Dynamically cross-linked polyethylene-like materials with reversible self-reporting properties

Alessandro Torri,[1] Chiara Paravidino,[2] Gabriele Giovanardi,[a] Francesco Rispoli,[a] Fabrizio Moroni,[3] Alessandro Pedrini,[1] Enrico Dalcanale,[1] Alberto Fina,[2*] and Roberta Pinalli[1*]

[1] Department of Chemistry, Life Sciences and Environmental Sustainability and INSTM UdR Parma, University of Parma, Parco Area delle Scienze 17/A, 43124 Parma, Italy
[2] Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Viale Teresa Michel 5, 15121 Alessandria, Italy
[3] Dipartimento di Ingegneria dei Sistemi e delle Tecnologie Industriali University of Parma, Parco Area delle Scienze 181/A, 43124 Parma, Italy

Summary

Materials and Methods

Unless stated otherwise, all reactions were conducted in flame-dried glassware under an atmosphere of nitrogen using anhydrous solvents (either freshly distilled or passed through activated alumina columns). All reagents and solvents were purchased from certified commercial sources and used as received, without further purification. For synthesis, all anhydrous solvents (either freshly distilled or passed through activated alumina columns) have been used. Rhodamine **6G** was purchased from TCI Chemicals (product number R0039). TMSPEDA was purchased from ABCR (product number AB131042). Pristine PE-HEMA was provided by Saudi Basic Industries Corporation (Sabic) with 2.1 mol% of HEMA content calculated by NMR spectroscopy. Silica Gel for chromatographic separation was purchased from Sigma-Aldrich in technical grade, pore size 60 Å, 230-400 mesh particle size, 43-60 μm particle size. Thin layer chromatography was performed using TLC Analytical Chromatography F254®, Merck.

Nuclear Magnetic Resonance. ^{1}H and ^{13}C spectra were recorded on Bruker 400 MHz AVANCE, using $CDCl_3$ as solvent. All chemical shifts (δ) were reported in parts for million (ppm) relative to proton resonances resulting from incomplete deuteration of NMR solvents. The abbreviations: s, d, t, m and bs indicated the spectrum peaks referred to: singlet, doublet, triplet, multiplet and broad singlet, respectively. The coupling constant (J) are expressed in Hz.

MS Spectrometry. ESI-MS characterization experiments were performed on a Waters ACQUITY Ultra Performance LC HO6UPS-823M with ESI source ionization (electrospray ionization) in positive modality.

HR-MS. High-Resolution ESI-MS characterization experiments were performed on a LTQ ORBITRAP XL Thermo with ESI source ionization (electrospray ionization) in positive modality and new generation Ion Trap FT Orbitrap as analyzer.

Thermogravimetric Analysis (TGA). TGA analyses have been achieved using a Perkin Elmer TGA 8000 with gas controller GC10 (pure air/nitrogen), Mettler Toledo. Samples were heated at 800 °C at a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC). Differential scanning calorimetry was performed on a DSC6000 from Perkin Elmer. DSC measurements were carried out under nitrogen between 0 and 200 °C at a scan rate of 10 °C min^{-1}. The sample weight was in the range of 5-10 mg. The transitions were measured in the second heating curves.

Dynamic Mechanical Analysis (DMTA). DMTA analyses were carried out on stripes with nominal dimensions 6x0.1x30 mm^3, cut from films obtained by solvent casting. Specimens were tested in tensile mode on a Q800 equipment (TA Instruments) at 2 °C/min heating rate (RT to 180 °C) and 1Hz frequency in strain-controlled mode, deformation amplitude at 0.05% and 0.01N preload. Specimens were conditioned at 23 °C and 50%RH for at least 48h before analyses.

Rheological analysis. Small angle oscillatory shear tests were carried out on an ARES rheometer (TA Instruments) operated with a 25 mm parallel plate geometry and 1 mm thickness samples obtained by compression moulding. Dynamic frequency sweep tests were carried out to determine G', G'' and complex viscosity (η*) between 0.1 and 100 rad/s at 1% strain (linear viscoelasticity) at temperatures between 120 °C and 200 °C.

Compression Molding. Polymer films for scratching tests and stress strain measurements were printed by compression molding using a *Gibitre Laboratory Press Drive* at 150 °C applying 15000 kg for 3 minutes. Specimens were compression molded on a Collins P200T press at 150 °C, 100 bar hydraulic pressure for 4 minutes, followed by water cooling to 50°C before extraction.

Stress-strain. Mechanical tests were conducted taking the ASTM-D-882 standard (ASTM-D-882 "Tensile Properties of Thin Plastic Sheeting") as reference, adapting the specimen geometry and test conditions to enhance the color appearance during the test. The tests were carried out at room temperature on bars with nominal dimensions (width) x 0.7 (thickness) x 80 (length) mm^3, which were cut from plates obtained by compression molding to have a free length of 40 mm between the grips for the measurements. Testing were

performed using an Instron 4400, electromechanical testing machine, equipped with a 30 kN load cell. The test speed was set to 250 mm/min and at least 3 repetitions were performed for each condition. The stress-strain curve was recorded for each specimen. From the stress-strain curve, the following parameters were calculated for each: i) Elastic modulus (E), determined as the slope of the initial linear region of the stress-strain curve. ii) Ultimate tensile strength (UTS), identified as the maximum stress the specimen withstood. iii) Strain at failure, defined as the last strain value recorded just before the complete specimen separation.

Gel Permeation Chromatography (GPC): GPC was performed on a Polymer Char GPC-IR system using a IR5 MCT detector A column set of three 3 columns PLgel Olexis (300 x 7,5 mm) was used. Samples were dissolved in trichlorobenzene (TCB) and the runs were performed at 160°C.

Synthesis of functionalized rhodamine 1

Rhodamine **1** was synthesized according to a procedure adapted from literature [31].

Ethanolamine (383 mg, 0.38 mL, 6.28 mmol, 6 eq) was added to a solution of rhodamine **6G** (500 mg, 1.05 mmol, 1 eq) in dry acetonitrile ACN (10 mL), and the reaction was refluxed overnight under mechanical stirring. As the reaction progressed, a pink precipitate formed. The reaction progress was monitored by TLC using ethyl acetate (EtOAc) as eluent. Once the complete disappearance of rhodamine **6G** was observed, the precipitate was filtered and washed with water. The obtained solid was purified by liquid chromatography on silica gel using 100% EtOAc as the eluent. The product was obtained as a white solid (418 mg, yield = 87%) and characterized by ^{1}H-NMR spectroscopy in $CDCl_3$. ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz) δ (ppm) = 7.92 (dd, J=8 Hz, 1H, Hi), 7.45 (m, 2H, Hg, Hh), 7.04 (d, J=8 Hz, 1H, Hf), 6.35(s, 2H, He), 6.28 (s, 2H, Hc), 4.16 (bs, 1H, Hm), 3.53 (bs, 1H, Hl), 3.44 (t, 2H, Hk), 3.25 (t, 2H, Hj), 3.21 (q, 4H, Hb), 1.92 (s, 6H, Hd), 1.32 (t, 6H, Ha).

ESI-MS: m\z = calculated for $C_{28}H_{30}N_3O_3$ $[M-H]^-$ 456.23, experimental value for $[M-H]^-$ 456.30

Synthesis of functionalized rhodamine 2

Rhodamine **2** was synthesized according to a procedure adapted from literature [31].

Rhodamine **1** (500 mg, 1.09 mmol, 1eq.) was added to a suspension of K_2CO_3 (906 mg, 6.56 mmol, 6 eq) and KI (4 mg, 0.02 mmol, 0.02 eq) in 2-bromoethanol (4 g, 2.3 mL, 30 mmol, 30 eq). The resulting red suspension was stirred mechanically at 110°C for 24 hours. The disappearance of Rhodamine **1** was monitored via TLC (DCM : MeOH 96:4). The solvent was then evaporated under high vacuum, and the resulting crude solid was dissolved in 25 mL of dichloromethane (DCM) and washed with 1M HCl (3 x 50 mL). The acidic aqueous phases were collected, neutralized with 1M NaOH, and formed a suspension. DCM was added 3 times to the suspension, and the extracted organic phases were combined and dried over Na_2SO_4. The solvent was evaporated under high vacuum, and the crude was purified by liquid chromatography on silica gel using a mixture of DCM : MeOH (96:4) as the eluent. Rhodamine **2** was obtained as a white solid with a yield of 65% (387 mg). ^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz) δ (ppm) = 7.99 (dd, J=8 Hz, 1H, Hi), 7.53 (m, 2H, Hg, Hh), 7.07 (m, 1H, Hf), 6.93(s, 2H, He), 6.52 (s, 2H, Hc), 4.25 (bs, 1H, Hm), 3.94 (br, 1H, Ho), 3.65 (m, 4H, Hn), 3.48 (t, J=4 Hz, 2H, Hk), 3.26 (m, 6H, Hj, Hl), 3.05 (q, 4H, Hb), 2.13 (s, 6H, Hd), 1.05 (s, 6H, Ha).

