SUPPLEMENTARY MATERIALS

Polyamidoamine-based photostabilizers for cotton fabrics

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[1]H-NMR characterization of PAAs

The chemical structure of M-GLY, M-LEU, M-ARG and M-GLU at 0 and 100 h of UV irradiation was assessed by ^{1}H-NMR, collecting spectra in D_2O at pH 4.5 and at 25 °C using a Bruker Advance DPX-400 NMR spectrometer (Milan, Italy) operating at 400.13 MHz. Parameters: scan number 32, relaxation delay, *d1*, 10.0 s, receiver gain automatically measured and set by the instrument.

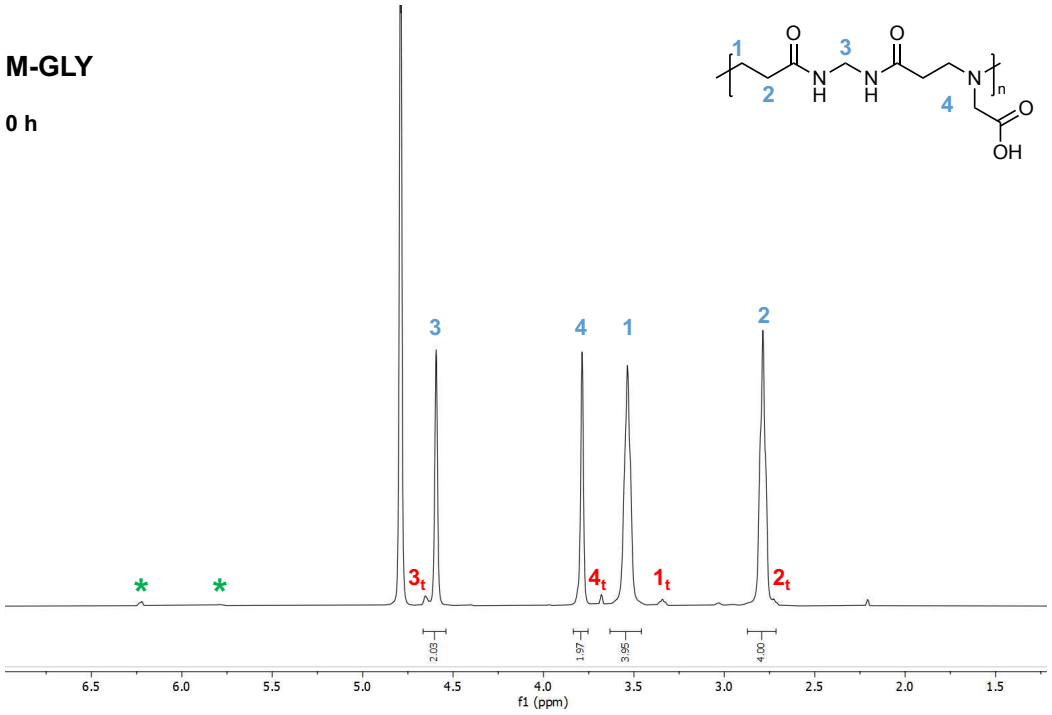

Figure S1. ^{1}H-NMR spectrum of M-GLY at 0 h UV irradiation.
The 1_t - 4_t peaks are ascribed to the glycine-based terminals. Green asterisks indicate traces of the vinyl-based terminals.

