Electronic Supplementary Material (ESI) for RSC Advances.

A novel strategy to polyurethanes with improved mechanical properties by photoactivation of amidocoumarin moieties.

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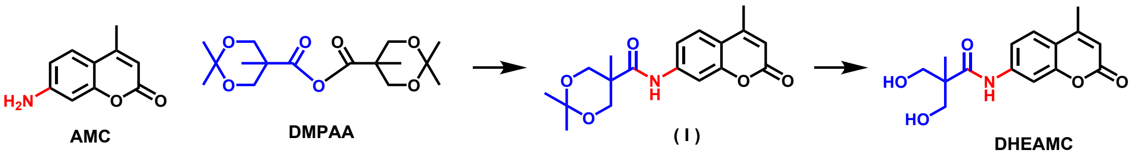
Synthetic route for the preparation of **DHEAMC**.



NMR-Data of Compounds

Compound (I):

^{1}H-NMR (400 MHz, DMSO-δ^6) δ: 9.68 (s, 1H), 7.82 (d, J = 1.9 Hz, 1H), 7.72 (d, J = 8.7 Hz, 1H), 7.59 (dd, J = 8.7, 1.9 Hz, 1H), 6.26 (s, 1H), 4.16 (d, J = 11.9 Hz, 2H), 3.75 (d, J = 11.9 Hz, 2H), 2.40 (s, 3H), 1.40 (s, 3H), 1.31 (s, 3H), 1.18 (s, 3H).

^{13}C-NMR (101 MHz, DMSO-δ^6) δ: 173.19, 159.99, 153.51, 153.02, 142.16, 125.69, 115.86, 115.17, 112.39, 106.37, 97.61, 65.19, 41.83, 25.04, 22.39, 18.07, 17.95.

Compound DHEAMC:

^{1}H-NMR (400 MHz, DMSO- δ^6) δ: 9.68 (br, 1H), 7.83 (d, J = 2.0 Hz, 1H), 7.69 (d, J = 8.7 Hz, 1H), 7.54 (dd, J = 8.7, 2.0 Hz, 1H), 6.24 (s, 1H), 4.94 (br, 2H), 3.75 – 3.46 (m, 4H), 2.39 (s, 3H), 1.13 (s, 3H).

^{13}C-NMR (101 MHz, DMSO- δ^6) δ: 174.61, 160.09, 153.59, 153.10, 142.51, 125.59, 115.77, 114.84, 112.15, 106.10, 64.01, 50.20, 17.97, 17.27.

