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A new cycloadduct based on quadricyclane and perfluorocyclohexene: synthesis, metathesis polymerization and gas-transport properties of the obtained polymer

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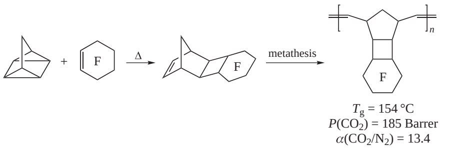
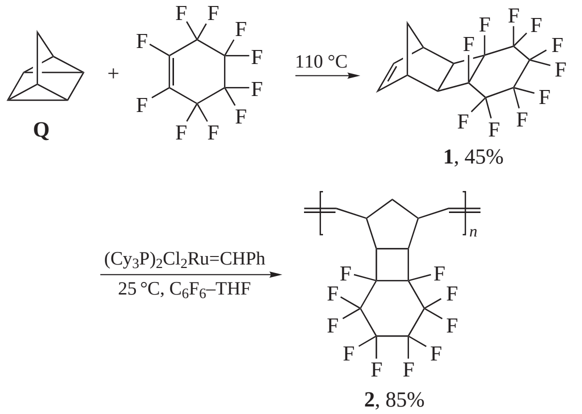
A new fluorine-containing tricyclononene was synthesized by [2σ + 2σ + 2π]-cycloaddition of quadricyclane with perfluorocyclohexene. This cycloadduct was subjected to ring-opening metathesis polymerization. Gas-transport properties of the obtained polymer were estimated.



Norbornene and its derivatives are very attractive monomers for macromolecular design of new polymer materials due to their high polymerization reactivities.[1–4] Tricyclo[4.2.1.0^{2,5}]non-7-enes have a heightened activity in polymerization because of their special structure containing 4-membered cycle in *exo*-position of norbornene moiety. Obviously, substituents linked with this fragment are located further away from the double bond. *exo*-Tricyclononenes are usually prepared by regio- and stereoselective [2σ+2σ+2π]-cycloaddition reaction[5–8] of quadricyclane (**Q**) with olefins.

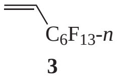
Earlier we have synthesized a new class of highly gas permeable polymer materials[3,9] on the basis of Si-containing tricyclononenes. The development of these materials became challenging due to discovery of certain relationships between a polymer structure and its gas permeability, which depended on the structure of a polymer chain, number of Si-containing substituents per a monomer unit and their nature.[3,9,10] The highest gas permeability was observed when Me_3Si substituents were located in main polymer chains as side groups. The similar effect could be expected if rigid fluoroorganic groups are introduced into a monomer unit of a polymer.[11–13]

In this work we synthesized a new norbornene type monomer by [2σ+2σ+2π]-cycloaddition reaction of perfluorocyclohexene with **Q**, and polymerized it in order to establish the influence of this fluorine-containing group on gas-transport parameters (Scheme 1). The desired monomer **1** was obtained in a moderate yield.[†] The cycloaddition of perfluorocyclohexene and **Q** slowly proceeded only on heating in contrast to some earlier studied Si-containing alkenes.[14] The reaction gave mostly one stereoisomer (98%), which was *exo* in tricyclononene moiety. The orientation of perfluorocyclohexenylene was ultimately established using NMR spectra and X-ray analysis (Figure 1).[‡]



Scheme 1

It is known that **Q** can successfully undergo cycloaddition with alkenes bearing electron-withdrawing substituents.[5] Although C_nF_m groups possess strong electron-withdrawing properties, it is difficult to predict the reactivity of fluorinated alkenes in the cycloaddition reaction with **Q**.[15,16] Herein, we discovered that acyclic fluoro alkenes **3**–**6** did not react properly with **Q**, probably,



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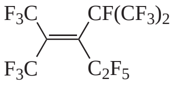

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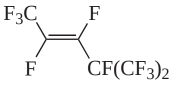