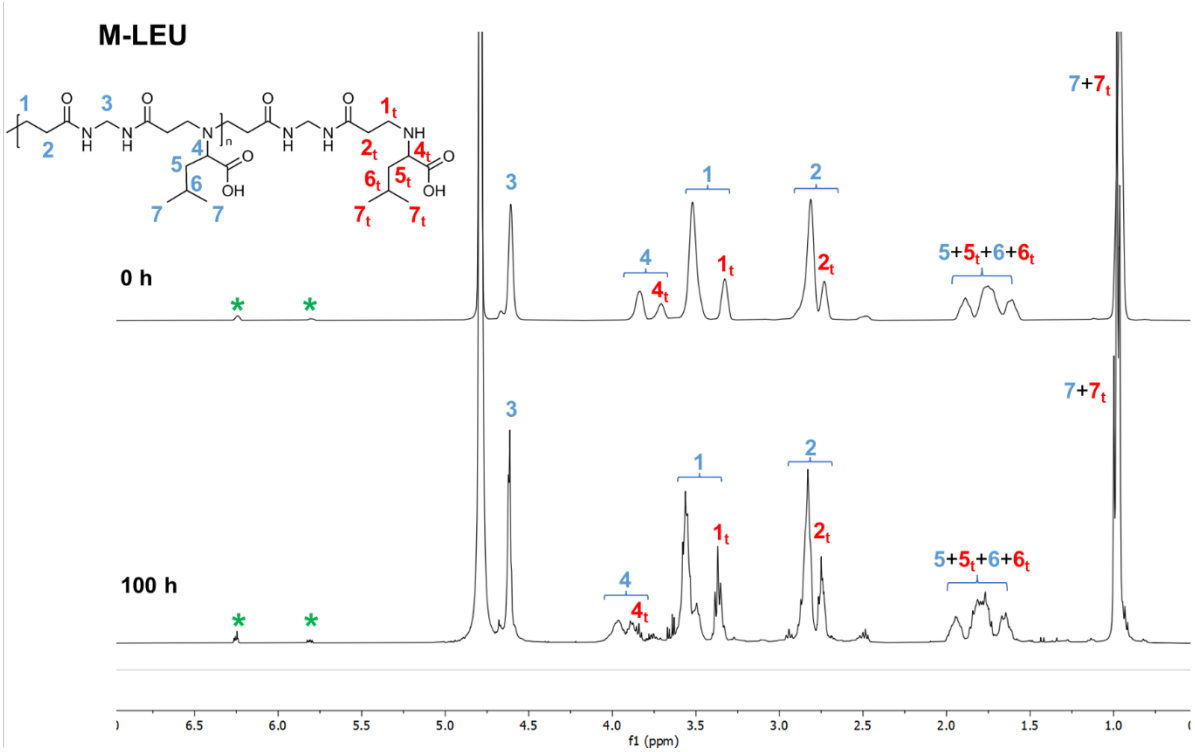

Figure S2. ^{1}H-NMR spectra of M-LEU at 0 and 100 h UV irradiation. Green asterisks indicate traces of the vinyl-based terminals. Small changes in the positions of the resonance peaks are due to the pH-dependence of the PAA proton magnetization.

