Supporting information

A novel, highly gas-permeable polymer representing a new class of silicon-containing polynorbornens as efficient membrane materials

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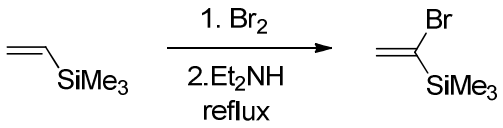
1.Synthesis of PTCNSi2g

Synthesis of 1-bromo-1-trimethylsilylethene. [1]



Scheme S1.

A three-necked, round-bottomed flask equipped with a mechanical stirrer and a dropping funnel was charged with 86.1 g (0.86 mol) of vinyltrimethylsilane**.** The content of the flask was cooled to −78° and 163 g (52 mL, 1.02 mol) of bromine was added dropwise over 1 hour. The cooling bath was removed, and the red viscous mixture was allowed to warm to room temperature. The flask was fitted with an efficient water-cooled condenser and 407 g (575 mL, 5.57 mol) of diethylamine was cautiously added with continued stirring. After the addition was complete, the reaction mixture was heated at reflux for 12 hours, during which time a precipitate of diethylamine hydrobromide formed. The salt was separated from the cooled suspension by filtration and washed with several 300-mL portions of diethyl ether. The ether filtrate was carefully washed, first with 100-mL portions of 10% hydrochloric acid until the aqueous layer remains acidic, then with 100 mL of water and 200 mL of saturated aqueous sodium chloride. The ether solution was dried with anhydrous magnesium sulfate, concentrated, and distilled under reduced pressure. Yield: 115 g (75 %), b.p. 72–75° (120 mmHg)

^{1}H ($CDCl_3$): 6.25 (d, ^{2}J = 2 Hz, 1H, CH_2=), 6.16(d, ^{2}J = 2 Hz, 1H, CH_2=), 0.18 (s, 9H, Si(CH_3)$_3$) (Figure S1).

^{13}C ($CDCl_3$):138.9, 129.3, -2.2 (Figure S2).

^{29}Si ($CDCl_3$):-0.23 (Figure S3).

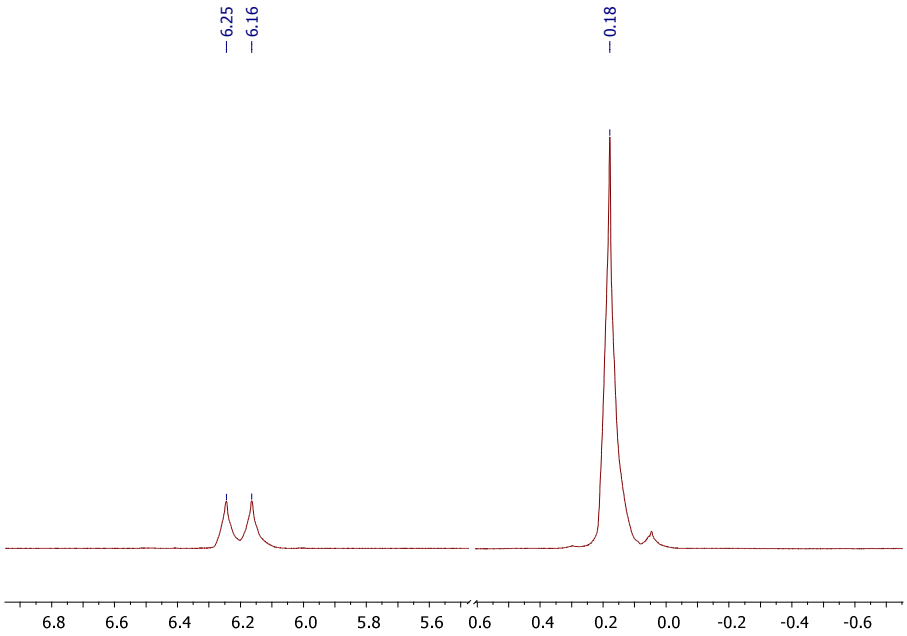


Figure S1. ^{1}H NMR spectrum of 1-bromo-1-trimethylsilylethene ($CDCl_3$).

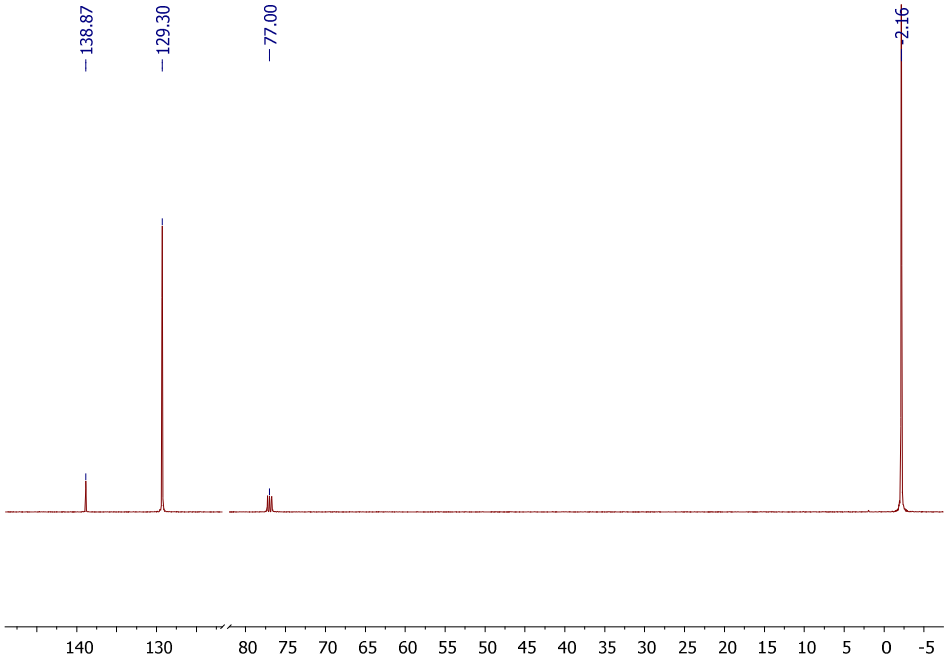


Figure S2. ^{13}C NMR spectrum of 1-bromo-1-trimethylsilylethene($CDCl_3$).

