Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Perfluoroalkylated alternating copolymer possessing solubility in fluorous liquids and imaging capabilities under high energy radiation

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EXPERIMENTAL

Materials

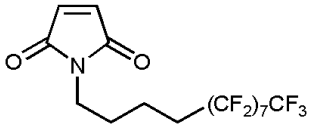
Toluene, maleic anhydride and anhydrous THF were purchased from Sigma-Aldrich and used as received. 1,1,1,2,3,3-Hexafluoro-4-(1,1,2,3,3,3-hexafluoropropoxy)pentane (PF-7600) was bought from 3M Korea and used without further purification.

Equipment

^{1}H NMR spectra were recorded on a Avance III400 (400 MHz) spectrometer at ambient temperature using the c hemical shift of a residual protic solvent ($CHCl_3$ at δ 7.24 ppm) as a reference. All chemical shifts were quoted i n parts per million (ppm) relative to the internal reference, and the coupling constants, *J*, were reported in Hz. Signal multiplicity was indicated as follows: s (singlet), d (doublet) and t (triplet). Attenuated total reflectance (ATR) FT-IR spectra were recorded on a Bruker VERTEX 80V. Size exclusion chromatography (SEC) was carried out on a Yo unglin GPC system (YL9100) equipped with a refractive index detector and a series of two columns (PL gel Mixed-C 5 µm and PL gel Mixed-D 5 µm) by eluting 1,3-dichloro-1,1,2,2,3-pentafluoropropane (Asahiklin™ AK-225G) at 35 °C. Monodisperse PMMA (molecular weight from 860 to 2,200,000 g mol^{-1}, Shodex™, Showa-Denko) was used as a reference standard for the SEC experiments. Electron beam (e-beam) lithography was carried out on a NANOBEAM NB3 exposure tool operating at an acceleration voltage of 80 kV with a probe current of 1.0 nA. Developed patterns of the polymer films were observed by scanning elect ron microscopy (SEM, Nanobeam NB3, 80 KeV) after sputter-coating of Pt. The nanoindentation tests were p erformed by a nano-indenter (Nanomechanics, USA) with a continuous stiffness measurement (CSM) te chnique. A Berkovich diamond tip was used in all the experiments.

Synthesis

1-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecyl)-1H-pyrrole-2,5-dione (R_FMi, 3) by using maleic anhydride



R_FMi (3)

To a magnetically stirred solution of 5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecan-1-amine (8.20 g, 16.7 mmol) in a mixture of CH_2Cl_2 (50 cm^3) and acetone (5 cm^3) was added maleic anhydride (1.63 g, 16.7 mmol) at ambient temperature. The solution was stirred for 2 h. The solvent was then distilled off under reduced pressure, and NaOAc (2.27 g, 16.7 mmol) and Ac_2O (40 cm^3) were added to the residue. It was stirred for 4 h at 110 °C. The reaction was quenched by the addition of Et_2O (120 cm^3). The recovered organic layer was washed with water (120 cm^3), brine (100 cm^3), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, EtOAc : hexane = 1 : 4) and crystallized from MeOH to give **R_FMi** (**3**) as a white solid (1.20 g, 13%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.69 (s, 2 H), 3.54 (t, *J* = 6 Hz, 2 H), 2.15-2.00 (m, 2H), 1.73-1.55 (m, 4H).