ESI-MS: m\z = calculated for $C_{32}H_{49}N_3O_5$ $[M+H]^+$ 546.30, experimental value for $[M+H]^+$ 546.35.

Synthesis of functionalized rhodamine 3

3-Isocyanatopropyltrimethoxysilane (167.5 mg, 154 µL, 0.81 mmol, 3.5 eq) was slowly added to a solution of rhodamine **2** (127.2 mg, 0.23 mmol, 1 eq) and dibutyltin dilaurate (DBTL, catalytic amount) in dry DCM (1.5 mL). The reaction was stirred mechanically at 40 °C in a dark environment for 16 hours. The solvent was then evaporated under high vacuum, and the resulting yellow oil was triturated in hexane (3 x 10 mL) and filtered. The target rhodamine **3** was obtained as a yellow solid in quantitative yield (270 mg) and fully characterized by NMR spectroscopy and HR ESI-MS.

^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz) δ (ppm) = 7.96 (m, 1H, Hg), 7.50 (m, 2H, Hf, He), 7.06 (m, 1H, Hd), 6.89(s, 2H, Hb), 6.42 (s, 2H, Ha), 4.14 (m, 4H, Hj), 3.57 (m, 28H, Ho, Hq), 3.24 (m, 4H, Hp, Hk), 3.16 (m, 6H, Hl), 3.08 (m, 4H, Hh), 2.06 (s, 6H, Hc), 1.64 (m, 6H, Hm), 1.04 (t, 6H, Hi), 0.65 (m, 6H, Hn).

^{13}C NMR ($CDCl_3$, 25 °C, 100 MHz) δ (ppm) = 168.80, 168.59, 156.94, 156.58, 156.05, 153.80, 151.48, 151.22, 150.29, 147.26, 132.81, 130.51, 129.96, 129.73, 128.46, 123.93, 123.10, 118.63, 113.30, 109.80, 96.42, 70.60, 69.78, 69.48, 69.20, 67.87, 64.84, 64.65, 63.92, 63.07, 62.35, 61.93, 51.97, 51.42, 50.83, 50.66, 47.83, 43.98, 43.49, 39.57, 23.27, 17.83, 16.79, 12.37, 6.40.

HR ESI-MS: m/z = calculated for ($C_{53}H_{85}N_6O_{17}Si_3$) $[M+H]^+$ 1161.5291, experimental value for $[M+H]^+$ 1161.5279.

General procedure to prepare the crosslinked material

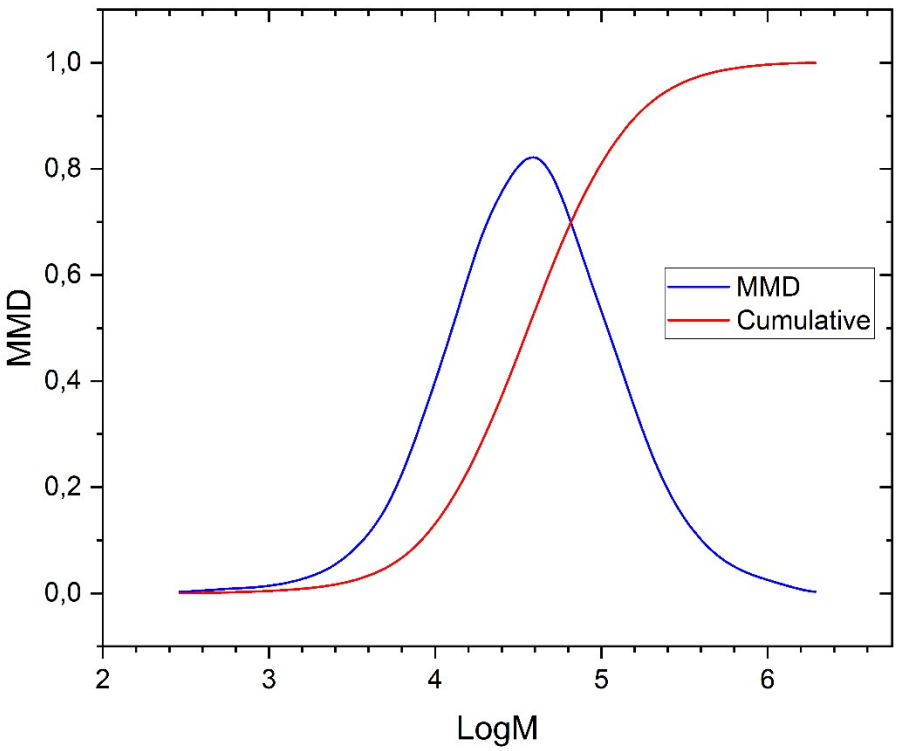
For the reaction stoichiometry calculations reported in Table 1 of the main text, it was assumed that all the –SiOMe groups of both Rhodamine **3** and TMSPEDA are capable of reacting with PE-HEMA hydroxyl groups.
The crosslinker (Rhodamine **3** or TMSPEDA) was added to a solution of PE-HEMA in ortho-dichlorobenzene (7 mL per gram of polymer) at 100 °C under magnetic stirring. The mixture was stirred at 100°C till it reached a viscosity high enough to prevent stirring (around 48 hours). The reaction was quenched by pouring the hot mixture into cold hexane. The resulting solid was recovered by filtration and dried under vacuum at 80 °C.

For the preparation of the sample CAN-Rhdisp 2, Rhodamine **1** was dissolved in ortho-dichlorobenzene at 100 °C together with PE-HEMA. Then, TMSPEDA was added, and the reaction proceeded as described before.

Table S1: GPC data and melt flow index (MFI) for PE-HEMA 2.1 mol%

	Mw (Kg/mol)[a]	**Mn (Kg/mol)[a]**	**PDI**	**MFI (g/10 min)[b]**
PE-HEMA 2.1%	75.9	17.0	4.48	2.58

