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Synthesis and Gas-Separation Properties of Metathesis Poly(3-Fluoro-3-Pentafluoroethyl-4,4-bis(trifluoromethyl)tricyclonene-7)

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Abstract—Metathesis polymerization of 3-fluoro-3-pentafluoroethyl-4,4-bis(trifluoromethyl)tricyclononene-7 (F-PTCN) and the properties of the resulting polymer, particularly gas permeability, have been studied. It has been found that F-PTCN exhibits high thermal stability. The gas separation parameters of the material ($P(O_2) = 60$ Barrer, $P(CO_2) = 240$ Barrer) are close to those of fluorinated polynorbornenes studied previously. The newly synthesized fluorinated metathesis polytricyclononene has a lower gas permeability than metathesis polytricyclononene bearing two Me_3Si groups in the monomer unit, but it is significantly superior to the latter in gas separation selectivity for some gas pairs.

Keywords: tricyclononenes, metathesis polynorbornenes, fluorinated polymers, gas permeability

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INTRODUCTION

At present, there are a great number of highly permeable glassy polymers and a search for new materials for membrane technology is running on. This search is caused by a significant increase in the membrane technology market and disadvantages of the existing polymer membranes whose performance characteristics do not correspond to the complete set of required properties. The polymers that traditionally attract attention as promising materials include perfluorinated amorphous polymers and polymers containing fluorine in the pendant groups or in the backbone. Perfluorinated copolymers exhibit special thermodynamic and transport properties, in particular fairly high selectivities in the separation of He/CH_4, CO_2/CH_4 mixtures [1–2]. There are extensive data on the transport properties of polymers containing, for example, CF_3 or $C(CF_3)_2$ pendant groups. In the mid-1990s, two new metathesis polynorbornenes with F-containing substituents were synthesized and studied [3, 4]. These polymers had fairly high gas permeability parameters. However, these works have not been further evolved despite the attractive methods developed for the synthesis of norbornene derivatives [5–7] and the polymerization thereof [8–11]. In this context, it is of interest to derive new data on the effect of the structure of organofluorine substituents on the gas separation properties of the polymers. Therefore, in this study, a new metathesis polytricyclononene has been synthesized on the basis of one of the available fluoroolefins—perfluoro(2-methylpent-2-ene)—and the gas permeability of the material has been examined.

EXPERIMENTAL

The metathesis polymerization catalysts were Grubbs complexes (Aldrich) used without further purification. Perfluoro(2-methylpent-2-ene) was purchased from ZAO NPO PiM-Invest and used as received. Quadricyclane was synthesized as described in [12], dried over Na, and recondensed in a vacuum. The inhibitor was 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) purchased from Aldrich. Toluene and tetrahydrofuran (THF) were dehydrated over sodium and stored over sodium wire under argon.

NMR spectra were recorded on Bruker MSL-300 and Bruker DRX 400 NMR spectrometers. ^{1}H-NMR and ^{19}F-NMR spectra were recorded at a frequency of 300.13 and 376.5 MHz, respectively. Signals were attributed with respect to residual protons of $CDCl_3$ (7.24 ppm) and C_6D_6 (7.15 ppm) in the ^{1}H NMR spectra and to the peak of C_6F_6 (−162.90 ppm) in the ^{19}F-NMR spectra.

Gas chromatography–mass spectrometry analysis was conducted on a Finnigan MAT 95 XL instrument (ionization energy, 70 eV; mass range, 20–800 amu; resolution, 1000; source temperature, 200°C; scan rate, 1 s/mass decade) and an HP 6890+ chromatograph equipped with a 30 m × 0.25 mm capillary column coated with the DB-5 phase (polydimethylsiloxane containing 5% phenyl groups) using helium as the carrier gas (at a split ratio of 1 : 30).

Calorimetric studies were conducted on a Mettler TA-4000 differential scanning calorimeter with a DSC-30 cell at a rate of temperature increase of 20 deg/min in an argon atmosphere. Thermogravimetric analysis (TGA) was conducted using a PerkinElmer TGA-7 instrument at a rate of temperature increase of 10 deg/min.