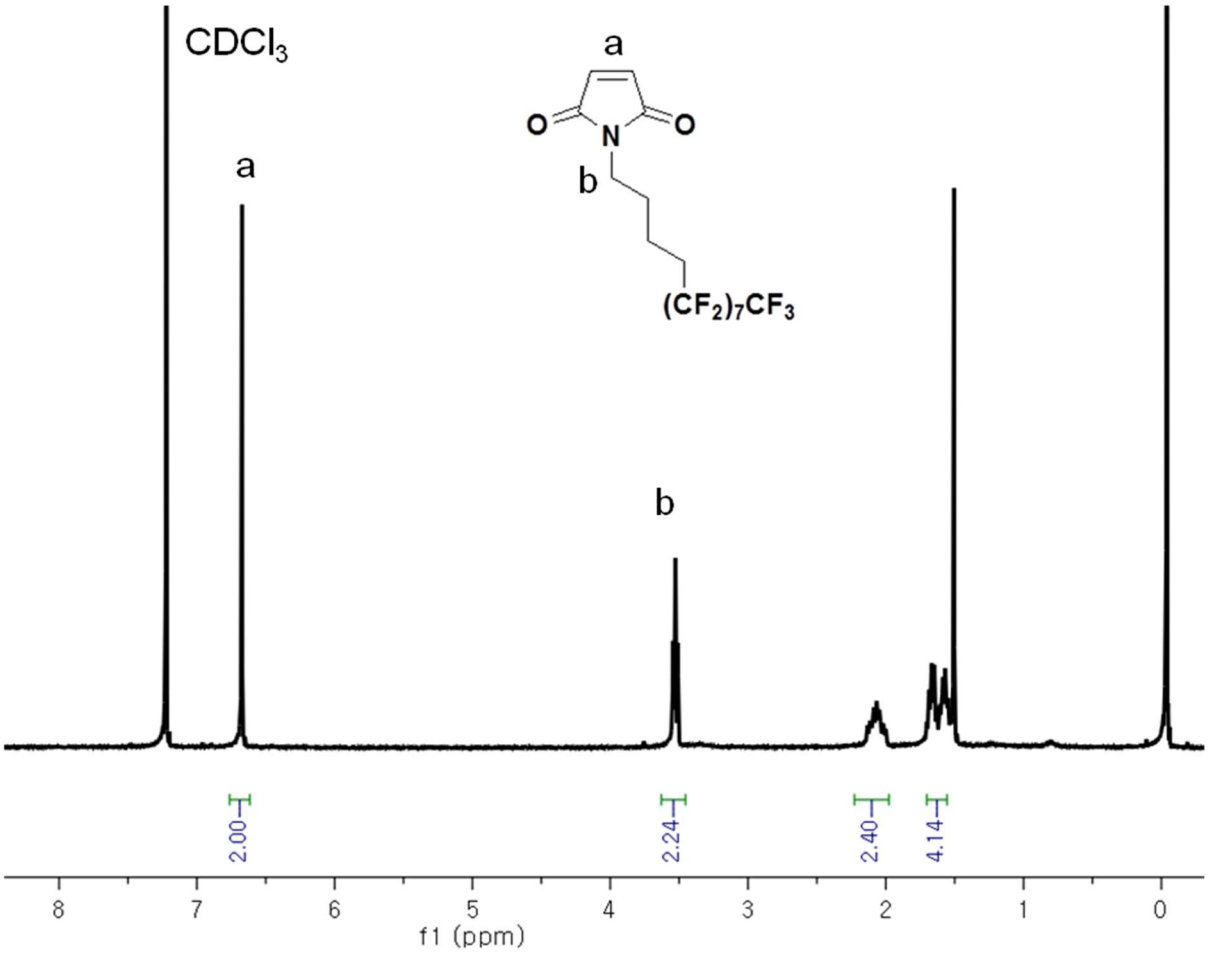


Fig. S1 : ^{1}H NMR of R_FMi (3) synthesized by using maleic anhydride

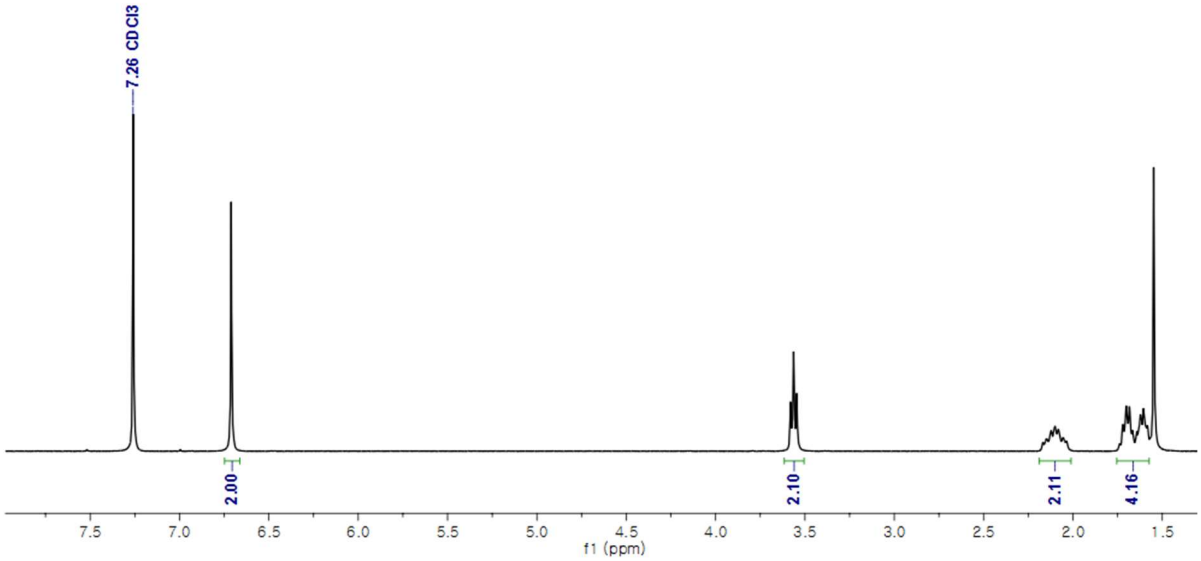
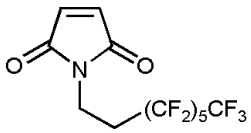
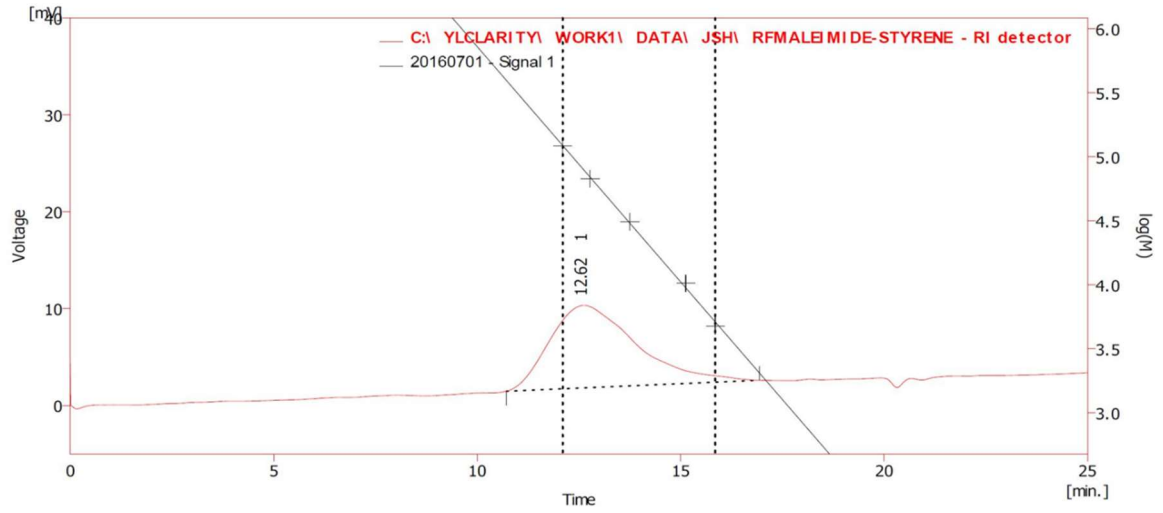


Fig. S2 : ^{1}H NMR of R_FMi (3) synthesized by using maleimide

1-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)-1H-pyrrole-2,5-dione



To a magnetically stirred solution of Ph_3P (2.70 g, 10.3 mmol) in THF (anhydrous, 50 cm^3) was added diisopropyl azodicarboxylate (2.08 g, 10.3 mmol) under a N_2 atmosphere at -78 °C. The mixture was stirred for 10 min, and another solution of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol (4.50 g, 12.4 mmol) in THF (10 cm^3) was added to the mixture at -78 °C. Maleimide (1.00 g, 10.3 mmol) was then added to the solution, and the reaction mixture was allowed to warm up to ambient temperature. After stirring for 12 h, the reaction was quenched and the crude product was recovered, which did not contain the desired product, 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)-1*H*-pyrrole-2,5-dione.