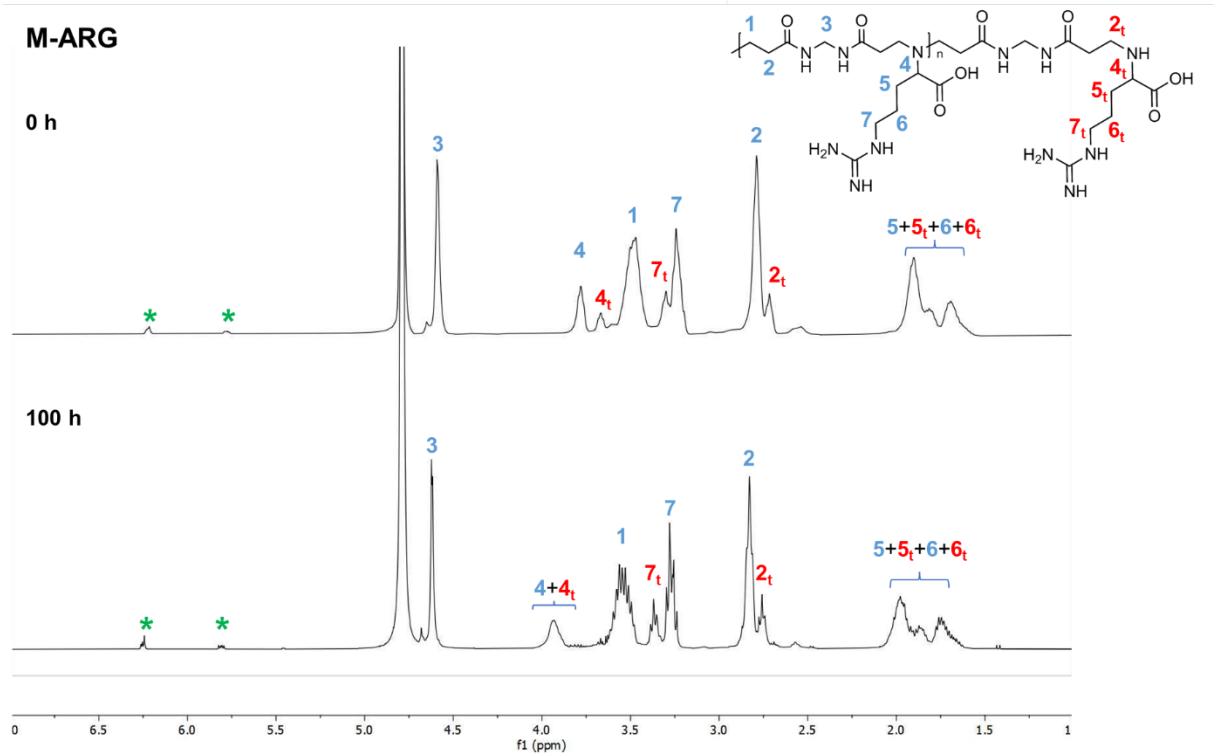

Figure S3. ^{1}H-NMR spectra of M-ARG at 0 and 100 h UV irradiation. The 4_t - 7_t peaks are ascribed to the glycine-based terminals. Green asterisks indicate traces of the vinyl-based terminals. Small changes in the positions of the resonance peaks are due to the pH-dependence of the PAA proton magnetization.

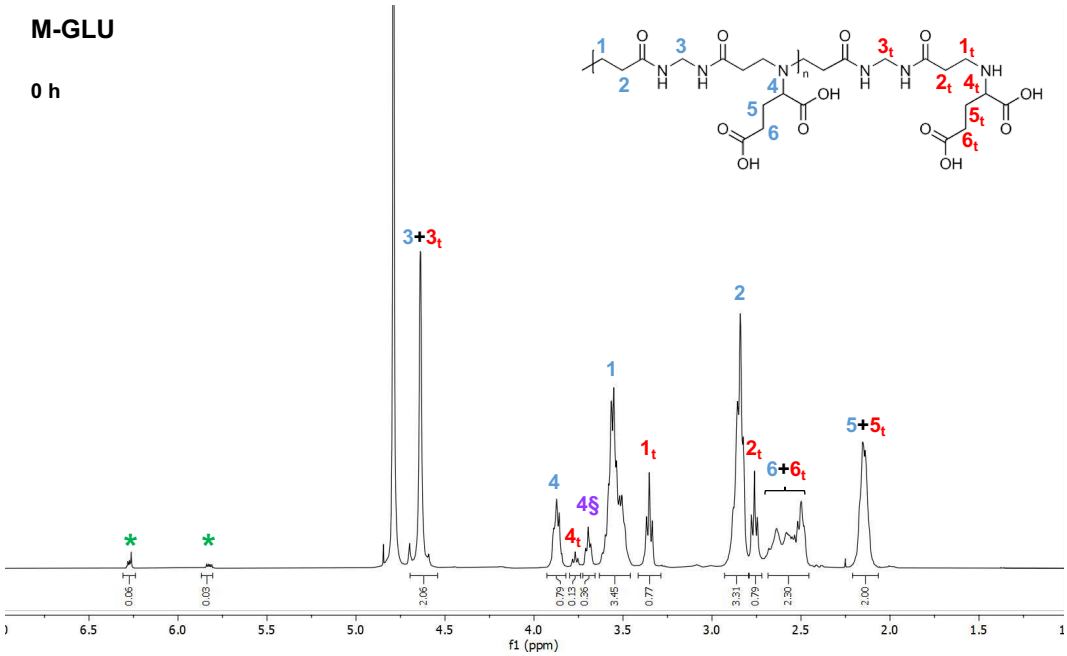

Figure S4. [1]H-NMR spectra of M-GLU at 0 UV irradiation. Green asterisks indicate traces of the vinyl-based terminals. The purple tilde on peak n°4 indicate differently protonated species.

Determination of the pKa values of PAAs and speciation diagrams

M-GLY: pK_a values were calculated in a previous work [1]. Speciation diagrams (Figure S5) were obtained by plotting the concentration fractions (α) of the different ionic species as a function of pH. The concentration fractions of M-GLY were calculated according to the following equations:

- Mass balance: $C_0 = C_{L+} + C_{L0} + C_{L-}$
- Equilibrium constants: $K_{a1} = \frac{C_{L0}\, C_{H+}}{C_{L+}}$; $K_{a2} = \frac{C_{L-}\, C_{H+}}{C_{L0}}$
- Concentration fractions:

$$C_{L+} = \frac{C_0\, {C_{H+}}^2}{{C_{H+}}^2 + K_{a1}\, C_{H+} + K_{a1}K_{a2}} = \frac{C_0\, {C_{H+}}^2}{D} \rightarrow \boldsymbol{\alpha_{L+}} = \frac{C_{L+}}{C_0} = \frac{{C_{H+}}^2}{D}$$

$$C_{L0} = \frac{C_0\, K_{a1}\, C_{H+}}{{C_{H+}}^2 + K_{a1}\, C_{H+} + K_{a1}K_{a2}} = \frac{C_0\, K_{a1}\, C_{H+}}{D} \rightarrow \boldsymbol{\alpha_{L0}} = \frac{C_{L0}}{C_0} = \frac{K_{a1}\, C_{H+}}{D}$$

$$C_{L-} = \frac{C_0\, K_{a1}K_{a2}}{{C_{H+}}^2 + K_{a1}\, C_{H+} + K_{a1}K_{a2}} = \frac{C_0\, K_{a1}K_{a2}}{D} \rightarrow \boldsymbol{\alpha_{L-}} = \frac{C_{L-}}{C_0} = \frac{K_{a1}K_{a2}}{D}$$

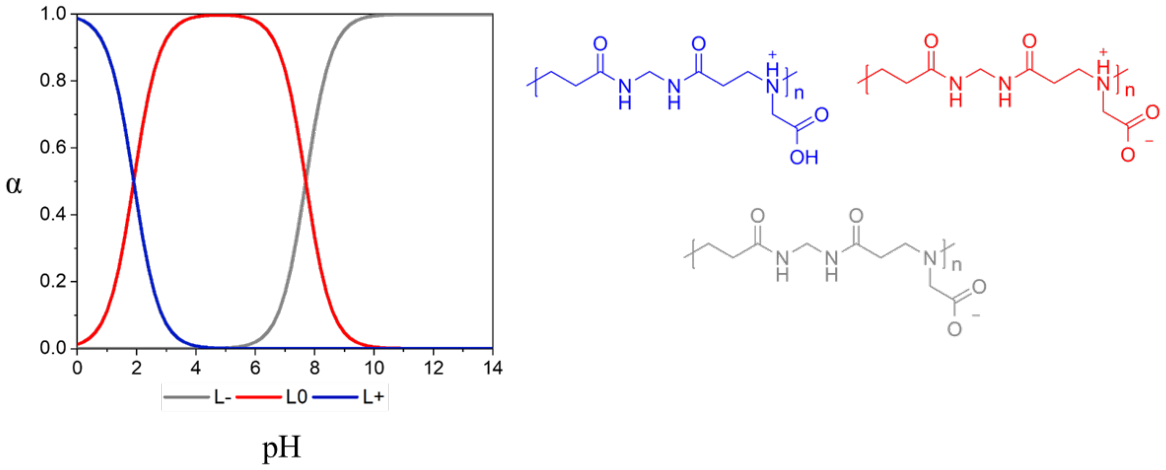

Figure S5. Speciation diagrams and chemical structures of the ionized repeat units of M-GLY.

M-LEU: the *pK_a* values were calculated in a previous work [2]. Speciation diagrams (Figure S6) were obtained by plotting the concentration fractions (α) of the different ionic species as a function of pH. The concentration fractions of M-LEU were calculated using the same equations used for M-GLY.

