Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Electrospun aggregation-induced emission active POSS-based porous copolymer films for detection of explosives

Hui Zhou,[a] Qun Ye,[a] Wei Teng Neo,[a] Jing Song,[a] Hong Yan,[a] Yun Zong,[a] Ben Zhong Tang*[b] T. S. Andy Hor,[a,c] and Jianwei Xu*[a]

jw-xu@imre.a-star.edu.sg; tangbenz@ust.hk

[a] *Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), 3 Research Link, Singapore 117602, Republic of Singapore.*
[b] *Department of Chemistry, Center for Display Research, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon Hong Kong (PR China)*
[c] *Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Republic of Singapore.*

* Corresponding author: Jianwei Xu and Bengzhong Tang

Email address: jw-xu@imre.a-star.edu.sg; tangbenz@ust.hk

Mailing address: 3 Research Link, Singapore 117602

Tel: 65-6872-7543

Fax: 65-6872-7528

Experimental

General. Caution: 2,4,6-trinitrotuluene (TNT) is highly explosive and should be handled only in very small quantities with care. All synthetic manipulations were carried out under an atmosphere of dry argon gas using standard vacuum-line Schlenk techniques. All solvents were degassed and purified before use according to standard literature methods. Diethyl ether, hexanes, tetrahydrofuran, and toluene were purchased from Aldrich Chemical Co. Inc. and distilled from sodium/benzophenone ketyl before use.

Materials. TNT was prepared from DNT and recrystallized twice from methanol. DNT, nitrotoluene and other nitroaromatics was purchased from Aldrich. 2,2′-azoisobutyronitrile (AIBN) was purchased from Aldrich and purified by crystallization before use. Other commercially available reagents and solvents were used as received.

Instrumentation. ^{1}H, ^{13}C and ^{29}Si nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 400-MHz NMR spectrometer in $CDCl_3$ at room temperature using tetramethylsilane (TMS) as an internal standard. Operating frequencies of the NMR spectrometer were 400.13 MHz (^{1}H), 100.61 MHz (^{13}C) and 79.49 MHz (^{29}Si). Electron impact mass spectra (EIMS) and high resolution MS (HRMS) were recorded using a Micromass 7034E mass spectrometer. Elemental analysis was conducted on a Perkin-Elmer 240C elemental analyzer for C, H, and N determination. UV-vis and fluorescence spectra were obtained using a Shimadzu UV3101PC UV-vis-NIR spectrophotometer and a Perkin-Elmer LS 50B luminescence spectrometer with a Xenon lamp as light source, respectively. Thermal analysis was performed on a Perkin-Elmer thermogravimetric analyzer (TGA 7) in nitrogen or in air at a heating rate of 20 ^{o}C min^{-1} and on a TA Instruments Differential Scanning Calorimetry (DSC) 2920 at a heating rate and a cooling rate of 5 ^{o}C min^{-1} in nitrogen. The BET surface area (S_{BET}) was analyzed by Brunauer-Emmett-Teller (BET) theory based on two "consistency criteria". The external surface area (S_{ext}) was determined by t-plot method, and then the micropore surface area (S_{mic}) was obtained by subtracting the S_{ext} from the S_{BET}. The total pore volume (V_t) was calculated from the amount adsorbed at a relative pressure P/P_0 of 0.988. N_2 capture Characterization: N_2 adsorption isotherms were obtained on a Micromeritics ASAP 2020 surface area and porosity analyzer at -195.8 °C. Before adsorption characterizations, each sample was degassed under vacuum for 12 h at 100 °C.

Electrohydrodyamic preparation.

Polymer solution was prepared by dissolving polymer into a chloroform/acetone co-solvent (1:1, volume ration), which was then stirred at room temperature for overnight, and filtered by 0.2 µm filter before using. The experimental setup used for electrohydrodynanic preparation consists of four major components: a high voltage power source, a syringe with a flat, blunt tipped needle, an aluminum collector, and a syringe pump. Processing parameters for electrohydrodynamic preparation are summarized in Table S1. The nano/microstructured polymer substrates collected on the grounded aluminum collector with glass slides were place in an oven to vacuum dry at 25 ^{o}C for 24 hours before use.

Synthesis of compounds and Polymers.

12-(4-(1,2,2-triphenylvinyl)phenoxy)dodecan-1-ol (**2**). Potassium carbonate (165.9 mg, 1.2 mmol) was added to a solution of 4-(1,2,2-triphenylvinyl)phenol (**1**)[17d] (418.1 mg, 1.2 mmol) and 12-bromo-1-dodecanol (265.2 mg, 1.0 mmol) in anhydrous DMF (10.0 mL). The reaction mixture was stirred at 85 ^{o}C for 6 h and then at 105 ^{o}C for 1 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified on silica gel using column chromatography with a dichloromethane and ethyl acetate (20:1) mixture as the eluent, giving the desired product as light yellow solid: 910.0 m g (85.4%). ^{1}H NMR ($CDCl_3$): δ 7.10-7.01 (m, 15H), 6.91 (d, 2H, J = 8.9 Hz), 6.61 (d, 2H, J = 8.9 Hz), 3.87 (t, 2H, J = 6.5 Hz), 3.64 (t, 2H, J = 6.67 Hz), 1.72 (m, 2H), 1.28 (m, 18H). ^{13}C NMR ($CDCl_3$): δ 157.9, 144.2, 140.8, 140.2, 136.1, 132.6, 131.5, 127.8, 127.7, 126.5, 126.3, 113.8, 68.1, 63.3, 33.0, 29.7, 29.6, 29.5, 26.2, 25.9. IR (thin film): ν = 3598, 3075, 3048, 2919, 2851, 1953, 1888, 1605, 1574, 1509, 1491, 1474, 1443, 1287, 1244, 1175, 1074, 1030, 825, 763, 748, 699, 624, 615 cm^{-1}. HRMS (ESI): [M + K^{+}] calcd for $C_{38}H_{44}O_2K$, m/z 571.2978;

found, m/z 571.2937.