	Max. RT	Start RT	End RT	Mn	Mw	PD	Height [mV]	Height [%]	Area [mV.s]	Area [%]
1	12.62	10.71	16.93	33770	77073	2.2823	8.52	100.00	1258.68	100.00

Fig S3 : GPC chromatogram and molecular weight information of P(R_FMi-St)

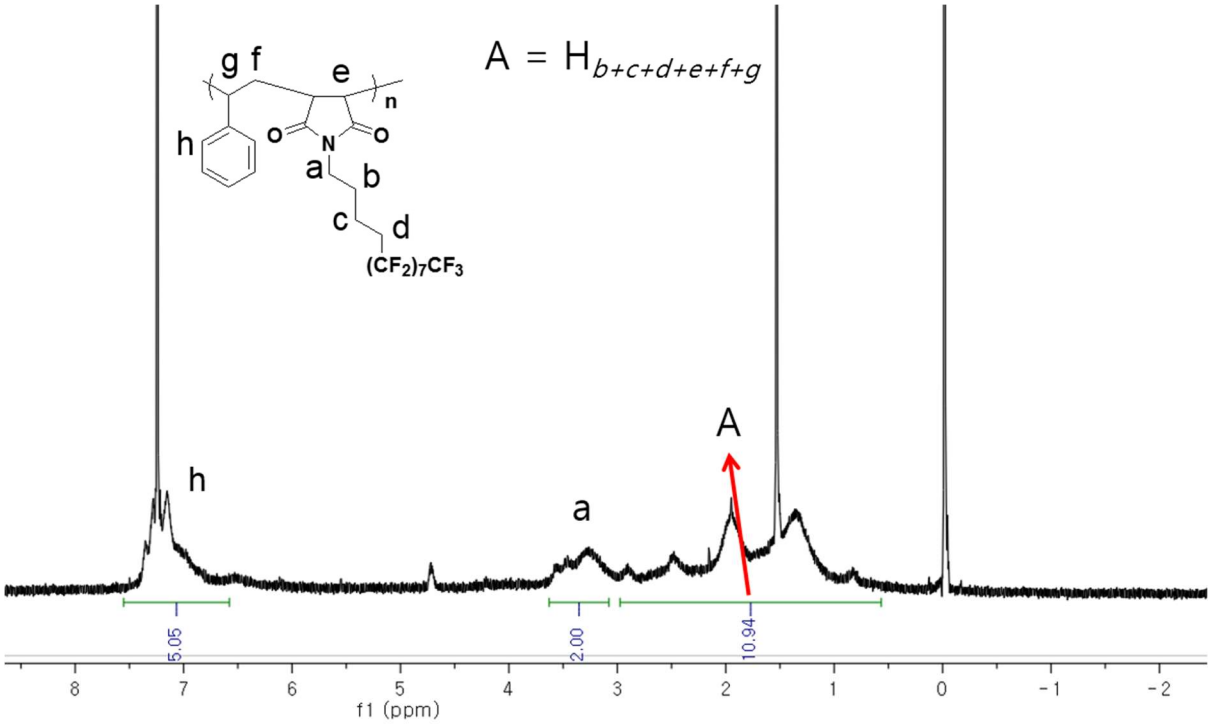
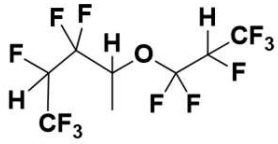


Fig. S4 : ^{1}H NMR of P(R_FMi-St)

(a)



(b)