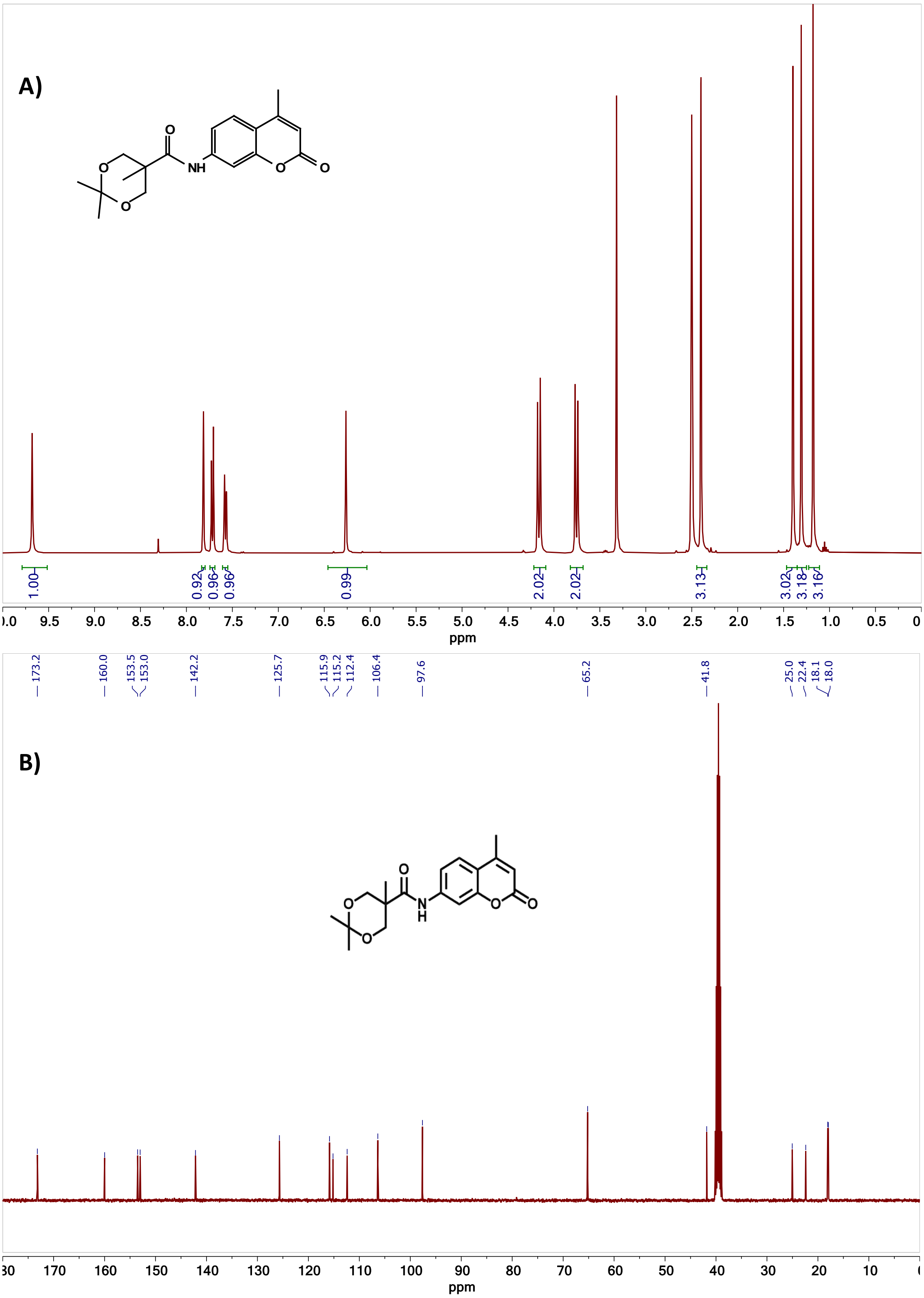


Fig. S1: A) ^{1}H-NMR and b) ^{13}C-NMR spectra of protected intermediate compound (I).