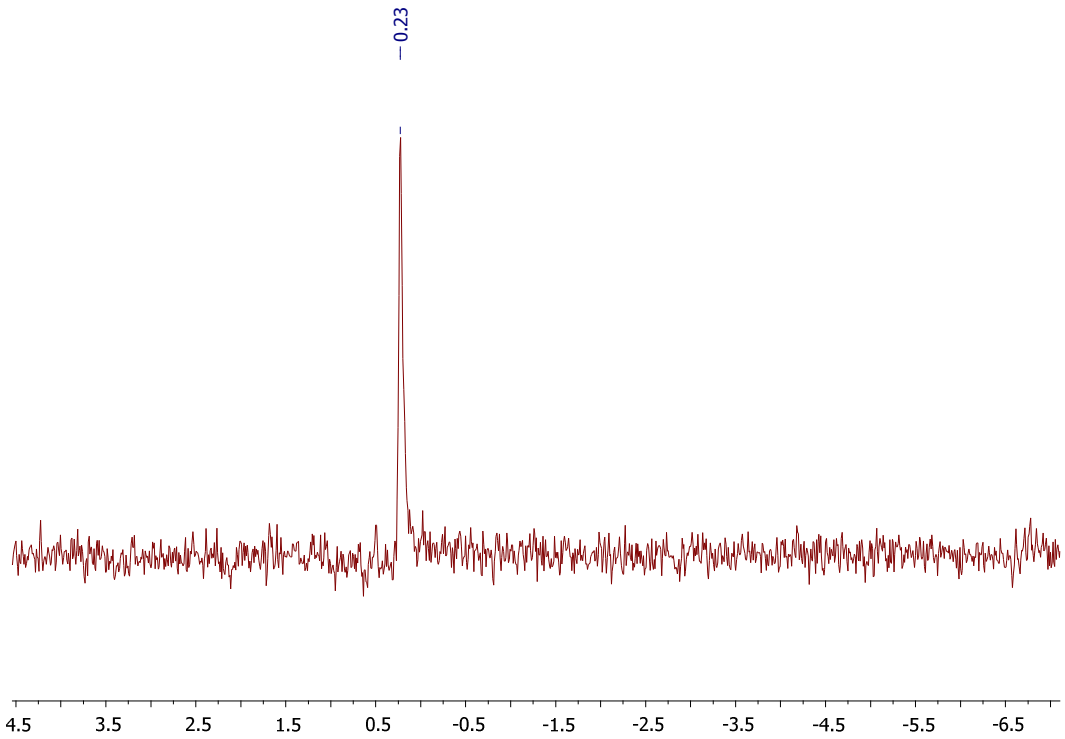
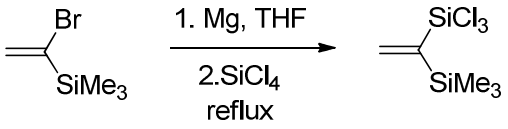


Figure S3. ^{29}Si NMR spectrum of 1-bromo-1-trimethylsilylethene ($CDCl_3$).

Synthesis of 1-trichlorosilyl-1-trimethylsilylethene. [2]



Scheme S2.

52 g (0.29 mol) of 1-bromo-1-trimethylsilylethene was used to form the Grignard reagent in 500 mL of THF. This was added to 88.0 g (0.52 mol, 59 mL) of pure $SiCl_4$ and the resulting mixture refluxed for 3 h. After cooling, excess $SiCl_4$ and the most of THF were removed by distillation under inert atmosphere. The remaining slurry was extracted with three 100 mL portions of hexane.

This solution was then distilled, the product boiling at 110-112 ^{o}C/98 mmHg was collected. Yield: 37.0 g (57%).

^{1}H ($CDCl_3$): 6.85 (d, ^{2}J = 4.8 Hz, 1H, CH_2=), 6.63 (d, ^{2}J = 4.8 Hz, 1H, CH_2=), 0.31 (s, 9 H) (Figure S4).

^{13}C ($CDCl_3$): 147.6, 147.4, -0.52 (Figure S5).

^{29}Si ($CDCl_3$): -0.26, -1.39 (Figure S6).

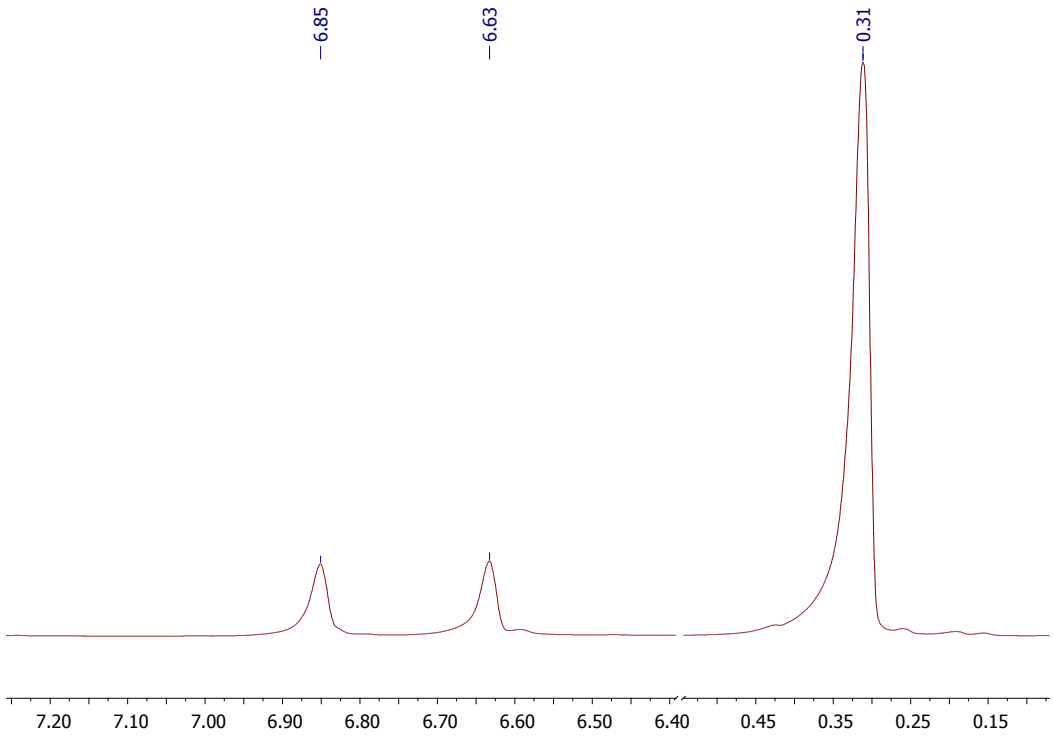


Figure S4. ^{1}H NMR spectrum of 1-trichlorosilyl-1-trimethylsilylethene ($CDCl_3$).

