Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2023

SUPPORTING INFORMATION

Pillar[5]arenes-based high-Tg thermosets for the capture of volatile organic compounds

Solenne Ritaine, Valentin Ternel, Patrice Woisel, Jérôme P. Claverie and Jonathan Potier**

Full experimental details, characterization and NMR spectra for all small molecule and polymeric products. (31 pages)

S. Ritaine, Prof. J. P. Claverie
Chaire de Recherche du Canada en Chimie des Matériaux Organiques Avancés
Université de Sherbrooke
2500 Bd. de l'Université, Sherbrooke, QC, J1K2R1, Canada
E-mail: Jerome.Claverie@USherbrooke.ca

S. Ritaine, V. Ternel, Prof. P. Woisel and Dr. J. Potier
Laboratoire UMET (Unité Matériaux Et Transformations)
Université de Lille et CNRS (UMR 8207)
Av. Paul Langevin, 59655 VILLENEUVE D'ASCQ CEDEX (France)
E-mail : jonathan.potier@univ-lille.fr

Table of contents

Instrumentation S3
Materials S3
Synthesis of 1-(2-bromoethoxy)-4-methoxybenzene S3
Synthesis of bromide copillar[5]arene S4
Synthesis of azide copillar[5]arene S5
Synthesis of amino copillar[5]arene S5
Synthesis of N-acryloyl-2-methylalanine S5
Synthesis of VDMA (2-Vinyl-4, 4-DiMethyl Azlactone) S6
Controlled radical polymerization of VDMA (Dpn = 200) S6
Synthesis of PVDMA grafted to functionalized amino-copillar[5]arene S7
Neutralization of polyazlactone of PVDMA grafted to functionalized amino-copillar[5]arene by butylamine S7
Formation of PVDMA-based materials crosslinked by xylylenediamine S7
NMR Spectra S9
Functionalization Studies S21
SEC Results S23
DSC Results S24

DMA Results S26
COV Tests S28
References.....S32

Instrumentation

NMR spectra were recorded on a Brucker Advance III HD, 300 MHz and 400 MHz, spectrometer. All NMR were made at room temperature in deuterated solvents: $CDCl_3$ and C_2D_6OS. Spectra were referenced based on the NMR solvent chemical shift(s).

DSC analyses were made on a TA Q100. Pans/lids used were standard aluminum hermetic pans/lids. All DSC samples were heated to a temperature of 25°C to 250°C taking the results every 10 °C/min. Two heating ramps were realized.

DMTA shear analysis were done on a DMA 1+ Mettler Toledo using shear clamp over a temperature range of 25 to 300 °C with a 5 °C/min heating ramp. Samples of 5 mm L × 5 mm W × 0.2 mm T were analyzed (needs two similar pieces of sample per analysis).

Materials

All chemicals were purchased from Sigma-Aldrich and used without further purification.

Synthesis of 1-(2-bromoethoxy)-4-methoxybenzene

4-methoxyphenol (10.1 g, 81.45 mmol, 1 eq) and potassium carbonate (35 g, 250 mmol, 3.07 eq) were dissolved in dry acetone (200 mL) and degassed under nitrogen. Then, 1,2-dibromoethane (35 mL, 420 mmol, 5.16 eq) diluted in dry acetone (65 mL) was introduced dropwise in the solution. The reaction was refluxed at 80 °C for 7 days under stirring and nitrogen. The solution was then filtered to remove potassium carbonate. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 (400 mL) and placed in a separatory

funnel. The organic phase was washed successively with 150 mL of a 0.5 M sodium hydroxide and 1 M hydrochloric acid solutions and a saturated solution of 1 M sodium chloride then dried over $MgSO_4$. After filtration, the solvent was evaporated and the residue was purified on flash chromatography (CH_2Cl_2/petroleum ether: 30/70 (v/v), Rf = 1). White powder (6.89 g) was obtained.

Yield: 37 %. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.88 (m, 4 H, Ar H), 4.28-4.17 (t, J = 6.3 Hz, 2 H, CH_2), 3.77 (s, 3 H, CH_3), 3.65-3.50 (t, J = 6.2 Hz, 2 H, CH_2).

Synthesis of bromide copillar[5]arene

1-(2-bromoethoxy)-4-methoxybenzene (840 mg, 3.6 mmol, 1 eq) and 1,4-dimethoxybenzene (8.53 g, 61.9 mmol, 17 eq) were dissolved in CH_2Cl_2 (350 mL). The mixture was bubbled under nitrogen at 0 °C. Paraformaldehyde (5.54 g, 184.6 mmol, 50 eq) was then introduced after 20 min and the iron (III) chloride (1.29 g, 7.9 mmol, 2.5 eq) was introduced after 30 min. Nitrogen bubbling was then stopped. The solution was left under stirring for 1 h at 0 °C and 3 h at room temperature under nitrogen. The mixture went from transparent to dark green. Then, water was added (100 mL). The mixture took on the color red. The solution was placed in a separatory funnel and washed twice with water and then with a saturated solution of sodium chloride and a final time with water. The organic phase was dried over $MgSO_4$, filtered, and evaporated. Red powder (5 g) was obtained. Crude product was then separated by flash chromatography (CH_2Cl_2/petroleum ether/EtOAc : 30/70/ppm (v/v), Rf = 0.86 (Bromide copillar[5]arene), Rf = 0.81 (DM-pillar[5]arene)) to recover 975 mg of bromide copillar[5]arene (white powder) and 525 mg of DM-pillar[5]arene (white powder).

Yield (Bromide copillar[5]arene) : 32 %. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.84-6.75 (m, 9 H, Ar H), 6.70 (s, 1 H, Ar H), 4.11-4.00 (t, J = 6.2 Hz, 2 H, CH_2), 3.87-3.78 (m, 10 H, CH_2), 3.75-3.64 (m, 27 H, CH_3), 3.53-3.44 (t, J = 6.2 Hz, 2 H, CH_2).

Yield (DM-pillar[5]arene): 19 %. ^{1}H NMR (300MHz, $CDCl_3$, δ): 6,85-6,73 (s, 10 H, Ar H), 3,83-3,73 (s, 10 H, CH_2), 3,73-3,61 (s, 30 H, CH_3).

Synthesis of azide copillar[5]arene

Bromide copillar[5]arene (3 g, 3.6 mmol, 1eq) and sodium azide (600 mg, 9.2 mmol, 2.6 eq) were dissolved in dry DMF (340 mL) and added into a round-bottom flask. The solution was bubbled with nitrogen for 20 min and was left under stirring and nitrogen for 2 days at room temperature. CH_2Cl_2 (100 mL) was then added to the flask. The organic phase was placed in a separatory funnel and washed with water (3 x 20 mL) and with saturated 1M sodium chloride solution (2 x 20 mL) before drying over $MgSO_4$. After filtration, the solvent was evaporated to lead to a white solid (2.7 g).

Yield: 94 %. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.82-6.70 (m, 9 H, Ar H), 6.65 (s, 1 H, Ar H), 3.90-3.70 (m, 12 H, CH_2), 3.70-3.60 (m, 27 H, CH_3), 3.45-3.35 (t, J = 5.0 Hz, 2 H, CH_2).

Synthesis of amino copillar[5]arene

Azide copillar[5]arene (2.96 g, 3.7 mmol, 1 eq) and $LiAlH_4$ (419 mg, 11 mmol, 3 eq) were dissolved in dry THF (60 mL). The solution was bubbled with nitrogen for 30 min and left under stirring and nitrogen for 2 days at room temperature. Water (300 mL) was then added to neutralize the $LiAlH_4$. Then an extraction with CH_2Cl_2 was carried out. The solution was dried with $MgSO_4$ before being evaporated. The pale-yellow powder obtained is purified on a silica gel column (CH_2Cl_2/methanol: 95/5 (v/v), Rf = 0.25). A white powder (2.36 g) was obtained.

Yield: 83%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.83-6.70 (m, 9 H, Ar H), 6.70-6.61 (s, 1 H, Ar H), 3.83-3.72 (m, 12 H, CH_2), 3.69-3.55 (m, 27 H, CH_3), 2.95-2.86 (t, J = 4.9 Hz, 2 H, CH_2).

Synthesis of N-acryloyl-2-methylalanine

2-aminoisobutyric acid (47.44 g, 0.46 mmol, 1eq) and hydroquinone (0.5 g) were added in a solution of NaOH (36.8 g, 0.92 mmol, 2 eq) in water (200 mL). The solution was left at 0 °C under nitrogen for 1 h until the dropwise addition of acryloyl chloride (41.63 g, 0.46 mmol, 1 eq) was complete. It was then left to stir for 2 h under nitrogen at room temperature. HCl (50 mL) was added to precipitate the product. It was washed with water and THF before filtering and pump-drying. A pink powder (51.8 g) was recovered.

Yield: 72 %. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 12.29-12.07 (s, 1 H, COOH), 8.33-8.10 (s, 1 H, NH), 6.36-6.17 (dd, J^2 = 17.1, J^3 = 10.1 Hz, 1 H, CH), 6.15-5.97 (dd, J^2 = 17.1, J^3 = 2.4 Hz, 1 H, CH_2), 5.70-5.45 (dd, J^2 = 10.0, J^3 = 2.4 Hz, 1 H, CH_2), 1.46-1.18 (s, 6 H, CH_3).

Synthesis of VDMA (2-Vinyl-4, 4-DiMethyl Azlactone)

N-acryloyl-2methylalanine (11.38 g, 72.4 mmol, 1 eq) was dissolved in dry acetone (76 mL) and dry triethylamine (10.6 g, 104.7 mmol, 1.5 eq). The solution was left at 0 °C under nitrogen for 1 h until the dropwise addition of ethyl chloroformate (8.64 g, 79.6 mmol, 1.1 eq) was complete. Stirred under nitrogen at room temperature for 20 h. The solution was washed with acetone before filtering. The filtrate was collected, a hydroquinone spatula was added to it before evaporating. A distillation was carried out (T = 30 °C, P = 0.2 mbar) to recover a slightly viscous transparent liquid (7.87 g).

Yield: 79 %. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 6.47-6.30 (dd, J^2 = 17.5, J^3 = 10.9 Hz, 1 H, CH), 6.23-6.10 (dd, J^2 = 17.6, J^3 = 1.1 Hz, 1 H, CH_2), 6.08-5.95 (dd, J^2 = 10.9, J^3 = 1.1 Hz, 1 H, CH_2), 1.45-1.28 (s, 6 H, CH_3).

Controlled radical polymerization of VDMA (Dpn = 200)

VDMA (4 g, 28.7 mmol, 400 eq), AIBN (1.20 mg, 7 µmol, 0.1 eq) and RAFT agent (18.1 mg, 0.72 mmol, 1 eq) were placed in a Schlenk and dissolved in dry toluene (8 g). Three freeze-

pump-thaw cycles were made. Then the mixture was stirred at 80 °C under nitrogen for 32 h. The solution was left cool before it is solubilized in THF (10 mL). The precipitation has been made in petroleum ether (240 mL) before filtering and pump-drying. A pale-yellow powder (3.19 g) was obtained.

Yield: 73 %. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 3.75-2.98 (br s, 1 H, CH), 2.25-1.76 (br s, 2 H, CH_2), 1.46-1.16 (s, 6 H, CH_3).

Synthesis of PVDMA grafted to functionalized amino-copillar[5]arene

PVDMA (500 mg, 3.6 mmol, 1 eq) and functionalized amino-copillar[5]arène (841 mg, 1.1 mmol, 0.3 eq) were dissolved in THF (150 mL). Then the solution was stirred at 60 °C under nitrogen for 24 h. The proportions were taken to have 30 % of Pillar[5]arene grafted to PVDMA chains. Subsequently, the mixture was precipitated in petroleum ether before filtering. A white powder (1.27 g) was recovered.

Yield: 95 %. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 7.12-6.54 (m, 3 H, Ar H), 4.20-3.50 (m, 12.1 H, CH_2 and CH_3), 2.35-1.83 (br s, 1 H, CH), 1.82-1.70 (q, J = 3.5 Hz, 2 H, CH_2), 1.03-1.75 (br s, 6 H, CH_3).

Neutralization of polyazlactone of PVDMA grafted to functionalized amino-copillar[5]arene by butylamine

PVDMA-30%Pilla (400 mg, 1.1 mmol, 1 eq) and butylamine (47 mg, 0.6 mmol, 0.6 eq) were dissolved in THF (100 mL). The proportions were taken to have 60 % of butylamine grafted to PVDMA chains. This mechanism was placed under nitrogen at 60 °C for 24 h. The solution was then precipitated in petroleum ether before filtering and pump-drying. A white powder (310 mg) was recovered.

Yield: 72 %. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 7.12-6.55 (m, 3 H, Ar H), 3.00-4.20 (m, 13.3 H, CH, CH_2 and CH_3), 1.75-1.03 (br s, 5.4 H, CH and CH_3), 1.03-0.52 (br s, 8H, CH_2 and CH_3).