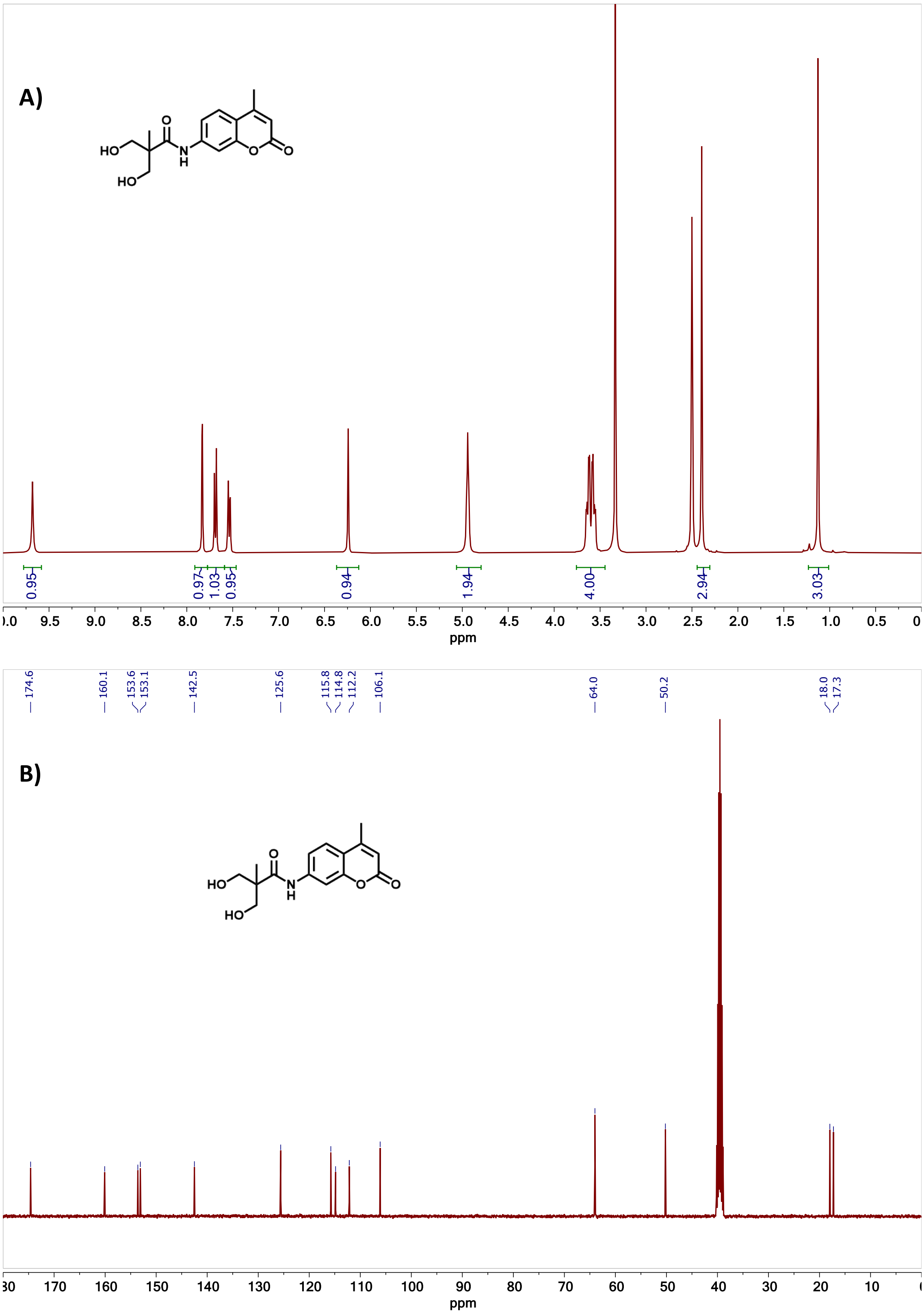


Fig. S2: A) ^{1}H-NMR and b) ^{13}C-NMR spectra of **DHEAMC**.