12-(4-(1,2,2-triphenylvinyl)phenoxy)dodecyl acrylate (**3**). 12-(4-(1,2,2-triphenylvinyl)phenoxy)dodecan-1-ol (**2**) (770.0 mg, 1.5 mmol) was dissolved in dry dichloromethane (10.0 mL). After adding 3.0 equiv. of triethylamine (607.0 μL, 4.5 mmol) to the solution, 2.0 equiv. of acryloyl chloride (235.0 μL, 3.0 mmol) were added drop wise at 0 °C. The mixture was then stirred at room temperature for 4 h. The ammonia salts were filtered off and the solvent was evaporated. The crude product was purified on silica gel using column chromatography with a dichloromethane and hexane (1:2) mixture as the eluent, giving the desired product white solid 866.9 mg (yield: 94.0%). ^{1}H NMR ($CDCl_3$): δ 7.10-7.02 (m, 15H), 6.91 (d, 2H, J = 8.9 Hz), 6.62 (d, 2H, J = 8.9 Hz), 6.40 (dd, 1H, J = 1.6, 17.2 Hz), 6.12 (dd, 1H, J = 10.5, 17.5 Hz), 5.81 (dd, 1H, J = 1.6, 10.5 Hz), 4.15 (t, 2H, J = 6.7 Hz), 3.87 (t, 2H, J = 6.7 Hz), 1.71 (m, 4H), 1.45-1.25 (m, 16H). ^{13}C NMR ($CDCl_3$): δ 157.9, 144.2, 140.8, 140.2, 136.1, 131.5, 130.4, 128.9, 127.9, 127.7, 126.5, 126.4, 113.8, 68.0, 64.9, 29.7, 29.6, 29.5, 29.4, 28.8, 26.2, 26.1. IR (thin film): ν = 3435, 3048, 2920, 2851, 1953, 1883, 1725, 1633, 1604, 1574, 1509, 1492, 1475, 1442, 1407, 1293, 1243, 1192, 1.74, 1029, 984, 823, 810, 762, 747, 699, 614 cm^{-1}. HRMS (ESI): [M + Na$^+$] calcd for $C_{41}H_{46}O_3Na$, m/z 609.3345; found, m/z 609.3328.

General Procedure for Polymerizations. All polymers were prepared by free radical polymerization of the corresponding monomers in the presence of AIBN. A solution of 0.50 mmol of monomer and 1.5 mg of AIBN dissolved in 1.0 mL of dry THF was degassed by three freeze/thaw cycles. The solutions were stirred for 48 h at 70 °C in sealed vessels. The viscous solutions were then precipitated into methanol and the solid filtered off. The polymer was re-dissolved in 5.0 mL of THF and re-precipitated. The polymer was then filtered and dried under vacuum at 60 °C for 72 hours.

*Polymer **P1***. Yield: 52.9%; ^{1}H NMR ($CDCl_3$): δ 7.04 (m, 15H), 6.90 (m, 2H), 6.60 (m, 2H), 4.03 (br, 2H), 3.84 (br, 2H), 2.28 (br, 1H), 1.71 (m, 2H), 1.59 (m, 3H), 1.45-1.22 (m, 17H). ^{13}C NMR ($CDCl_3$): δ 157.8, 144.2, 144.1, 140.7, 140.1, 136.0, 132.6, 131.5, 131.4, 131.3, 127.8, 127.7, 127.6, 126.5, 126.3, 113.7, 67.9, 29.8, 29.7, 29.6, 29.5, 28.8, 26.3, 26.2, 26.1. Anal. Calcd for $(C_{41}H_{46}O_3)_n$: C, 83.92; H, 7.09. Found: C, 83.77; H, 7.27.

Polymer ***P2*.** Yield: 51.5%; ^{1}H NMR ($CDCl_3$): δ 7.03 (m, 45H), 6.90 (m, 6H), 6.61 (m, 6H), 4.03 (br, 10H), 3.85 (br, 6H), 2.27 (br, 5H), 1.85 (m, 17H), 1.71 (m, 11H), 1.61 (m, 6H), 1.40 (m, 6H), 1.28 (m, 48H), 0.96 (d, 84H), 0.61 (d, 32H). ^{13}C NMR ($CDCl_3$): δ 157.8, 144.2, 144.1, 140.7, 140.1, 136.0, 132.6, 131.6, 131.5, 131.4, 127.8, 127.7, 127.6, 126.5, 126.3, 113.7, 67.9, 29.8, 29.7, 29.6, 29.5, 29.4, 28.8, 26.2, 26.1, 25.9, 25.8, 24.1, 23.9, 22.6, 22.5, 8.5. ^{29}Si NMR ($CDCl_3$): δ -59.0. Anal. Calcd for $(C_{191}H_{282}O_{37}Si_{16})_n$: C, 70.10; H, 7.87, Si, 8.35. Found: C, 69.95; H, 7.98, Si, 8.29.

Polymer ***P3*.** Yield: 50.7%; ^{1}H NMR ($CDCl_3$): δ 7.03 (m, 15H), 6.90 (m, 2H), 6.61 (m, 2H), 4.03 (br, 8H), 3.85 (br, 2H), 2.27 (br, 4H), 1.85 (m, 25H), 1.71 (m, 10H), 1.61 (m, 2H), 1.40 (m, 2H), 1.28 (m, 16H), 0.96 (d, 126H), 0.61 (d, 48H). ^{13}C NMR ($CDCl_3$): δ 157.8, 144.2, 144.1, 140.8, 140.1, 136.0, 132.6, 131.6, 131.5, 131.4, 127.8, 127.7, 126.5, 126.3, 113.7, 67.9, 66.6, 64.8, 29.8, 29.5, 25.9, 25.8, 24.0, 23.9, 22.6, 22.5, 22.3, 8.5. ^{29}Si NMR ($CDCl_3$): δ -59.0. Anal. Calcd for $(C_{143}H_{262}O_{45}Si_{24})_n$: C, 50.88; H, 7.82, Si, 19.97. Found: C, 50.69; H, 8.01, Si, 19.91.

Polymer ***P4***. Yield: 48.1%; ^{1}H NMR ($CDCl_3$): δ 7.03 (m, 15H), 6.90 (m, 2H), 6.61 (m, 2H), 4.03 (br, 14H), 3.85 (br, 2H), 2.27 (br, 7H), 1.85 (m, 52H), 1.71 (m, 16H), 1.61 (m, 2H), 1.40 (m, 2H), 1.28 (m, 16H), 0.96 (d, 252H), 0.61 (d, 96H). ^{13}C NMR ($CDCl_3$): δ 157.8, 144.2, 140.7, 140.1, 136.0, 132.6, 131.6, 131.5, 131.4, 127.8, 127.7, 127.6, 126.5, 126.3, 113.7, 67.9, 66.6, 29.8, 29.7, 29.6, 29.5, 28.8, 26.2, 26.1, 25.9, 25.8, 24.1, 24.0, 23.9, 22.6, 22.5, 8.4. ^{29}Si NMR ($CDCl_3$): δ -59.0. Anal. Calcd for $(C_{245}H_{478}O_{87}Si_{48})_n$: C, 47.74; H, 7.82, Si, 21.87. Found: C, 47.61; H, 7.95, Si, 21.69.

