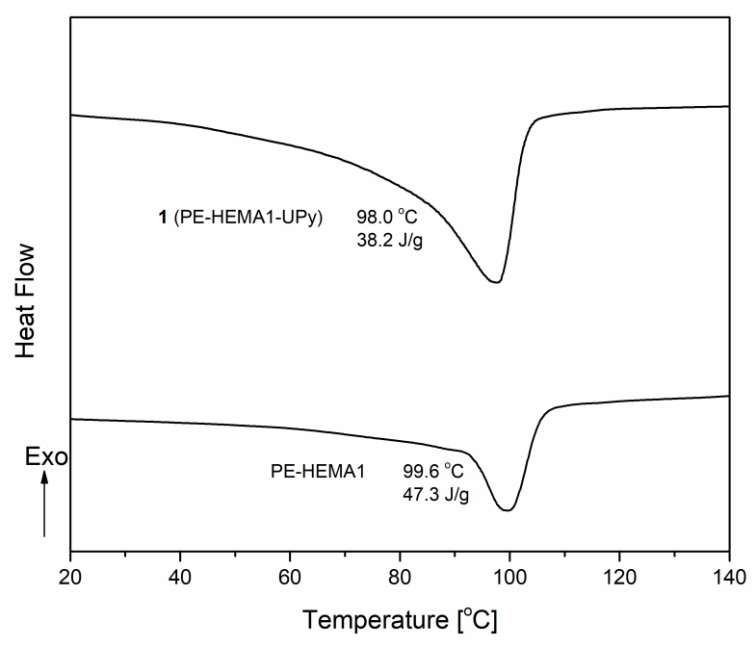

Figure S7. DSC second heating curves of PE-HEMA1 and polymer **1** (PE-HEMA2-UPy).

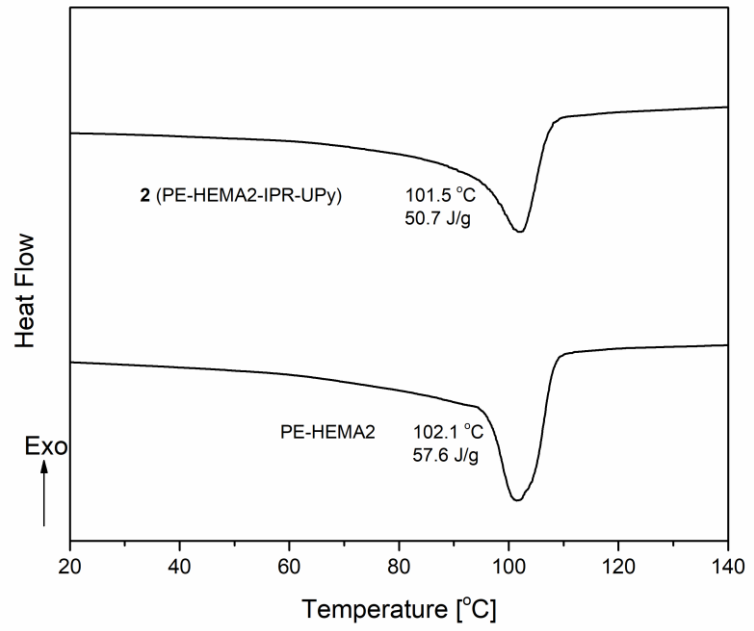

Figure S8. DSC second heating curves of PE-HEMA2, and polymer **2** (PE-HEMA2-IPR-UPy).