X-ray diffraction measurements were conducted on a DRON-3M diffractometer in the transmission mode (an asymmetric detector-focusing primary-beam quartz monochromator) using CuK_α radiation. Diffraction patterns were recorded in a step scan mode in increments of $\Delta 2\theta = 0.04°$ with an acquisition time of $\tau = 10$ s.

To examine gas permeability, films with a thickness of 50–80 μm were cast from 2–5% polymer solutions in C_6F_6. After evaporation of the solvent, the films were evacuated to constant weight at room temperature for 2 days. Gas permeability coefficients were measured on a chromatographic setup at 22–24°C and a partial pressure differential of the penetrant of 1 atm [13].

All procedures on the synthesis and polymerization of monomers were conducted in a dry argon atmosphere.

Monomer Synthesis

Perfluoro(2-methylpent-2-ene) (30 g, 0.1 mol) and quadricyclane (14.7 g of 94% purity (6% norbornadiene-2,5), 0.15 mol) were placed in a 100-mL ampoule. The mixture was frozen, evacuated, and then thawed with the vacuum switching valve closed. The degassing procedure was repeated three times. The ampoule was sealed off in a vacuum and heated at 95°C for 24 h. After that, the ampoule was open and the unconverted reactants and the by-product (norbornadiene-2,5) were distilled off at atmospheric pressure. The target monomer was distilled in a vacuum (5 mm, 78–80°C [14]). The yield was 83% (32.5 g). The NMR spectra (^{1}H and ^{13}C) were consistent with those previously published [14].

^{1}H NMR ($CDCl_3$): 6.35–6.05 m (1H, CH=CH), 3.38 br. s (0.07H), 3.28 br. s, 3.18 br. s (1.93H), 2.79–2.55 m (1H), 2.43–2.22 m (1.93H), 2.17–2.09 m (0.07H), 1.39 d (1H, $^2J = 10.2$ Hz).

Mass spectrum: 392 (2%, M^+), 373 (5%, M^+–F), 92 (17%, M^+–C_6F_{12}), 66 (100%, $C_5H_6^+$).

Metathesis Polymerization

A 15-mL Schlenk reactor was charged with 1.0 g of the monomer (2.55 mmol) and 8 mL of hexafluorobenzene; after that, 0.4 mL (0.003 M, 1.2×10^{-3} mmol) of the second-generation Grubbs carbene complex solution in THF was poured into the reactor under constant stirring. The reaction mixture was stirred at room temperature for 6 h and then admixed to vinyl ethyl ether (0.02 mL) to deactivate the catalyst and the 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) inhibitor (3–4 mg). The polymer was precipitated in ethanol containing 0.5 wt % 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol). The coagulated polymer was filtered, washed with a fresh solution of 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) in ethanol and dried in a vacuum. After that, the polymer was redissolved in hexafluorobenzene containing the oxidation inhibitor, reprecipitated with ethanol, and dried in a vacuum at 40°C to constant weight (the procedure was repeated twice).

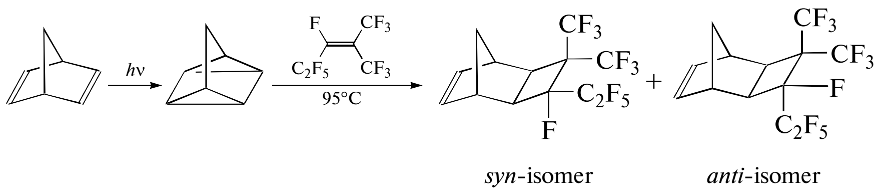
^{1}H NMR (C_6D_6/C_6F_6): 5.59–5.09 m (1H, CH=CH), 3.84–2.69 m (4H), 2.45–1.87 m (1H, C(9)H_2), 1.52–1.14 m (1H, C(9)H_2).

^{19}F NMR (C_6D_6/C_6F_6): −58.0–(−)60.4 (CF_3), −64.4–(−)66.7 (CF_3), −77.9–(−)80.2 (CF_3), −119–(−)121.5 (CF_2), −123.2–(−)125.7 (CF_2), −178.2–(−)179.8 (CF).