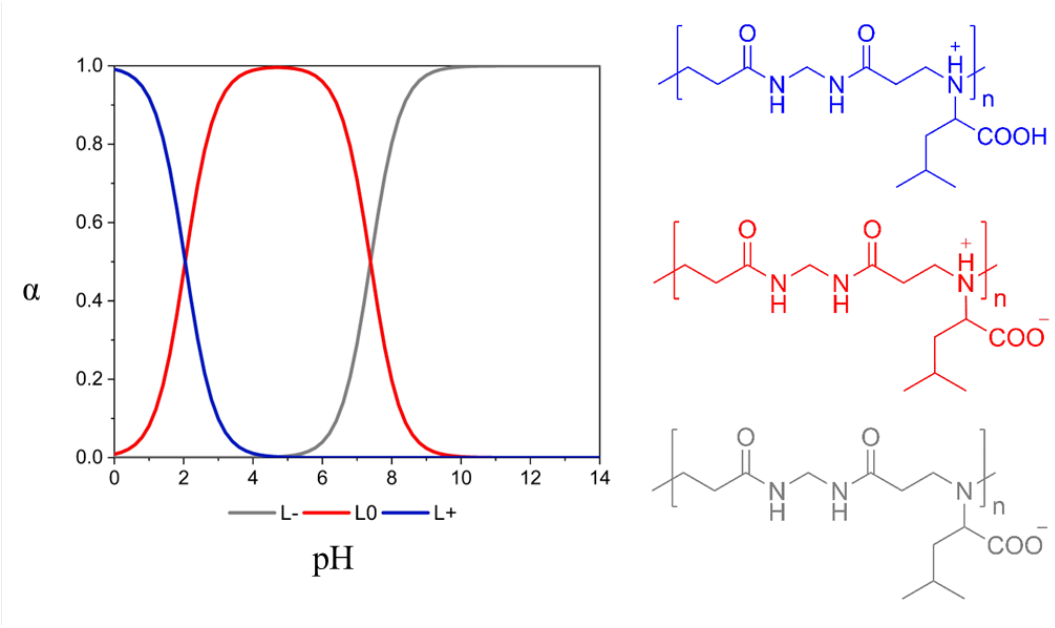

Figure S6. Speciation diagram and chemical structures of the ionized repeat units of M-LEU.

M-ARG: the pK_a values were calculated in a previous work [3]. Speciation diagrams (Figure S7) were obtained by plotting the concentration fractions (α) of the different ionic species as a function of pH. The concentration fractions of M-ARG were calculated according to the following equations:

- Mass balance: $C_0 = C_{L2+} + C_{L+} + C_{L0} + C_{L-}$
- Equilibrium constants: $K_{a1} = \frac{C_{L+}\, C_{H+}}{C_{L2+}}$; $K_{a2} = \frac{C_{L0}\, C_{H+}}{C_{L+}}$; $K_{a3} = \frac{C_{L-}\, C_{H+}}{C_{L0}}$;
- Concentration fractions:

$$C_{L2+} = \frac{C_0\, {C_{H+}}^3}{{C_{H+}}^3 + {C_{H+}}^2 K_{a1} + C_{H+} K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3}} = \frac{C_0\, {C_{H+}}^3}{D} \rightarrow \boldsymbol{\alpha_{L2+}} = \frac{C_{L2+}}{C_0} = \frac{{C_{H+}}^3}{D}$$

$$C_{L+} = \frac{C_0 {C_{H+}}^2 K_{a1}}{D} \rightarrow \boldsymbol{\alpha_{L+}} = \frac{C_{L+}}{C_0} = \frac{{C_{H+}}^2 K_{a1}}{D}$$

$$C_{L0} = \frac{C_0\, C_{H+} K_{a1} K_{a2}}{D} \rightarrow \boldsymbol{\alpha_{L0}} = \frac{C_{L0}}{C_0} = \frac{C_{H+} K_{a1} K_{a2}}{D}$$

$$C_{L-} = \frac{C_0\, K_{a1} K_{a2} K_{a3}}{D} \rightarrow \boldsymbol{\alpha_{L-}} = \frac{C_{L-}}{C_0} = \frac{K_{a1} K_{a2} K_{a3}}{D}$$