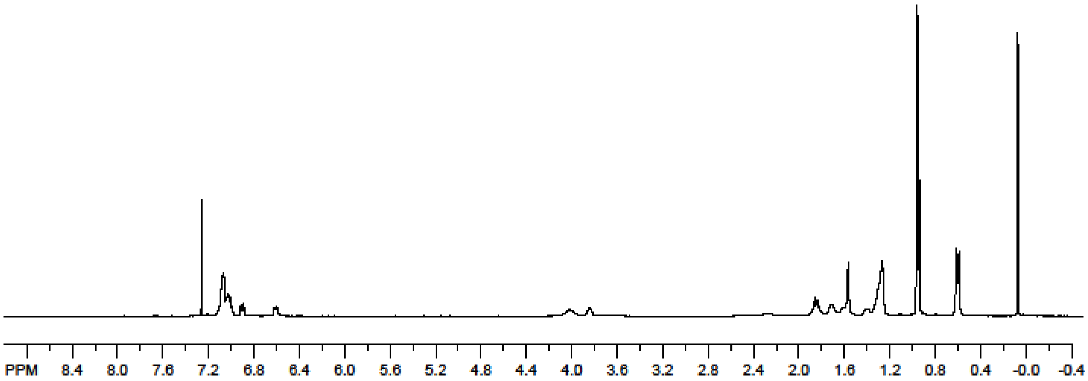


Fig. S1 ^{1}H NMR spectrum of polymer **P2** in $CDCl_3$.

Table S1 Processing parameters for electrohydrodynamic preparation (**F1**-**F6**), drop coating (**F7**) and spin coating preparation (**F8**).

Film	polymer	Concentration (wt%)	Voltage (kV)	Flow rate (mL/h)	Distance (cm)	Time (h)
F1	**P1**	2.0	9.7	4.0	10.0	1.0
F2	**P2**	2.0	9.7	4.0	10.0	1.0
F3	**P3**	2.0	9.7	4.0	10.0	1.0
F4	**P4**	2.0	9.7	4.0	10.0	1.0
F5	**P4**	5.0	9.7	4.0	10.0	1.0
F6	**P4**	10.0	9.7	4.0	10.0	1.0
F7	**P4**	2.0	Drop coating			
F8	**P4**	2.0	Spin coating			

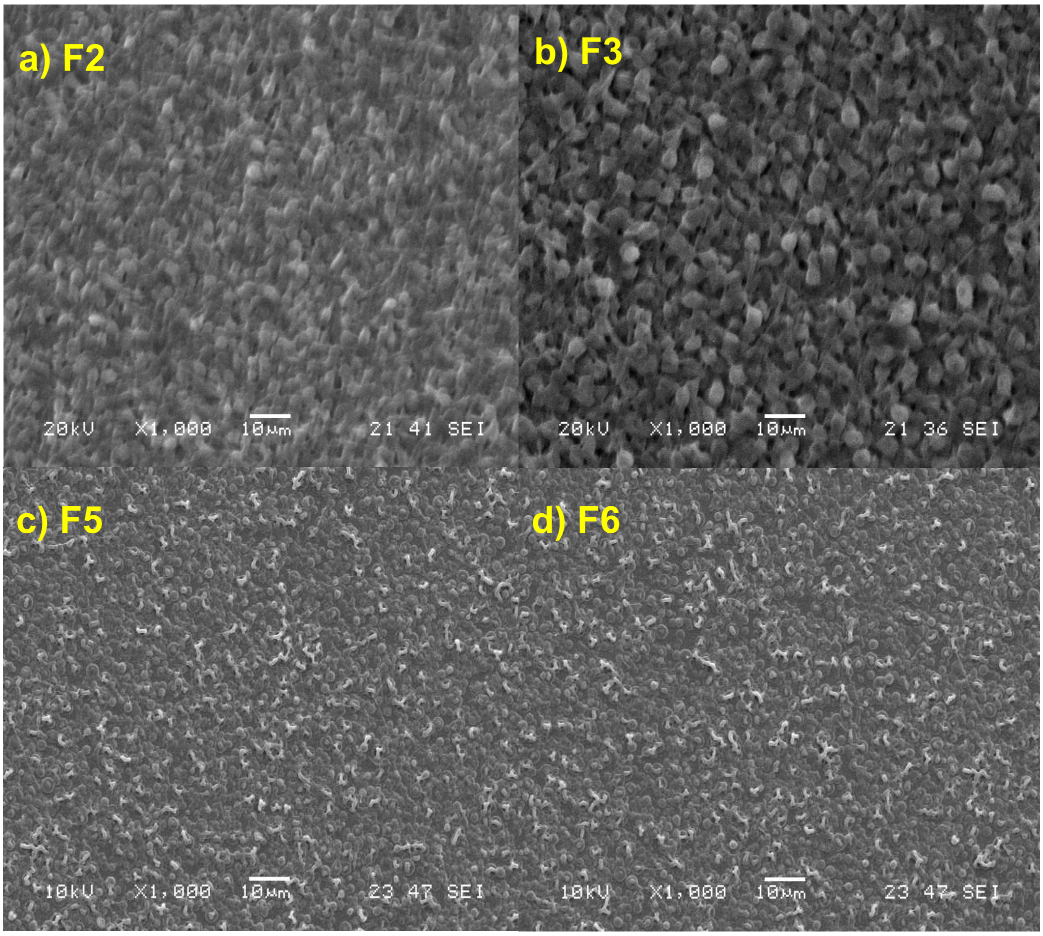


Fig. S2 SEM images of films produced by electrohydrodynamic preparation: (a) **F2**, (b) **F3**, (c) **F5** and (d) **F6**. See processing parameters in Table S1.

