Electronic Supplemental Information (ESI):

An optimised synthesis of high performance radiation-grafted anion-exchange membranes

Lianqin Wang, Emanuele Magliocca, Emma L. Cunningham, William E. Mustain, Simon D. Poynton, Ricardo Escudero-Cid, Mohamed M. Nasef, Julia Ponce-González, Rachida Bance-Souahli, Robert C. T. Slade, Daniel K. Whelligan, and John R. Varcoe.

Table S1 Summary of the conditions used to synthesise RG-AEM(Cl^-)s, and their select properties, for the purpose of optimising the surfactant amount and the grafting temperature. All electron-beam irradiations were carried out on 25 µm ETFE using 30 KGy absorbed doses in air. All grafting steps were carried out in grafting mixtures containing 5%vol vinylbenzyl chloride (VBC) monomer in water diluent and with prior N_2 purging. All means ± sample standard deviations are from *n* = 3 repeats.

RG-AEM(Cl^-):	E-a	E-b	E-c	E-d	E-e	E-f	E-g	E-h	E-i
1-octyl-2-pyrrolidone (%vol)	0.5	0.5	0.5	**1**	1	1	1.5	1.5	1.5
Temperature (°C)	70	65	60	**70**	65	60	70	65	60
DoG (%)	67	57	38	**69**	64	33	71	51	46
IEC / mmol g^{-1}	2.00 ± 0.02	1.85 ± 0.05	1.58 ± 0.31	**2.22± 0.08**	1.82 ± 0.10	1.62 ± 0.15	1.90 ± 0.04	1.74 ± 0.13	1.60 ± 0.48
WU (%)	50	43	34	**55**	47	34	61	39	30

Table S2 Summary of the conditions used to synthesise the thicker RG-AEM(Cl^-)s, using 50 µm ETFE, and their key properties. All electron-beam irradiations were carried out in air. All grafting steps were carried out at 70°C in solutions containing 1%vol 1-octyl-2-pyrrolidone (surfactant) with prior N_2 purging. All means ± sample standard deviations are from *n* = 3 repeats.

RG-AEM(Cl^-):	E_{50}-R	E_{50}-1	E_{50}-2	E_{50}-3	E_{50}-4	E_{50}-5
e^--beam dose / kGy	70	40	40	**40**	40	40
[VBC] (%vol)	20	5	5	**5**	5	5
Propan-2-ol:H_2O diluent	1:0	0:1	1:3	**1:1**	3:1	1:0
DoG (%)	44	41	49	**51**	22	0.4
IEC / mmol g^{-1}	1.69±0.07	1.20±0.16	1.59±0.03	**1.59±0.06**	0.96±0.04	< 0.1
WU (%)	45 ± 4	44 ± 3	32 ± 4	**38 ± 2**	13 ± 2	< 1
T_{dry} / µm	70 ± 4	74 ± 5	71 ± 2	**69 ± 2**	64 ± 2	50 ± 2
TPS (%)	27 ± 1	22 ± 2	14 ± 2	**30 ± 2**	6 ± 1	< 1
σ(80°C, hydrated)/ mS cm^{-1}	44 ± 2	37 ± 1	40 ± 5	**43 ± 2**	23 ± 1	< 1

Table S3 Micelle size distributions at 25°C in the various grafting mixtures used (that also contained 1%vol 1-octyl-2-pyrrolidinone and 5% VBC monomer). A Zetasizer Nano S (Malvern Instruments) was used for the micelle size analyses.

Propan-2-ol (%vol)	UPW (%vol)	Micelle size distribution / nm
94	0	274 ± 13
70.5	23.5	403 ± 150
47	47	551 ± 31
23.5	70.5	665 ± 176
0	94	863 ± 143