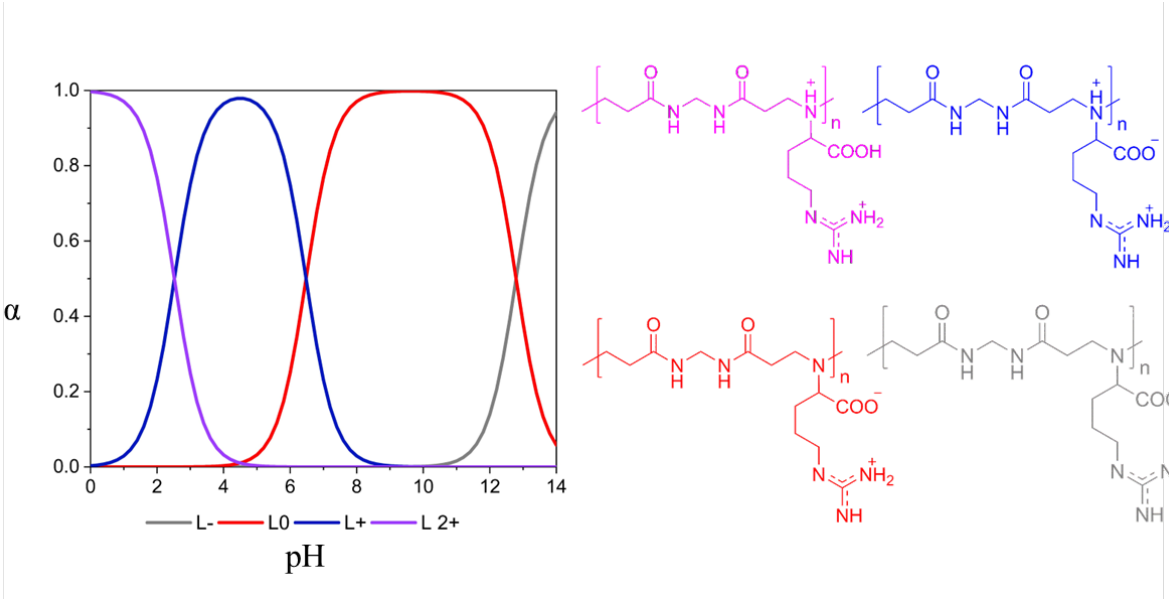

Figure S7. Speciation diagram and chemical structures of the ionized repeat units of M-ARG.

M-GLU: the pK_a values were calculated in a previous work [4]. Speciation diagrams (Figure S8) were obtained by plotting the concentration fractions (α) of the different ionic species as a function of pH. The concentration fractions of M-GLU were calculated according to the following equations:

- Mass balance: $C_0 = C_{L+} + C_{L0} + C_{L-} + C_{L2-}$
- Equilibrium constants: $K_{a1} = \frac{C_{L0}\, C_{H+}}{C_{L+}}$; $K_{a2} = \frac{C_{L-}\, C_{H+}}{C_{L0}}$; $K_{a3} = \frac{C_{L2-}\, C_{H+}}{C_{L-}}$
- Concentration fractions:

$$C_{L+} = \frac{C_0\, {C_{H+}}^3}{{C_{H+}}^3 + {C_{H+}}^2 K_{a1} + C_{H+} K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3}} = \frac{C_0\, {C_{H+}}^3}{D} \rightarrow \boldsymbol{\alpha_{L+}} = \frac{C_{L+}}{C_0} = \frac{{C_{H+}}^3}{D}$$

$$C_{L0} = \frac{C_0\, {C_{H+}}^2 K_{a1}}{D} \rightarrow \boldsymbol{\alpha_{L0}} = \frac{C_{L0}}{C_0} = \frac{{C_{H+}}^2 K_{a1}}{D}$$

$$C_{L-} = \frac{C_0\, C_{H+} K_{a1}K_{a2}}{D} \rightarrow \boldsymbol{\alpha_{L-}} = \frac{C_{L-}}{C_0} = \frac{C_{H+} K_{a1}K_{a2}}{D}$$

$$C_{L2-} = \frac{C_0\, K_{a1}K_{a2}K_{a3}}{D} \rightarrow \boldsymbol{\alpha_{L2-}} = \frac{c_{L2-}}{c_0} = \frac{K_{a1}K_{a2}K_{a3}}{D}$$