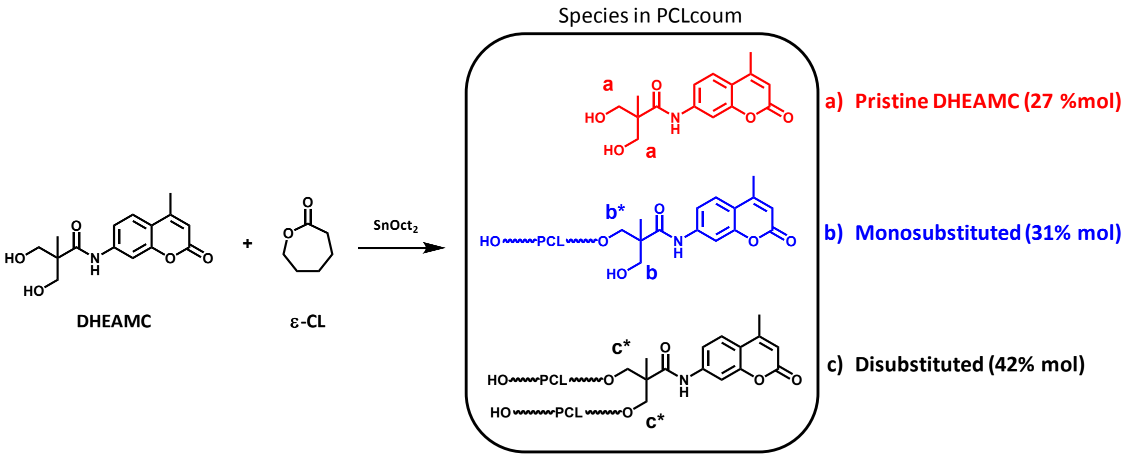


Fig. S3: Chemical structures and loading content (in mol) of all detected