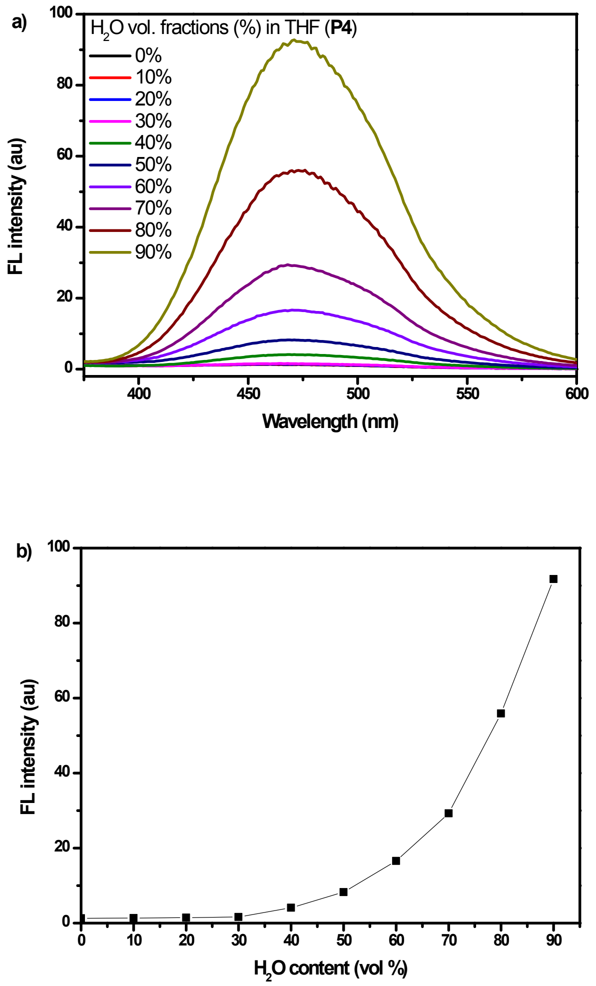


Fig. S3 (a) Fluorescence spectra of polymer **P4** in THF/H_2O mixtures with different H_2O contents (λ_{ex} = 318 nm, [**P4**] = 100.0 μg•mL^{-1}, inserted pictures are photographs of **P4** solutions taken under UV illumination (λ_{ex} = 365 nm)). (b) Fluorescence intensity maximum of **P4** in THF/H_2O mixtures ([**P4**] = 100.0 μg•mL^{-1}).

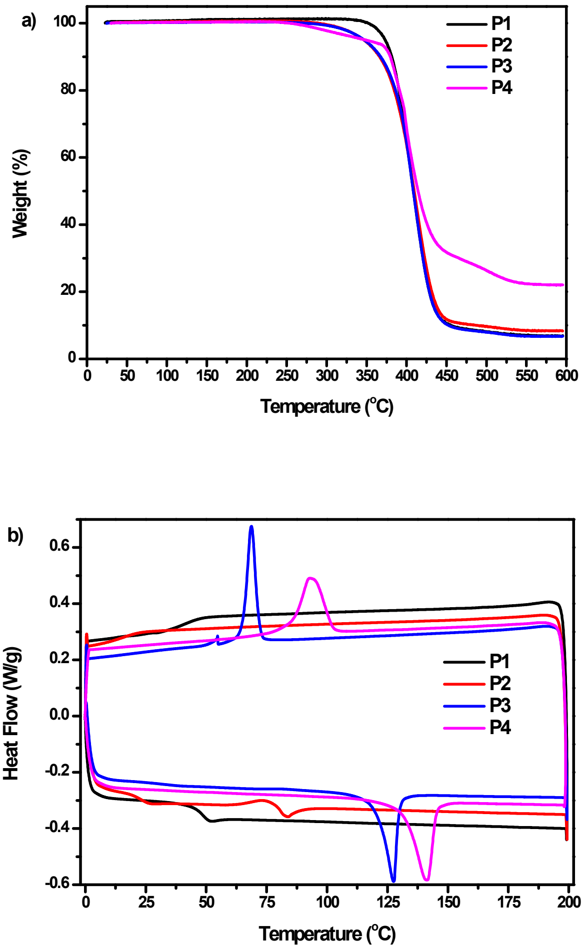


Fig. S4 (a) TGA thermograms of polymers **P1-4** under nitrogen at a heating rate of 20 ^{o}C•min^{-1}. (b) DSC thermograms of polymers **P1-4** under nitrogen at a heating rate of 10 ^{o}C•min^{-1}.

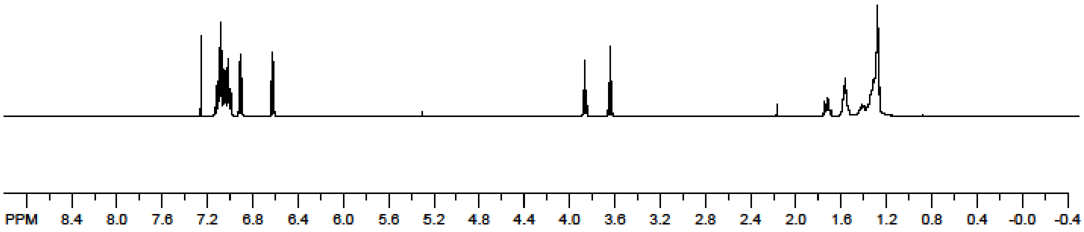


Fig. S5 ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

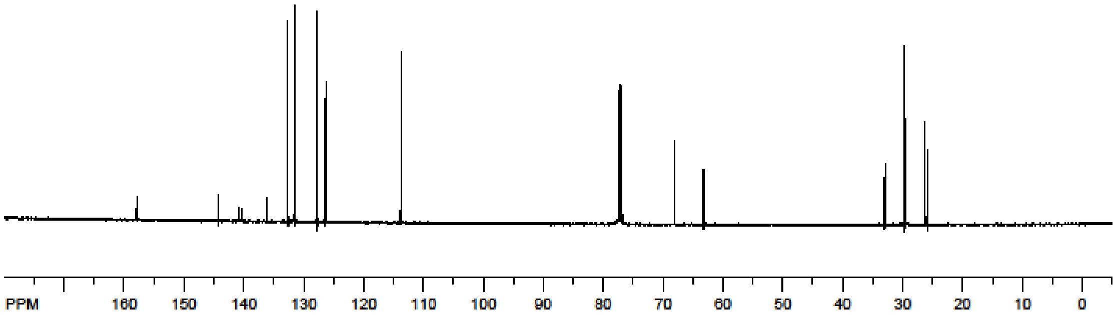
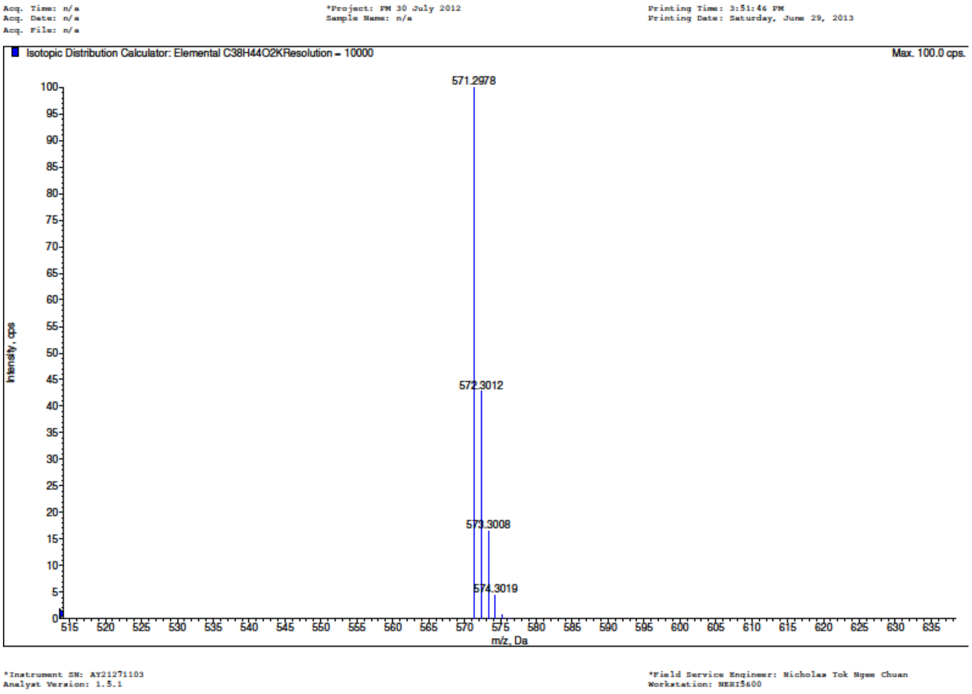


Fig. S6 ^{13}C NMR spectrum of compound **2** in $CDCl_3$.