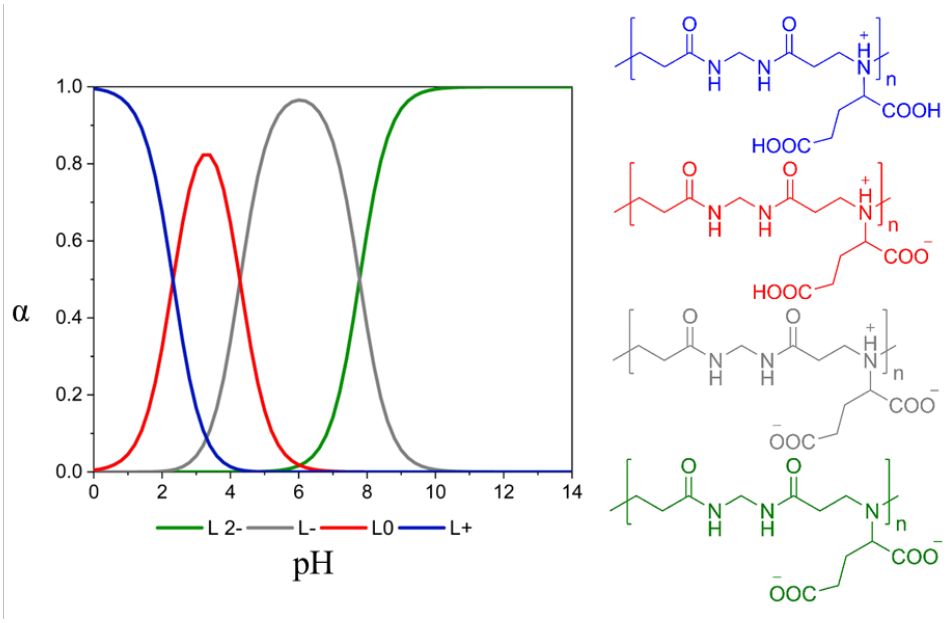

Figure S8. Speciation diagram and chemical structures of the ionized repeat units of M-GLU.

FT-IR/ATR characterization

COT, COT/M-GLY, COT/M-LEU, COT/M-ARG and COT/M-GLU were analyzed at 0 and 100 h of UV irradiation by attenuated total reflectance (ATR) Fourier transform infrared spectroscopy (FT-IR). FT-IR/ATR spectra were recorded at room temperature, in the 4000 - 600 cm^{-1} wavenumber range, with 32 scans and 4 cm^{-1} resolution, using a Perkin-Elmer Frontier FT-IR/FIR spectrophotometer (Milano, Italy), equipped with a ZnSe crystal characterized.