RESULTS AND DISCUSSION

Monomer Synthesis

The desired monomer was synthesized as described in [14]. The synthesis is based on the regio- and stereospecific reaction of [2σ + 2σ + 2π]-cycloaddition of quadricyclane, which is the product of photochemical isomerization of norbornadiene-2,5, and perfluoro(2-methylpent-2-ene) (Scheme 1).



syn-/anti- = 7/93
Yield of monomer mixture 83%

Scheme 1. Synthesis of the monomer.

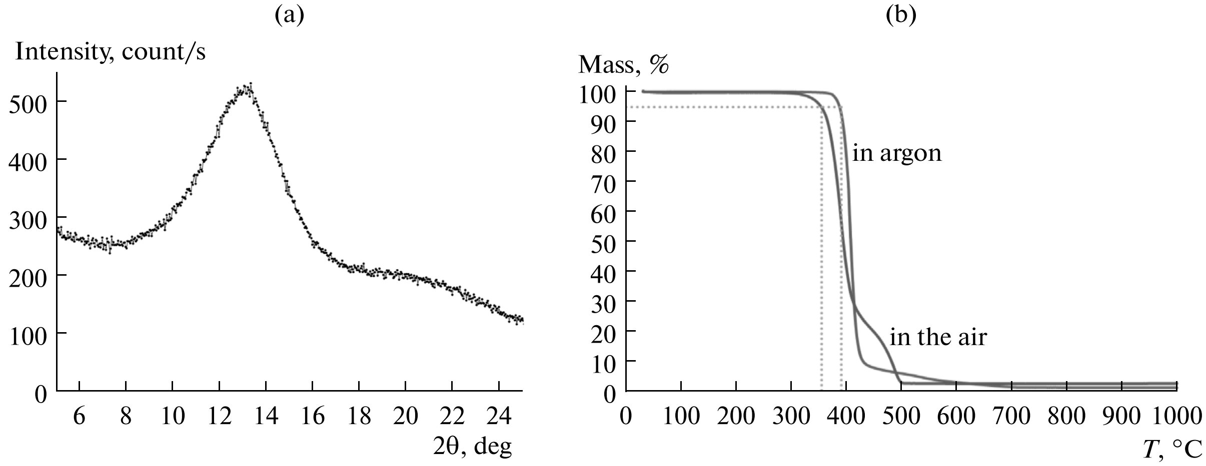
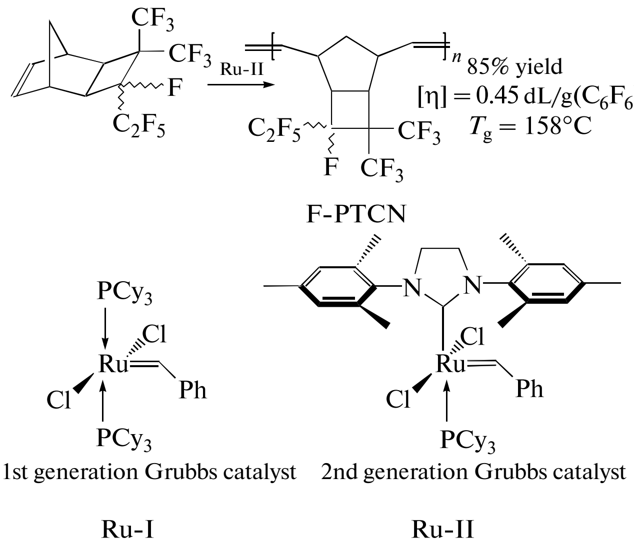


Fig. 1. (a) Diffraction pattern and (b) TGA curves for F-PTCN.

Quadricyclane can react with olefins only if the latter comprise electron acceptor substituents. In this case, despite the presence of strong electron acceptor groups in perfluoro(2-methylpent-2-ene), the reaction occurred only under heating, unlike some vinylchlorosilanes [15–16]. However, it should be noted that the single-step synthesis of fluorinated tricyclononene is simpler than the previously developed two-step procedure for the preparation of silicon-substituted monomers of this kind [15–17]; in addition, the former is based on commercially available fluoroolefin. An increase in the time of reaction between quadricyclane and perfluoro(2-methylpent-2-ene) provided the production of the target tricyclononene with a higher yield (83% for 24 h) than in the previously described case (56% for 12 h [14]). After reaction, the monomer was isolated as a mixture of two isomers (*syn*- and *anti*-); the monomer structure was confirmed by NMR spectroscopy and mass spectrometry.