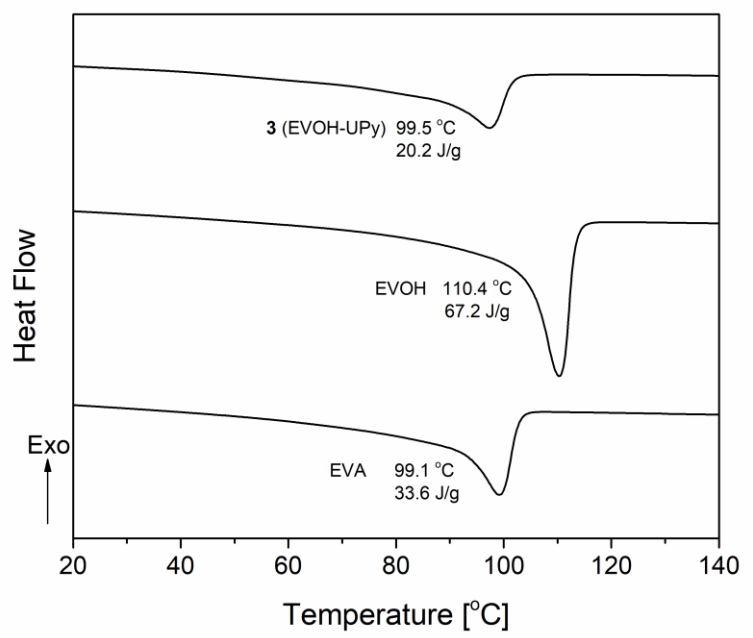

Figure S9. DSC second heating curves of EVA, EVOH and polymer **3** (EVOH-UPy).

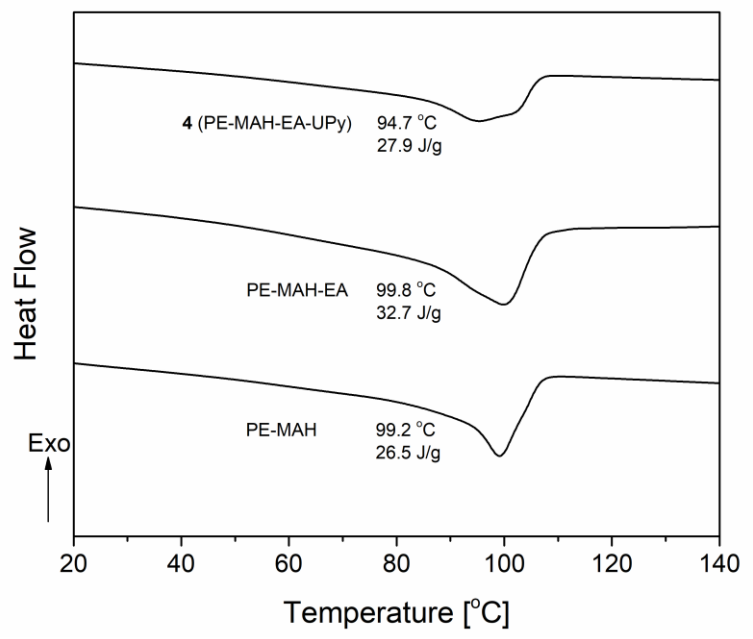

Figure S10. DSC second heating curves of PE-MAH, PE-MAH-EA and polymer **4** (PE-MAH-EA-UPy).

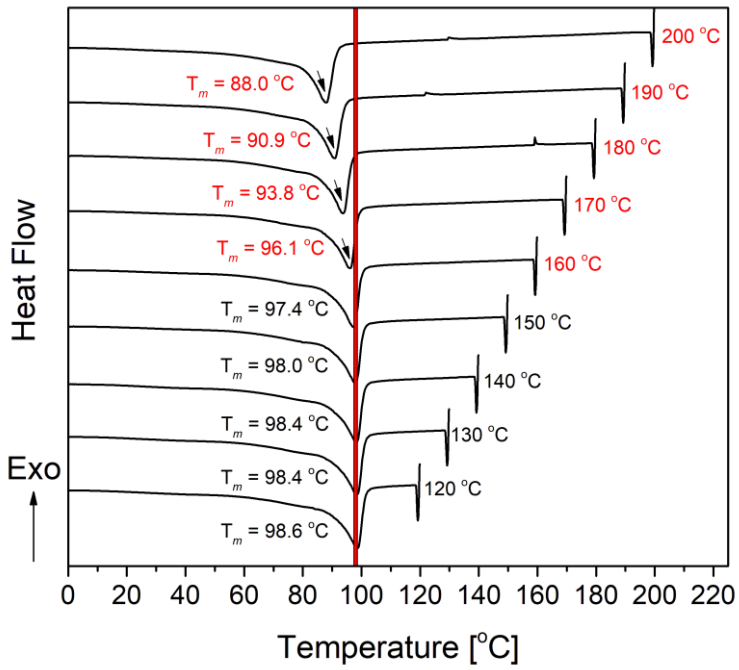

Figure S11. DSC heating curves of polymer **3** (EVOH-UPy), maximal temperature was increased by 10 °C each time starting from 120 °C.