Formation of PVDMA-based materials crosslinked by xylylenediamine

PVDMA-30%Pilla (4 g, 9.4 mmol, 1 eq) was dissolved in a minimum of DMSO to be able to solubilize the product. Xylylenediamine (1.27 g, 9.4 mmol, 1 eq) was added to the solution which was stirred. This solution was then placed in an aluminium cup which was placed in the oven at 90 °C overnight and then at 150 °C overnight. An orange material was obtained (5 mm L × 5 mm W × 0.2 mm T).

NMR Spectra

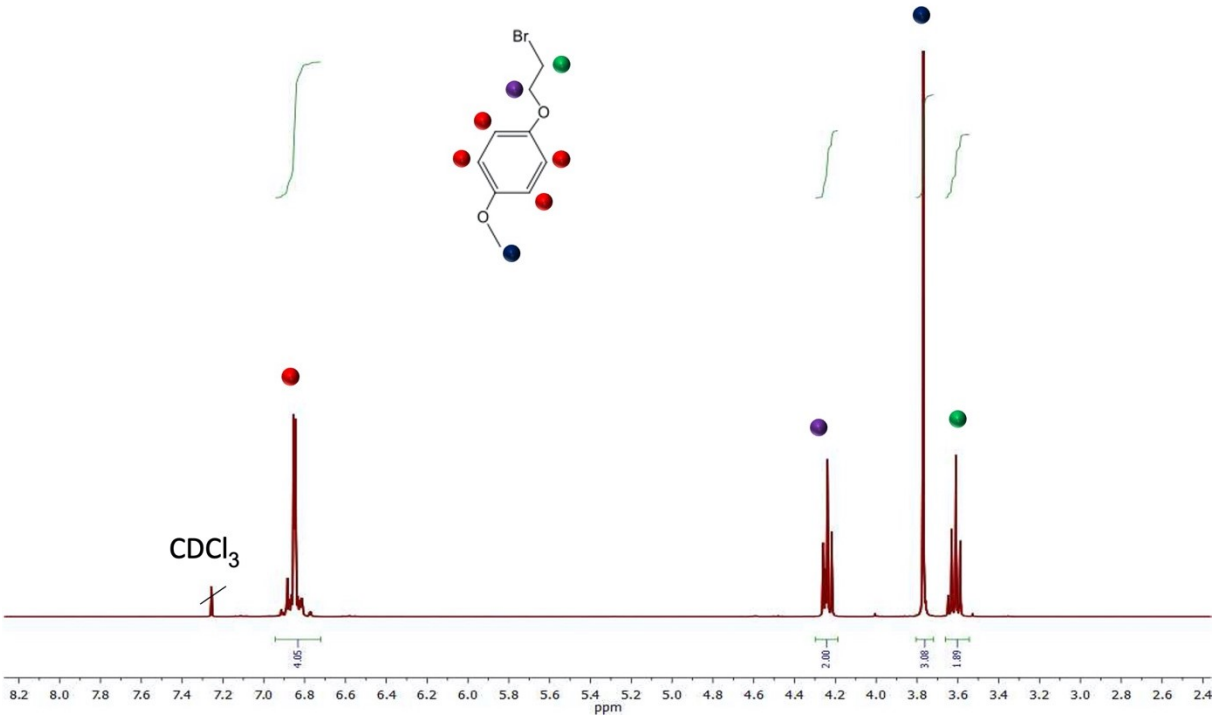


Figure S1. ^{1}H NMR (300 MHz, $CDCl_3$, δ) of 1-(2-bromoethoxy)-4-methoxybenzene at room temperature.

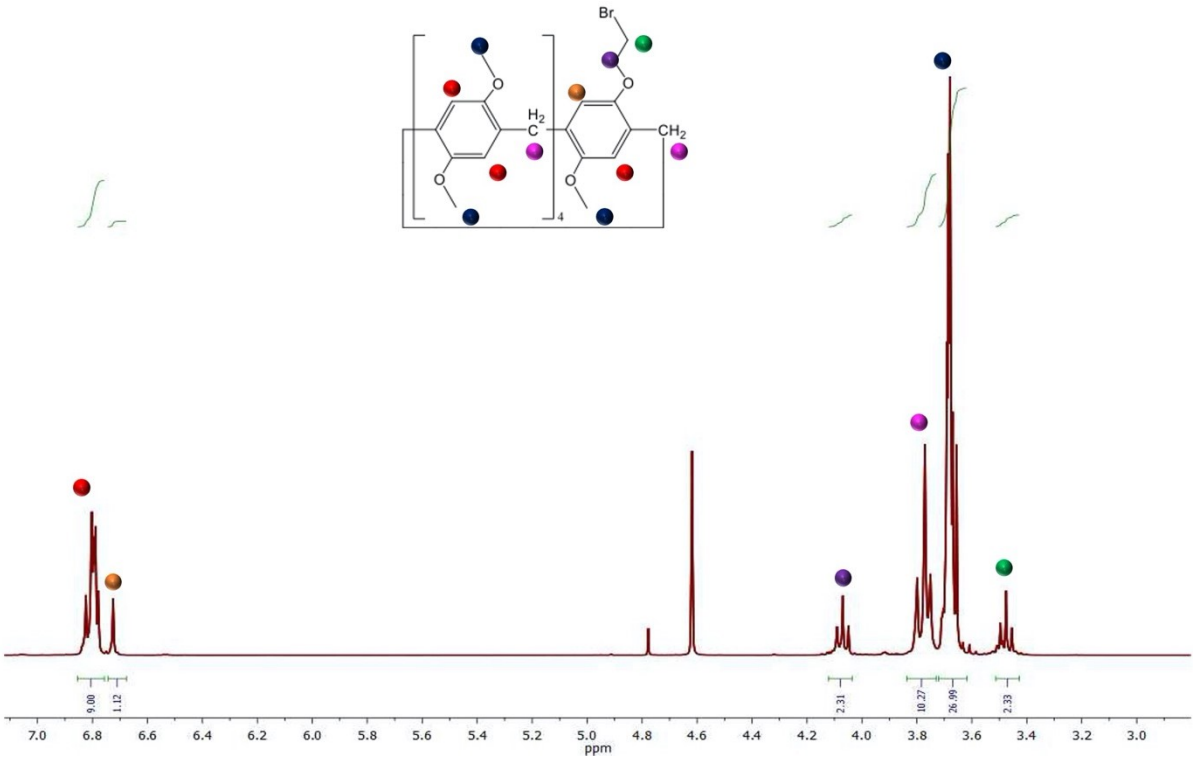


Figure S2. ^{1}H NMR (300 MHz, $CDCl_3$, δ) of bromide copillar[5]arene at room temperature.

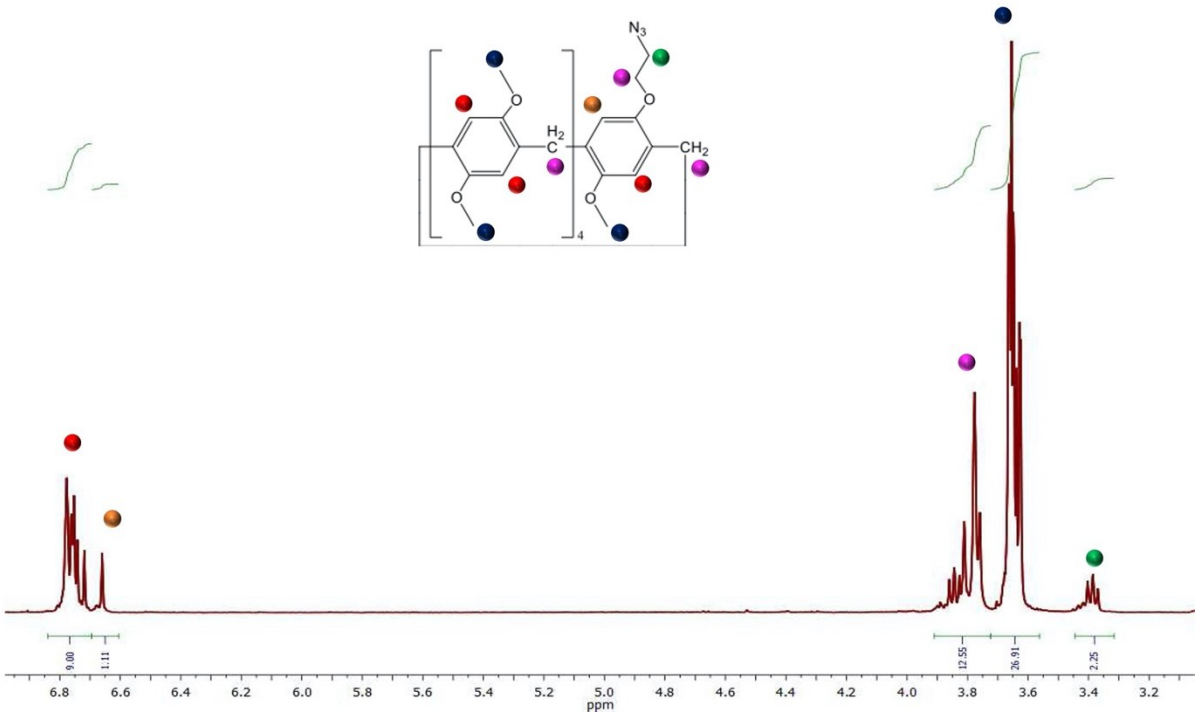


Figure S3. ^{1}H NMR (300 MHz, $CDCl_3$, δ) of azide copillar[5]arene at room temperature.

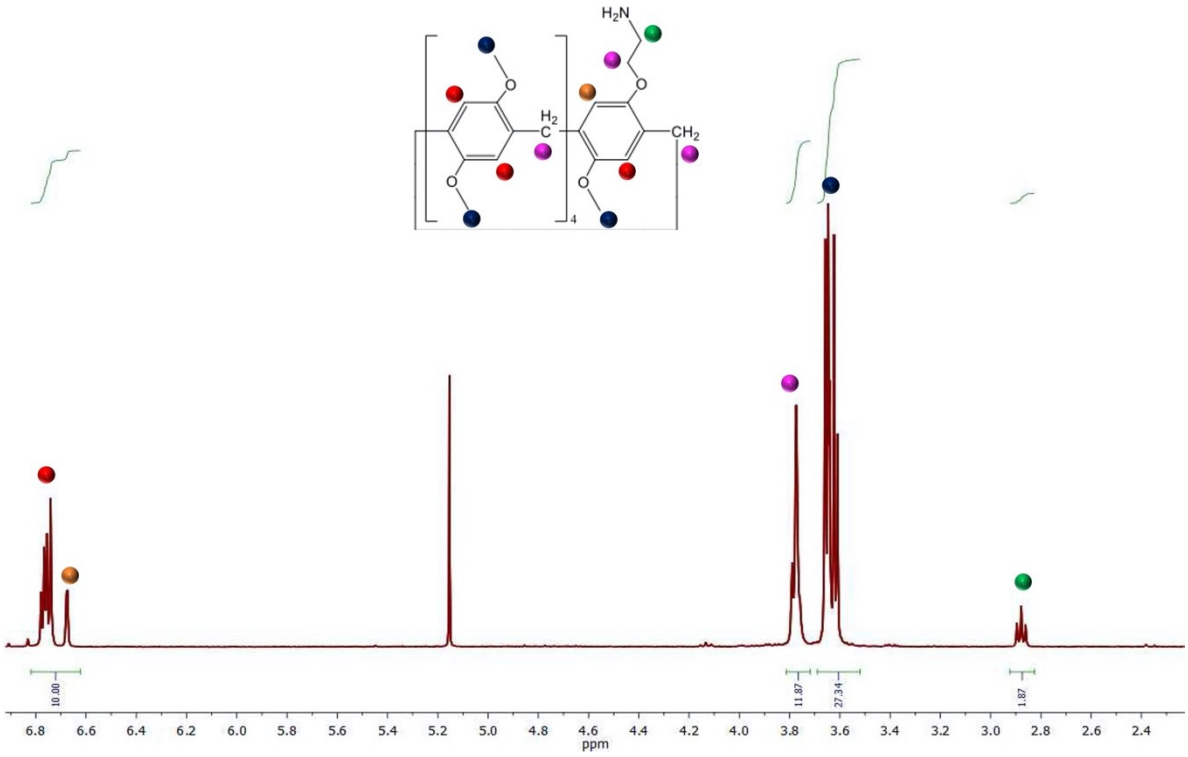


Figure S4. ^{1}H NMR (300 MHz, $CDCl_3$, δ) of amino copillar[5]arene at room temperature.