[a] det. via GPC, 160°C, TCB as solvent
[b] T = 190°C, load = 2.16 Kg


1,0
0,8
0,6
0,4
0,2
0,0
MMD
2
3
4
5
6
LogM
MMD
Cumulative

NMR Spectra

Rhodamine 1

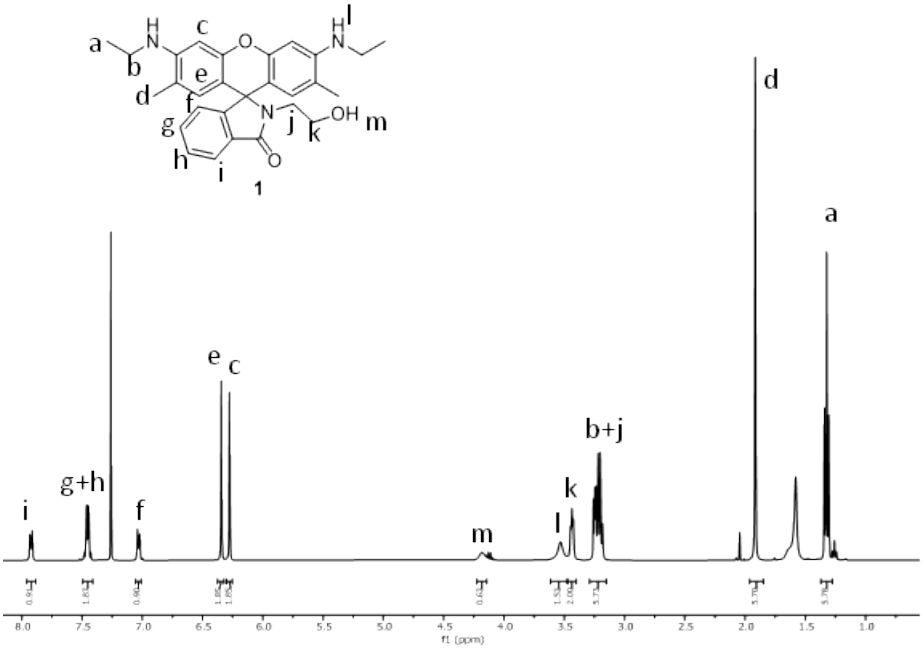


Figure S1. ^{1}H-NMR ($CDCl_3$, 25°C, 400MHz) spectrum of Rhodamine **1**

Rhodamine 2

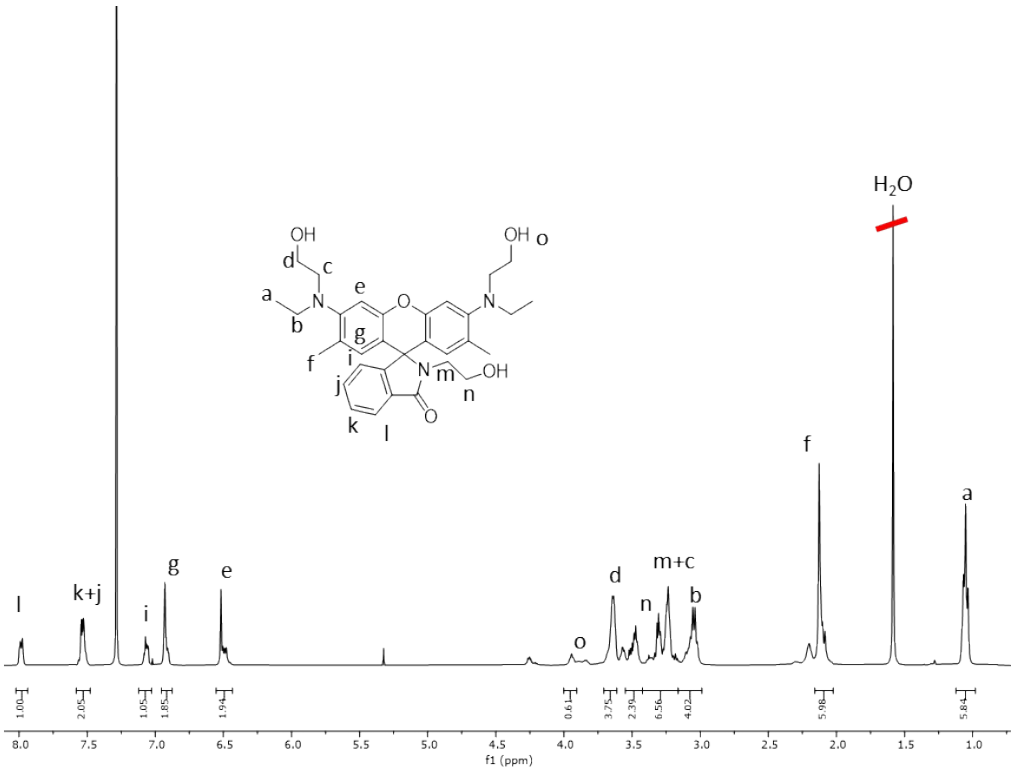


Figure S2. ^{1}H-NMR ($CDCl_3$, 25°C, 400MHz) spectrum of Rhodamine **2**