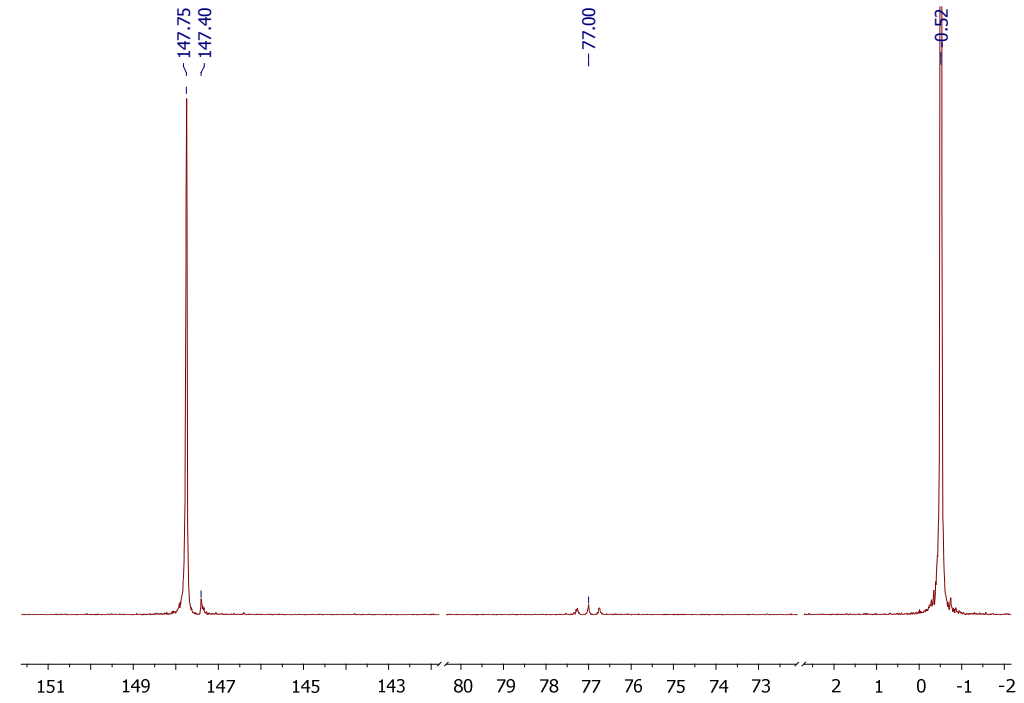


Figure S5. ^{13}C NMR spectrum of 1-trichlorosilyl-1-trimethylsilylethene ($CDCl_3$).

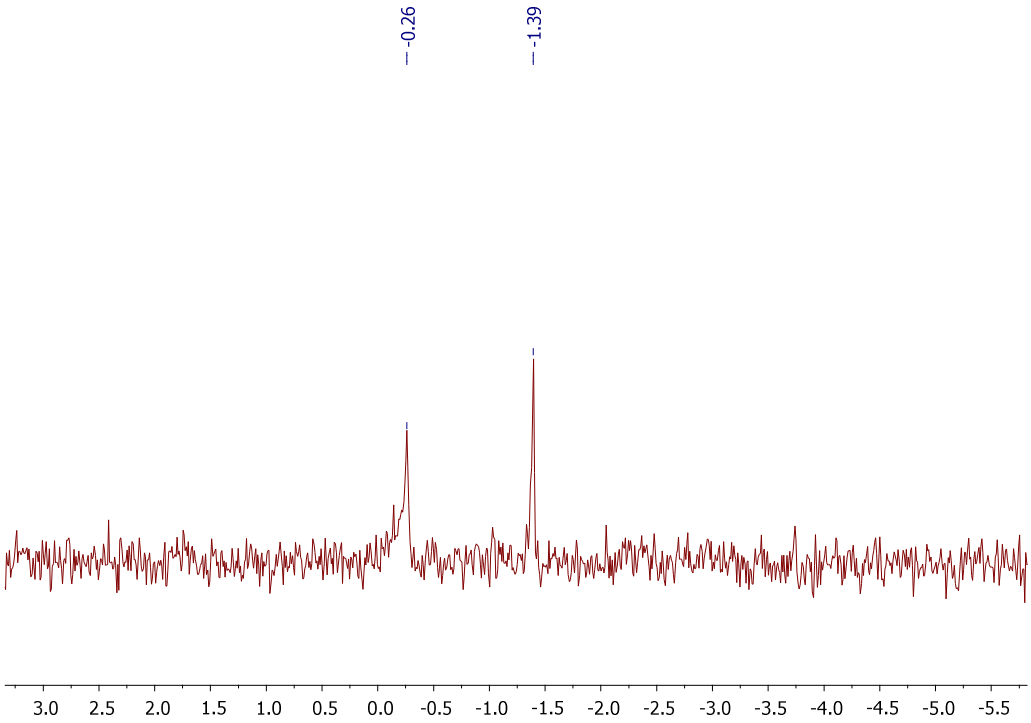
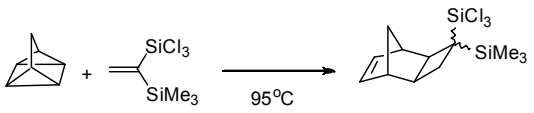


Figure S6. ^{29}Si NMR spectrum of 1-trichlorosilyl-1-trimethylsilylethene ($CDCl_3$).

Synthesis of 3-trichlorosilyl-3-trimethysilyltricyclononene-7.



Scheme S3.

An oven-dried ampoule equipped with a magnetic stirring bar and preliminary evacuated and filled with argon was charged with 23.0 g (0.25 mol) of quadricyclane and with 39.0 g (0.17 mol) of 1-trichlorosilyl-1-trimethylsilylethene under argon The ampoule was sealed and heated at 95 °C for 150 h. The conversion was controlled by ^{1}H-NMR. The reaction mixture was concentrated and separated from the light fractions under reduced pressure (0.05 mmHg, 60 °C). The residue was the cycloadduct (*syn-/anti*-isomers) was obtained as colorless oil. Yield: 48.9 g (90%).

^{1}H ($CDCl_3$): 5.66-5.53 (m, 2H, C*H*=C*H*), 2.98 (br.s, 0.7H), 2.70 (br.s, 0.3H), 2.40 (br.s, 1H), 2.18-1.45 (m, 5H), 1.12-1.03 (m, 1H) -0.03 –(-0.07) (m, 9H, $SiMe_3$) (Figure S7).

^{13}C ($CDCl_3$) : 135.6, 135.2, 135.1, 135.0, 45.0, 44.9, 44.1, 43.9, 43.8, 42.5, 42.1, 42.0, 36.8, 36.7, 26.86, 26.13, 23.8, 23.5, 2.0, -1.4 (Figure S8).

^{29}Si ($CDCl_3$): 9.8, 8.2, 6.9, 0.4 (Figure S9).