Acq. Time: n/a
Acq. Date: n/a
Acq. File: n/a

*Project: PM 30 July 2012
Sample Name: n/a

Printing Time: 3:51:46 PM
Printing Date: Saturday, June 29, 2013

Isotopic Distribution Calculator: Elemental C38H44O2KResolution = 10000

Max. 100.0 cps.

*Instrument SN: AY21271103
Analyst Version: 1.5.1

*Field Service Engineer: Nicholas Tok Ngee Chuan
Workstation: NERI5600

Fig. S7 HRMS spectrum of compound **2**.

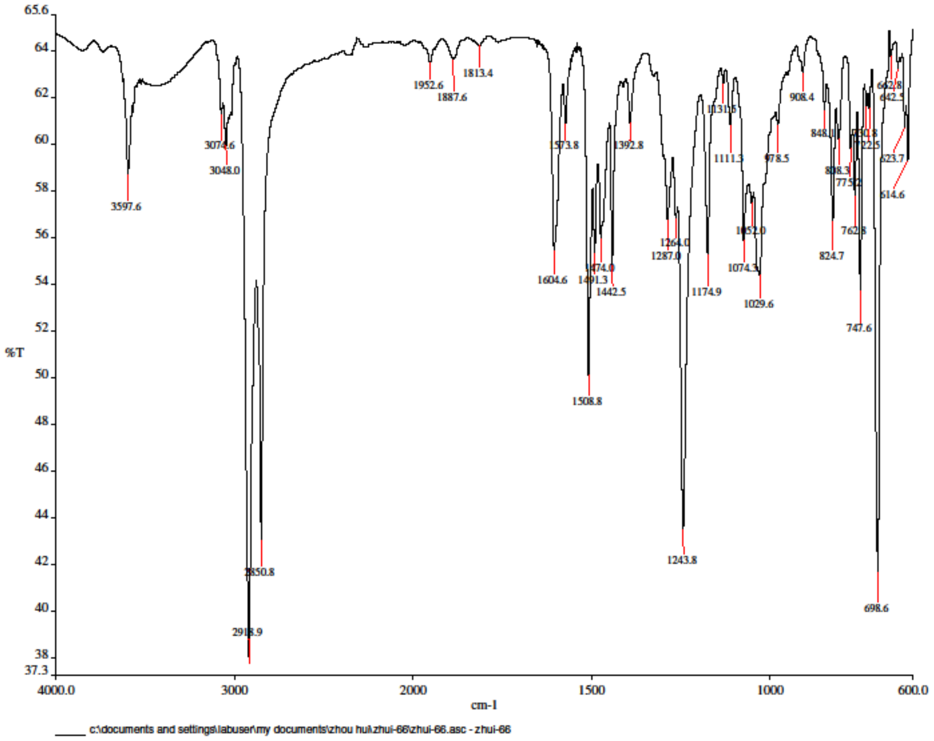


Fig. S8 FTIR spectrum of compound **2**.