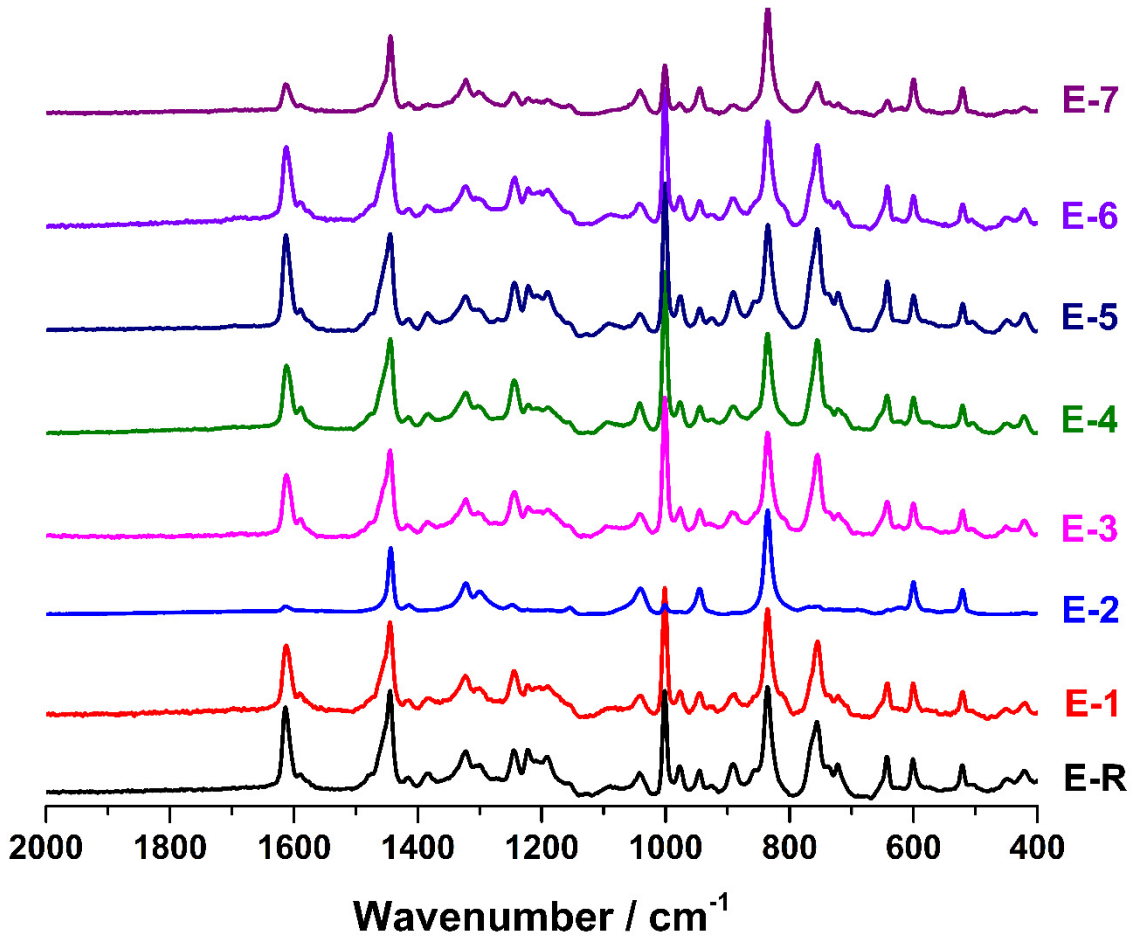


Figure S1 The Raman spectra (λ = 780 nm laser) of all the RG-AEMs synthesised from 25 μm ETFE (discussed in the main article). The spectra were normalised to the intensity of the ETFE-derived peak at 835 cm^{-1} for ease of visual comparison.