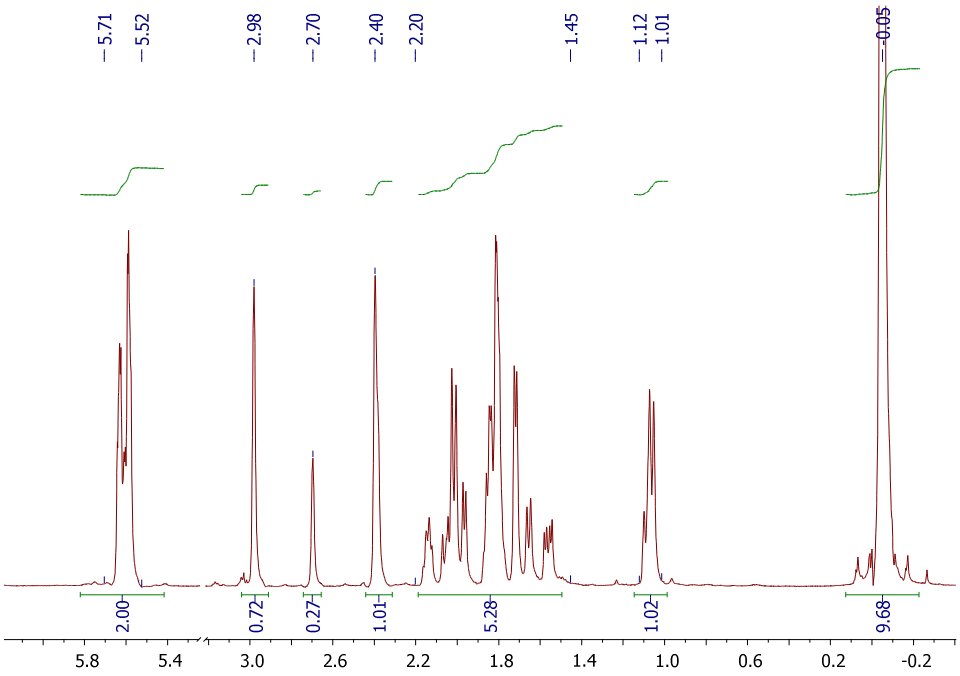


Figure S7. ^{1}H NMR spectrum of 3-trichlorosilyl-3-trimethysilyltricyclononene-7 ($CDCl_3$).

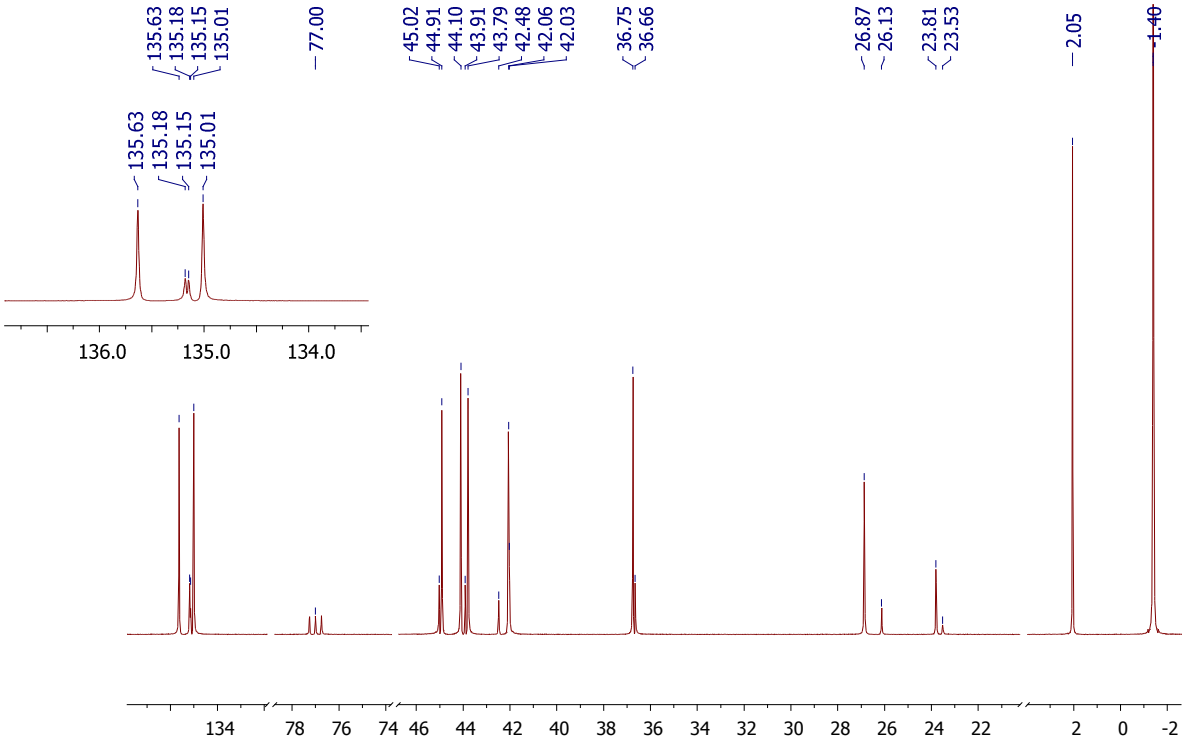


Figure S8. ^{13}C NMR spectrum of 3-trichlorosilyl-3-trimethysilyltricyclononene-7 ($CDCl_3$).

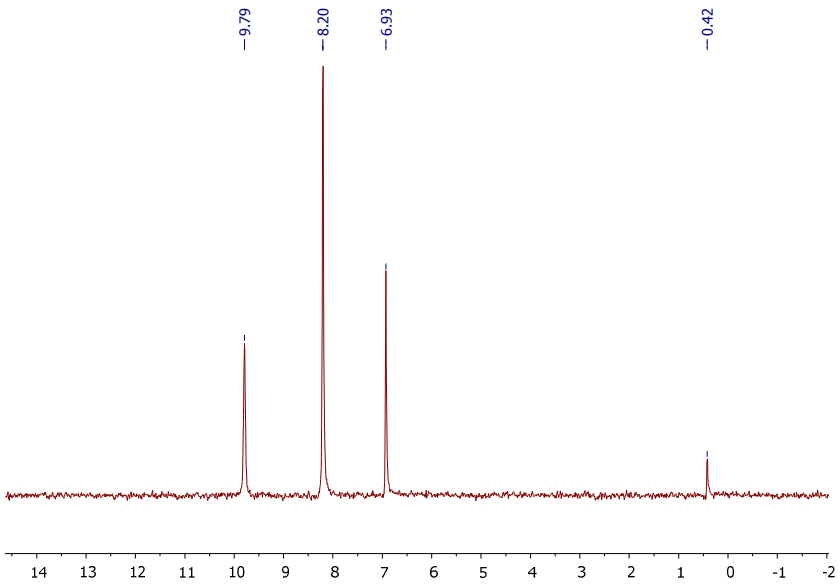
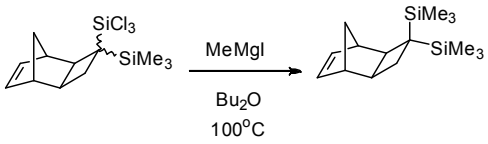


Figure S9. ^{29}Si NMR spectrum of 3-trichlorosilyl-3-trimethysilyltricyclononene-7 ($CDCl_3$).

Synthesis of 3,3-bis(trimethylsilyl)tricyclononene-7 (TCNSi2g).



Scheme S4.