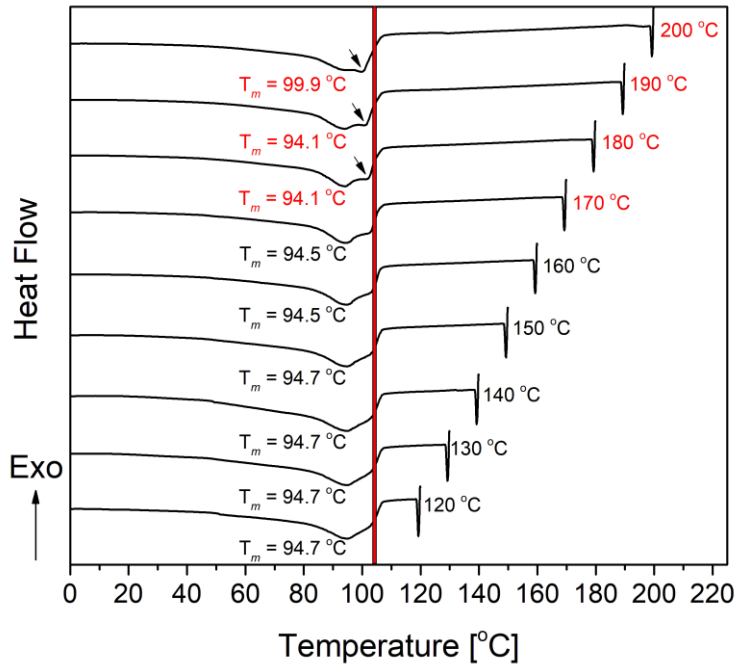

Figure S12. DSC heating curves of polymer **4** (PE-MAH-EA-UPy) maximal temperature was increased by 10 °C each time starting from 120 °C.

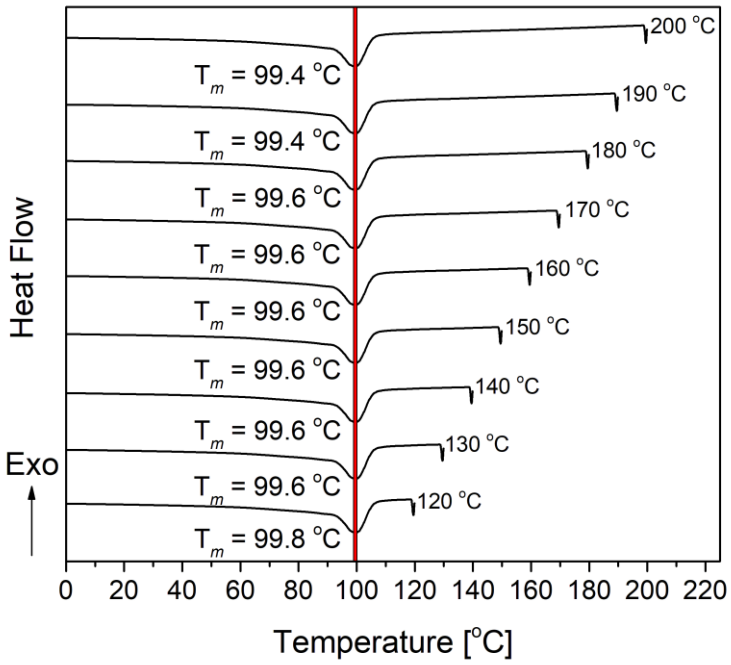

Figure S13. DSC heating curves of PE-HEMA1, maximal temperature was increased by 10 °C each time starting from 120 °C.

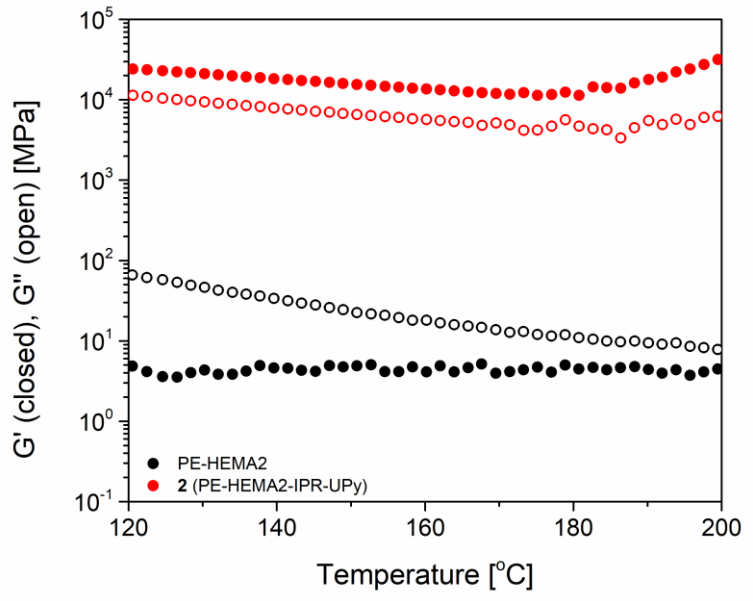

Figure S14. Rheology temperature sweep curves of PE-HEMA2 and polymer **2** (PE-HEMA1-UPy).