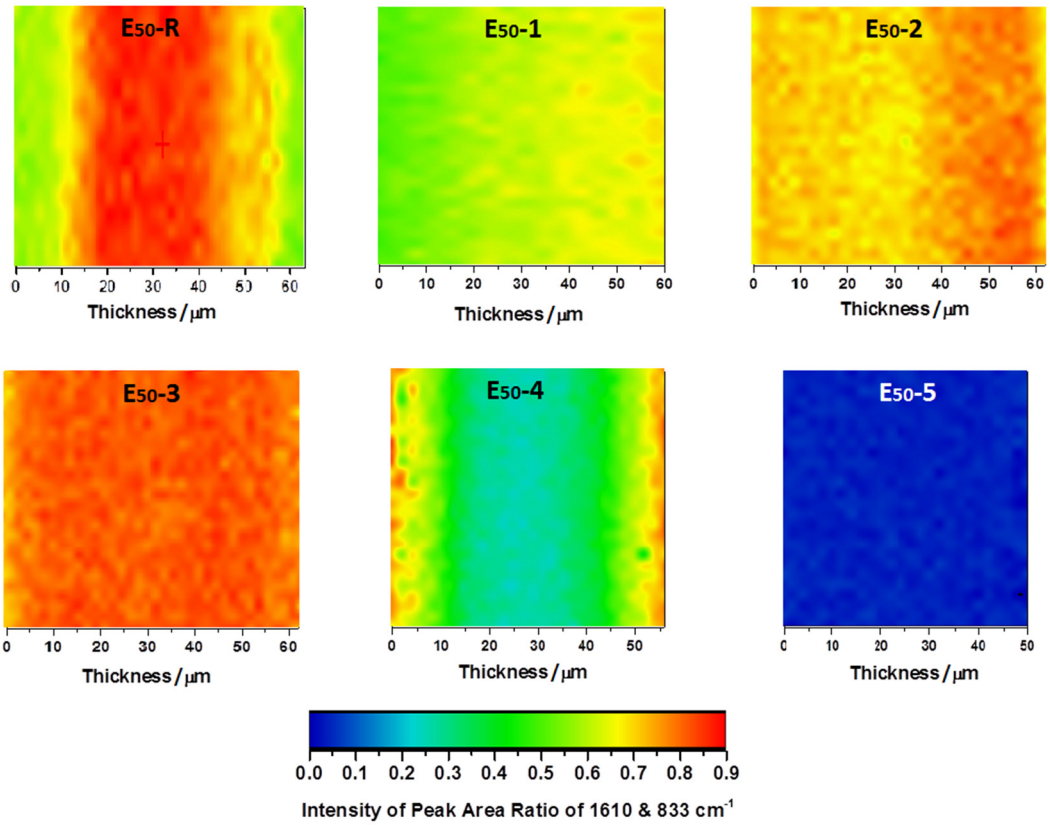


Figure S2 Raman micro-spectroscopic analysis of randomly selected cross-sections of the ETFE-*g*-poly(VBC) intermediate membranes for all the thicker RG-AEMs synthesised from the 50 μm ETFE. The through-plane direction is from left to right in these maps. The maps show the *relative* area of the aromatic ring breathing band at 1610 cm^{-1} (related to the poly(VBC) grafts) normalised to the area of the CF_2 stretches at 833 cm^{-1} (related to the ETFE film).

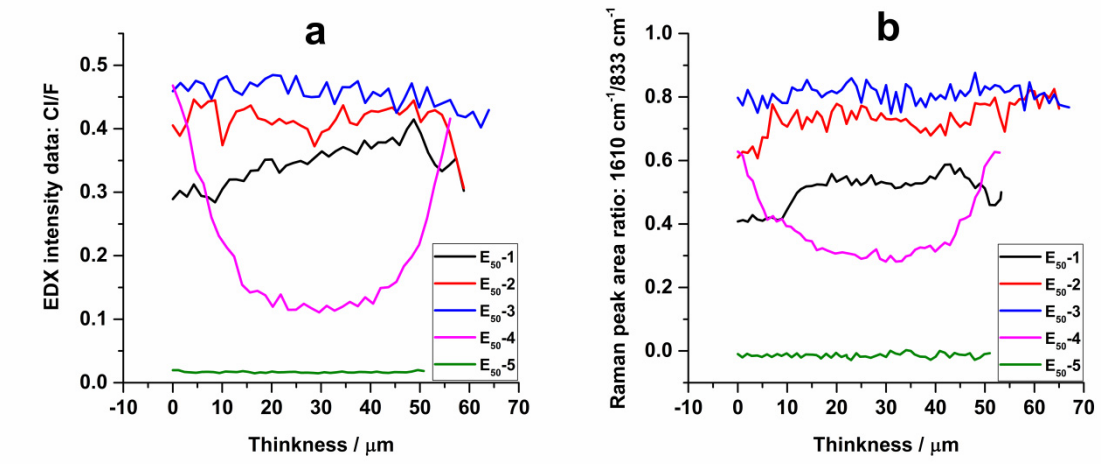


Figure S3 (a) EDX & (b) Raman line data of the ETFE-*g*-poly(VBC) intermediate membranes for all the thicker RG-AEMs synthesised from the 50 μm ETFE. The through-plane direction is from left to right in these line maps.