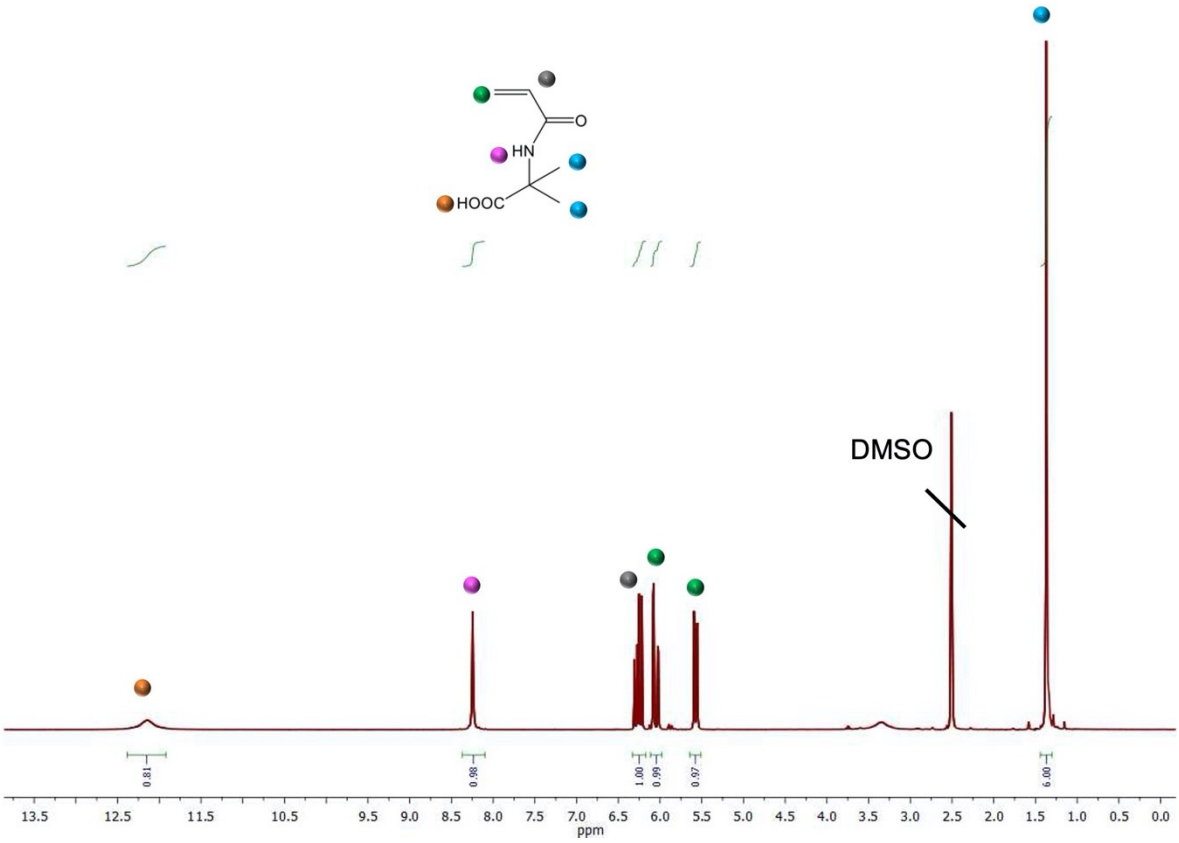


Figure S5. ^{1}H NMR (300 MHz, DMSO-d_6, δ) of N-acryloyl-2-methylalanine at room temperature.

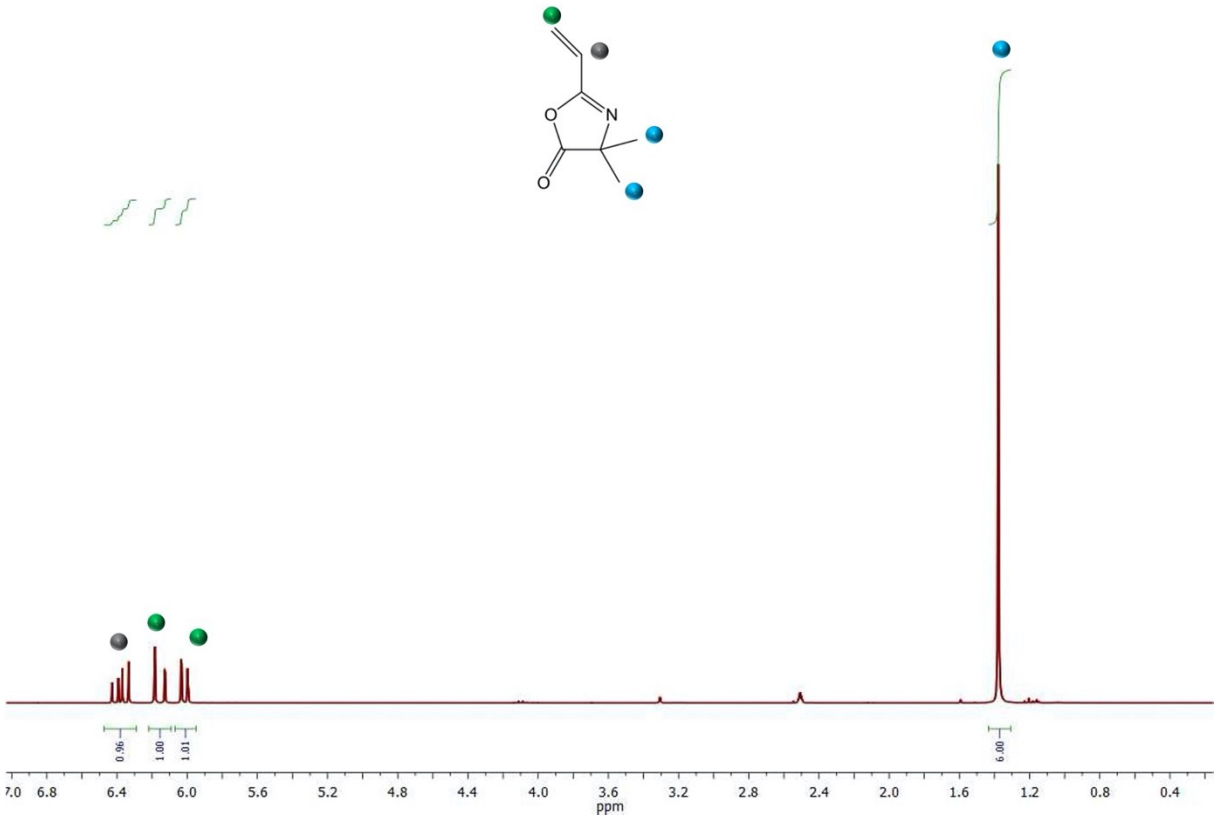


Figure S6. ^{1}H NMR (300 MHz, DMSO-d_6, δ) of VDMA (2-Vinyl-4, 4-DiMethyl Azlactone) at room temperature.

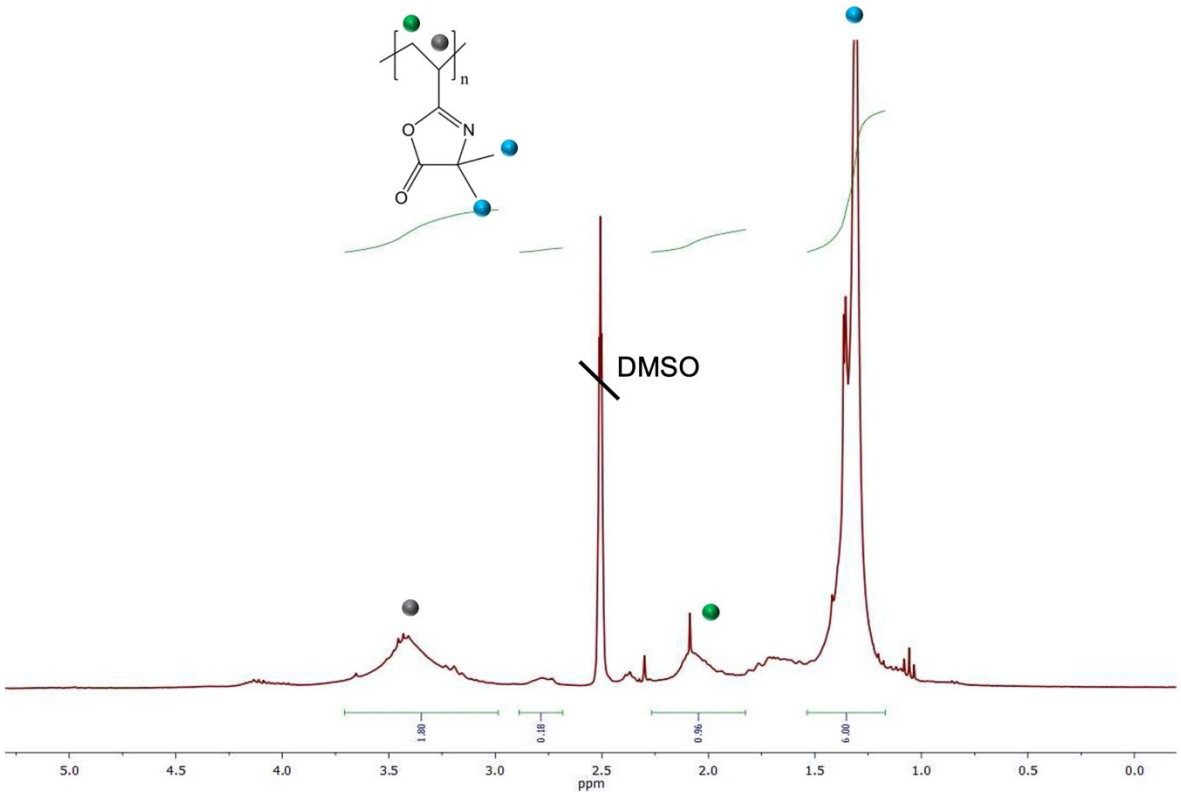


Figure S7. ^{1}H NMR (300 MHz, DMSO-d_6, δ) of PVDMA (Poly-2-Vinyl-4, 4-DiMethyl Azlactone) at room temperature.

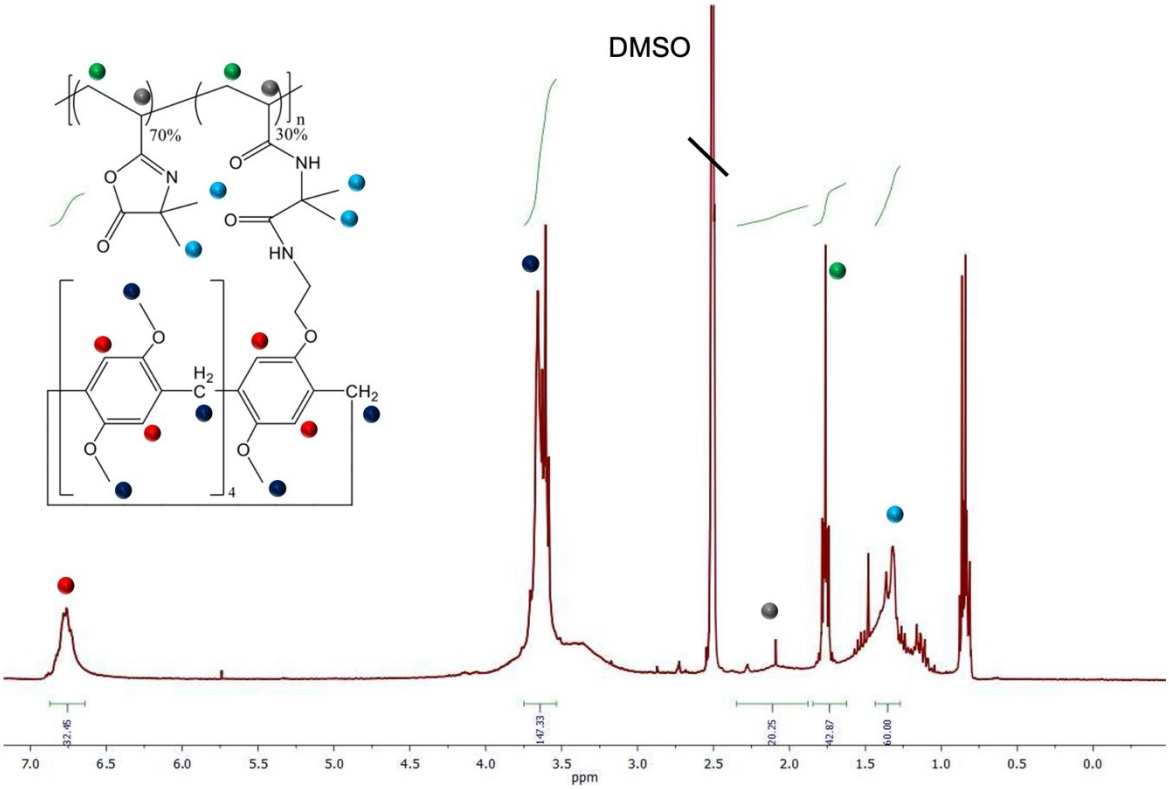


Figure S8. ^{1}H NMR (300 MHz, DMSO-d_6, δ) of PVDMA grafted to 30% functionalized amino-copillar[5]arene at room temperature.