Metathesis Polymerization

Owing to the presence of a double bond in the strained norbornene moiety, the synthesized monomer was active in metathesis polymerization over both first- and second-generation Grubbs catalysts (Ru-I and Ru-II, respectively; Scheme 2). However, in this case, the activities of the catalysts were significantly different. The use of the Ru-II catalyst led to the formation of the respective polymer with considerably higher yields (80–90% compared to 20–30% for the Ru-I catalyst under the same conditions). Polymerization was conducted in a mixture of solvents (C_6F_6 and THF) that provided a fairly high solubility of both the polymer (C_6F_6) and the catalysts (THF).



Scheme 2. Metathesis polymerization of fluorinated tricyclononene.

The metathesis polymerization resulted in the high-yield production of new fluorinated polytricyclononene (F-PTCN) exhibiting film-forming properties required for gas-permeability studies. It was found that F-PTCN is an amorphous polymer (Fig. 1a), which has a glass-transition temperature of about 160°C and exhibits high thermal stability in both an inert atmosphere and the air (Fig. 1b).

Examination of the properties of F-PTCN revealed that this material is readily soluble in hexafluorobenzene, swells in *N*,*N*-dimethylformamide, acetone, and THF, and is insoluble in toluene, chloroform, hexane, and diethyl ether. The polymer forms transparent colorless films from solutions in hexafluorobenzene. The

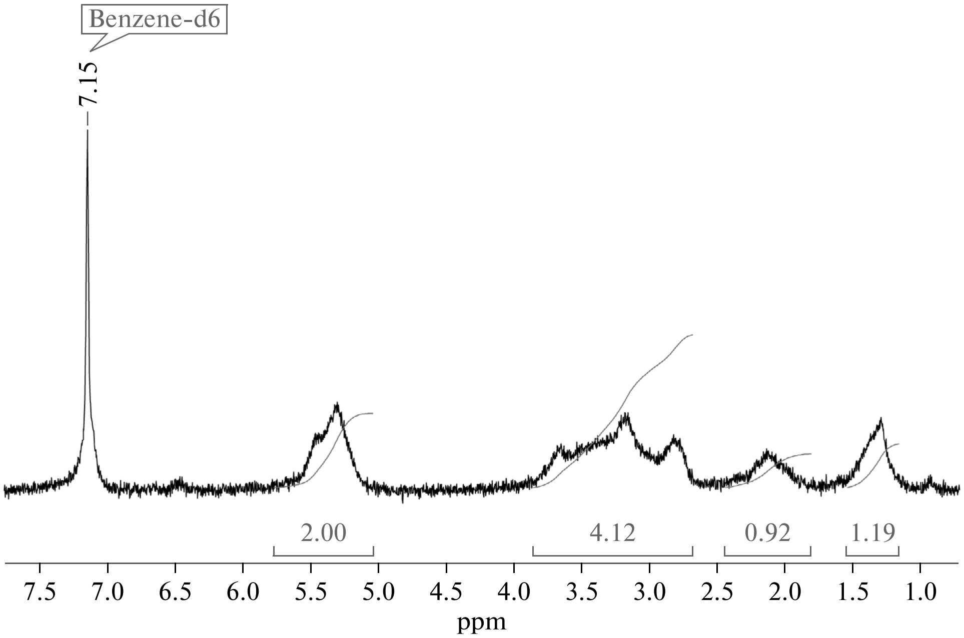


Fig. 2. ^{1}H NMR spectrum of metathesis poly(3-fluoro-3-pentafluoroethyl-4,4-bis(trifluoromethyl)tricyclononene-7) (C_6D_6/C_6F_6).

F-PTCN structure was confirmed by NMR spectroscopy (Fig. 2).