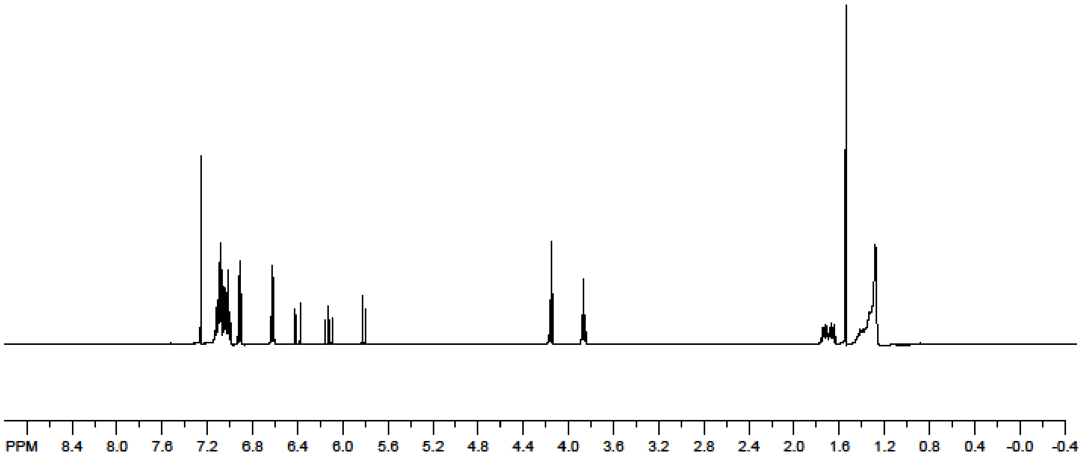


Fig. S9 ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

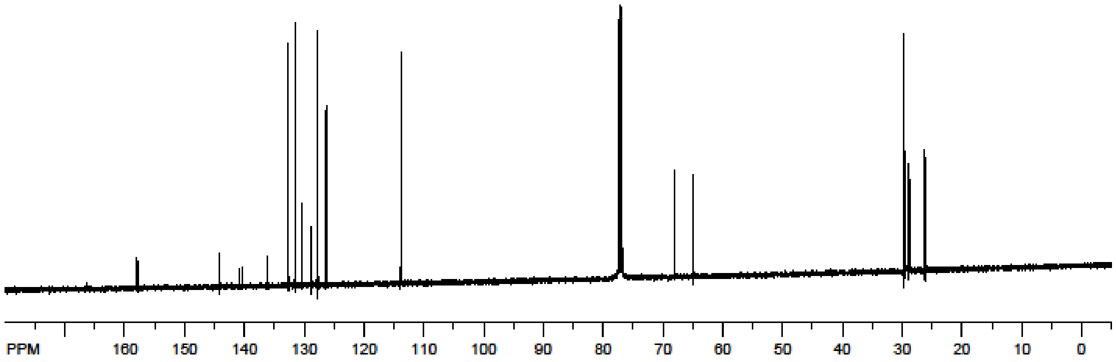
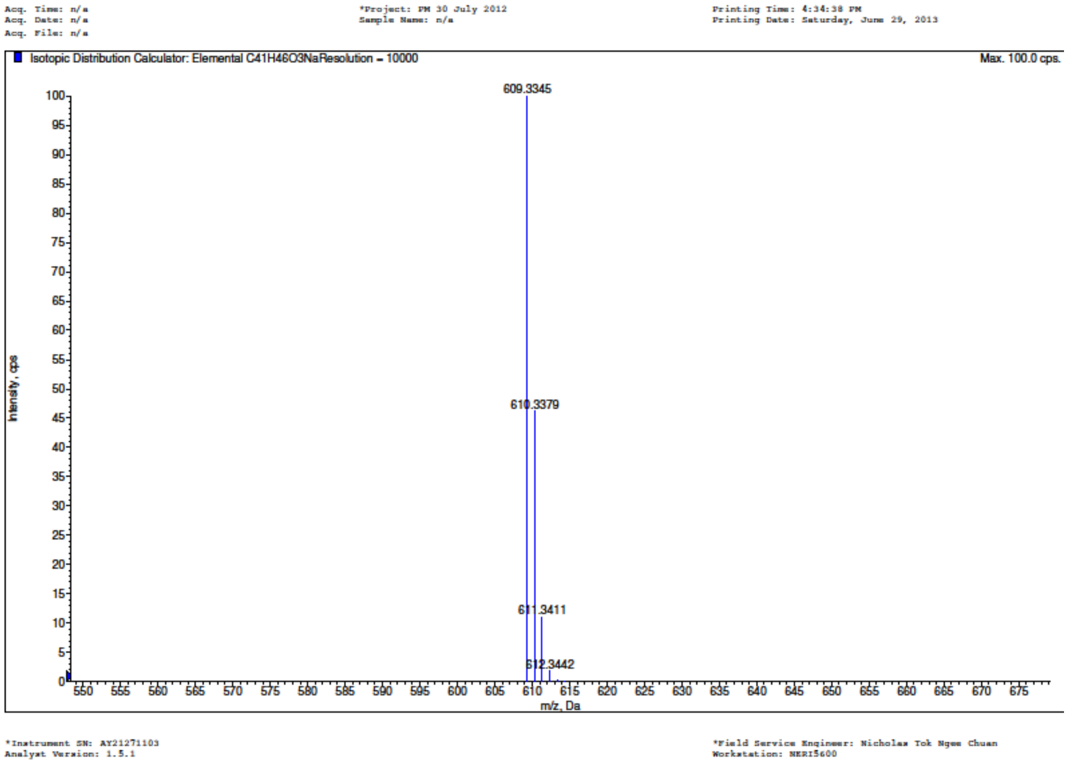


Fig. S10 ^{13}C NMR spectrum of compound **3** in $CDCl_3$.



Acq. Time: n/a
Acq. Date: n/a
Acq. File: n/a

*Project: PM 30 July 2012
Sample Name: n/a

Printing Time: 4:34:38 PM
Printing Date: Saturday, June 29, 2013

Isotopic Distribution Calculator: Elemental C41H46O3NaResolution = 10000

Max. 100.0 cps.

*Instrument SN: AY21271103
Analyst Version: 1.5.1

*Field Service Engineer: Nicholas Tok Ngee Chuan
Workstation: NERI5600

Fig. S11 HRMS spectrum of compound **3**.

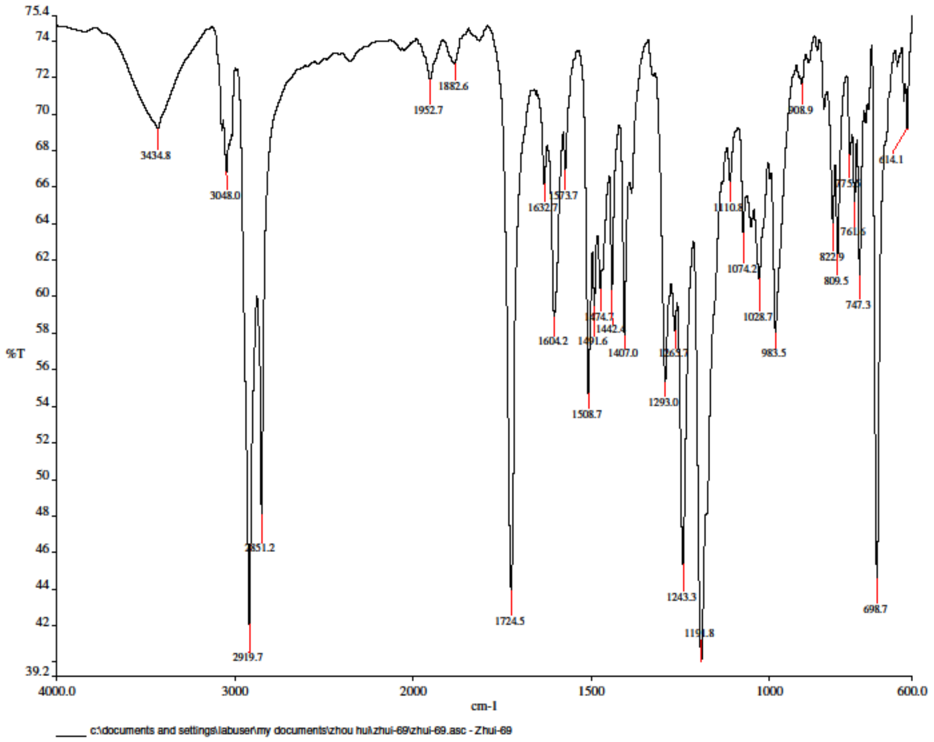


Fig. S12 FTIR spectrum of compound **3**.

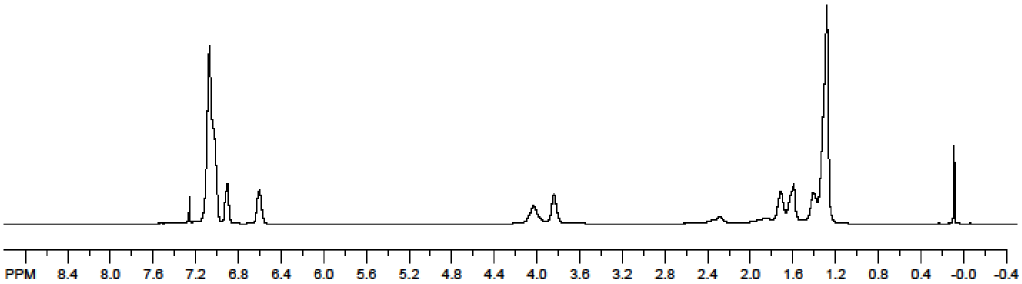


Fig. S13 ^{1}H NMR spectrum of polymer **P1** in $CDCl_3$.