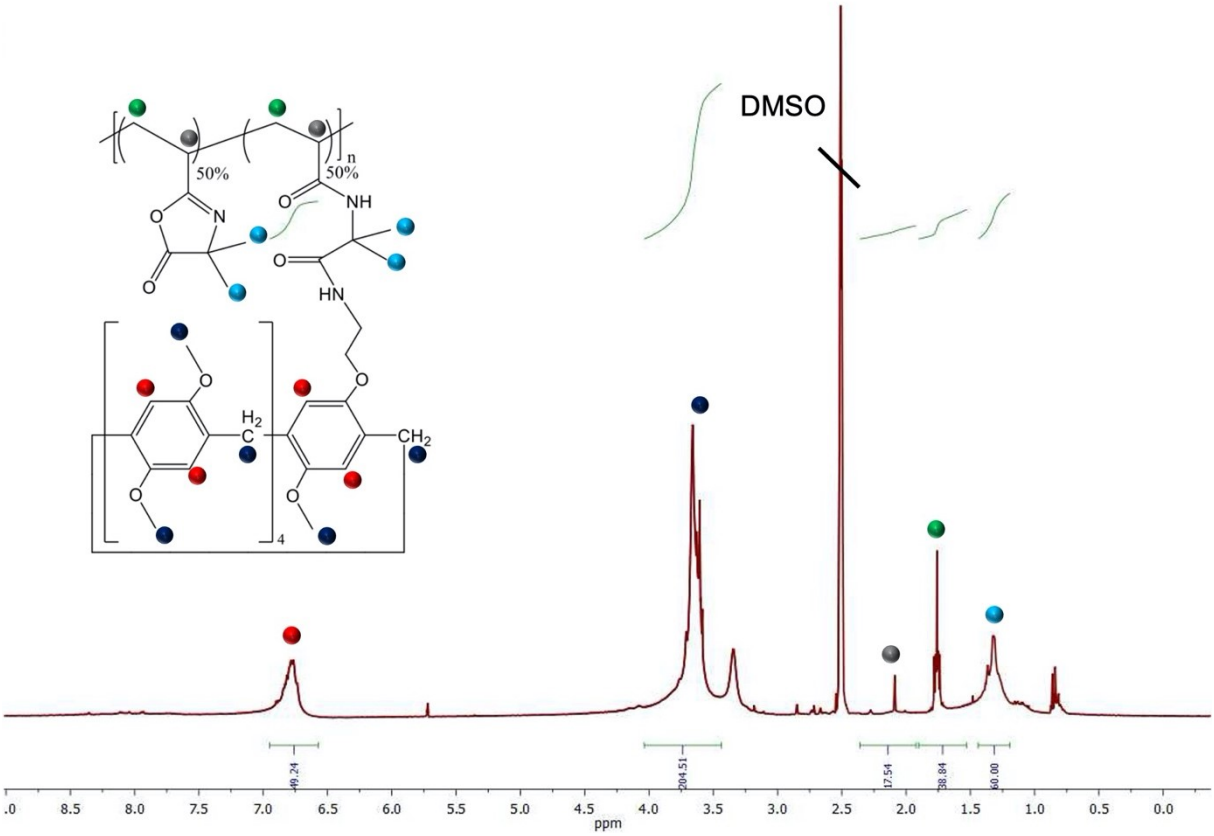


Figure S9. ^{1}H NMR (300 MHz, DMSO-d_6, δ) of PVDMA grafted to 50% functionalized amino-copillar[5]arene at room temperature.

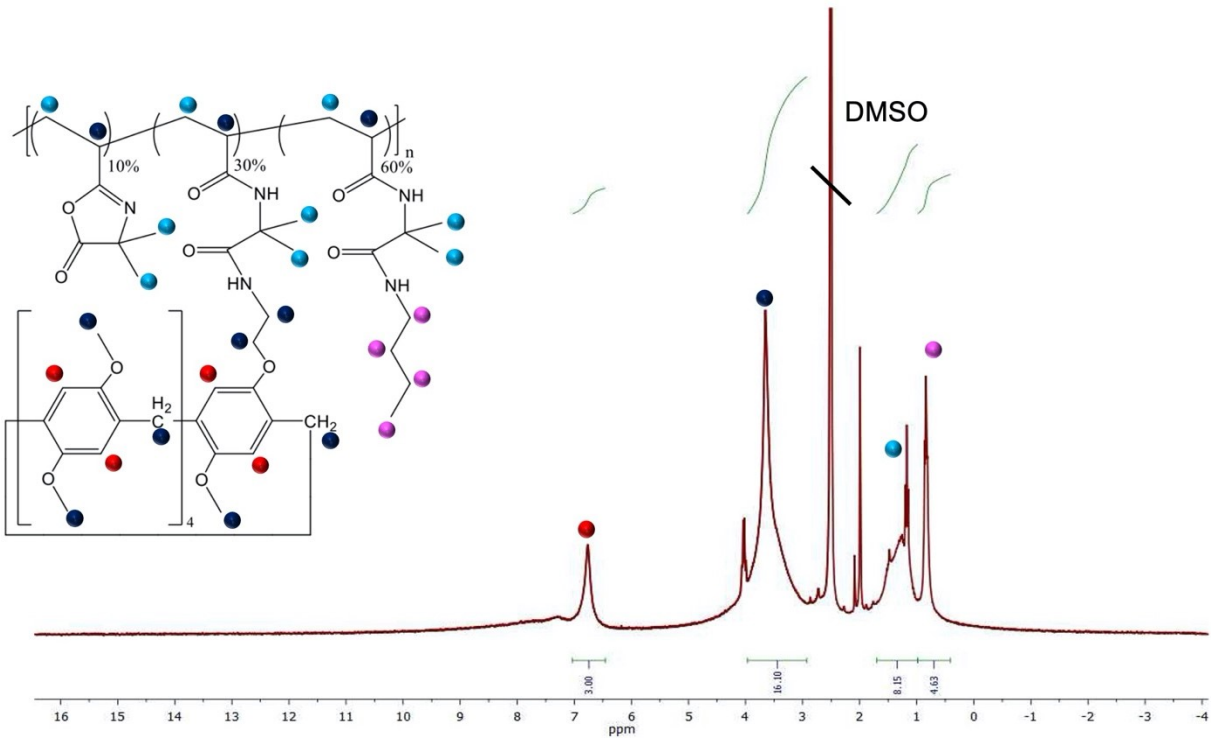


Figure S10. ^{1}H NMR (300 MHz, DMSO-d_6, δ) of PVDMA grafted to 30% functionalized amino-copillar[5]arene and 60% butylamine at room temperature.

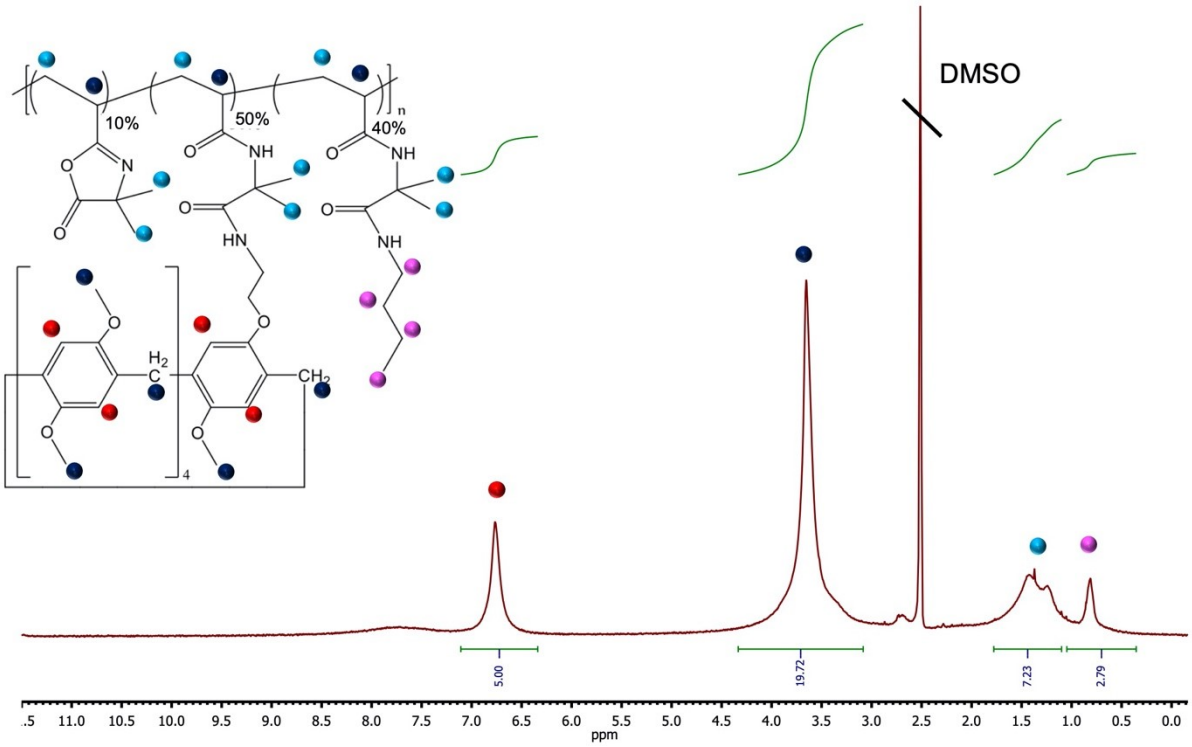


Figure S11. ^{1}H NMR (300 MHz, DMSO-d_6, δ) of PVDMA grafted to 50% functionalized amino-copillar[5]arene and 40% butylamine at room temperature.

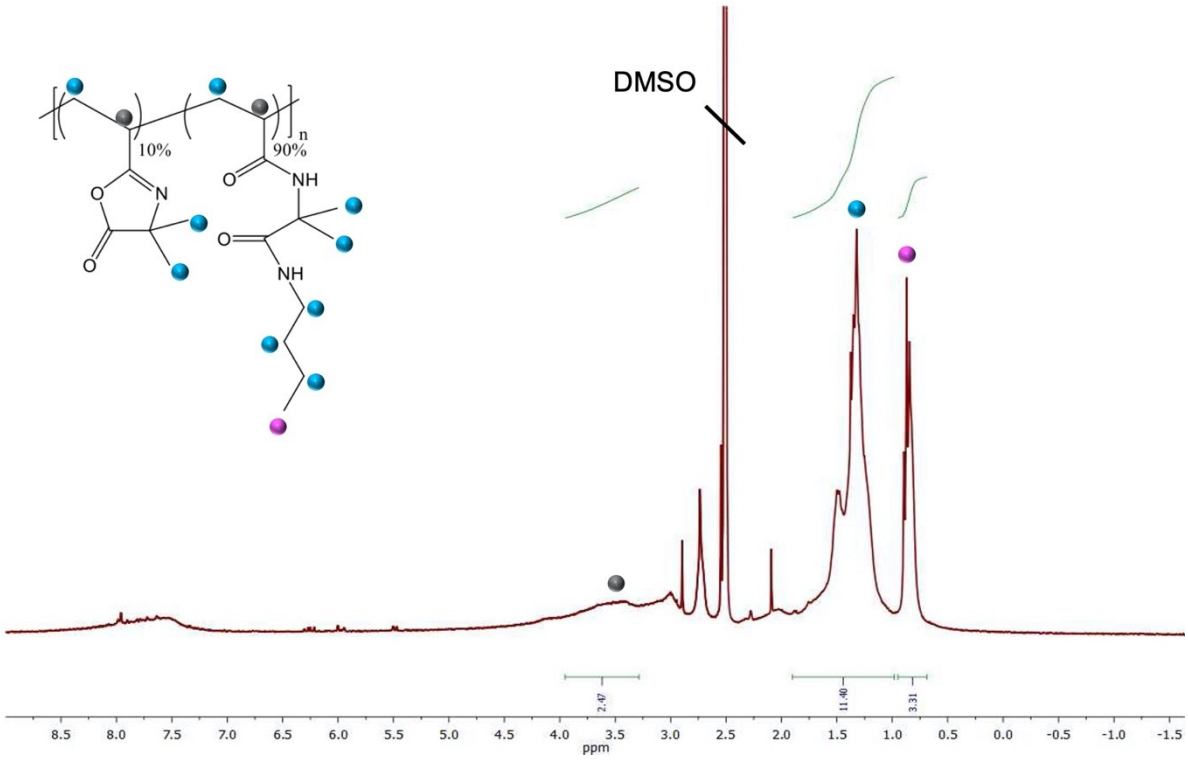


Figure S12. ^{1}H NMR (300 MHz, DMSO-d_6, δ) of PVDMA grafted to 90% butylamine at room temperature.