To a MeMgI solution prepared from Mg (15.3 g, 0.63 mol) and methyl iodide (81.1 g, 0.57 mol) in di-*n*-butyl ether (250 mL) 3-trichlorosilyl-3-trimethysilyltricyclononene-7 (27.9 g, 85.6 mmol) in di-*n*-butyl ether (10 mL) was added dropwise heated to reflux and then heated additionally at 100°C for 15h. The reaction mixture was poured into cooled water. The water fraction was extracted with diethyl ether (5 × 70 mL). Combined organic fractions were dried over $MgSO_4$ and solvents were evaporated under reduced pressure (1 mmHg). The residue was purified by flash chromatography (the height of silicagel padw was 10 cm, the eluent was hexane). The product was obtained as a transparent oily liquid. Yield 83% (18.7 g). NMR data is consistent with literature data. [3]

^{1}H ($CDCl_3$): 5.97-5.79 (m, 2H, C*H*=C*H*), 2.88 (br.s, 1H), 2.59 (br.s, 1H), 2.11-2.04 (m, 1H), 2.01 (d, 1H,^{2}J=8.7Hz), 1.94-1.86 (m, 1H), 1.83 (d, 1H,^{3}J=6.8Hz),1.72-1.63 (m, 1H), 1.26 (d, 1H,^{2}J=8.7Hz), 0.07 (br.s, 18H, 2$SiMe_3$) (Figure S10)

^{13}C ($CDCl_3$): 136.1, 134.6, 45.8, 42.2, 43.05, 42.1, 37.0, 26.1, 13.9, 2.2, 1.2 (Figure S11).

^{29}Si ($CDCl_3$): 4.9, -0.1 (Figure S12).

MS (EI): 264, M^+ (2%), 249, $[M\text{-}CH_3]^+$ (1%), 73, $[SiMe_3]^+$ (100%) (Figure S13).

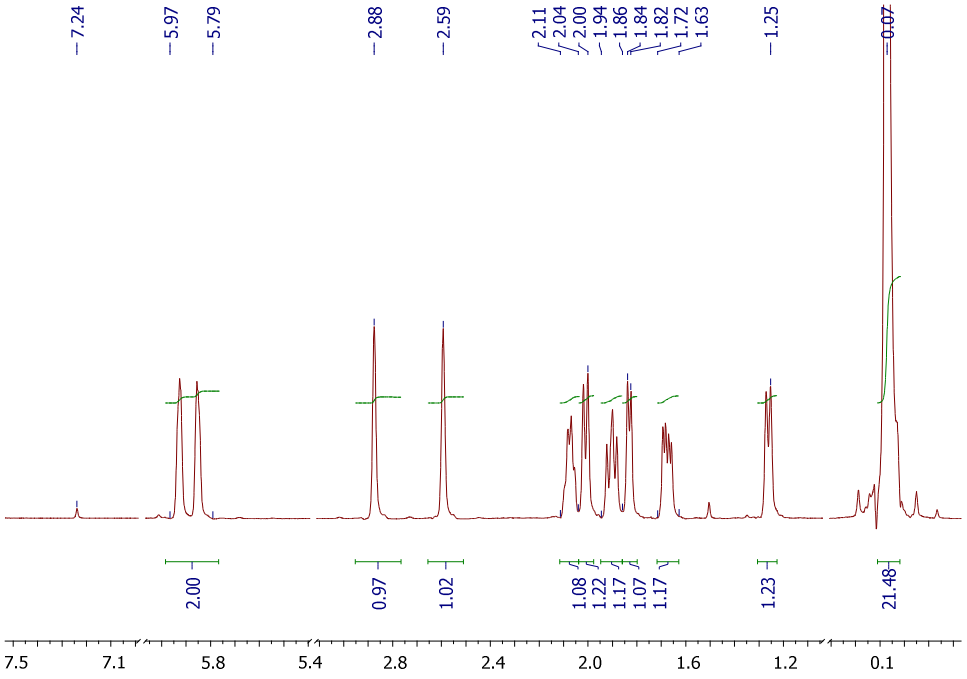


Figure S10. ^{1}H NMR spectrum of 3,3-bis(trimethylsilyl)tricyclononene-7 ($CDCl_3$).

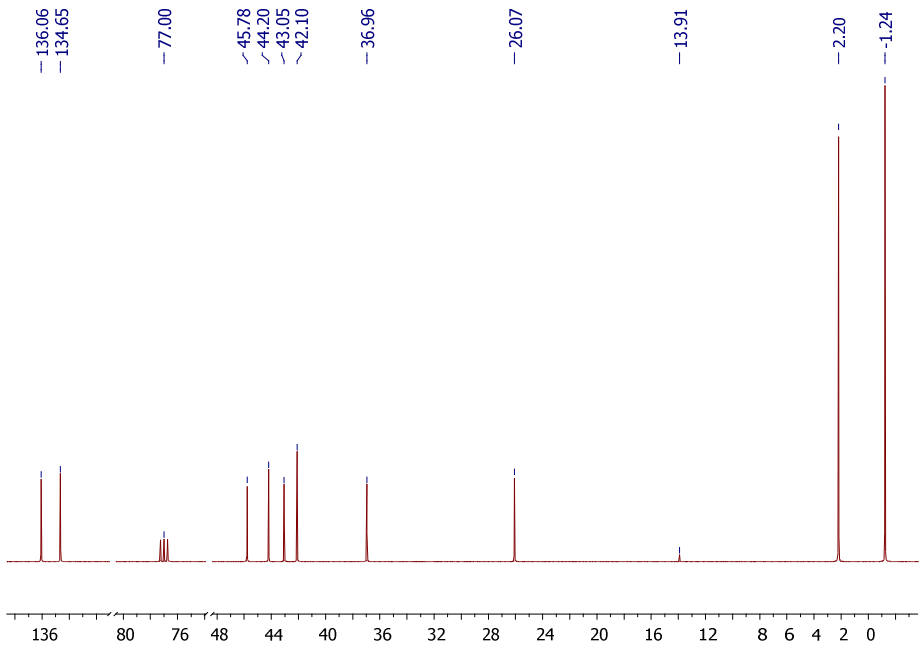


Figure S11. ^{13}C NMR spectrum of 3,3-bis(trimethylsilyl)tricyclononene-7 ($CDCl_3$)

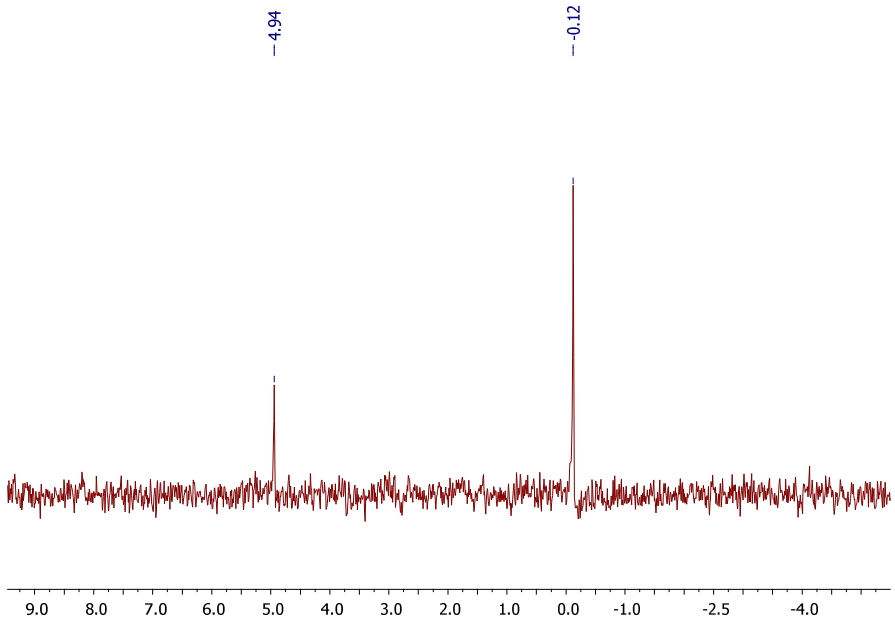


Figure S12. ^{29}Si NMR spectrum of 3,3-bis(trimethylsilyl)tricyclononene-7 ($CDCl_3$)