Rhodamine 3

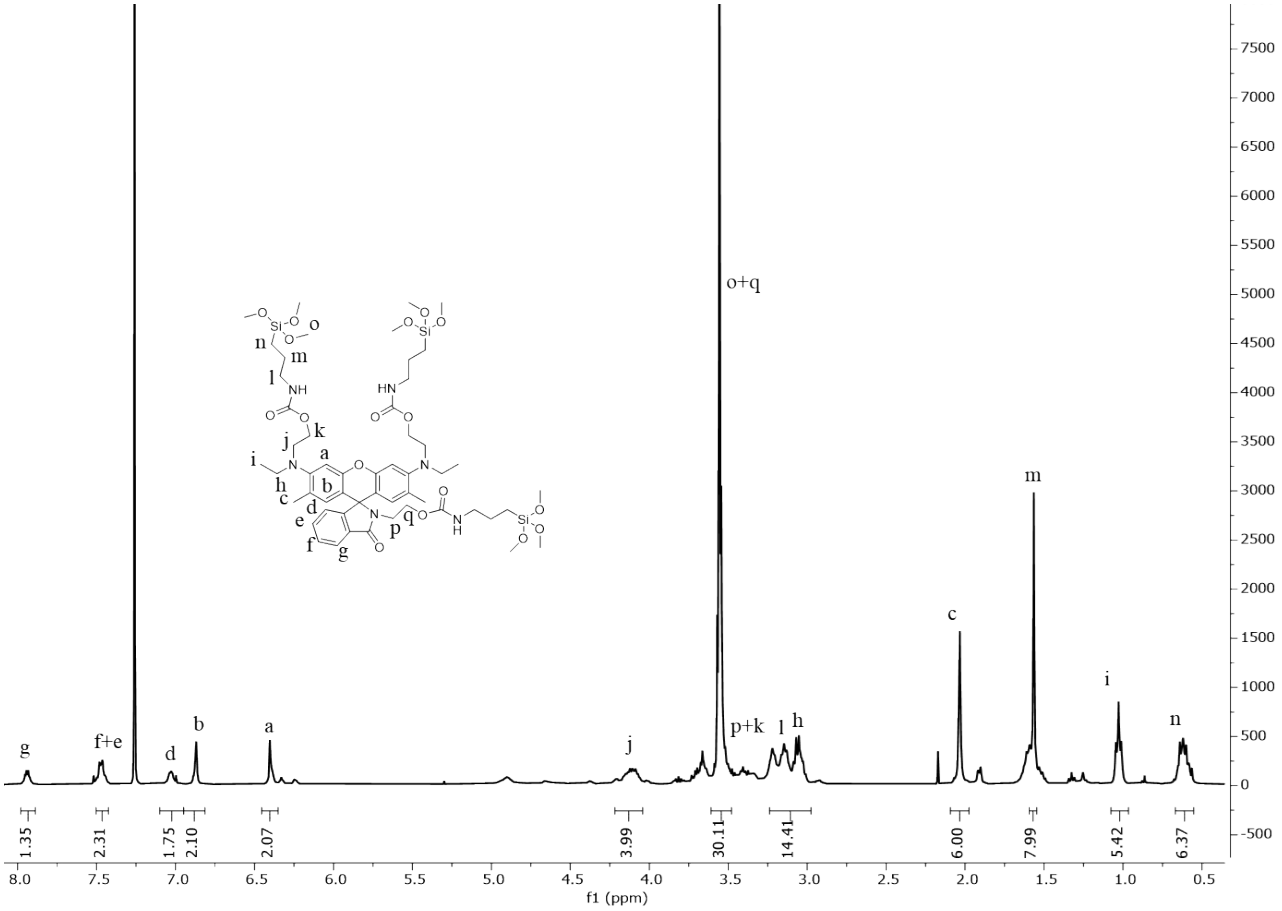


Figure S3. ^{1}H-NMR ($CDCl_3$, 25°C, 400MHz) spectrum of Rhodamine **3**

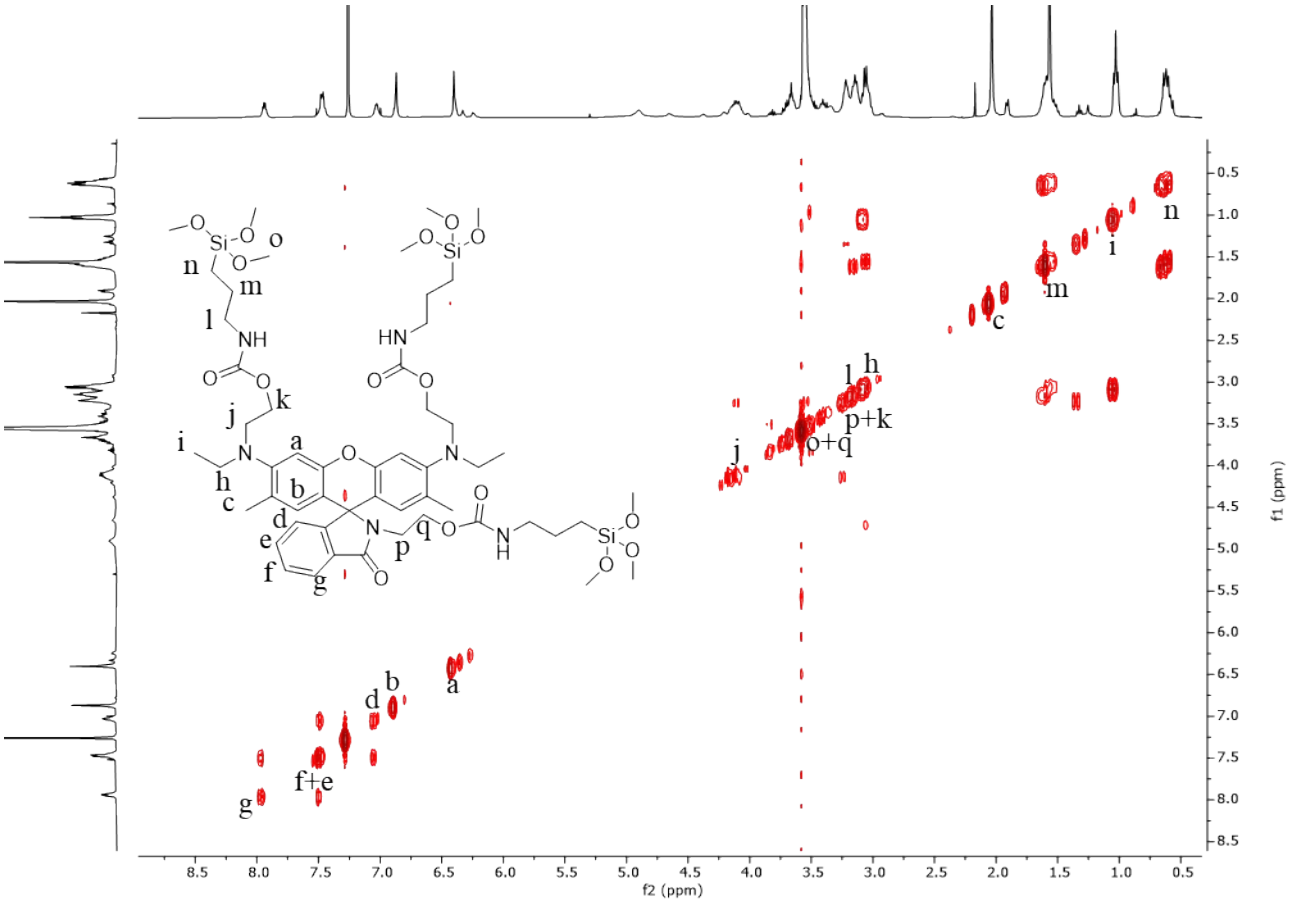


Figure S4. COSY-NMR ($CDCl_3$, 25°C, 400MHz) Spectrum of Rhodamine **3**

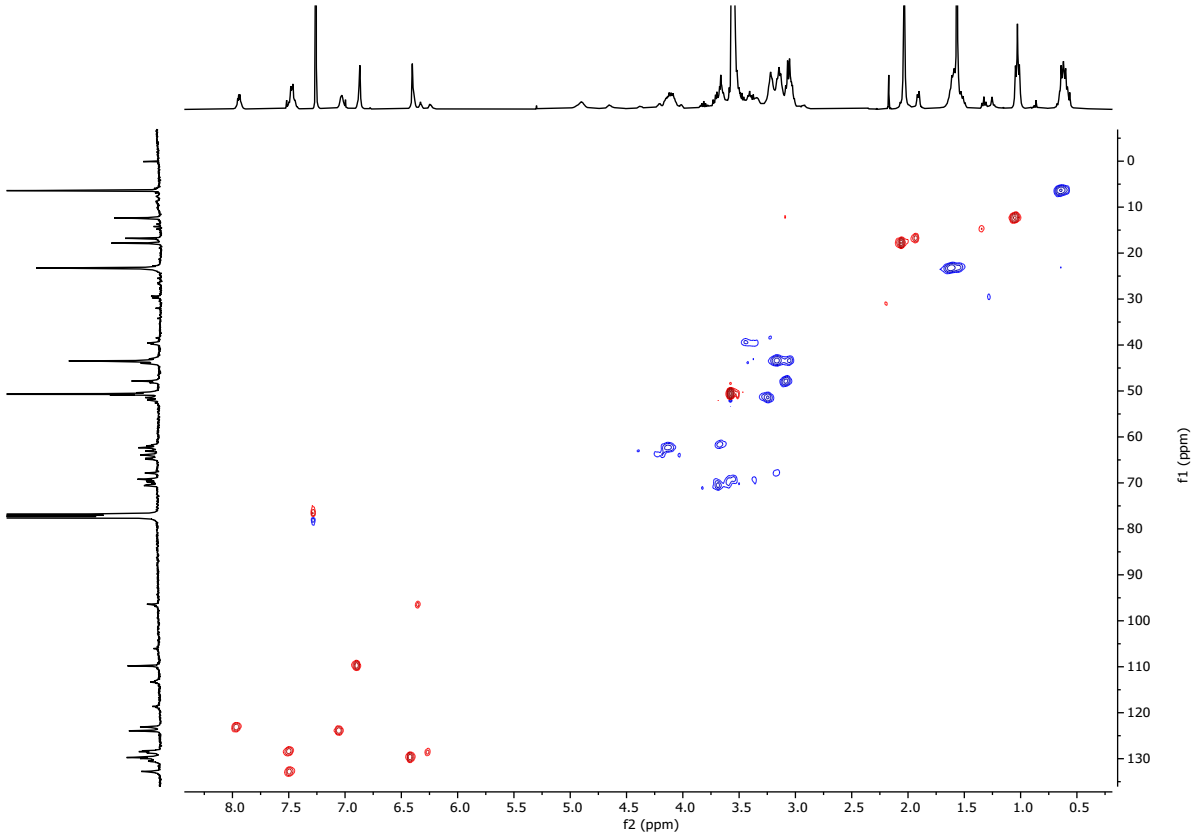


Figure S5. HSQC-NMR ($CDCl_3$, 25°C, 400MHz) Spectrum of Rhodamine **3**

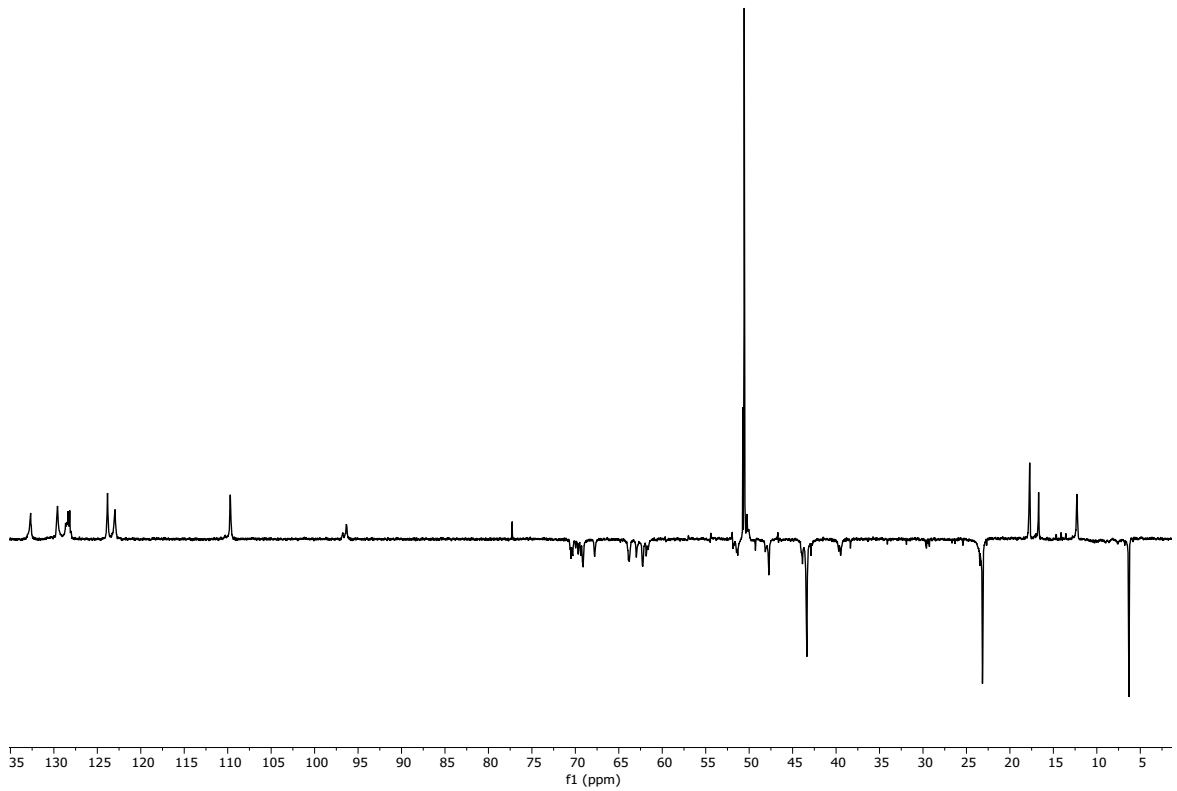