Functionalization Studies

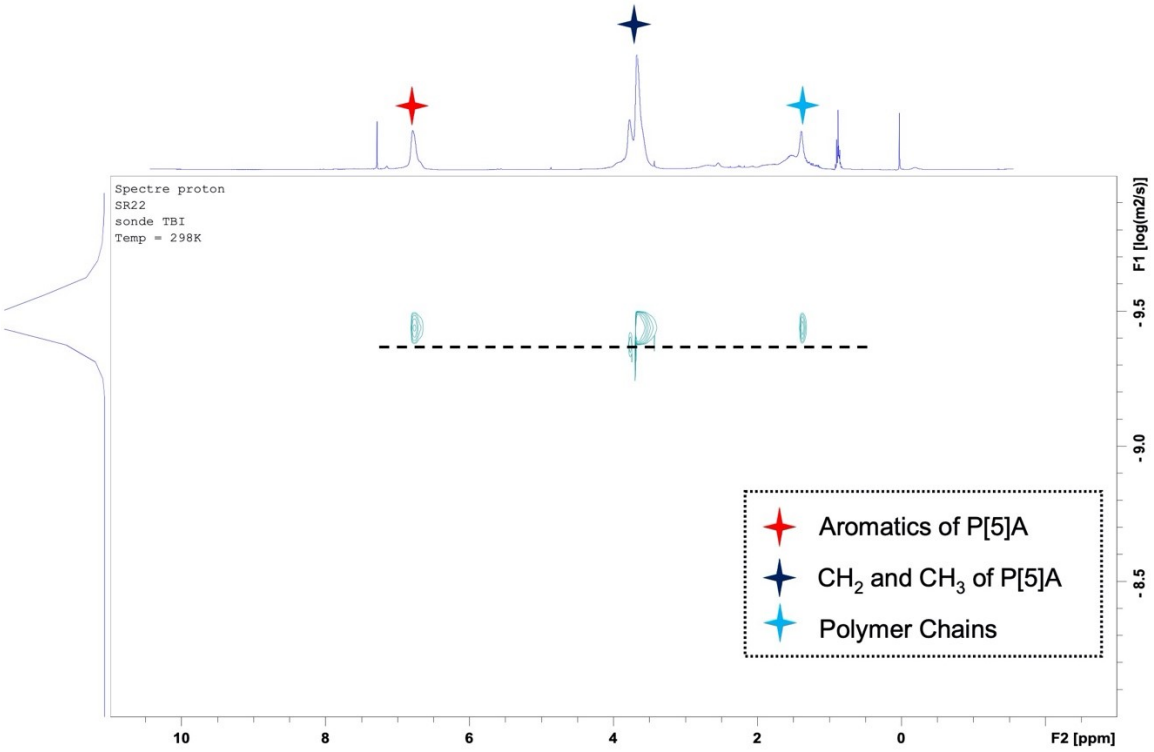


Figure S13. ^{1}H NMR DOSY (400 MHz, DMSO-d_6, δ) of PVDMA grafted to 50% functionalized amino-copillar[5]arene at room temperature.

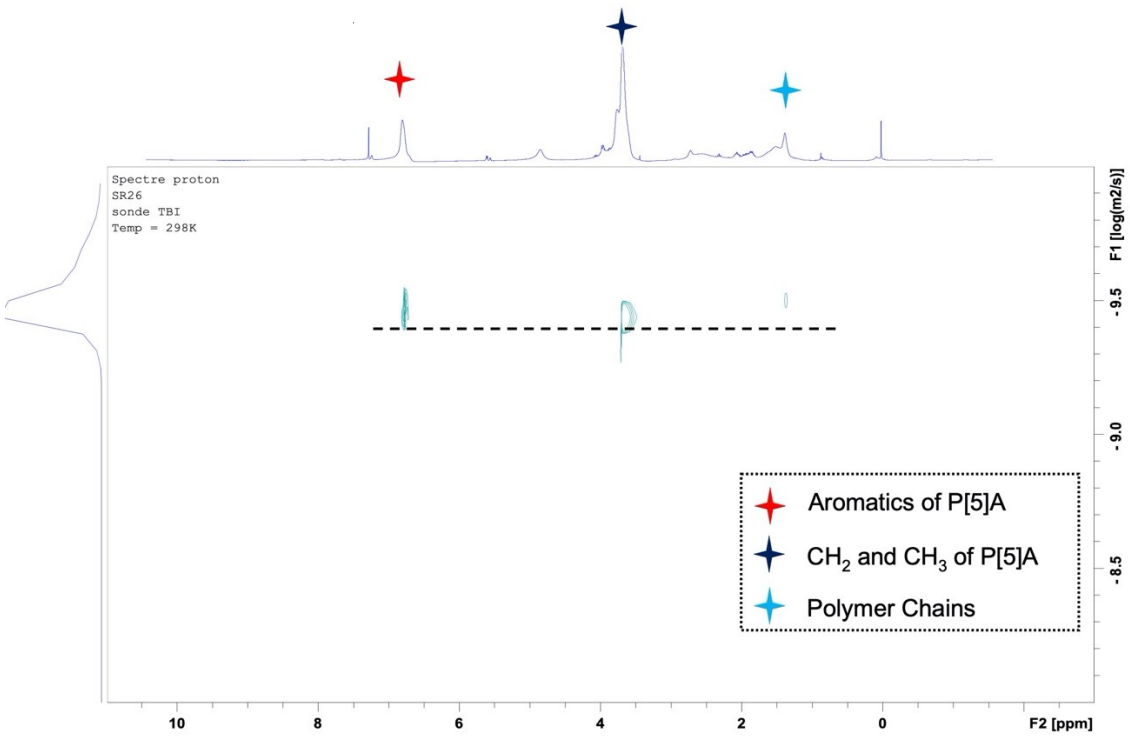


Figure S14. ^{1}H NMR DOSY (400 MHz, DMSO-d_6, δ) of PVDMA grafted to 60% functionalized amino-copillar[5]arene at room temperature.

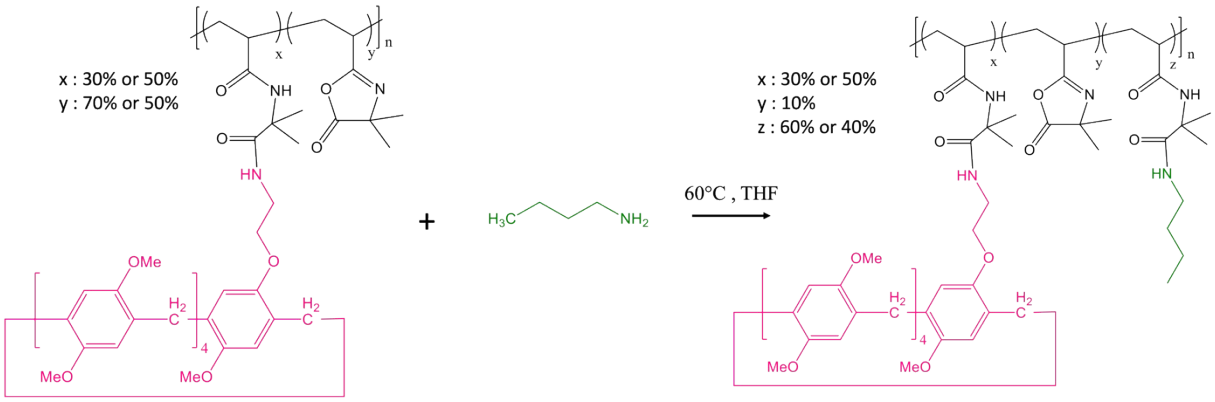


Figure S15. Functionalization reaction of 60 or 40% butylamine on PVDMA chains.

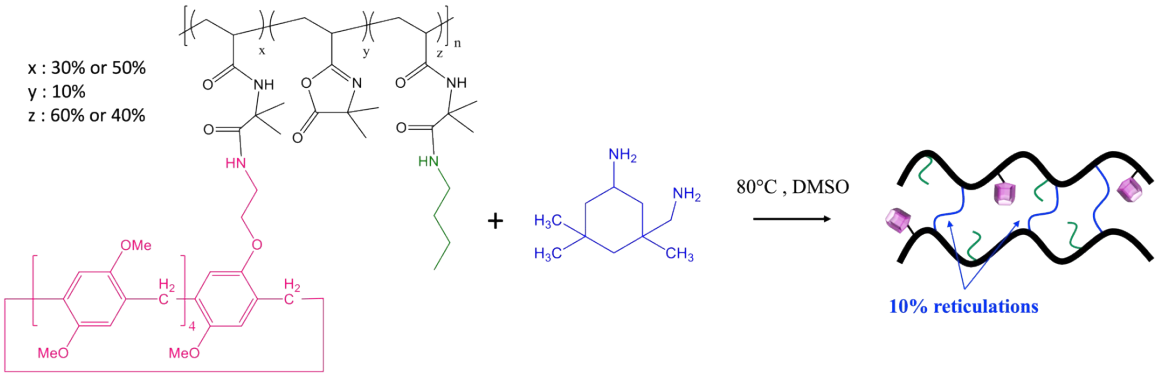


Figure S16. Formation of reticulation in the material by adding 10 mol.% isophorone diamine.

SEC Results

DP_n	% P[5]A	% Butylamine	M_n	M_w	M_v	M_z	Đ
89	0	0	$9{,}545\times10^3$ ±(12,768%)	$1{,}088\times10^4$ ±(12,768%)	/	$1{,}237\times10^4$ ±(28,550%)	1,1 ±(18,057%)
261	0	0	$3{,}625\times10^4$ ± (6,331%)	$4{,}613\times10^4$ ± (2,865%)	$5{,}390\times10^4$ ± (0,905%)	$5{,}421\times10^4$ ± (5,696%)	1,3 ±(6,949%)
89	0	90	$9{,}726\times10^3$	$1{,}291\times10^4$	/	$1{,}754\times10^4$	1,3
89	30	0	$1{,}024\times10^4$	$1{,}440\times10^4$	$1{,}799\times10^4$	$1{,}852\times10^4$	1,4
89	50	0	$7{,}235\times10^4$	$7{,}542\times10^4$	$7{,}755\times10^4$	$7{,}872\times10^4$	1,0
89	30	60	Non soluble				
89	50	40	Non soluble				
261	30	0	Non soluble				
261	50	0	Non soluble				

Figure S17. GPC results for each PVMA functionalized with P[5]A and/or butylamine in THF at 658nm.

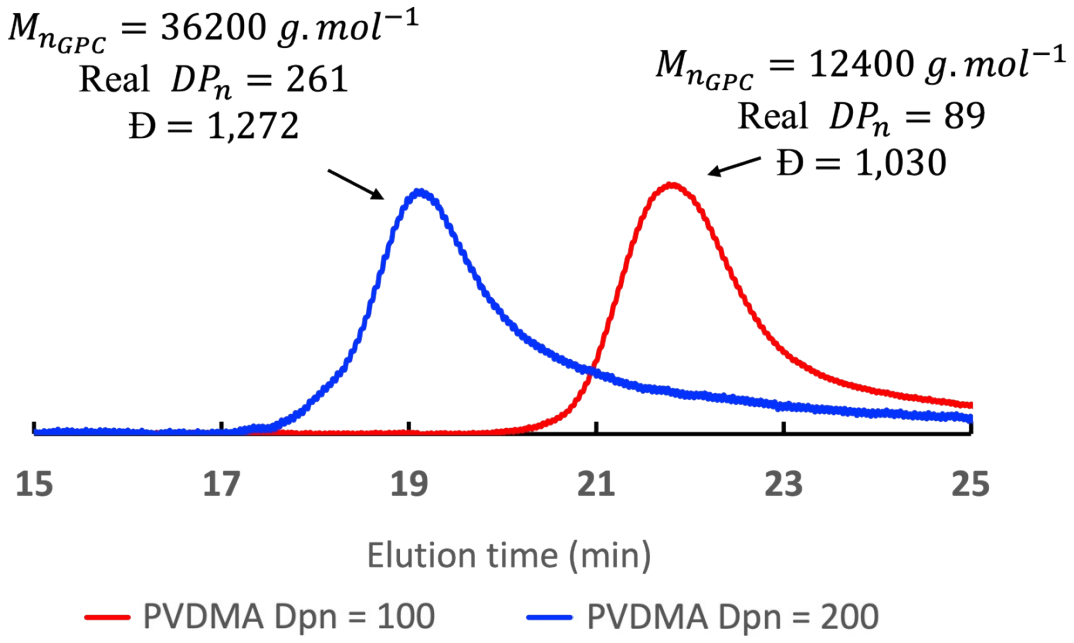
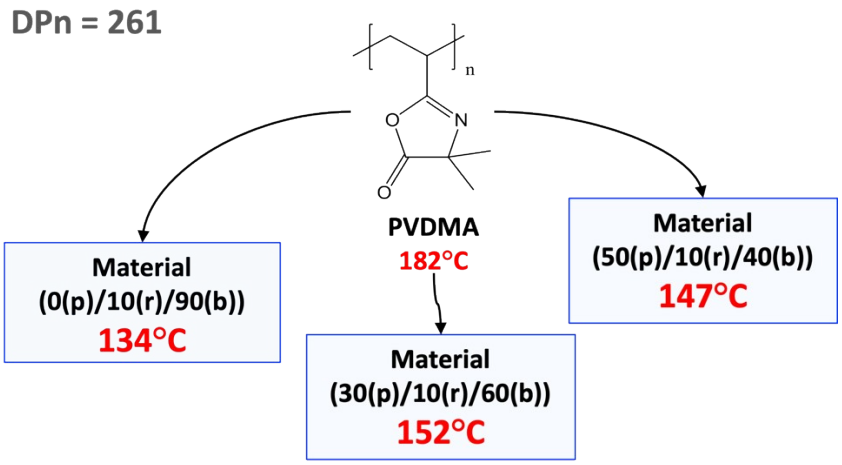


Figure S18. SEC obtained for PVDMA Dpn = 100 and Dpn = 200

DSC Results



Dpn = 89	Dpn = 261					Dpn = 89	Dpn = 261
Name	Name	% P[5]A	% Reticulation	% Butylamine	State	Tg (°C)	Tg (°C)
1	2	0	0	0	Powder	**124**	**182**
0(p) / 0(r) / 90(b)	0(p) / 0(r) / 90(b)	0	0	90	Powder	**103**	**108**
0(p) / 10(r) / 90(b)	0(p) / 10(r) / 90(b)	0	10	90	Material	**132**	**134**
30(p) / 0(r) / 0(b)	30(p) / 0(r) / 0(b)	30	0	0	Powder	**123**	**115**
50(p) / 0(r) / 0(b)	50(p) / 0(r) / 0(b)	50	0	0	Powder	**116**	**110**
30(p) / 0(r) / 60(b)	30(p) / 0(r) / 60(b)	30	0	60	Powder	**107**	**113**
50(p) / 0(r) / 40(b)	50(p) / 0(r) / 40(b)	50	0	40	Powder	**119**	**111**
1-30	2-30	30	10	60	Material	**144**	**152**
1-50	2-50	50	10	40	Material	**135**	**147**

Figure S19. Tg of PVDMA materials at different percentages of P[5]A, reticulation and butylamine, obtained by DSC thermogram heated at a rate of 10°C / min (second heating ramp 25 – 250°C).