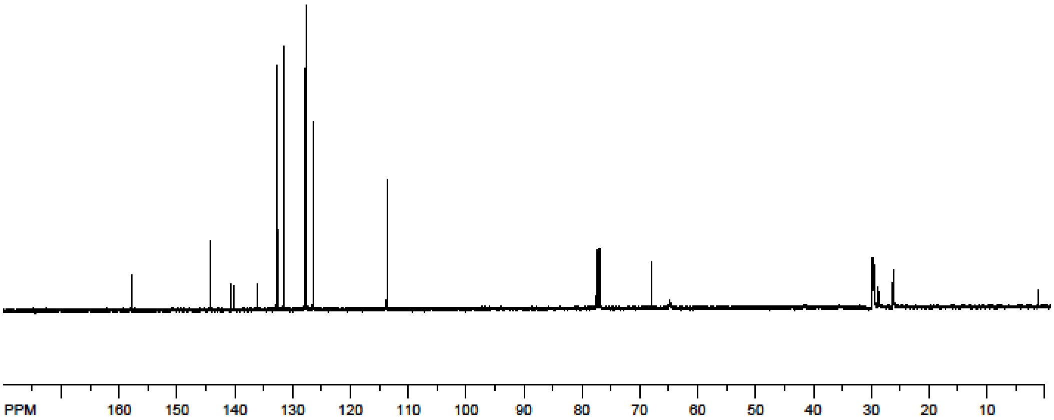


Fig. S14 ^{13}C NMR spectrum of polymer **P1** in $CDCl_3$.

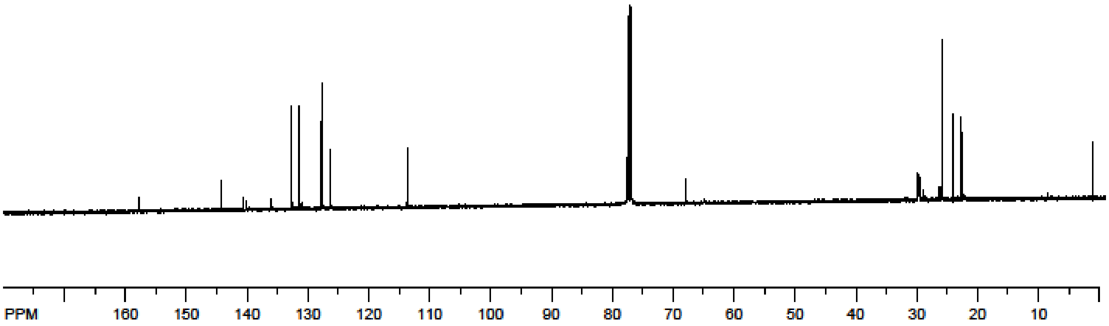


Fig. S15 ^{13}C NMR spectrum of polymer **P2** in $CDCl_3$.

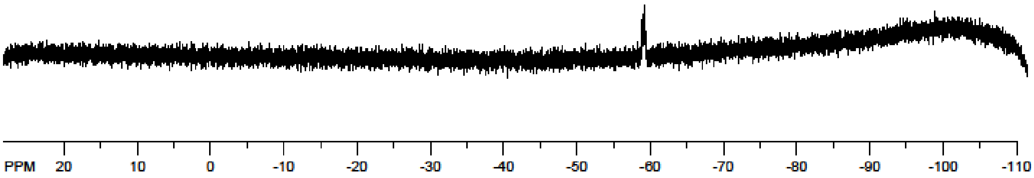


Fig. S16 ^{29}Si NMR spectrum of polymer **P2** in $CDCl_3$.

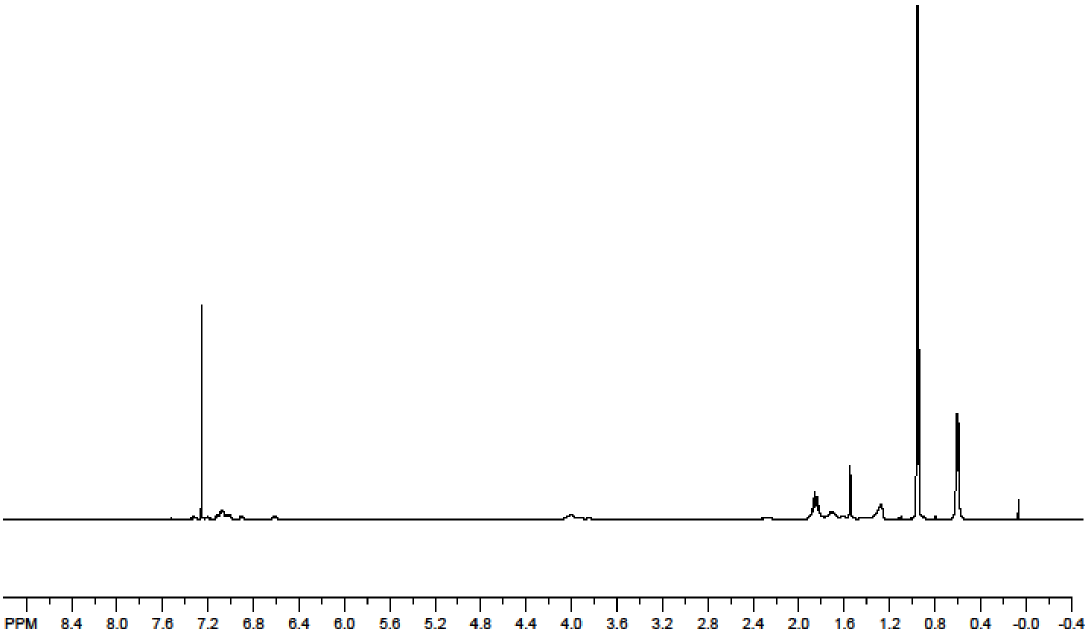


Fig. S17 ^{1}H NMR spectrum of polymer **P3** in $CDCl_3$.