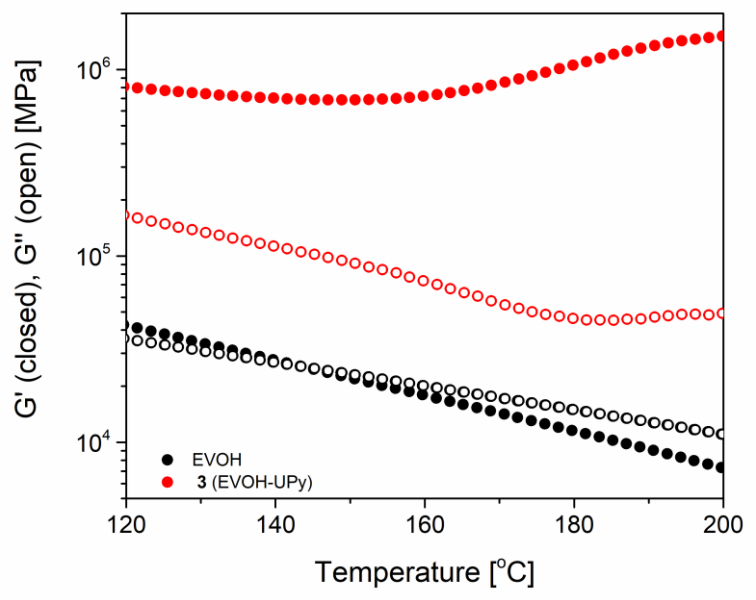

Figure S15. Rheology temperature sweep curves of EVOH and polymer **3** (EVOH-UPy).

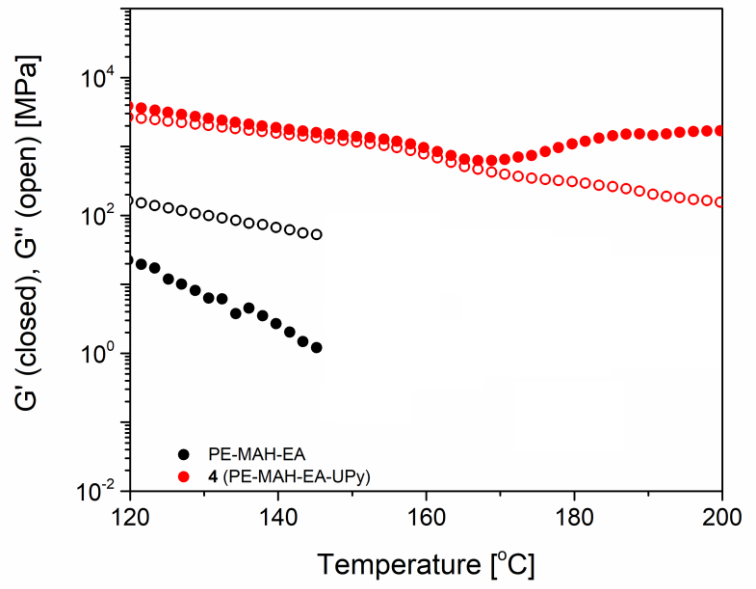

Figure S16. Rheology temperature sweep curves of PE-MAH-EA and polymer **4** (PE-MAH-EA-UPy).