Figure S6. DEPT135-NMR ($CDCl_3$, 25°C, 100MHz) Spectrum of Rhodamine **3**

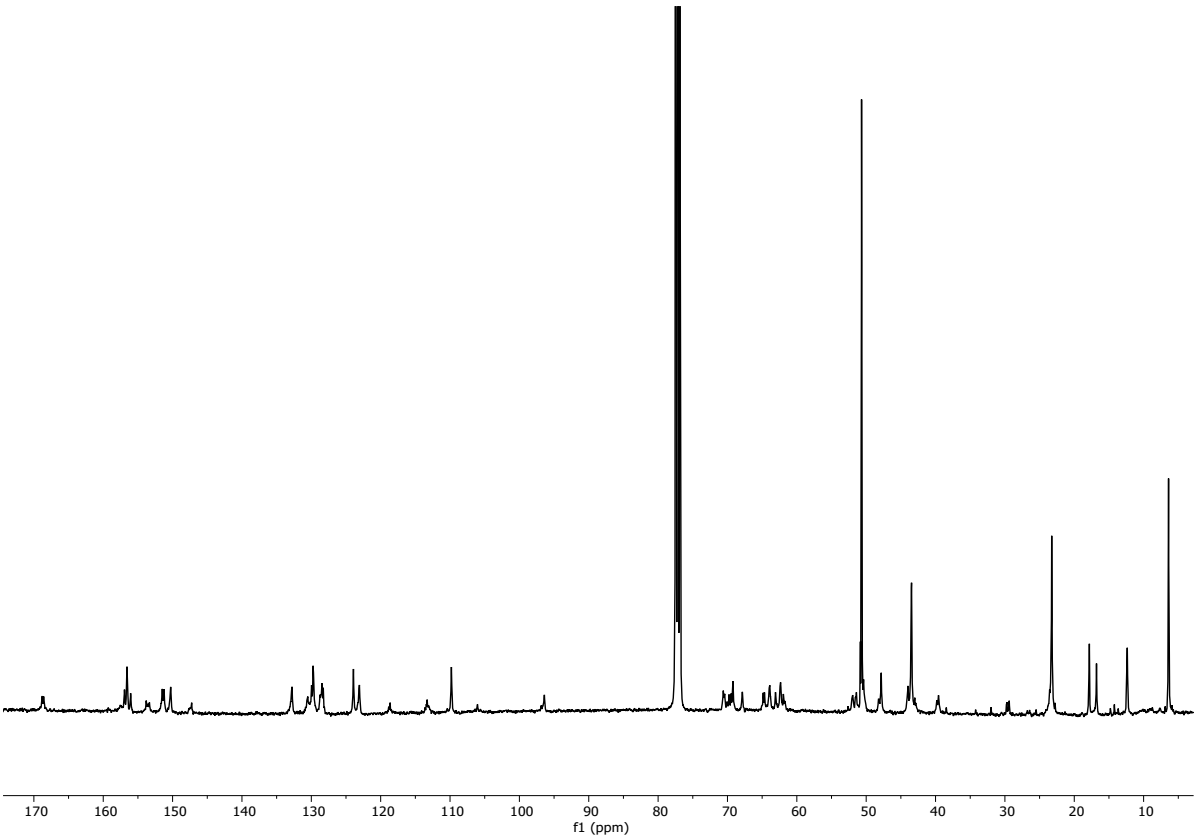


Figure S7. ^{13}C-NMR ($CDCl_3$, 25°C, 100MHz) Spectrum of Rhodamine **3**

DSC Analyses

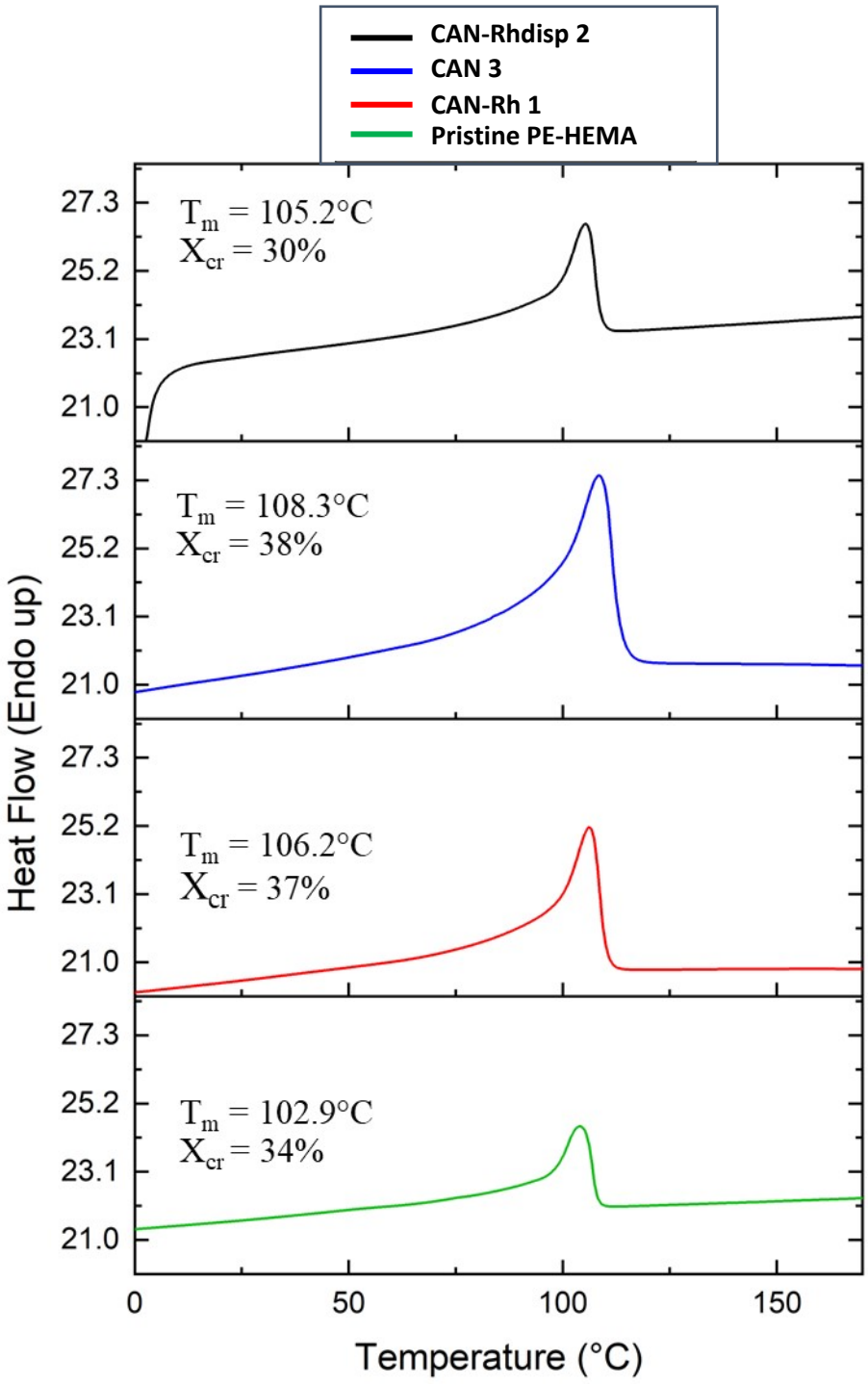


Figure S8. DSC second heating ramp of pristine PE-HEMA (green trace), CAN-Rh 1 (red trace), CAN 3 (blue trace), CAN-Rhdisp 2 (black trace).