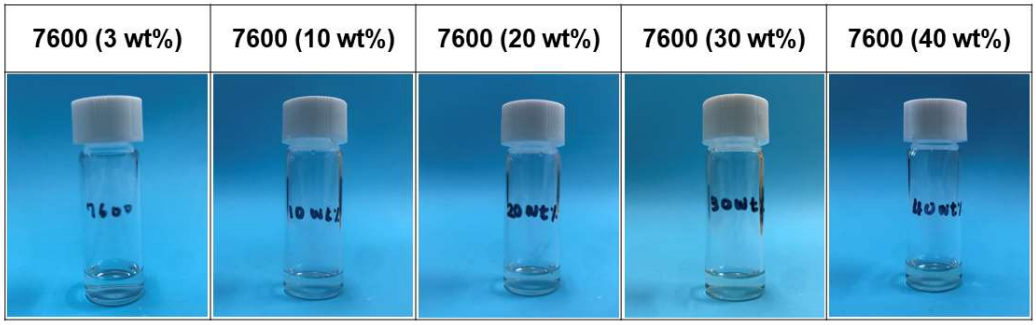


Fig S5 : (a) Chemical structure of a fluorous solvent (PF-7600) and (b) solubility test of P(R_FMi-St) in PF-7600.

Analysis of dissolution behaviour of P(R_FMi-St) by a quartz crystal microbalance (QCM)

To prepare samples for QCM experiment, 5 wt% solution **P(R_FMi-St)** in PF-7600 was spin-coated onto a QCM electrode made of quartz and Au (2.5 cm in diameter) at 1,000 rpm for 60 s to form a *ca*. 300 nm-thick film. It was baked at 110 °C for 60 s. The dissolution behaviour of **P(RFMi-St)** films was then investigated in PF-7600.

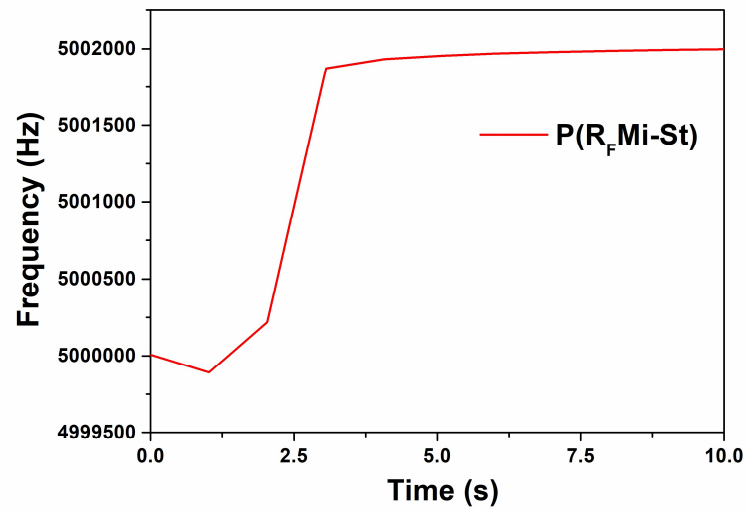


Fig S6 : Dissolution behaviour of P(R_FMi-St) in PF-7600 according to time by a QCM method.

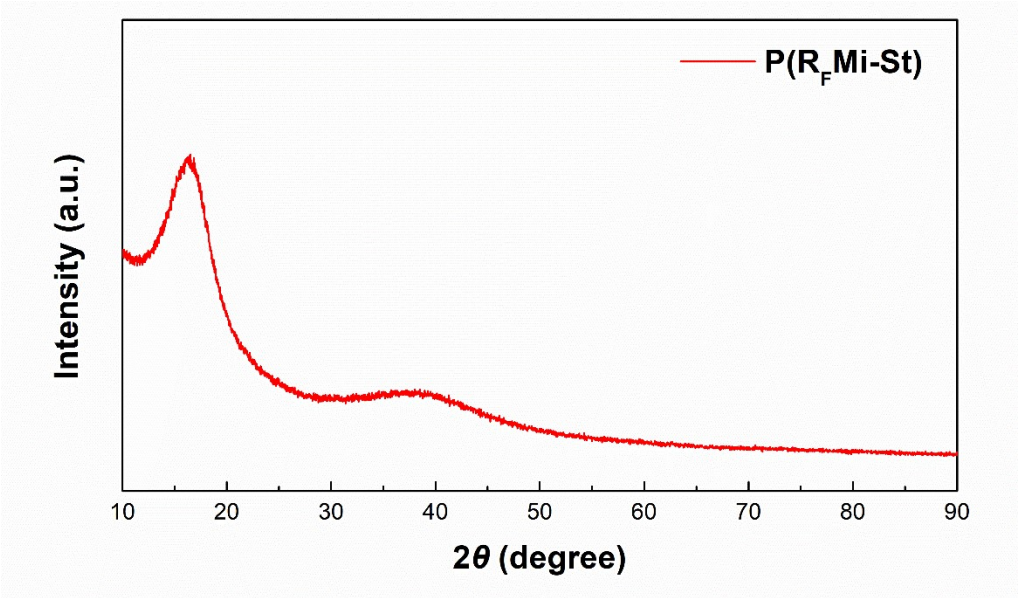


Fig S7 : Powder X-ray diffraction (XRD) spectrum of P(R_FMi-St).