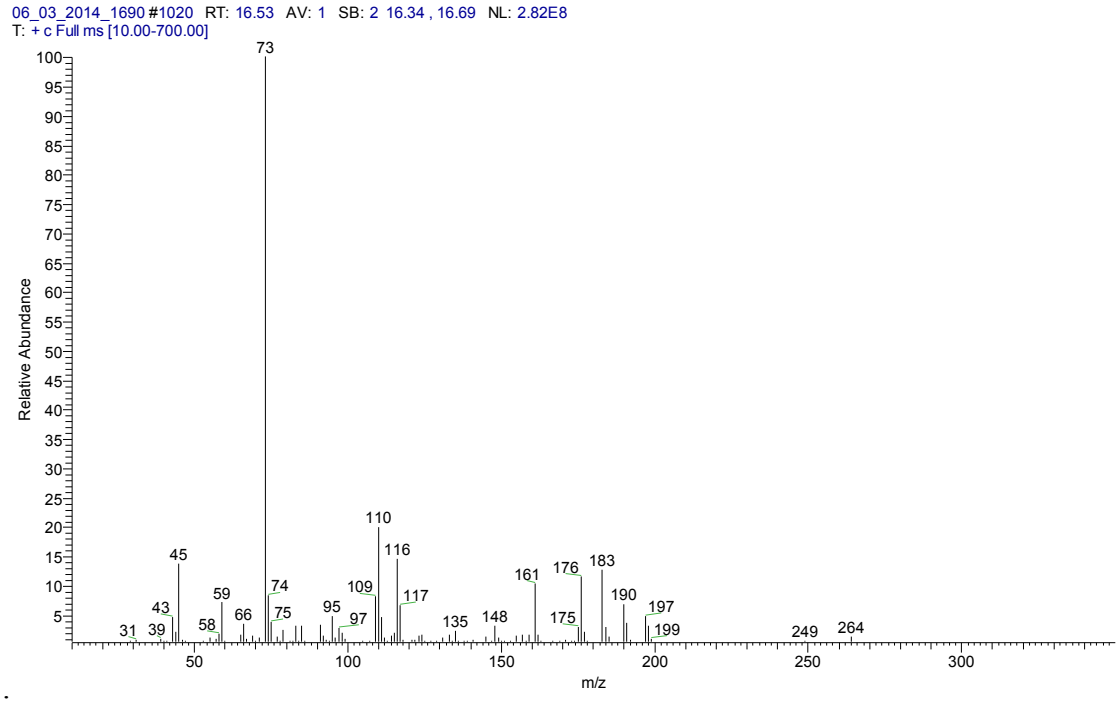


Figure S13. Mass-spectrum (EI) of 3,3-bis(trimethylsilyl)tricyclononene-7.

Addition polymerization of 3,3-bis(trimethylsilyl)tricyclononene-7 (PTCNSi2g).

In the typical procedure (the example is given for ratio **TCNSi2g**/$Pd(OAc)_2$/$[Ph_3C][B(C_6F_5)_4]$= 3200/1/5), the toluene solution of $Pd(OAc)_2$ (1.82 mL, $4.74 \cdot 10^{-3}$ mmol, 2.6 mM) and the monomer (4.0 g, 15.15 mmol) were introduced into round-bottom Schlenk flask equipped with a magnetic stirrer preliminary purged in vacuum and filled with argon. Polymerization was initiated by adding of 6.36 mM toluene solution of $[Ph_3C][B(C_6F_5)_4]$ (3.72 mL, $2.37 \cdot 10^{-2}$ mmol). The reaction mixture was continuously stirred for 24 h at ambient temperature (25^oC). The polymer was precipitated by ethanol, separated, washed by several portions of ethanol and dried in vacuum. It was twice reprecipitated by ethanol from toluene solution and dried in vacuum at 80-90^0C up to a constant weight. Yield: 2.0 g. (50%).

^1H (C_6D_6): 3.14-1.45 (m, 10H), 0.28 (br.s, 18H) (Figure S13)

^{13}C (C_6D_6): 57.4-38.4, 30.2, 20.8-15.8, 2.3, -0.7 (Figure S14).

^{29}Si (C_6D_6): 5.0, -0.9 (Figure S15).

IR (ATR): 2950, 2901, 2867, 1477, 1453, 1411, 1250, 1163, 1110, 1043, 982, 945, 829, 757, 677, 635 (Figure S16).

Elemental analysis: calculated: C, 68.10%; H, 10.67%. Found: C, 68.35%; H, 10.79%.

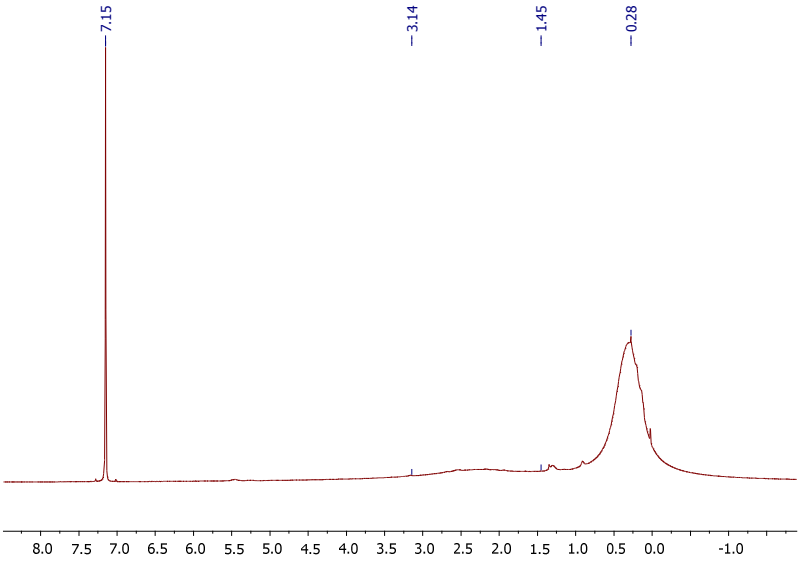


Figure S14. ^{1}H NMR spectrum of addition poly(3,3-bis(trimethylsilyl)tricyclononene-7) **PTCNSi2g** (C_6D_6).