Gel-Fraction Measurements

Gel-fraction measurements have been performed on 100 mg of crosslinked material heating the polymer in xylene at 100 °C for 18 hours. The samples have been then dried in high vacuum at 100 °C until the weight of the insoluble fraction remained constant.

All the crosslinked samples have shown a considerable amount of insoluble fraction as reported in **table S1**:

Table S2: Gel-fraction of pristine PE-HEMA and crosslinked polyethylene CAN-Rh 1, CAN-Rhdisp 2, CAN 3.

Material	Initial Mass [mg]	Final Mass [mg]	Gel-Fraction [%]	Swelling [%]
CAN-Rh 1	100	64	64	258
CAN-Rhdisp 2	100	72	72	330
CAN 3	100	69	69	307
PE-HEMA	100	-	-	

DMTA measurements on control materials

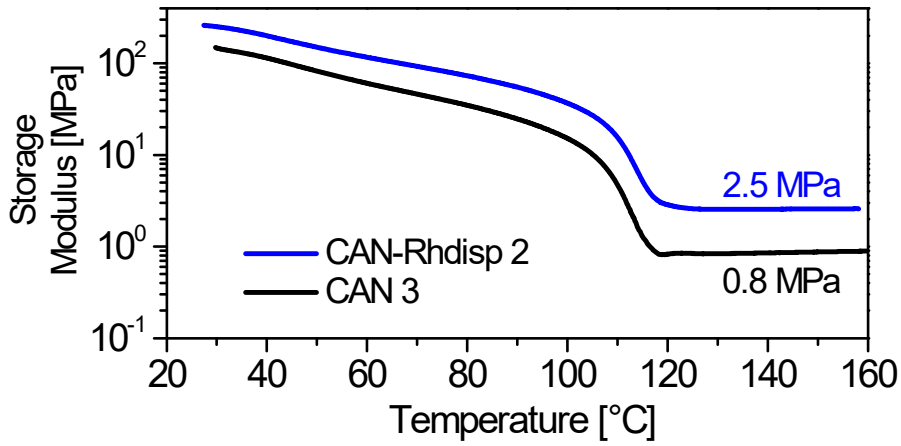


Figure S9. Storage Modulus vs Temperature of CAN-Rhdisp 2 and CAN 3. Tests are carried out on bars with nominal dimensions 6x1x30 mm^3, cut from plates obtained by compression moulding

TGA Measurements

Rhodamine 1

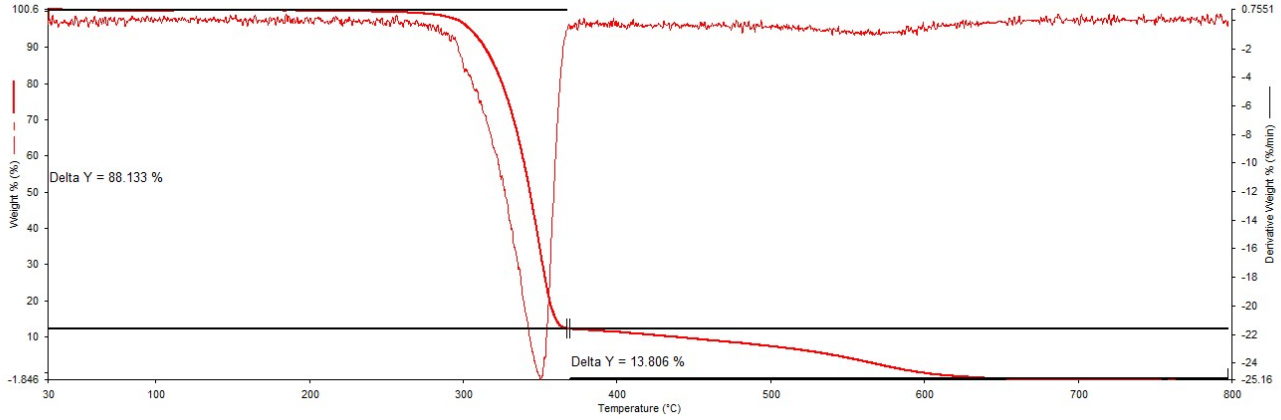


Figure S10. TGA measurement on Rhodamine **1**

Rhodamine 2

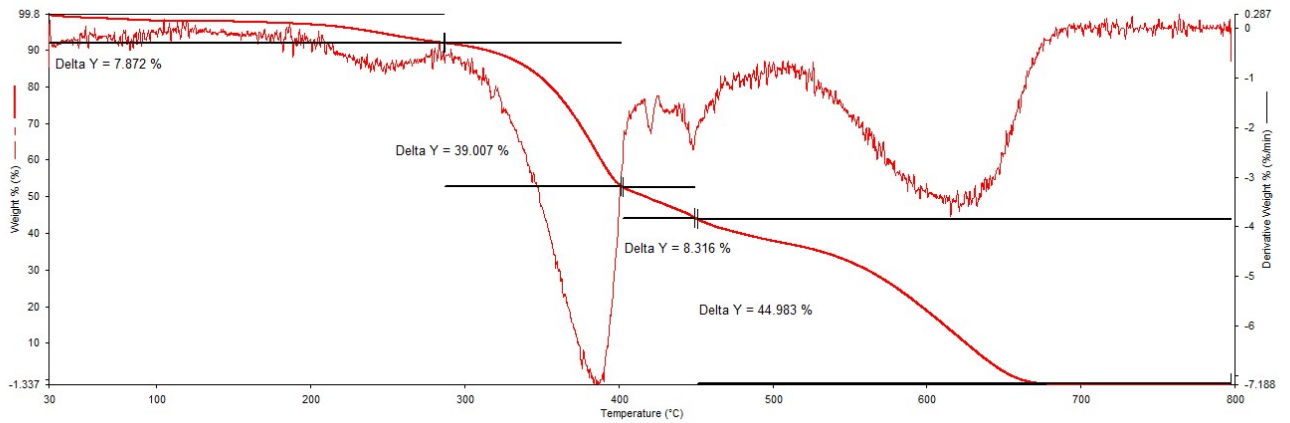


Figure S11. TGA measurement on Rhodamine **2**

Rhodamine 3

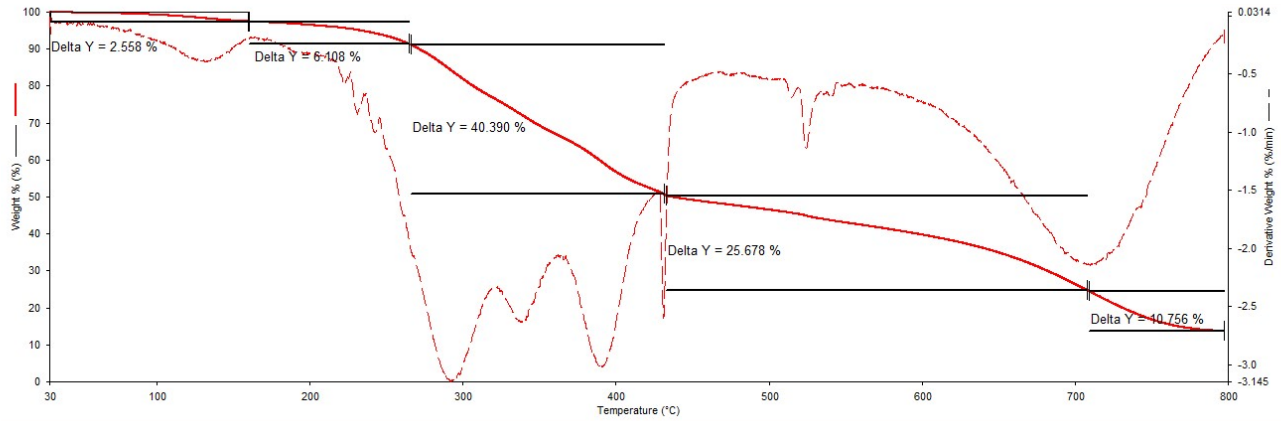


Figure S12. TGA measurement on Rhodamine **3**

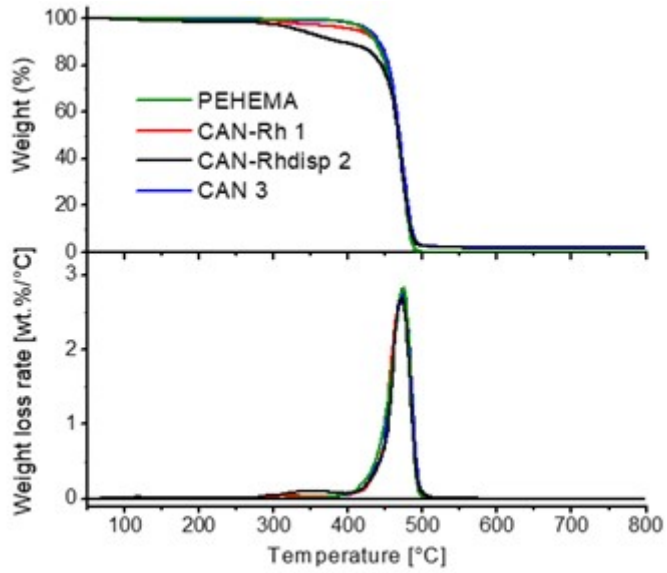


Figure S13. TGA measurement on heating (10°C/min) for CAN-Rh 1, CAN-Rhdisp 2 and CAN 3, compared to pristine PEHEMA