species in **PCLcoum**.

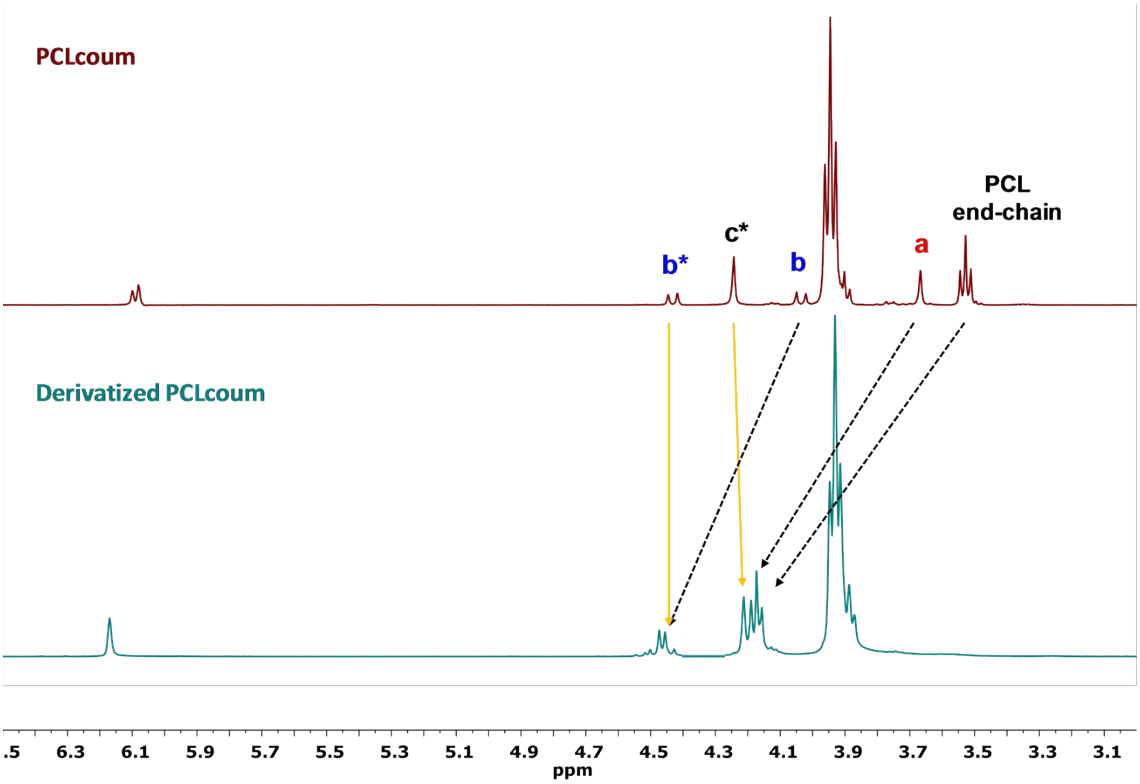
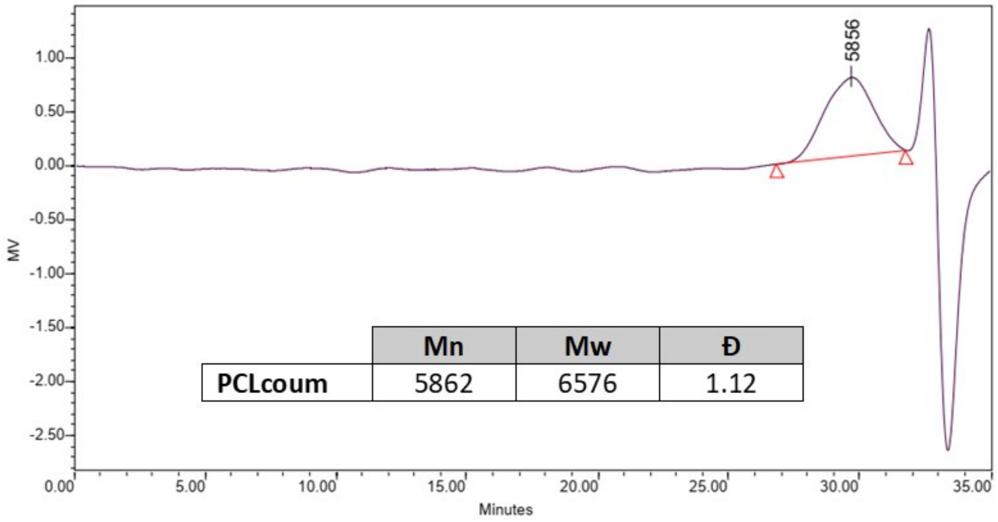