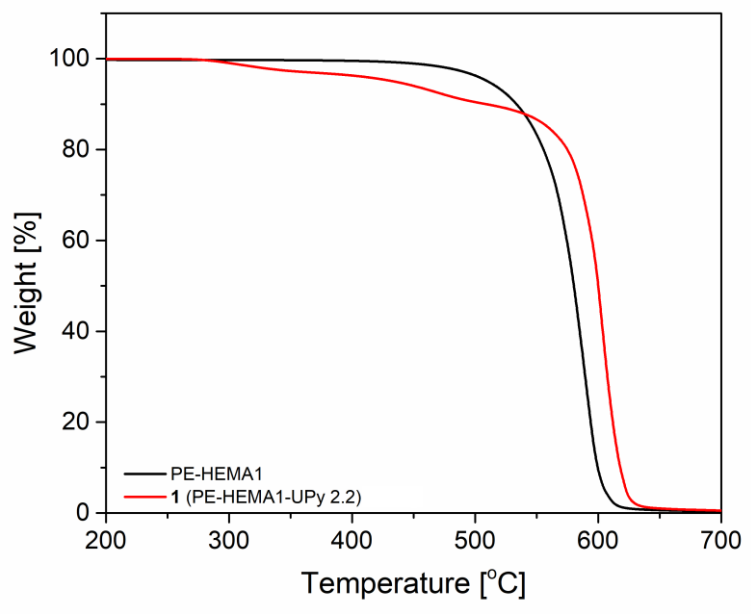

Figure S17. TGA curves of PE-HEMA1 and polymer **1** (PE-HEMA-UPy).

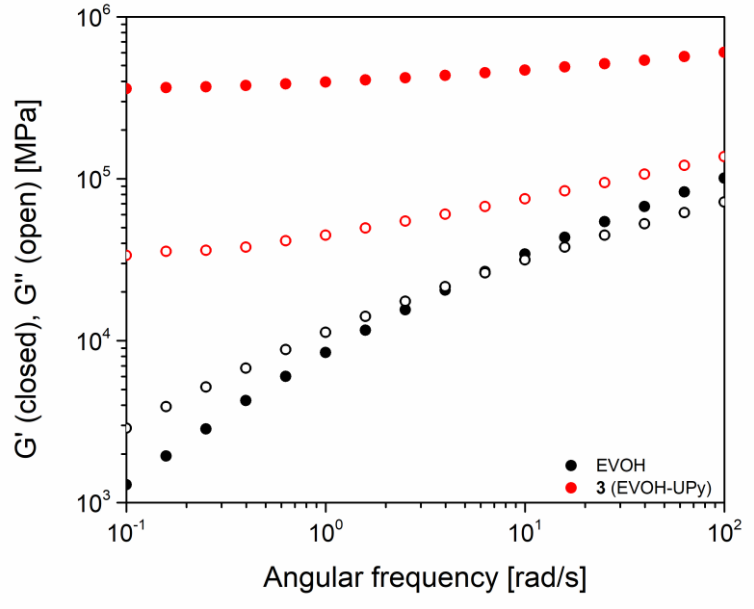

Figure S18. Rheology frequency sweep curves of EVOH and polymer **3** (EVOH-UPy).

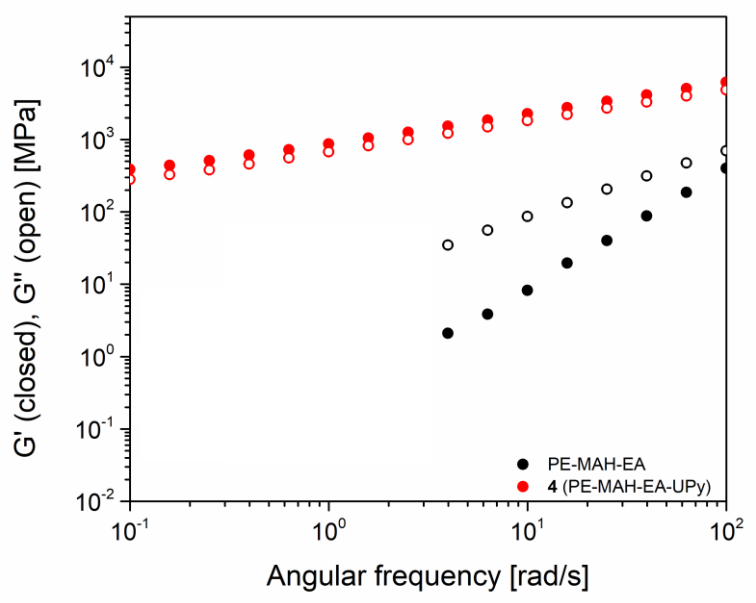

Figure S19. Rheology frequency sweep curves of PE-MAH-EA and polymer **4** (PE-MAH-EA-UPy)