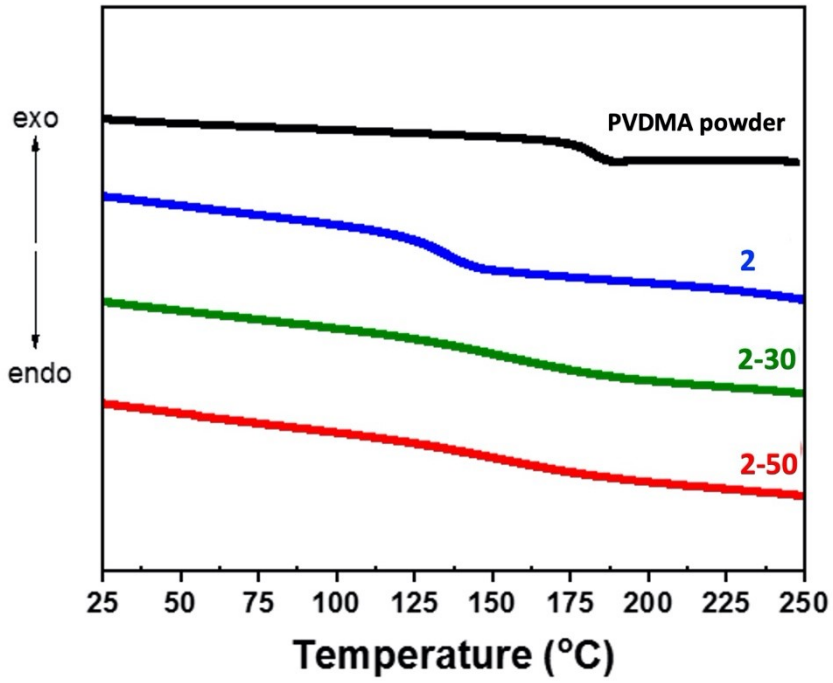


Figure S20. DSC thermograms of polymers heated at a rate of 10°C / min (second heating ramp 25 – 250°C) showing Tg.

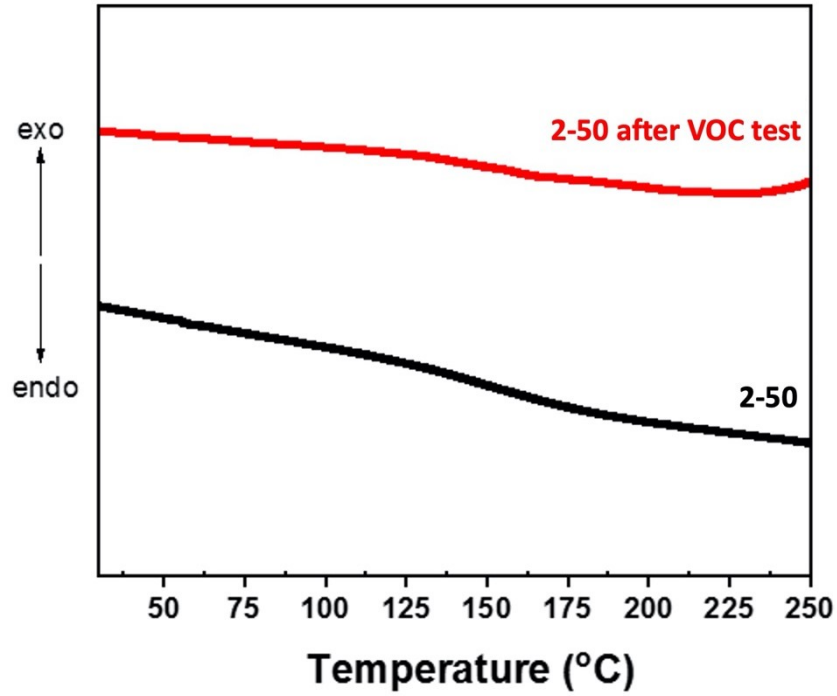


Figure S21. DSC thermograms of polymers heated at a rate of 10°C / min (second heating ramp 25 – 250°C) showing no modification of Tg before and after VOC test (VOC: Dibromoethane) on **2** material. 147 et 144 °C

DMA Results

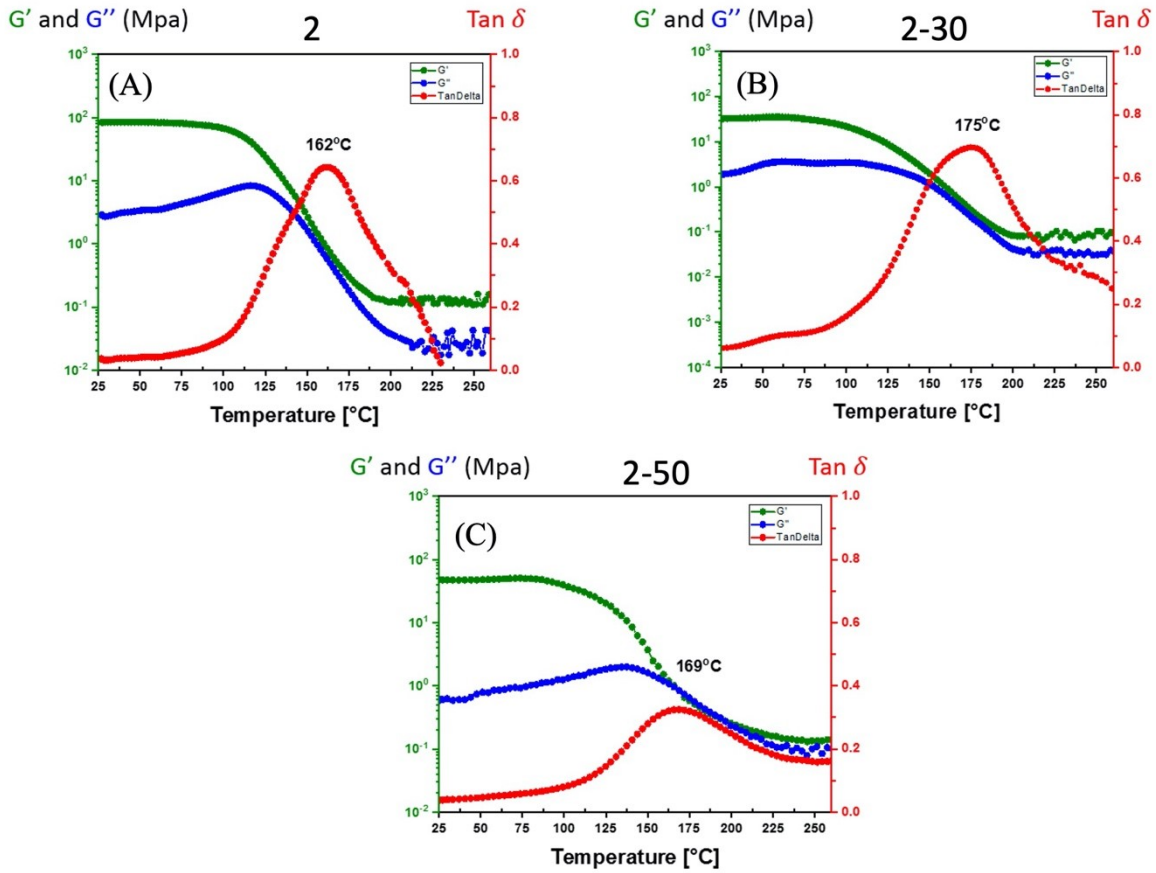


Figure S22. Storage modulus G′, loss modulus G'' and Tan(δ) versus temperature for **2** (A), **2-30** (B) and **2-50** (C) materials, obtained by shear DTMA.

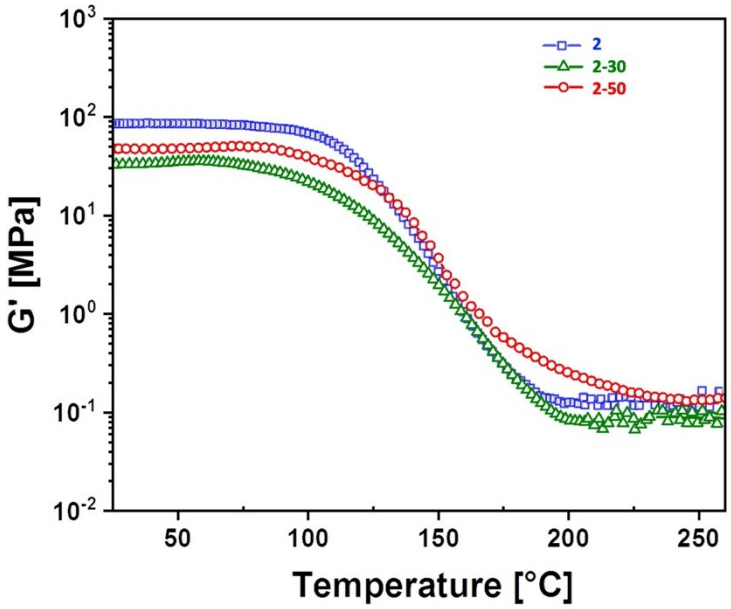


Figure 23. Storage modulus G′ versus temperature for **2** (□), **2-30** (Δ) and **2-50** (o) materials, obtained by shear DTMA.

COV Tests

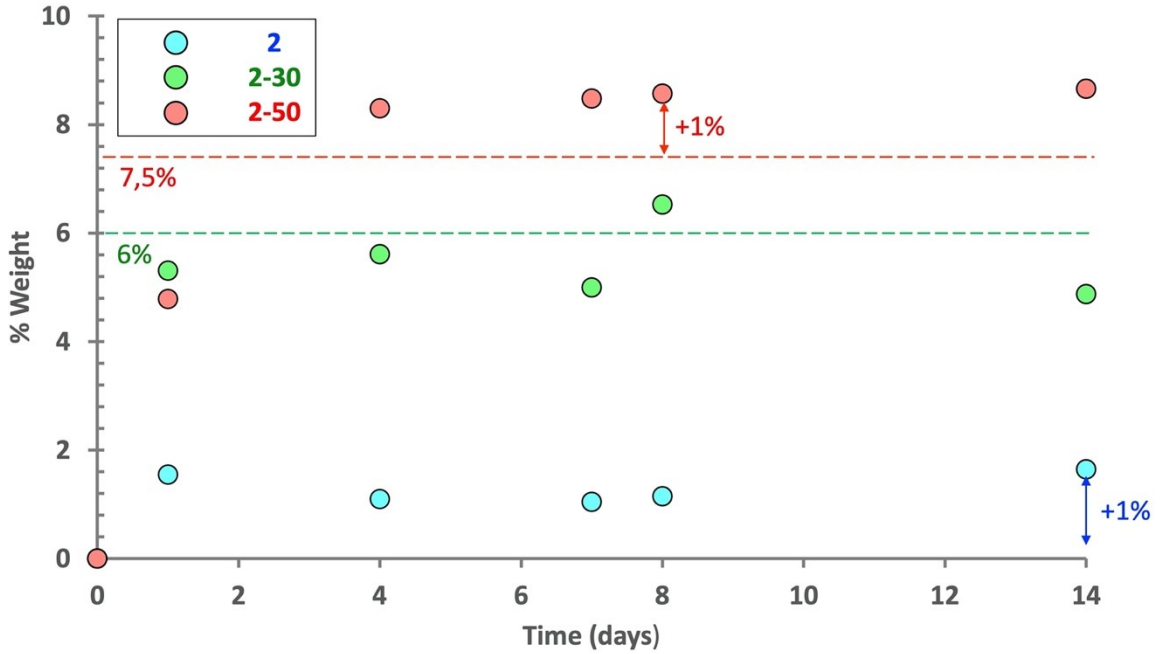


Figure S24. wt.% gain of materials **2**, **2-30** and **2-50** during 14 days in Dichloromethane vapors.