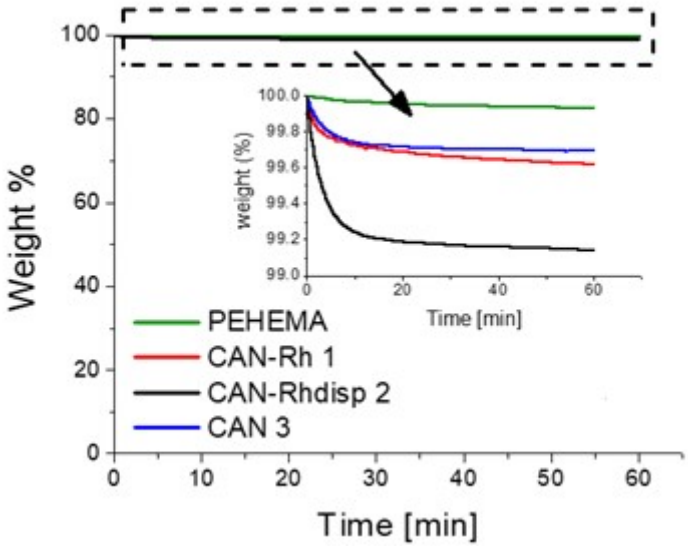


Figure S14. Isothermal (150°C) TGA measurement on CAN-Rh 1, CAN-Rhdisp 2 and CAN 3, compared to pristine PEHEMA. Inset shows large magnification to show minor weight loss difference between the different formulations

Film Preparation

Polymer films for self-reporting tests were prepared by compression moulding 2g of CAN-Rh 1.

The material was firstly heated at 150 °C for 1 minute and then hot pressed at constant temperature with a 15000 kg load for 3 minutes. After 3 minutes, keeping the material pressed, the hot plates have been cooled down to 25 °C with a cooling rate of 50 °C/min.