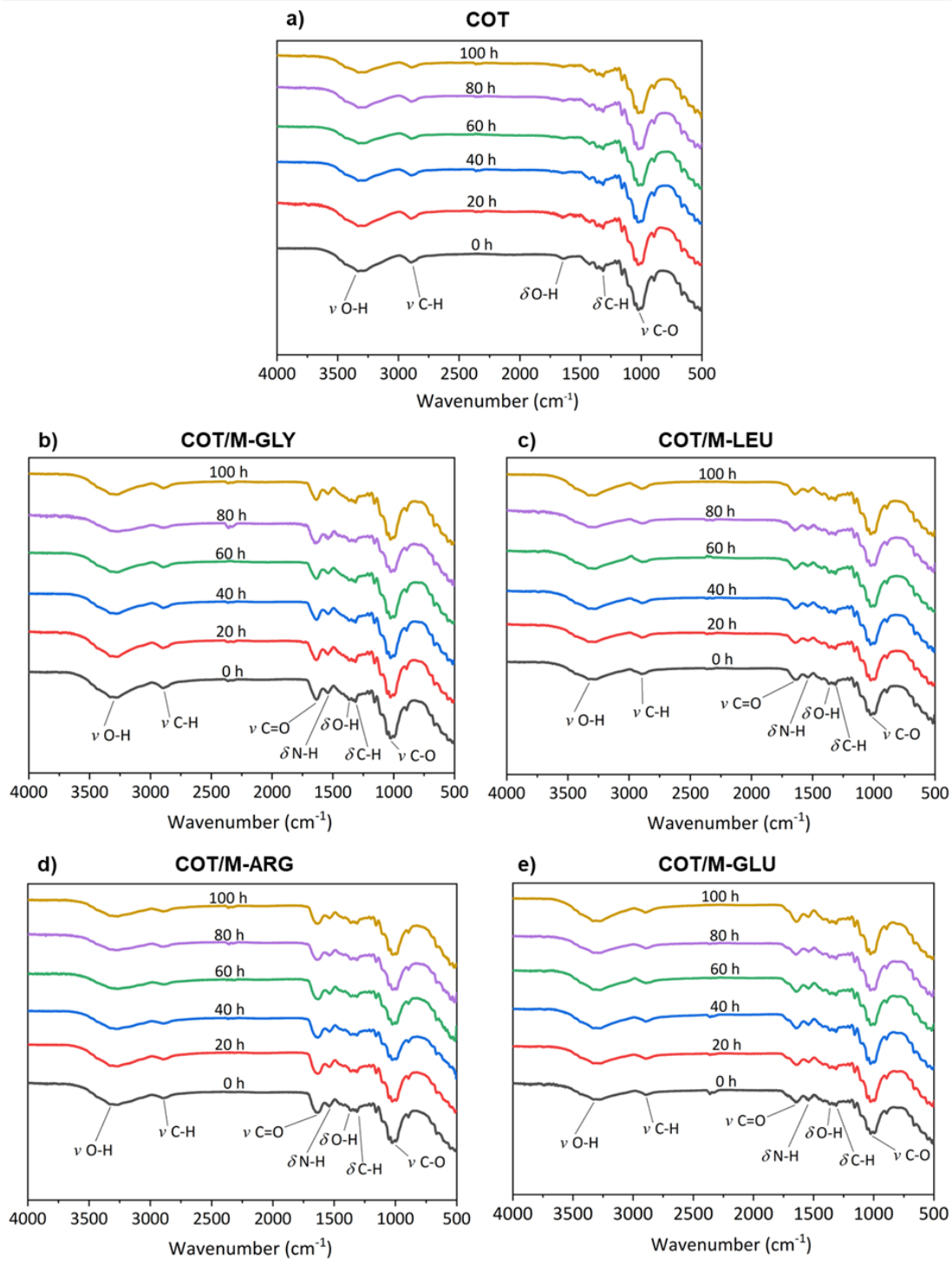

Figure S9. FT-IR/ATR spectra of COT, COT/M-GLY, COT/M-LEU, COT/M-ARG and COT/M-GLU analyzed at 0 and 100 h UV irradiation.

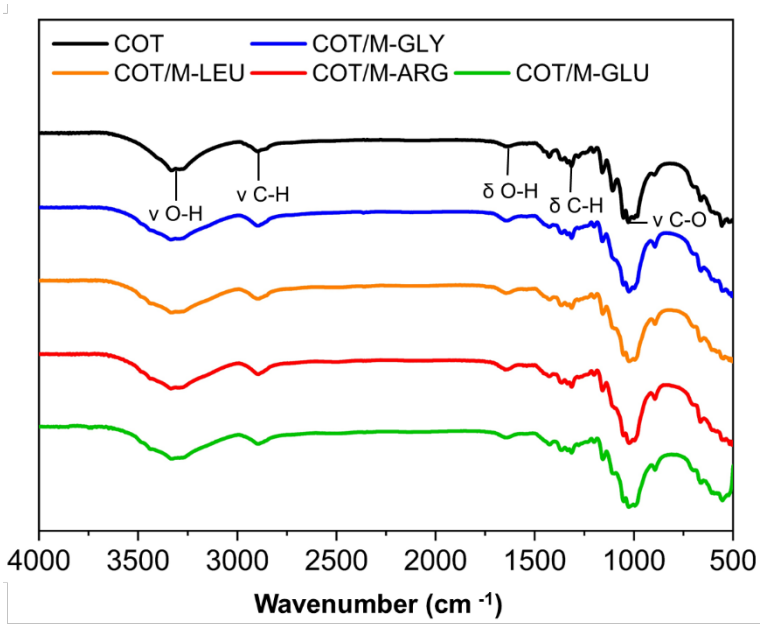

Figure S10. FT-IR/ATR spectrum of COT/M-GLY, COT/M-LEU, COT/M-ARG and COT/M-GLU after extraction.

References

1. Manfredi, A.; Carosio, F.; Ferruti, P.; Ranucci, E.; Alongi, J. Linear polyamidoamines as novel biocompatible phosphorus-free surface-confined intumescent flame retardants for cotton fabrics. *Polymer Degradation and Stability* **2018**, *151*, 52–64. doi:10.1016/j.polymdegradstab.2018.02.020.
2. F. Lazzari, A. Manfredi, J. Alongi, R. Mendichi, F. Ganazzoli, G. Raffaini, P. Ferruti, E. Ranucci, Self-structuring in water of polyamidoamino acids with hydrophobic side chains deriving from natural α-amino acids, Polymers 10(11) (2018) https://doi.org/10.3390/polym10111261
3. P. Ferruti, N. Mauro, L. Falciola, V. Pifferi, C. Bartoli, M. Gazzarri, F. Chiellini, E. Ranucci, Amphoteric, prevailingly cationic l-arginine polymers of poly(amidoamino acid) structure: synthesis, acid/base properties and preliminary cytocompatibility and cell-permeating characterizations, Macromol. Biosci. 14(3) (2014) 390-400, https://doi.org/10.1002/mabi.201300387
4. A. Beduini, F. Carosio, P. Ferruti, E. Ranucci, J. Alongi, Synergism between α-amino acid-derived polyamidoamines and sodium montmorillonite for enhancing the flame retardancy of cotton fabrics, Polym. Degrad. Stab. 225 (2024). https://doi.org/10.1016/j.polymdegradstab.2024.110764.