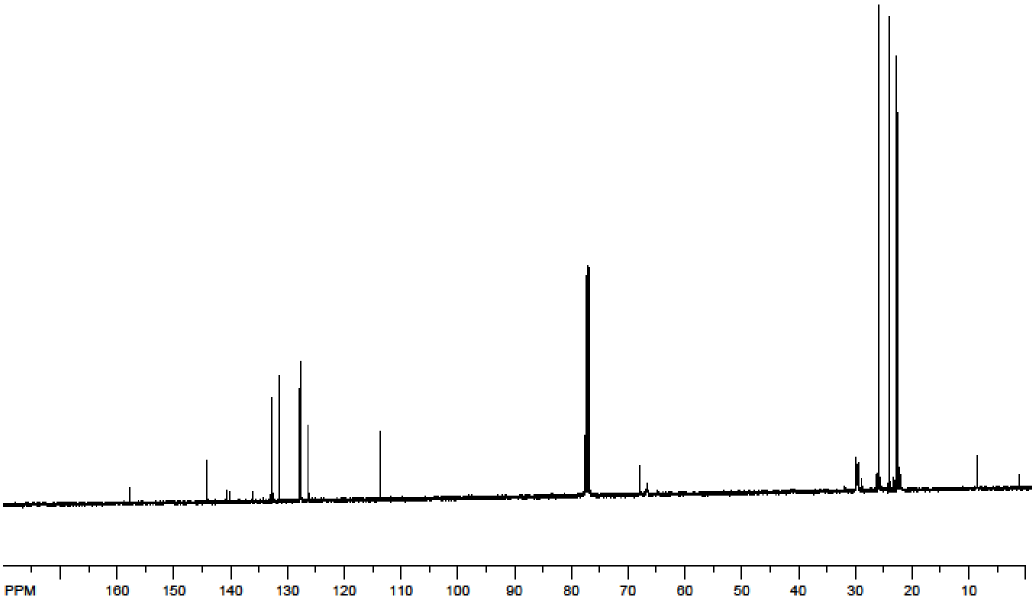


Fig. S18 ^{13}C NMR spectrum of polymer **P3** in $CDCl_3$.

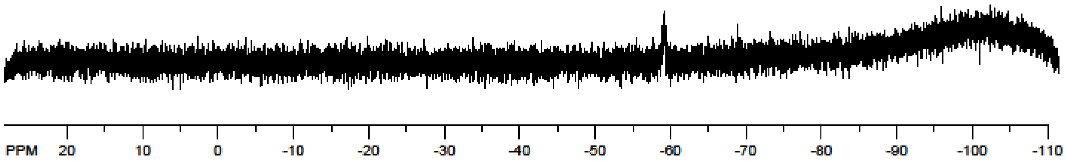


Fig. S19 ^{29}Si NMR spectrum of polymer **P3** in CDCl$_3$.

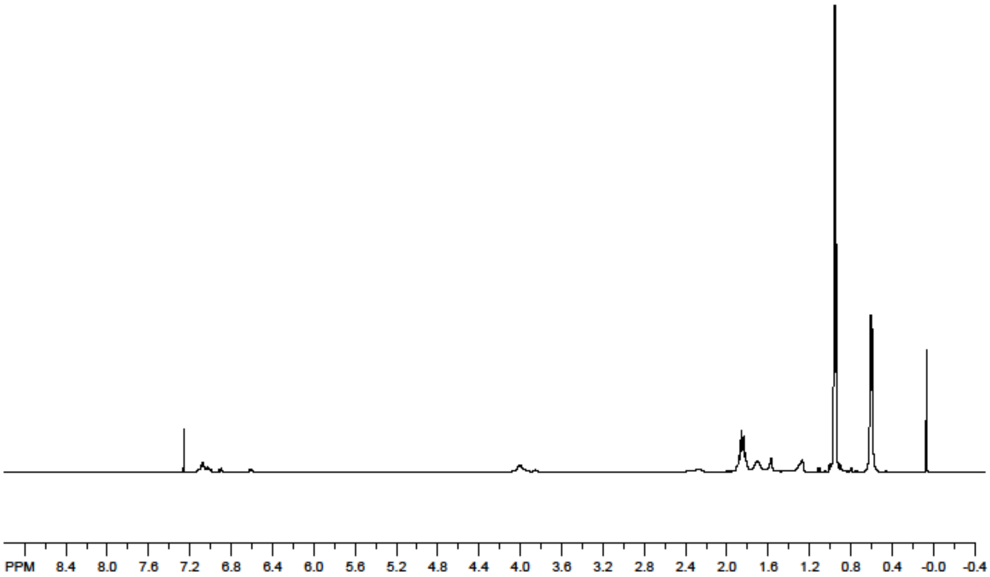


Fig. S20 ^{1}H NMR spectrum of polymer **P4** in CDCl$_3$.

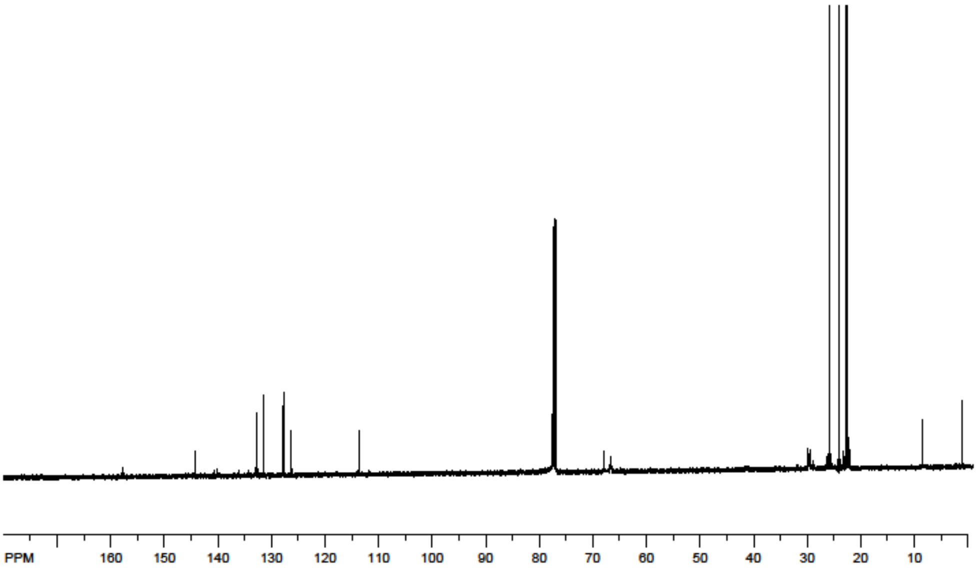


Fig. S21 ^{13}C NMR spectrum of polymer **P4** in CDCl$_3$.

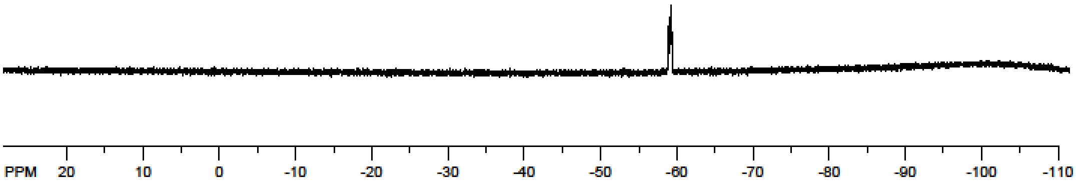


Fig. S22 ^{29}Si NMR spectrum of polymer **P4** in CDCl$_3$.