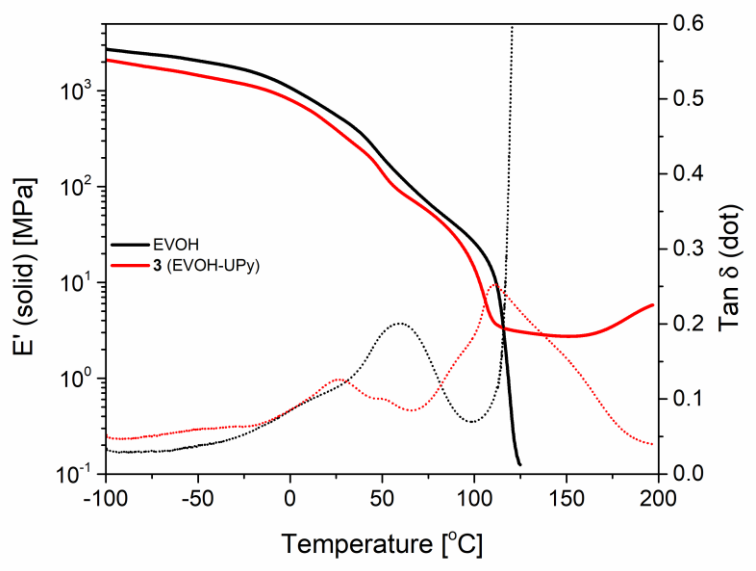

Figure S20. DMTA curves of EVOH and polymer **3** (EVOH-UPy).

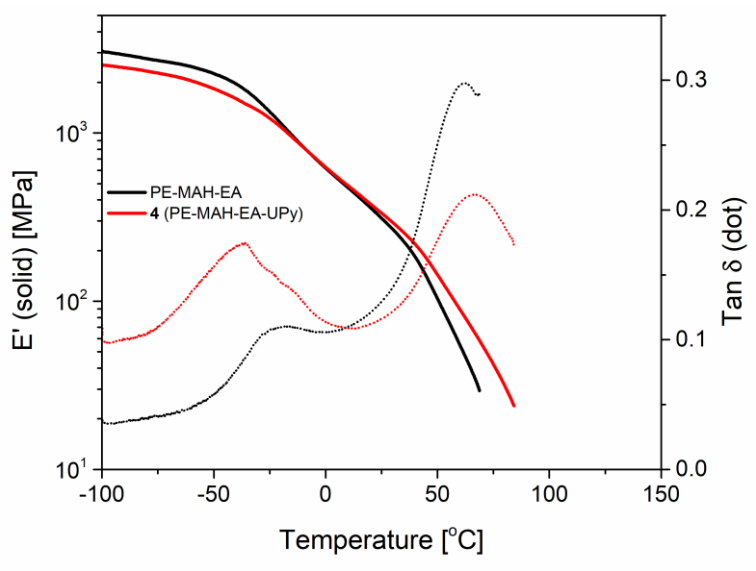

Figure S21. DMTA curves of PE-MAH-EA and polymer **4** (PE-MAH-EA-UPy)