Fig. S4: Comparison of ^{1}H-NMR spectra of pristine PCLcoum (in red) and derivatized PCLcoum (in green).

In this figure, the unaltered NMR signals after derivatization have been highlighted with a yellow arrow. These signals are labelled with the letters **b*** and **c***, corresponding to the methylol groups (CH_2-OH) that have previously reacted with a ε-caprolactone unit (CH_2O-*ε-CL*). Their position remains constant after derivatization, because these groups do not react with the fluorinated anhydride.

On the other hand, the signals that shift their position with the derivatization have been indicated with a dashed black arrow and correspond to the free methylol groups (CH2-OH) (labelled with **a** and **b**). Additionally, there is a third shifting signal that corresponds to PCL end-chain. The displacement of this set of signals always occurs downfield due to the deshielding carried out by the trifluoroacetyl group (CH_2-O-*$COCF_3$*).



	Mn	Mw	Đ
PCLcoum	5862	6576	1.12

Fig. S5: GPC curve, molecular weights (**Mn** and **Mw**) and polydispersity (**Đ**) for **PCLcoum**

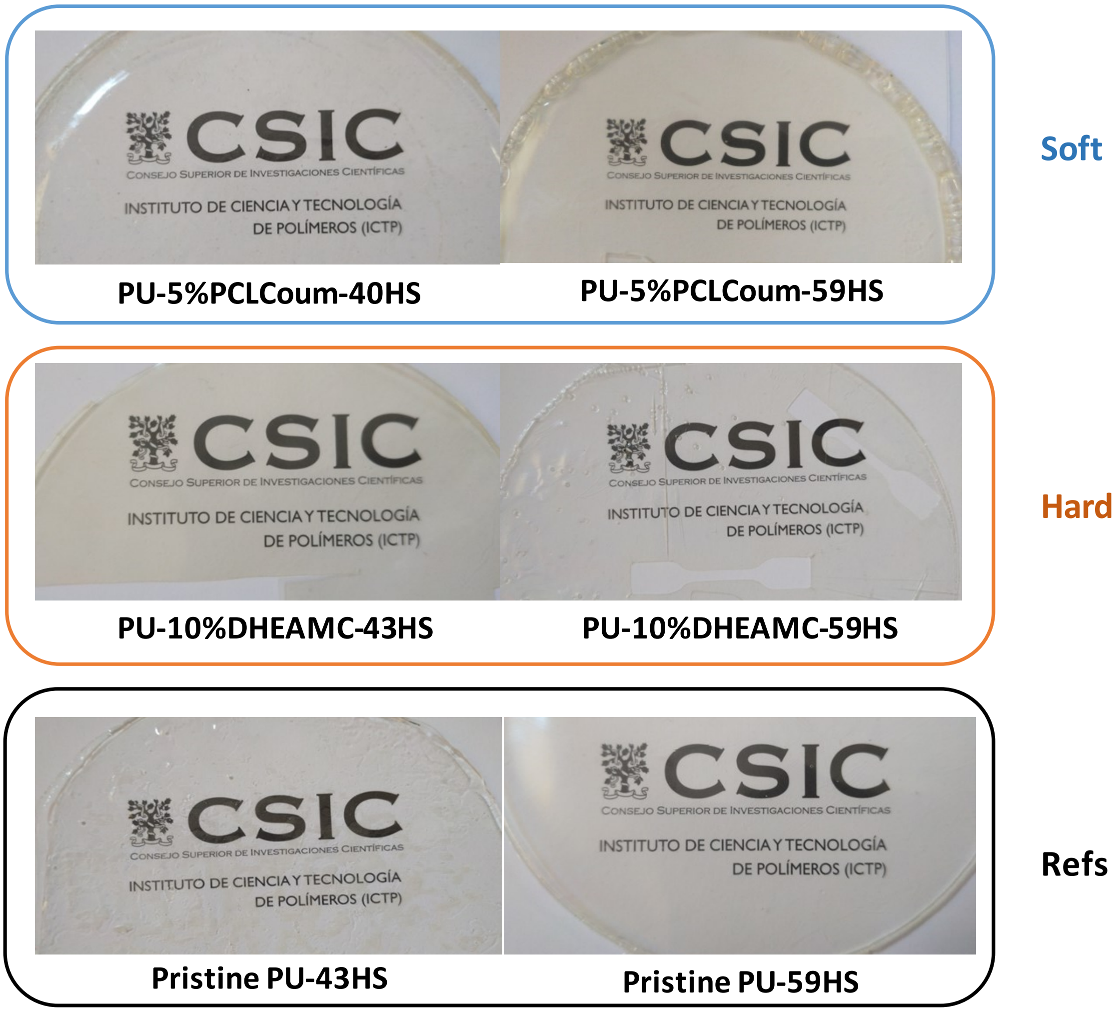


Fig S6: Photographs of the polyurethane coatings bearing coumarin in the soft segment (blue), in the hard segment (orange) and the reference systems (black).

Polyurethane	Thickness (µm)	Non-irrad		Irrad @365nm	
		Stress (MPa)	**Strain (%)**	**Stress (MPa)**	**Strain (%)**
PU-5%PCLcoum-40HS	148 ± 10	1.3 ± 0.2	> 1700	5.0 ± 1.5	1130 ± 54
PU-5%PCLcoum-59HS	220 ± 13	16.7 ± 4.2	790 ± 66	48.0 ± 7.4	540 ± 45
PU-10%PCLcoum-43HS	209 ± 17	31.8 ± 3.7	812 ± 25	37.5± 9.3	740 ± 19
PU-10%PCLcoum-59HS	204 ± 15	40.2 ± 2.9	300 ± 82	42.8± 8.8	270 ± 15
PU-5%DHEAMC-40HS	189 ± 24	0.4 ± 0.3	> 1700	77.2 ± 5.6	1050 ± 58
PU-5%DHEAMC-59HS	204 ± 11	1.6 ± 0.5	780 ± 35	56.8 ± 3.5	570 ± 57
PU-10%DHEAMC-43HS	156 ± 13	0.6 ± 0.2	> 1700	42.4 ± 4.7	900 ± 67
PU-10%DHEAMC-59HS	202 ± 16	2.9 ± 0.5	720 ± 140	74.3 ± 6.4	540 ± 50

Table S1: Mechanical properties (Max Stress and Strain) of the segmented polyurethanes before and after crosslinking by UV-light at 365nm for 180 min.