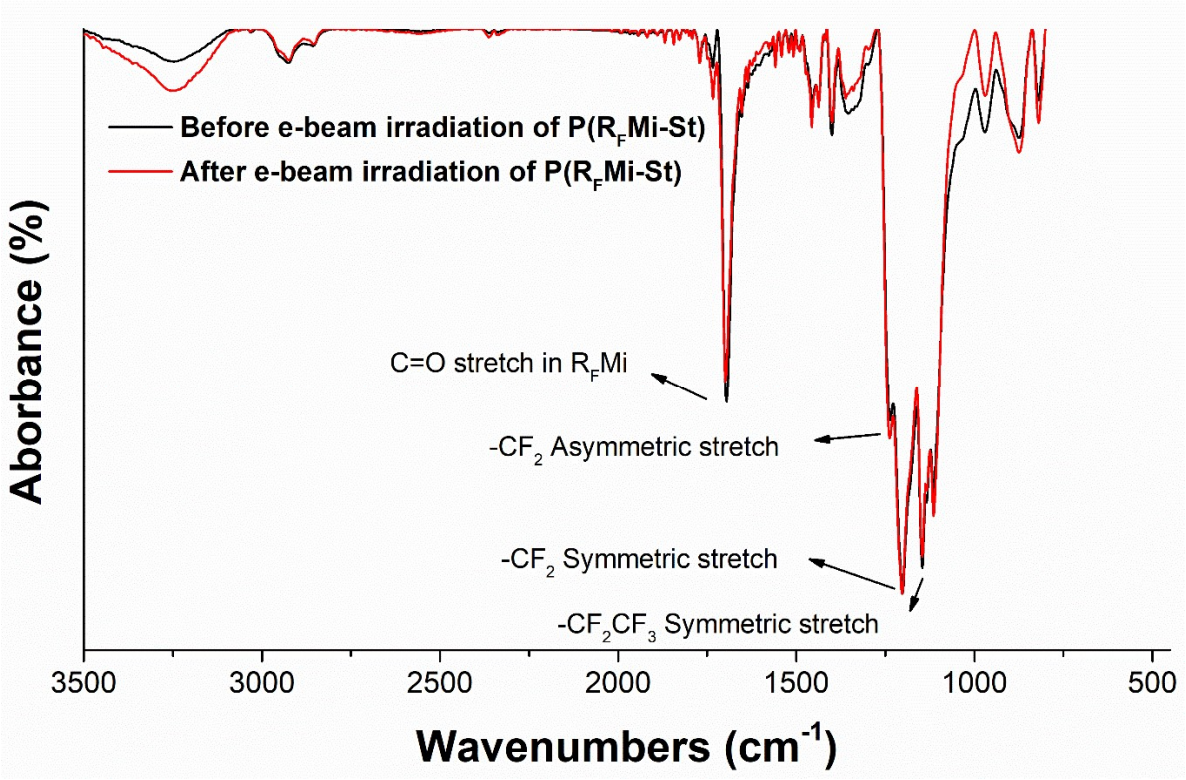


Fig S8 : FT-IR spectra of P(R_FMi-St) films on Si wafer before and after e-beam exposure.