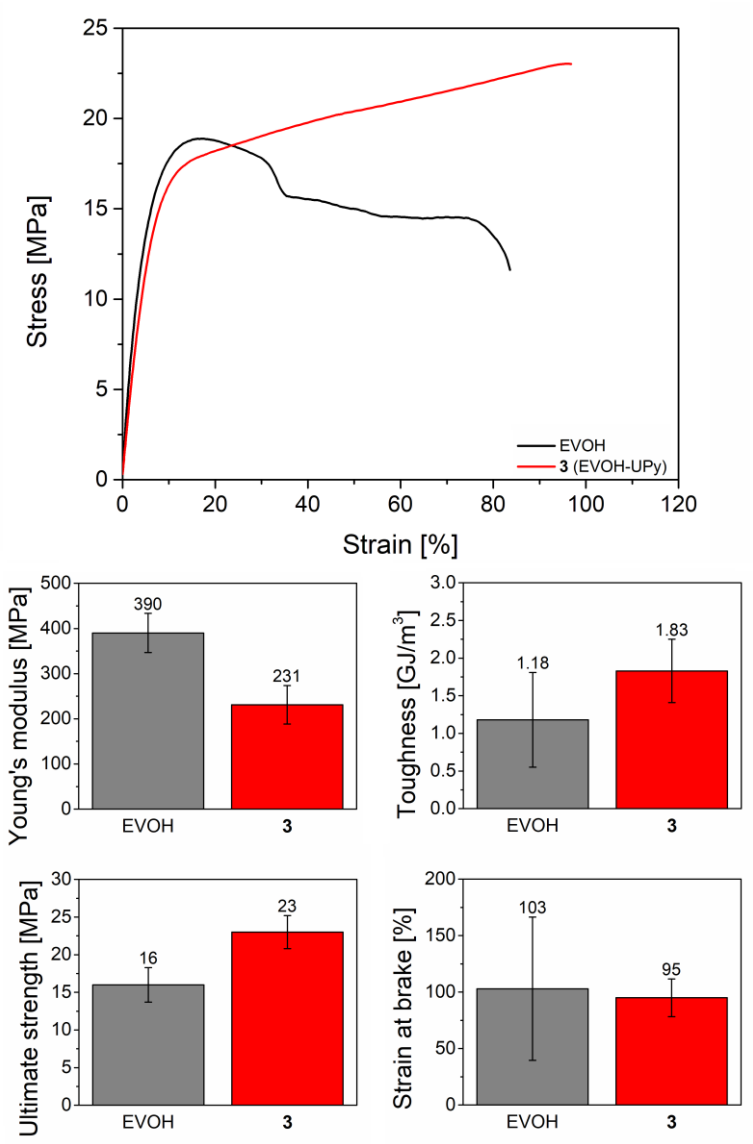

Figure S22. Representative stress-strain curves and Young's modulus, toughness, ultimate strength and strain at break of EVOH and polymer **3** (EVOH-UPy).

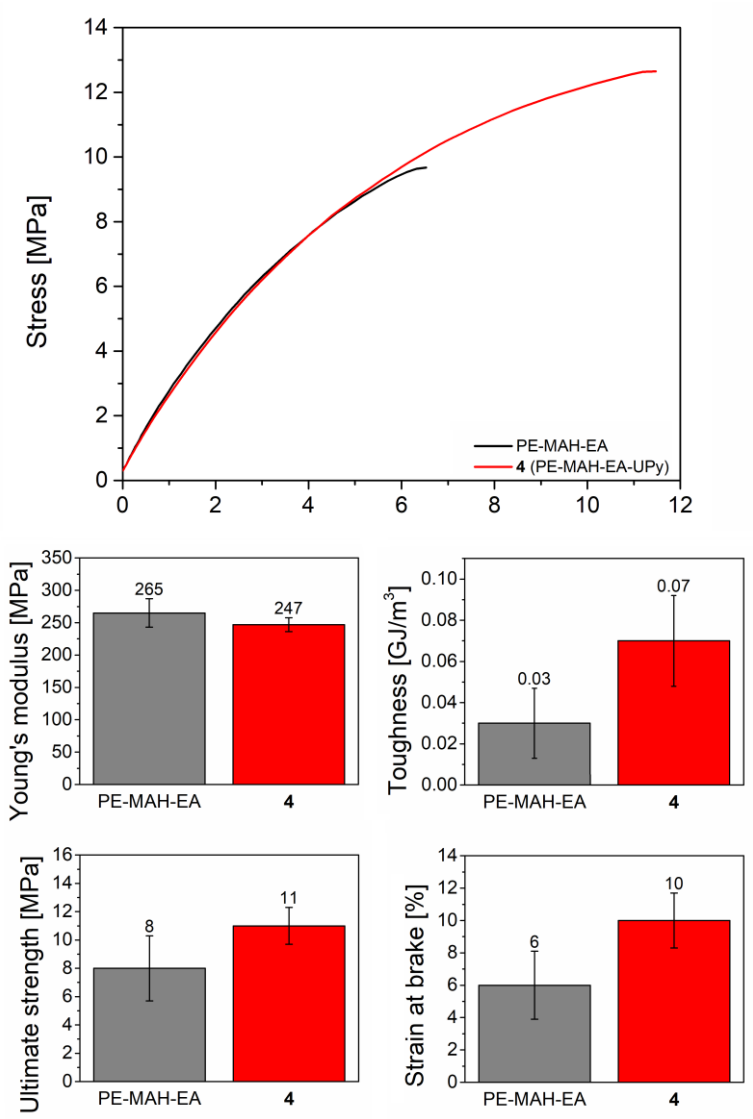

Figure S23. Representative stress-strain curves and Young's modulus, toughness, ultimate strength and strain at break of PE-MAH-EA and polymer **4** (PE-MAH-EA-UPy)