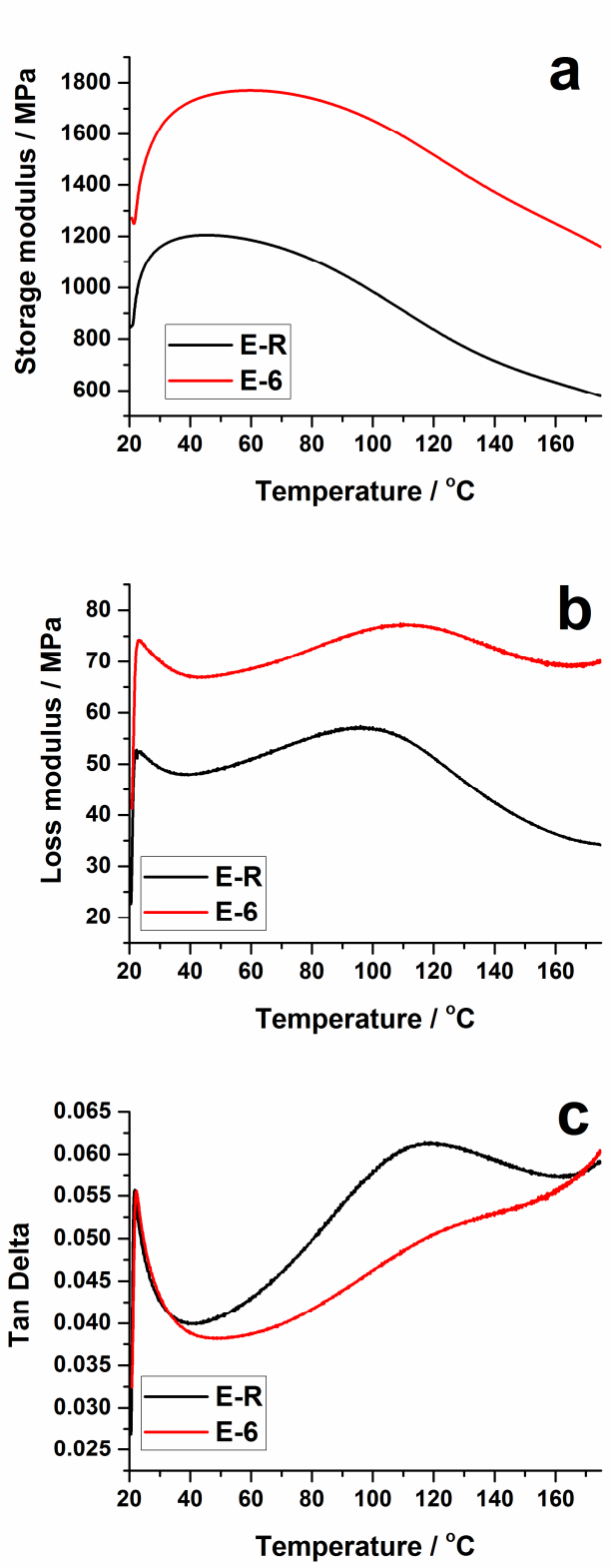


Figure S4 (a) Storage modulus, (b) Loss modulus, and (c) Tan δ Dynamic Mechanical Analysis (DMA) data for **E-R** & **E-6**. Measured at 1 Hz from 20 to 175˚C with a heating rate of 5°C min^{-1} on a TA Dynamic Mechanical Analysis Q800.