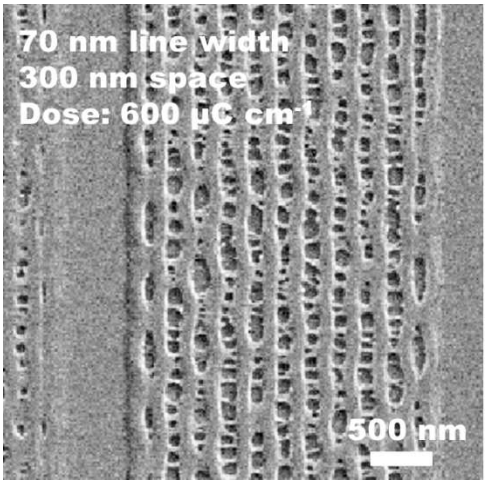


Fig S9 : SEM images of line and space patterns of a high molecular weight P(R_FMi-St) (Mn = 33,800 and *Đ*=2.3)

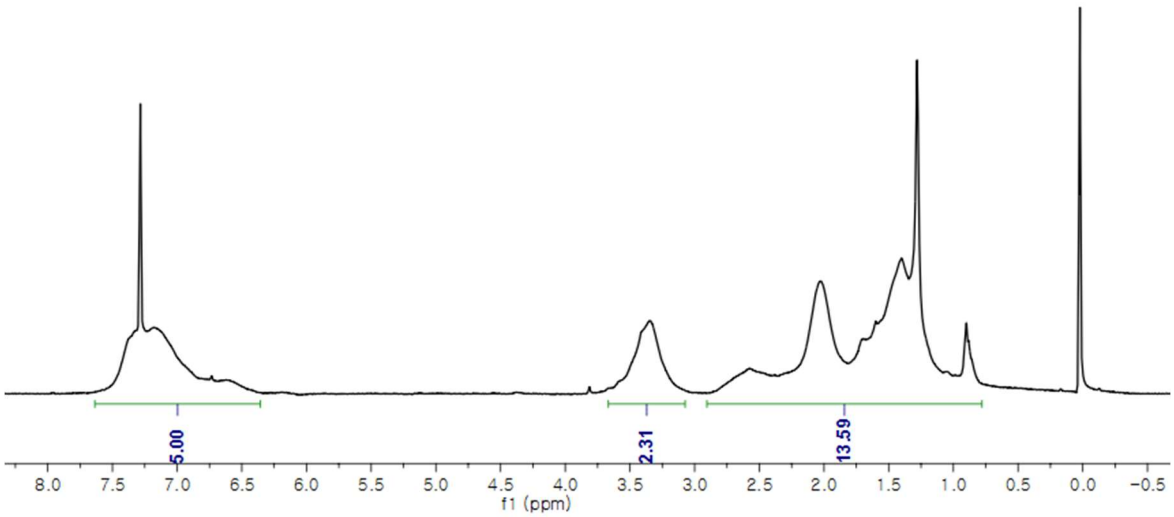
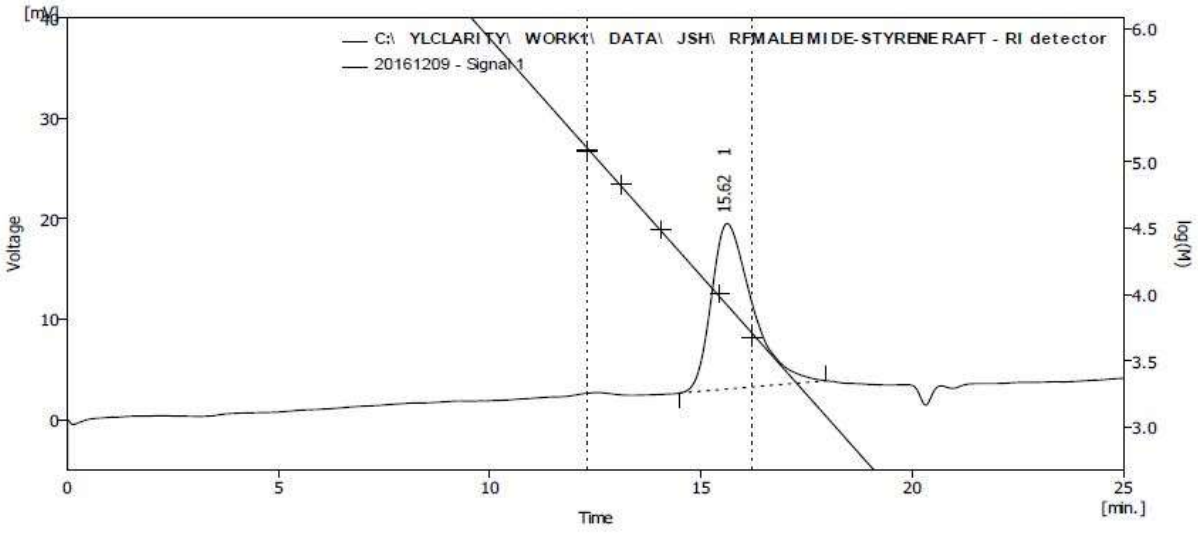
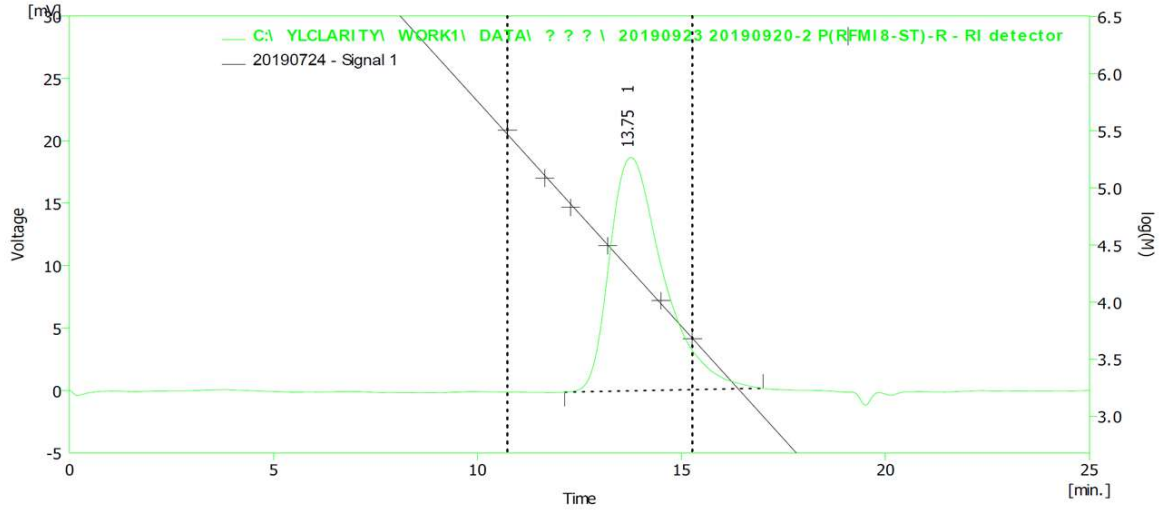