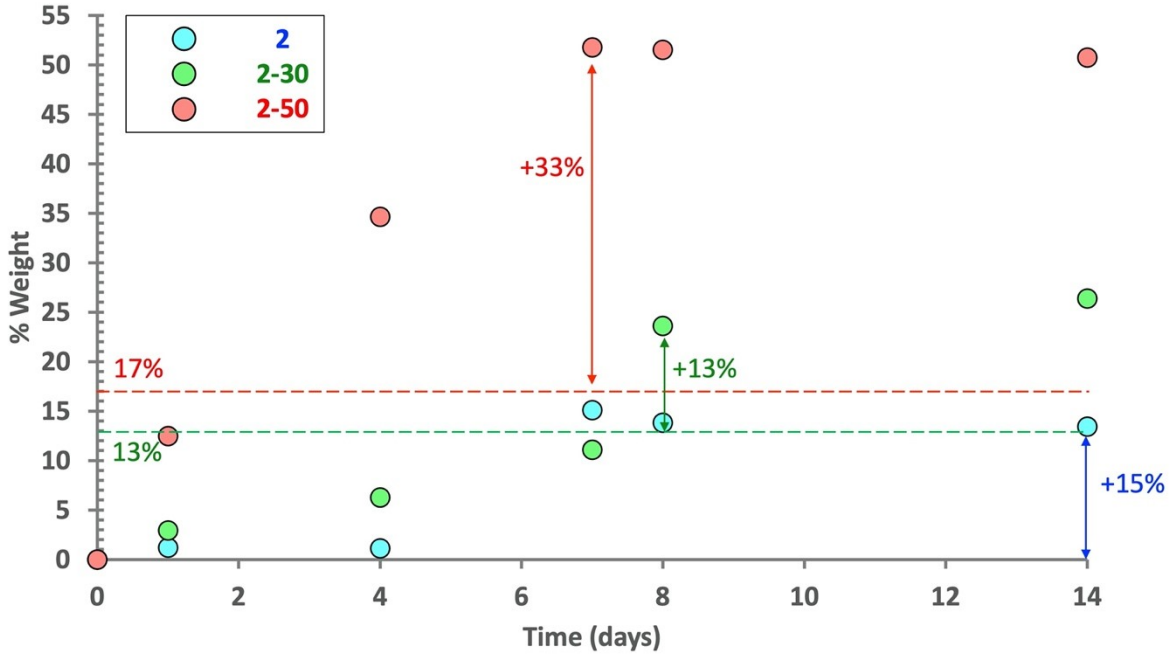


Figure S25. wt.% gain of materials **2**, **2-30** and **2-50** during 14 days in Dibromoethane vapors.

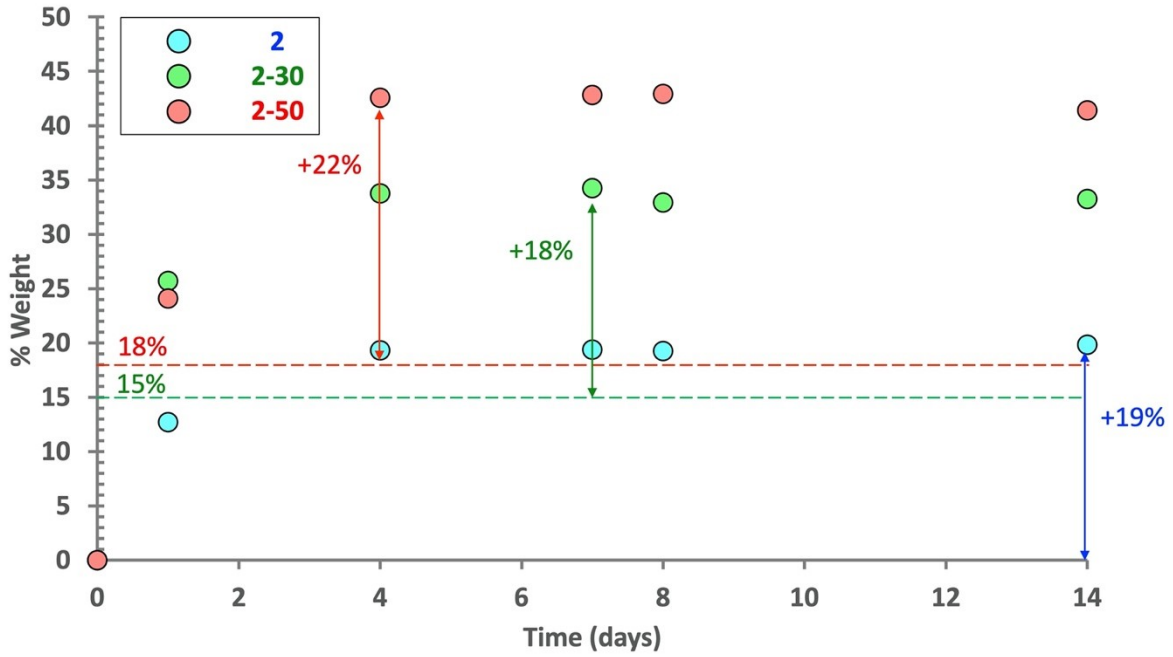


Figure S26. wt.% gain of materials **2**, **2-30** and **2-50** during 14 days in Dibromochloromethane vapors.

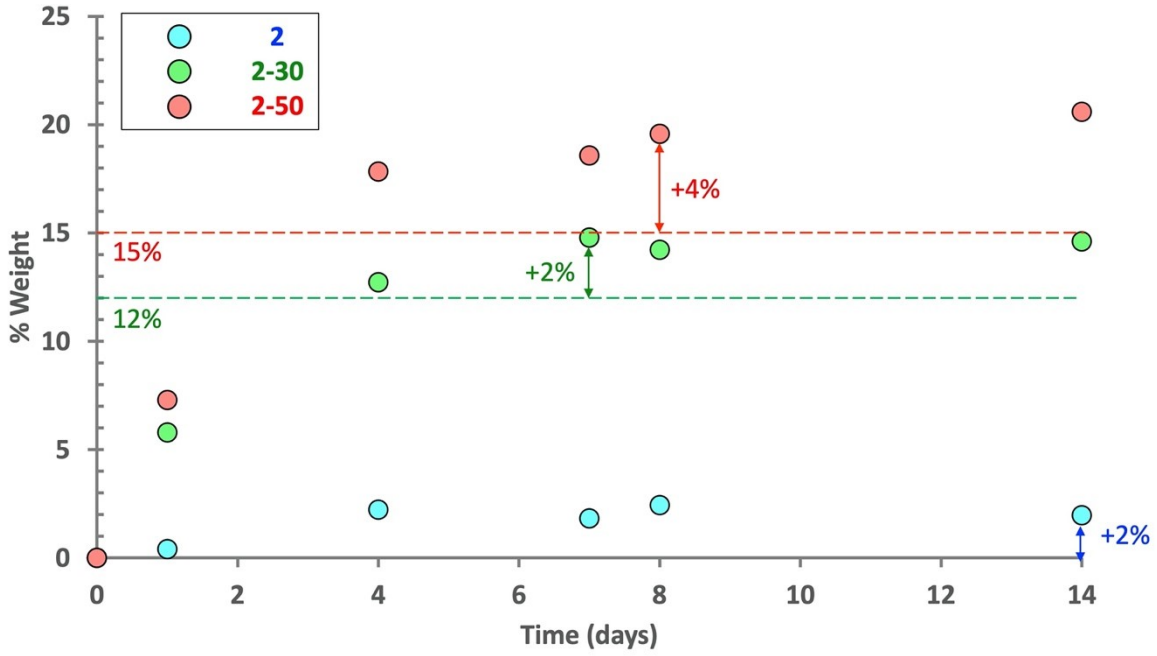


Figure S27. wt.% gain of materials **2**, **2-30** and **2-50** during 14 days in Tetrachloroethane vapors.

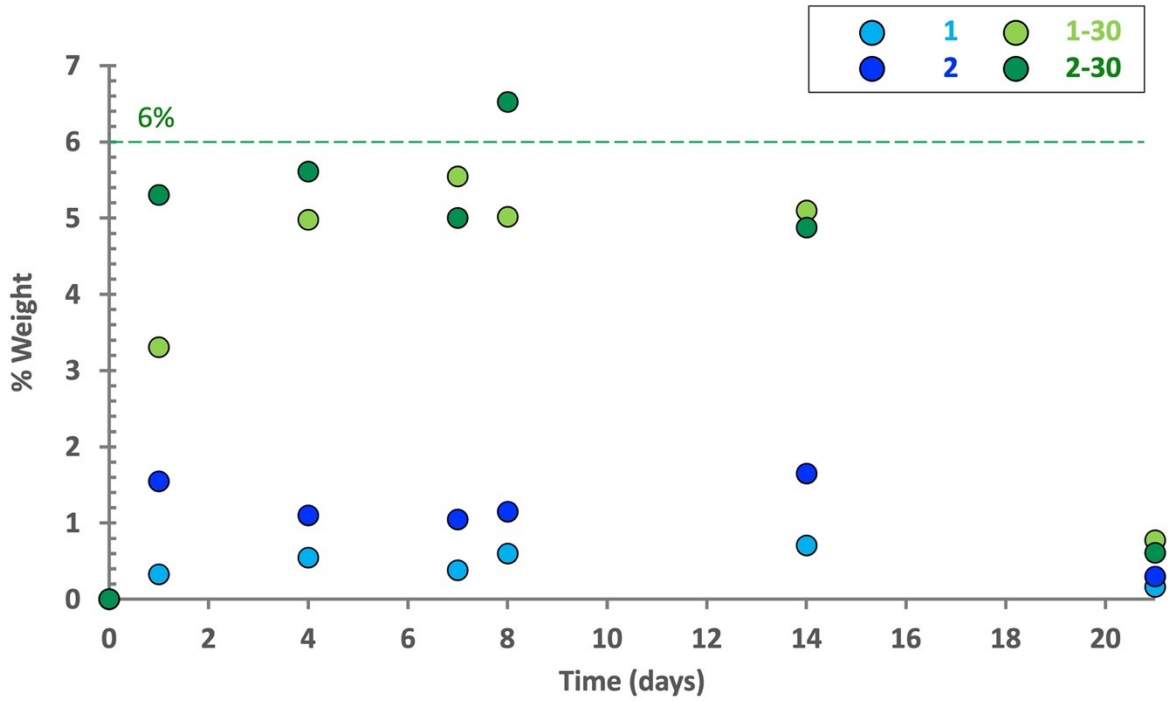


Figure S28. wt.% gain of materials **1**, **2**, **1-30** and **2-30** during 14 days in Dichloromethane vapors for **DPn = 89** and **Dpn = 261**.

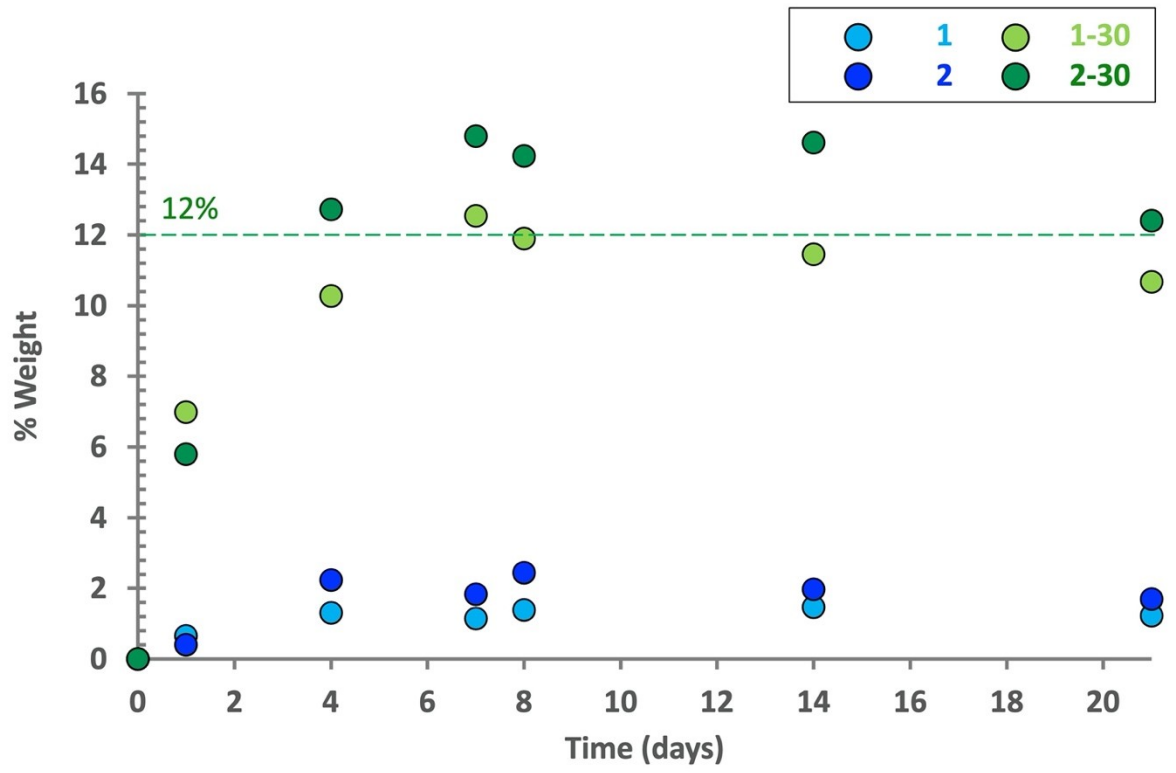


Figure S29. wt.% gain of materials **1**, **2**, **1-30** and **2-30** during 14 days in Tetrachloroethane vapors for **DPn = 89** and **Dpn = 261**.