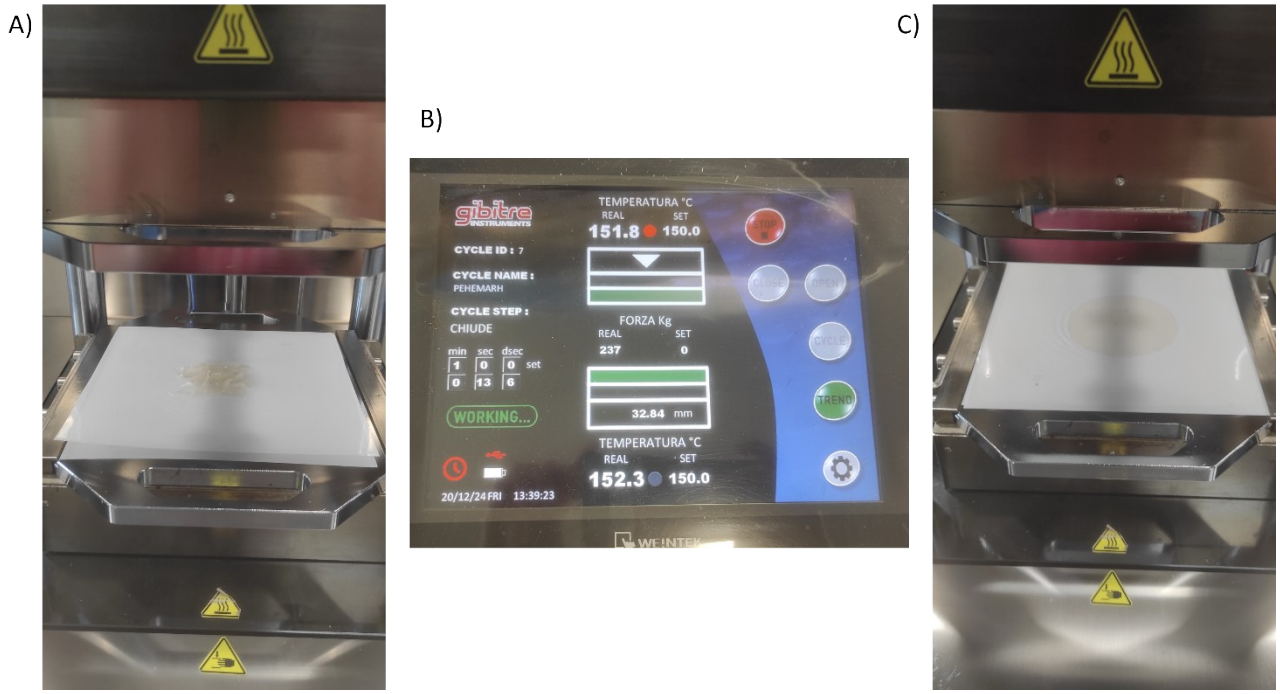


Figure S15. Film preparation

Tensile tests

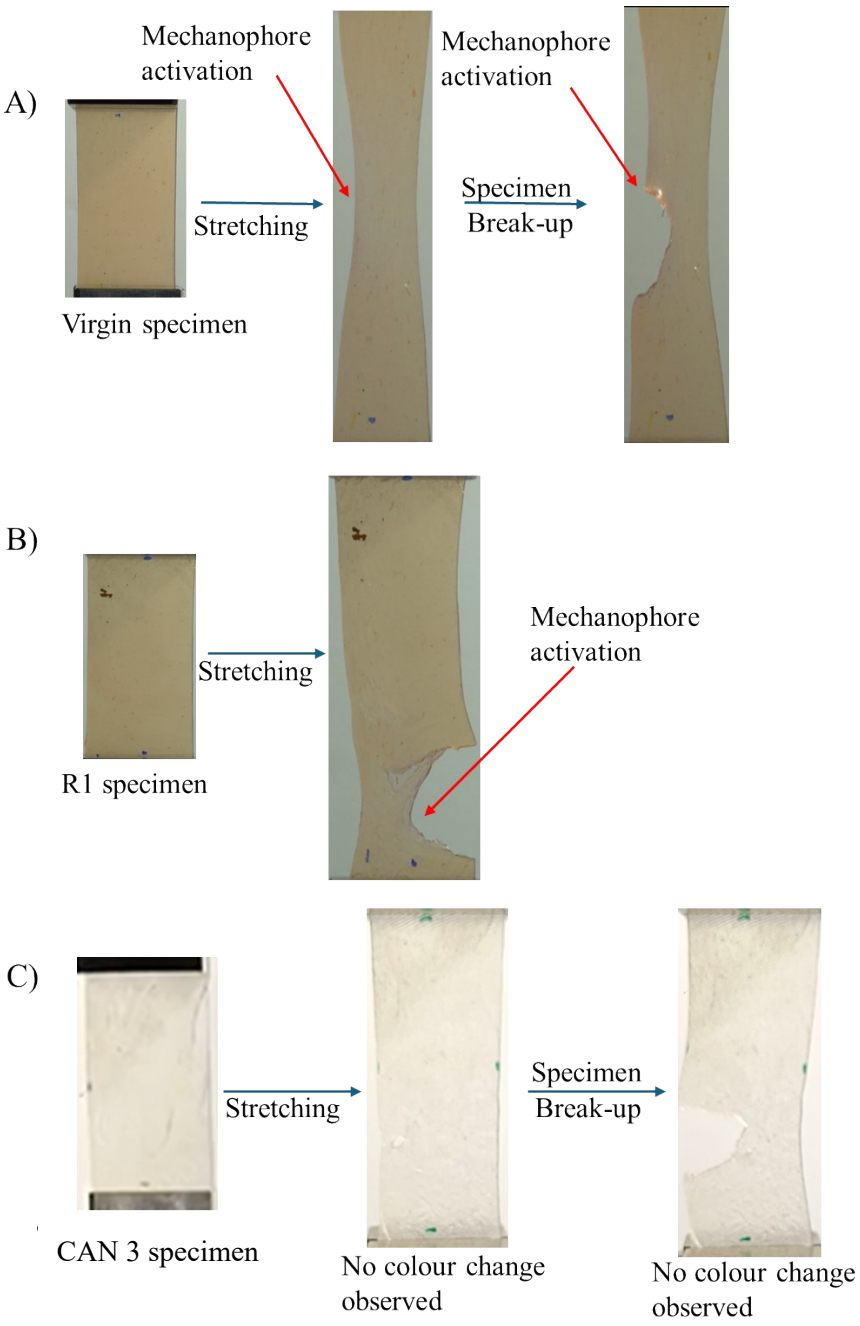


Figure S16. Self-reporting properties of A) virgin CAN-Rh 1 (V), B) recycled CAN-Rh 1 during stress-strain measurement; C) Control experiment with CAN-3 as reference.

Additional self-reporting, quenching and reversibility tests

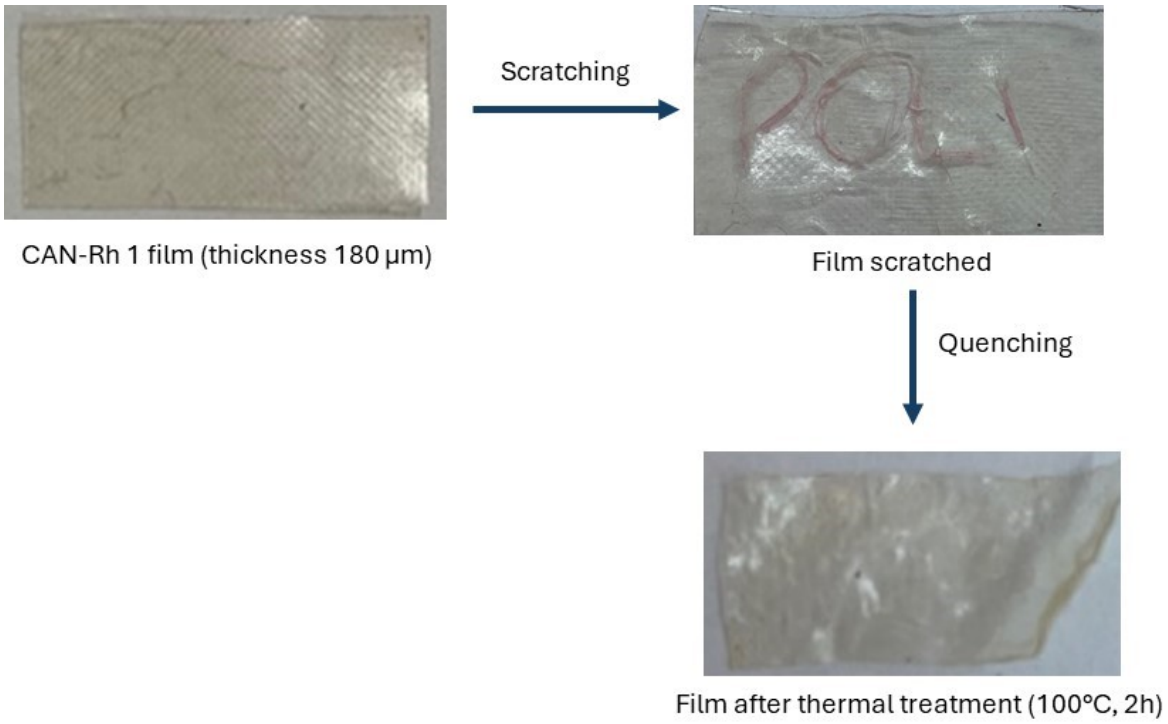


Figure S17. CAN-Rh 1 scratching and quenching test

It was observed that after the printing process the polymer film is completely transparent, when the polymer is scratched a clear pink coloration appears in correspondence of the mechanical damage. After a thermal treatment at 100°C for 2 hours, the material is completely healed and the mechanophore is completely quenched.

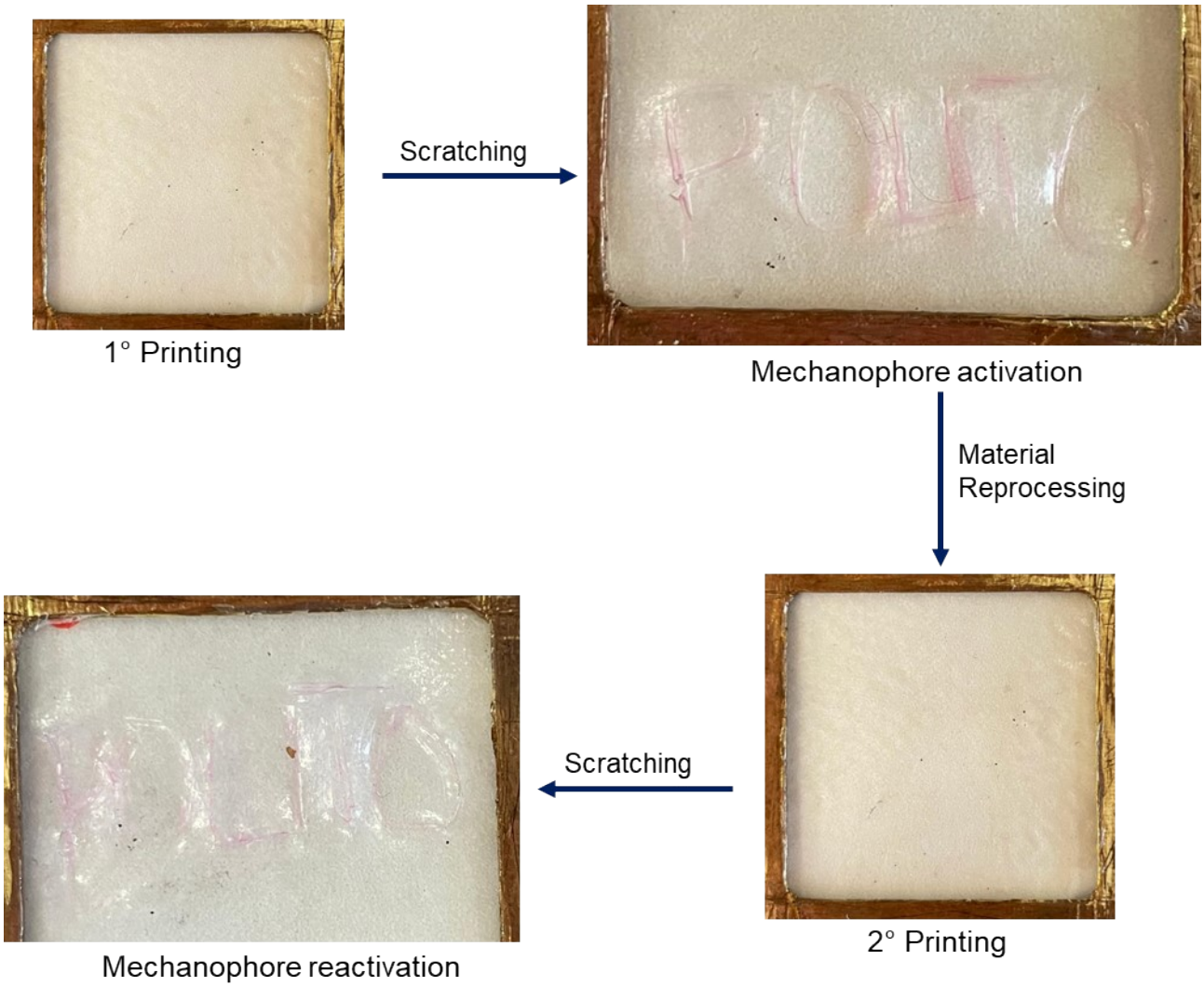


Figure S18. CAN-Rh 1 printing, activation, reprinting and reactivation test.