Fig. S10 : ^{1}H NMR spectrum of P(R_FMi-St)-R



	Max. RT	Start RT	End RT	Mn	Mw	PD	Height [mV]	Height [%]	Area [mV.s]	Area [%]
1	15.62	14.50	17.97	6255	7534	1.2044	16.47	100.00	1116.64	100.00

Fig S11 : GPC chromatogram and molecular weight information of P(R_FMi-St)-R



	Max. RT	Start RT	End RT	Mn	Mw	PD	Height [mV]	Height [%]	Area [mV.s]	Area [%]
1	13.75	12.14	17.00	11554	17309	1.4980	18.70	100.00	1714.42	100.00

Fig S12 : GPC chromatogram and molecular weight of P(R_FMi-St)-R

Mechanical properties measurement by nanoindentation

15wt% Solution of **P(R_FMi-St)** in PF-7600 was spin-coated on to a Si wafer and baked at 110 ° C for 1 min. The cast films (thickness *ca*. 650 nm) were exposed to e-beam with increasing doses of 100, 300, 500, 700, 900 and 1,100 µC cm^{-2}, and washed in PF-7600. A Berkovich diamond tip approached the polymer patterns with 100 nm s^{-1} and penetrated down to 300 nm with a strain rate of 0.05 s^{-1}. The vibration amplitude (2 nm) and frequency (100 Hz) were respectively used. Nine indentations were performed on each sample. The hardness and reduced modulus of the **P(R_FMi-St)** patches were compared with data collected at 200 nm penetration depth.