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[†] *3,4,4,5,5,6,6,7,7,8-Decafluorotetracyclo[8.2.1.0^{2,9}.0^{3,8}]tridec-11-ene* **1**. The cycloaddition reaction was performed according to the earlier developed procedures.[7,8] An oven-dried ampoule equipped with a magnetic stirring bar was charged with **Q** (8.2 g, 89.2 mmol) and perfluorocyclohexene (11.7 g, 44.6 mmol). The mixture was degassed. The ampoule was sealed and heated at 110 °C for 96 h (at higher temperatures the fast isomerization of **Q** into norborna-2,5-diene was observed). The reaction mixture was concentrated and separated from the light fractions under reduced pressure (2 Torr, 60 °C). The residue was sublimed and then crystallized from *n*-hexane. Yield 7.1 g (20.1 mmol), mp 52–54 °C. For characteristics, see Online Supplementary Materials.

[‡] *Crystal data for* **1**. Monocrystal of **1** for X-ray analysis was obtained after slow evaporation of *n*-hexane from the solution, M = 354.19, monoclinic, space group $P2_1/n$. At 120(2) K: a = 6.1614(5), b = 15.7377(13) and c = 12.8181(11) Å, V = 1223.29(18) Å^3, β = 100.198(2)°, Z = 4, d_{calc} = 1.923 g cm^{-3}, μ = 0.219 mm^{-1}. 9998 reflections were collected at

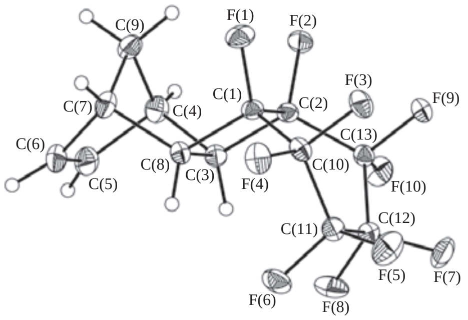


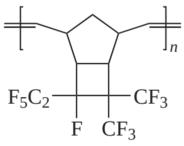
Figure 1 Molecular structure of **1**. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.

due to steric hindrance of bulky groups and/or unfavourable distribution of double bond π-electron density.

The obtained monomer **1** was subjected to ring-opening metathesis polymerization in the presence of the 1st generation Grubbs catalyst.[§] The corresponding polymer **2** was obtained in a good yield (see Scheme 1). The polymerization was performed in the C_6F_6–THF mixture to provide a good solubility of both the catalyst and the formed polymer. The polymer structure was confirmed with ^{1}H, ^{13}C and ^{19}F NMR spectroscopy. Polymer **2** was amorphous (WAXD analysis) and its glass transition temperature was about 154 °C (DSC). It is soluble in organofluorine solvents and possesses good film-forming properties (ε = 6%, σ = 44 MPa and E = 915 MPa).

The study of gas-transport properties[¶] of polymer **2** was performed for a series of gases (He, H_2, O_2, CO_2, N_2, CH_4, Table 1). The order of gas permeability for **2** is consistent with sequence He ≈ $CO_2 > H_2 > O_2 > N_2 > CH_4$ reproducing the behavior for highly gas permeable perfluorodioxole copolymers reported to date.[11,12]

It seemed interesting to compare the new polymer **2** with known **7** as they have[17] the same number of carbon atoms in side groups (Table 1). These polymers have close glass transition temperatures. Polymer **7** containing more branch substituents is more permeable than polymer **2**. A possible explanation for this difference is a looser packing of the main polymer chains for **7** which is confirmed by values of diffusion coefficients (Table 2). Ideal selectivities of **2** and **7** turned to be very close. The samples of polymer **7** obtained on using the 1st generation Grubbs catalyst (Ru-1) and the 2nd generation Grubbs catalyst (Ru-2) exhibit very close values of permeability. That can be explained by a weaker influence of the polymer microstructure on gas-transport parameters in comparison to the effect of a substituent nature. At the same time, polymer **2** possesses higher gas permeability coefficients than polymer **8** containing Me_3Si groups, although the former demonstrated lower selectivities.