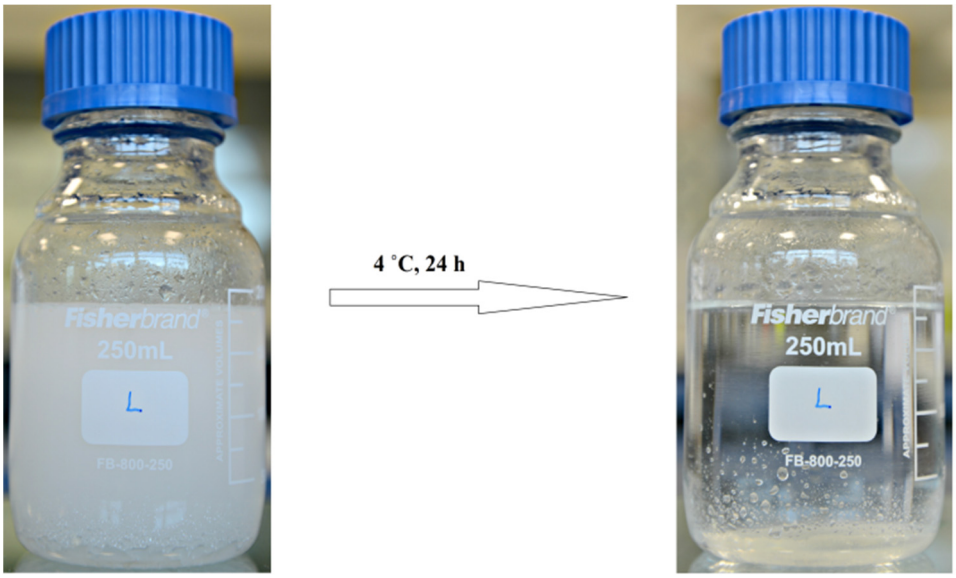
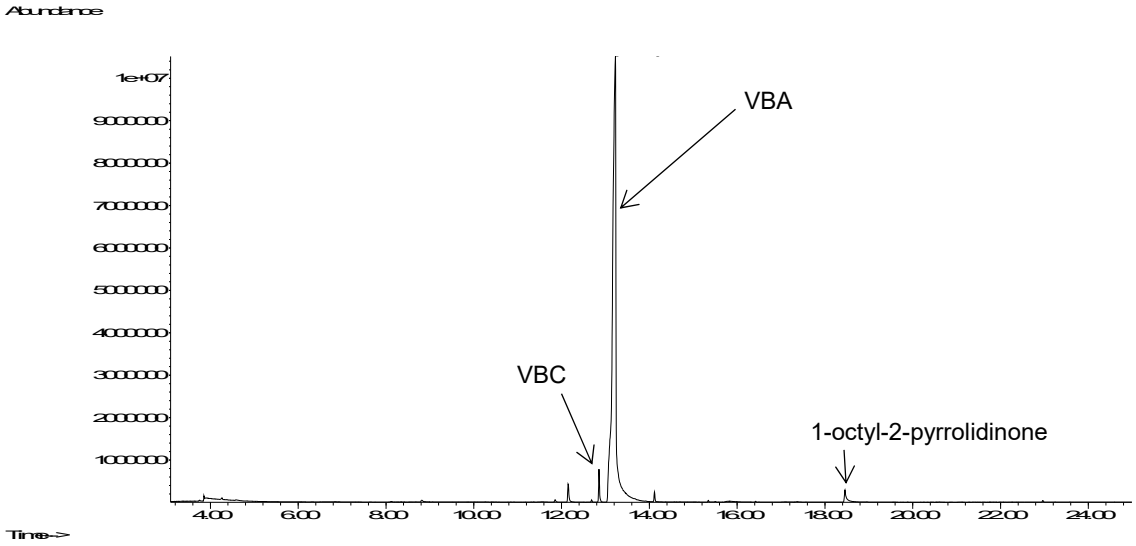


Figure S5 The residual grafting mixture used to make AEM **E-6A** before (left) and after (right) storage at 4°C for 24 h.

Aqueous layer:



Organic layer:

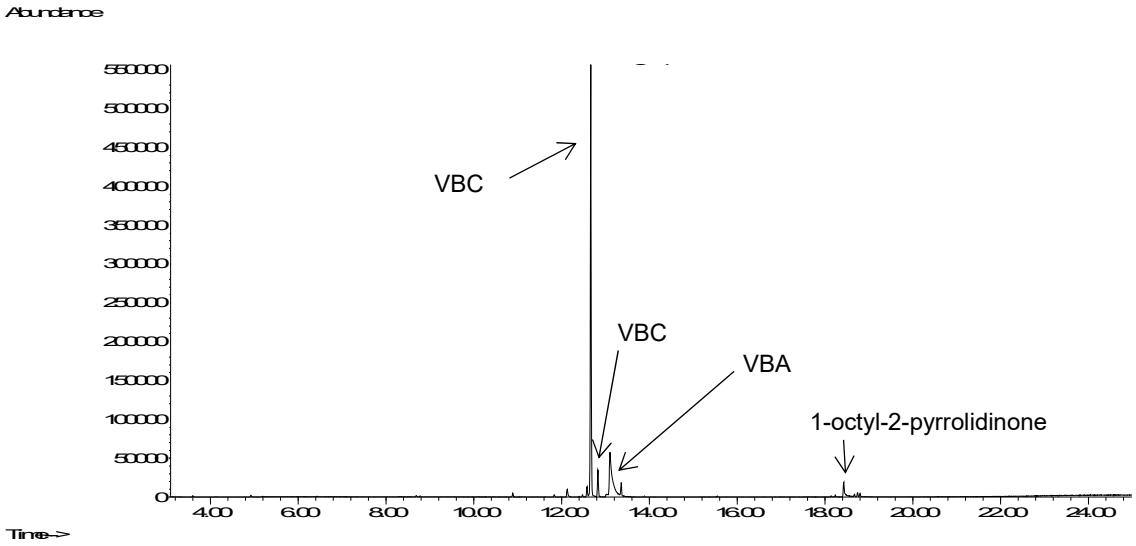


Figure S6 GCMS chromatograms of the aqueous and organic layers resulting from taking the grafting mixture used to produce **E-6B**, allowing it to stand at 4°C for 24 h and decanting. GCMS was carried out on an Agilent Technologies 7890A GC system connected to an Agilent Technologies 5975C inert XL EI/CI mass selective detector (MSD) operating in EI mode and the conditions were as follows: inj. vol. = 1 µL, inj. temp. = 250°C, column = Agilent HP-5MS (30 m × 0.25 mm), and the following oven temperature gradient: 0 – 10 min = 30 °C, 10 – 21 min = 30 – 250 °C (20°C min^{-1}).

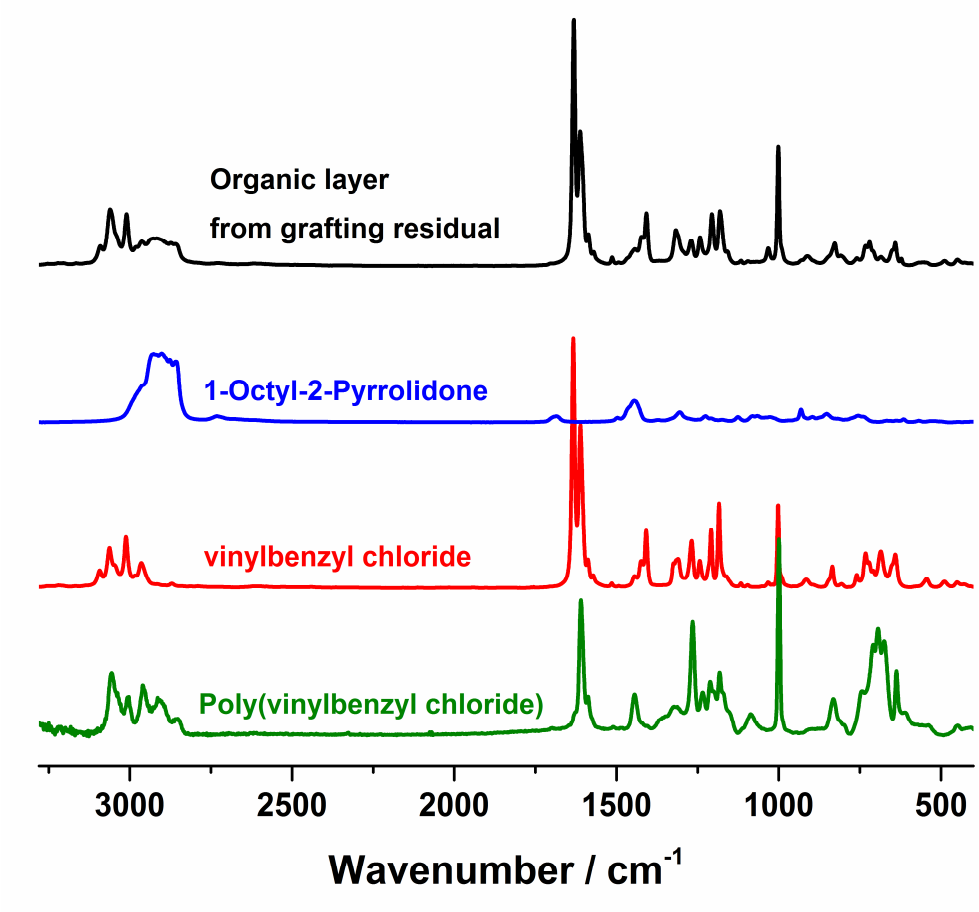


Figure S7 The Raman spectrum (λ = 532 nm laser) of organic layer recovered from the grafting mixture after the synthesis of AEM **E-6A**. The Raman spectra of vinylbenzyl chloride (VBC), poly(vinylbenzyl chloride), and 1-octyl-2-pyrrolidone are also shown.