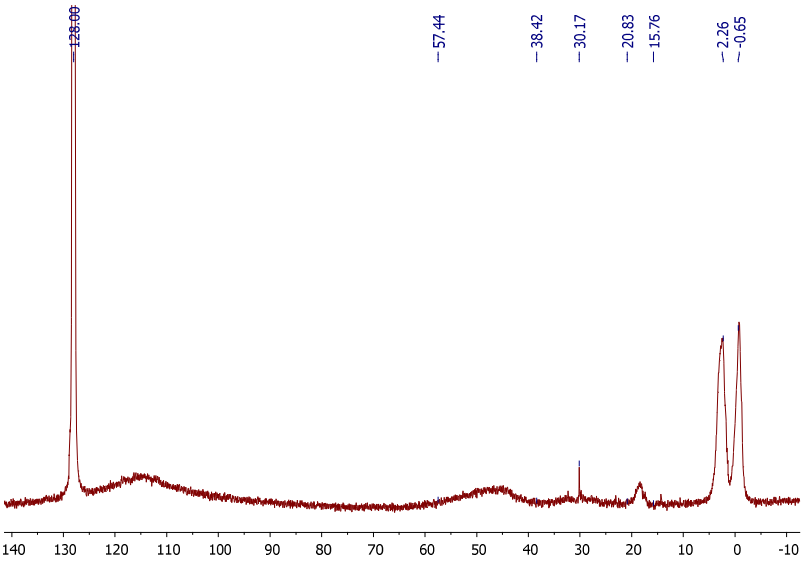


Figure S15. ^{13}C NMR spectrum of addition poly(3,3-bis(trimethylsilyl)tricyclononene-7) **PTCNSi2g** (C_6D_6).

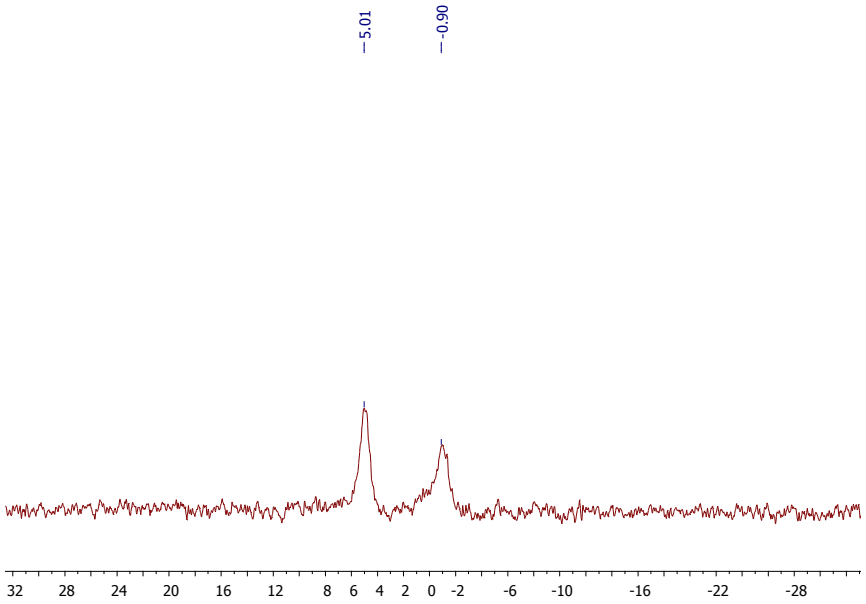


Figure S16. ^{29}Si NMR spectrum of addition poly(3,3-bis(trimethylsilyl)tricyclononene-7) (**PTCNSi2g**) (C_6D_6).

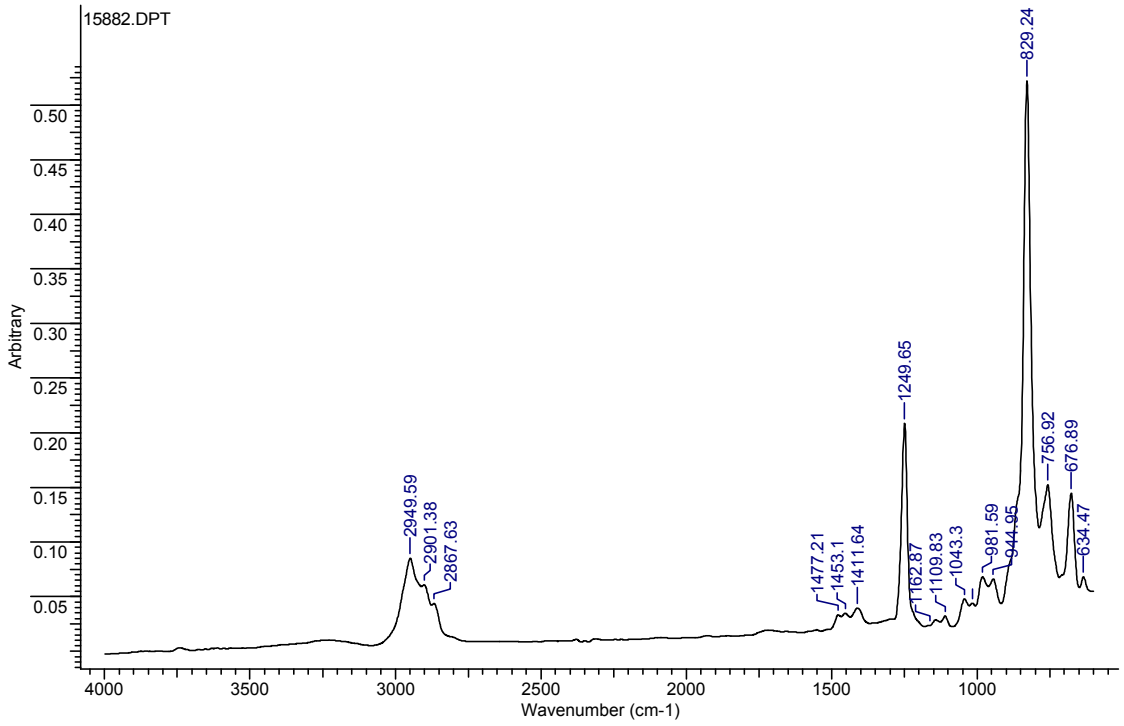


Figure S17. IR spectrum (ATR) of addition poly(3,3-bis(trimethylsilyl)tricyclononene-7) (**PTCNSi2g**).

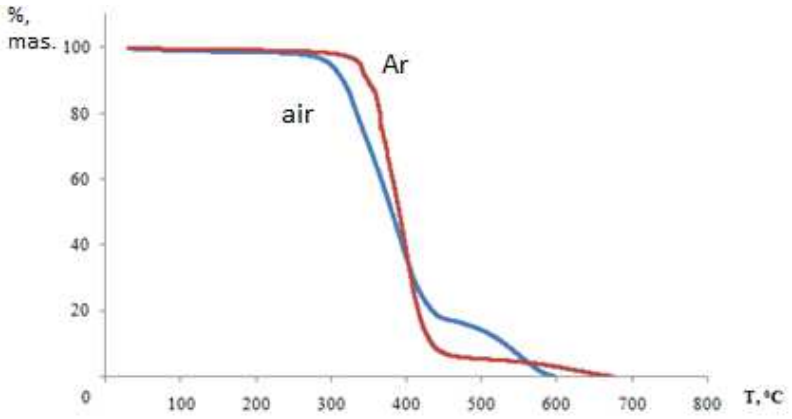


Figure S18. TGA of addition poly(3,3-bis(trimethylsilyl)tricyclononene-7) (**PTCNSi2g**).