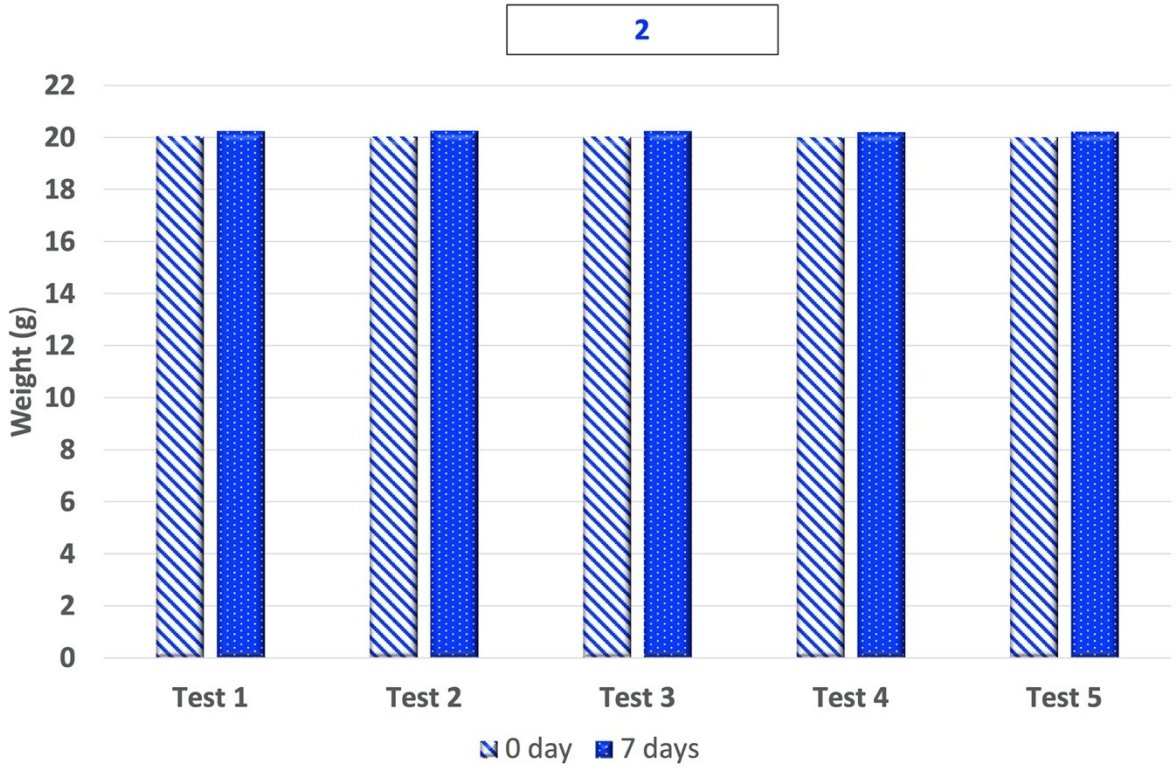


Figure S30. Repeatability of weight taken by material 2 in Dichloromethane.

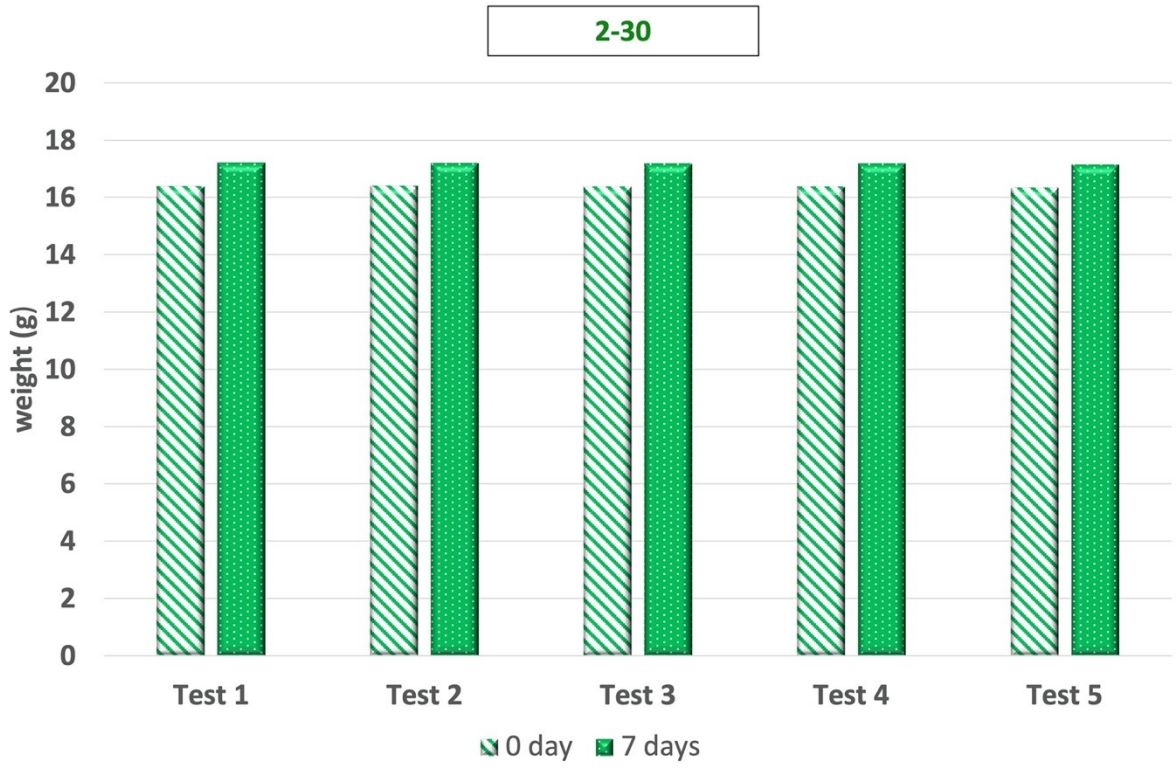


Figure S31. Repeatability of weight taken by material 2-30 in Dichloromethane.

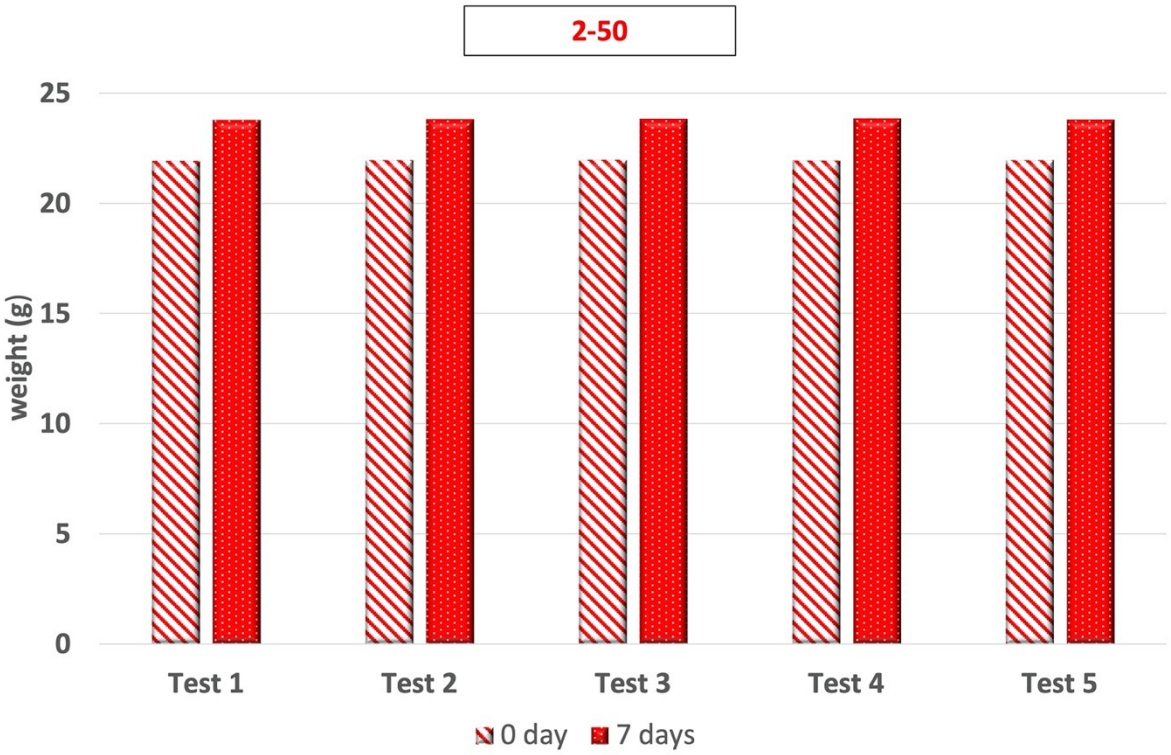


Figure S32. Repeatability of weight taken by material 2-50 in Dichloromethane.

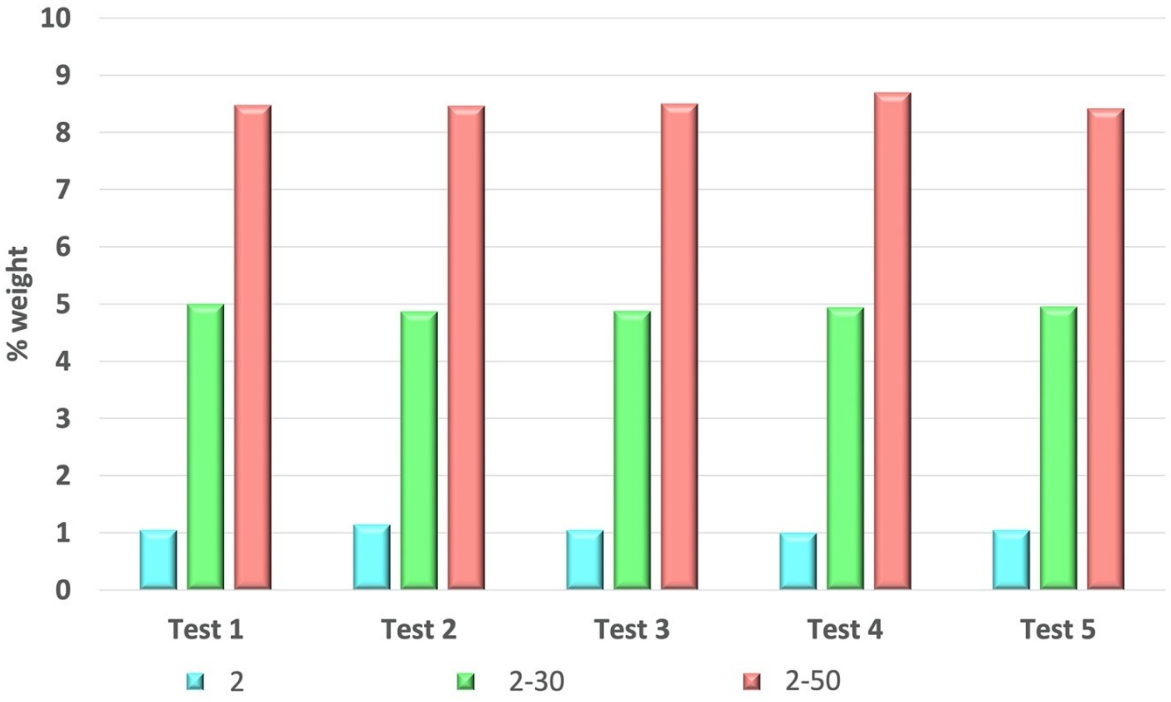


Figure S33. Complete graphic of repeatability of wt.% taken by materials 2, 2-30 and 2-50 in Dichloromethane.

VOCs selectivity factors	2-30	2-50
B/A	4.33	6.24
C/A	5.50	5.06
D/A	2.33	2.24
B/C	0.79	1.23
B/D	1.86	2.79
C/D	2.36	2.26

Figure S34. Selectivity factors of Pillar[5]arene-based thermosets to different VOCs