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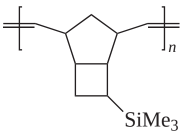

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Table 1 Gas permeability and ideal selectivities of metathesis polymers **2**, **7** and **8**.

Poly-mer	Meta-thesis catalyst used	T_g/°C	Permeability (P)/Barrer[a]						Ideal permeability selectivity, $\alpha(P_i/P_j)$		Ref.
			He	H_2	O_2	N_2	CO_2	CH_4	O_2/N_2	CO_2/N_2	
2	Ru-1	154	195	137	42	14	185	12	3.0	13.2	This work
7	Ru-1	150	262	203	68	23	277	20	3.0	12.0	This work
7	Ru-2	158	355	230	60	20	240	20	3.0	12.0	[17]
8	Ru-1	104	81	119	28	6.8	112	14.3	4.1	16.4	[3]

[a] 1 Barrer = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} (cmHg)$^{-1}$.

Table 2 Diffusivity coefficients and diffusivity selectivities of metathesis polymers **2** and **7** (measured in this work).

Polymer	Diffusivity (D)/10^{-7} cm^2 s^{-1}						Diffusivity selectivity, $\alpha(D_i/D_j)$	
	He	H_2	O_2	N_2	CO_2	CH_4	O_2/N_2	CO_2/N_2
2	290	88	5.3	2.5	2.6	0.7	2.12	1.04
7	310	110	7.8	3.7	4.3	1.3	2.11	1.16

In conclusion, a new fluorine-containing norbornene-type monomer was synthesized and its metathesis polymerization was performed. The gas-transport properties of the obtained polymer were studied and the influence of perfluorocyclohexenylene substituent on gas-transport parameters was estimated. The synthesized polymer possesses good gas permeability level. It was shown that for the design of new highly permeable fluorocontaining polymers it is more preferable to introduce rigid branched substituents in a polymer.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.03.013.

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2.07 < θ < 29.00°, 3255 independent reflections (R_{int} = 0.0253). The structure was refined with full-matrix least-squares on F^2, GOF = 1.014, R_1 = 0.0354 and wR_2 = 0.0892 (all data), R_1 = 0.0442 and wR_2 = 0.0956 [$I > 2\sigma(I)$]. For more details, see Online Supplementary Materials.

CCDC 1419546 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

[§] *Polymer* **2**. The solution of **1** in C_6F_6 (1:1 w/w, 4.8 g, 6.78 mmol) and 7 ml of C_6F_6 were placed into a round-bottom glass ampoule (V = 15 ml) equipped with a magnetic stirrer, which was preliminary degassed and filled by argon. Polymerization was initiated by addition of the 1st generation Grubbs catalyst $(PCy_3)_2Cl_2Ru{=}CHPh$ in THF (4.52×10^{-3} mmol, 1 ml). After 24 h, the inhibitor, 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol), and vinyl ethyl ether were added and the mixture was allowed to stay for 10 min. Then the polymer solution was precipitated by ethanol with the inhibitor, separated, washed by several portions of ethanol and dried *in vacuo*. The polymer **2** was twice reprecipitated by ethanol from its C_6F_6 solution and dried *in vacuo* at 50 °C up to a constant weight. Yield 2.04 g (85%). [η] = 0.85 dl g^{-1} (C_6F_6, 25 °C). For characteristics, see Online Supplementary Materials.

[¶] The gas-transport properties were studied on the precision TimeLag_GKSS setup equipped with a pressure sensor Baratron with sensitivity to 10^{-7} bar (MKS Instruments) at 30 °C. Permeability coefficients of **7** in ref. 17 were determined using a setup with gas chromatographic analysis of permeates.

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