2. Brief description of the method for determination solubility coefficients

A new method for determining the solubility coefficients of gases in polymers combines the advantages of the static and dynamic approaches to sorption estimation. It allows one to determine the equilibrium characteristics of sorption for small quantities of samples (0.1–0.2 g) and at low (<0.5 atm) partial pressures of the gas under investigation. It implies sorption of gases into a film sample with subsequent desorption into a chromatographic detector. Because of this, high sensitivity is provided. In the method it must be reliably separated the quantity of the sorbed gas and the gaseous molecules presenting in the gas phase of the vessel (loop) in which a polymer sample is placed. It is thus necessary at the first stage to measure quantity of gas in the loop volume without the studied material, i.e., to determine *empty* volume. This procedure can be performed at different partial pressures of the studied gas. At the second stage, a membrane material with known weight is placed in the loop, through which the studied gas with known partial pressure is purged up to a complete saturation. The gas is then desorbed by the carrier gas into a chromatographic detector to determine the total quantity of gas. The third stage of measurements consists of evaluating the quantity of sorbed gas by subtracting the quantity of gaseous phase in the sorption space (loop) from the total quantity detected by thermal conductivity detector. The detection unit was the detector of a

Kristallux 4000M gas chromatograph equipped with a thermal conductivity sensor. The sorption–desorption unit of the instrument is a chromatographic loop connected to six-port injection valve. The ribbon films were placed into sorption tubular cell (inner diameter 2 mm, length of the tube was app. 40 mm). The masses of the polymer in the cells were 0.0231 and 0.0114 g respectively. The former sample was used to measure sorption isotherms of light gases (N_2, O_2, CH_4 and CO_2) and initial parts of isotherms of C_2-C_4 hydrocarbons, whereas the second one – to evaluate sorption isotherms of the C_2-C_4 alkanes in the whole pressure range. More details of the new sorption technique and calculations can be found elsewhere.[4]

3.Gas-transport data

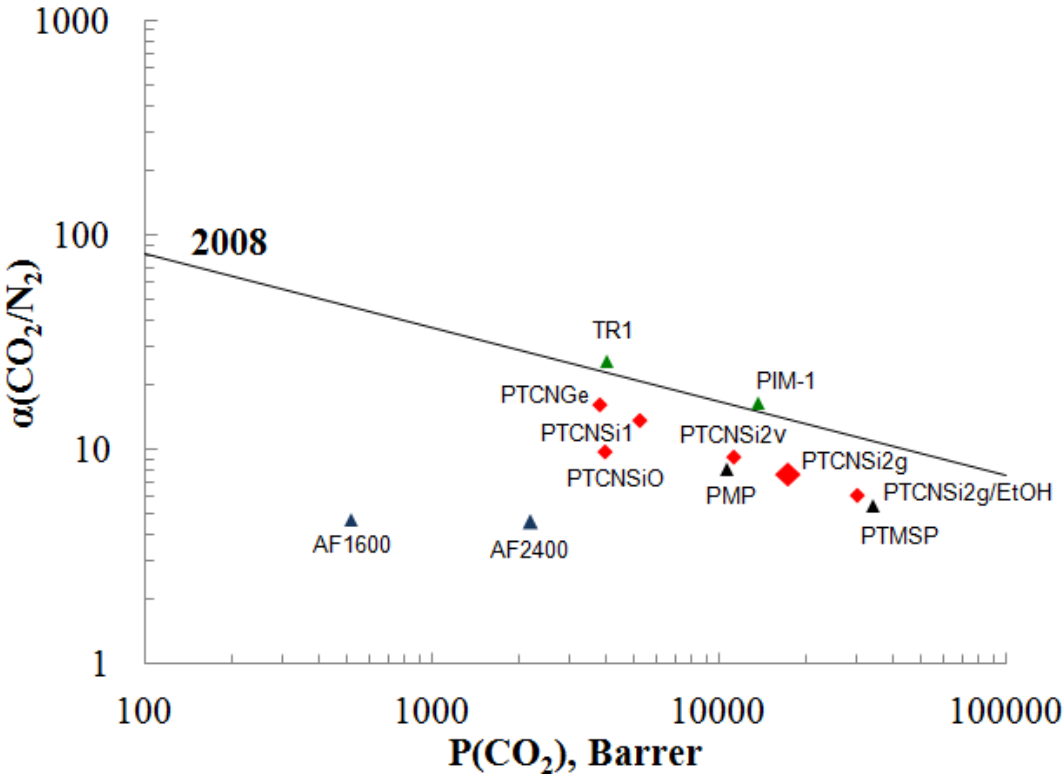


Figure S19. Robeson diagram for gas pair CO_2/N_2.

Aging

Since highly permeable polymers are prone to fast aging we have measured gas permeability of the films of **PTCNSi2g** in time. The measurements were performed with both as cast and EtOH treated films for about 40 days. The results are given in Tables S1 and S2.

Table S1. Changes in permeability of **PTCNSi2g** of as cast film

Time, days	P, kBarrer				Selectivity		
	O_2	N_2	CO_2	CH_4	O_2/N_2	CO_2/N_2	CO_2/CH_4
0	4.57	2.53	19.00	6.88	1.8	7.5	2.8
7	4.33	2.29	18.39	6.24	1.9	8.0	2.9
14	4.18	2.20	17.67	6.02	1.9	8.0	2.9
29	4.00	2.11	16.81	5.74	1.9	8.0	2.9
42	3.95	2.00	16.57	5.43	2.0	8.3	3.0

Table S2. Changes in permeability of **PTCNSi2g** of EtOH treated film

Time, days	P, kBarrer				Selectivity		
	O_2	N_2	CO_2	CH_4	O_2/N_2	CO_2/N_2	CO_2/CH_4
0	6.71	4.14	25.68	11.2	1.6	6.2	2.3
7	5.90	3.54	21.90	9.58	1.7	6.2	2.3
13	5.65	3.36	21.57	9.07	1.7	6.4	2.4
26	5.44	3.21	20.80	8.76	1.7	6.5	2.4
33	5.42	3.18	20.70	8.53	1.7	6.5	2.4
40	5.4	3.17	20.62	8.54	1.7	6.5	2.4

References

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3. Bermeshev, M. V.; Syromolotov, A. V.; Gringolts, M. L.; Lakhtin, V. G.; Finkelshtein, E. S., Synthesis of silicon-substituted tricyclononenes. *Tetrahedron Letters* **2011,** *52* (46), 6091-6093.
4. Nizhegorodova, Y. A.; Belov, N. A.; Berezkin, V. G.; Yampolskii, Y. P. *Russ. J. Phys. Chem.* **2015,** *89*, 502-509.