Gas Separation Properties

The permeability of F-PTCN was studied for a large set of gases (He, H_2, N_2, O_2, CO_2, CH_4). The determined gas permeability coefficients are listed in Table 1.

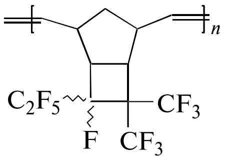
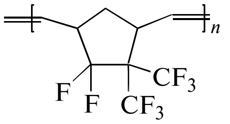
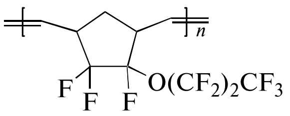
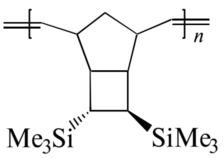
It is evident that, although the synthesized polymer is less gas-permeable than metathesis polytricyclononene comprising two Me_3Si groups per monomer unit, it exhibits permeability comparable to that of previously studied fluorine-substituted polynorbornenes. It is of interest to compare the selectivities (ideal separation factors) of F-PTCN and metathesis polytricyclononene comprising two Me_3Si groups per monomer unit as a "hydrocarbon" polymer with a close level of gas permeability. The ideal selectivities are listed in Table 2. It is evident that separation factors $\alpha(O_2/N_2)$ for the two polymers are close. Differences take place for pairs of gases containing hydrocarbons (CH_4) as a "slow" component. For example, F-PTCN exhibits significantly higher gas-separation selectivities for gas pairs (CO_2/CH_4, He/CH_4, H_2/CH_4) than those of the silicon-containing polymer (Table 2). This fact is attributed to a low solubility (and thus permeability) of hydrocarbons in F-containing polymers. The same relationship is observed for the He/H_2 gas pair for the new F-containing polymer. Figure 3 shows a Robeson diagram for the He/CH_4 pair. The position of F-PTCN in this diagram is near the upper bond of 1991.

An attractive combination of gas permeability and selectivity, as well as high thermal and chemical stability, makes it possible to regard F-PTCN as a promising material for hydrocarbon-resistant gas separation membranes.

CONCLUSIONS

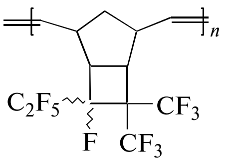
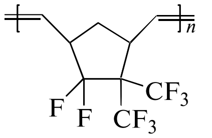
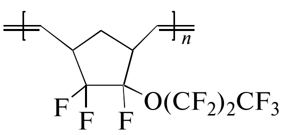
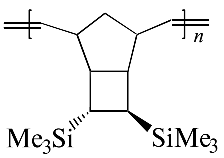
Thus, a new high-molecular-mass fluorinated polytricyclononene has been produced with a high yield by metathesis polymerization in the presence of the second-generation Grubbs catalyst; the properties of the product, particularly gas-separation characteristics, have been studied. It has been found that the synthesized polymer exhibits high thermal stability and gas separation properties comparable to those of previously studied fluorinated metathesis polynorbornenes. Comparison with slightly more permeable metathesis polytricyclononene comprising two Me_3Si groups per monomer unit has shown that the new polymer is significantly superior to the silicon-containing polytricyclononene in gas separation selectivity for gas pairs comprising methane or hydrogen.

Table 1. Gas permeability coefficients for metathesis polynorbornenes

Polymer	T_g, °C	Permeability, Barrer*						Reference
		He	H_2	O_2	N_2	CO_2	CH_4	
	158	355	230	60	20	240	20	This study
	169	–	166	50	17	200	13	[4]
	77	–	130	55	17	200	18	[4]
	129	227	332	89	24	396	55	[15]

1 Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg.

Table 2. Gas separation selectivity for metathesis polynorbornenes

Polymer	Selectivity $\alpha = P_i/P_j$						Reference
	O_2/N_2	CO_2/CH_4	He/H_2	He/CH_4	N_2/CH_4	H_2/CH_4	
	3.0	12.0	1.5	17.8	1.0	11.5	This study
	2.9	15.4	–	–	1.3	12.8	[4]
	3.2	11.1	–	–	0.9	7.2	[4]
	3.7	7.2	0.7	4.1	0.4	6.0	[15]

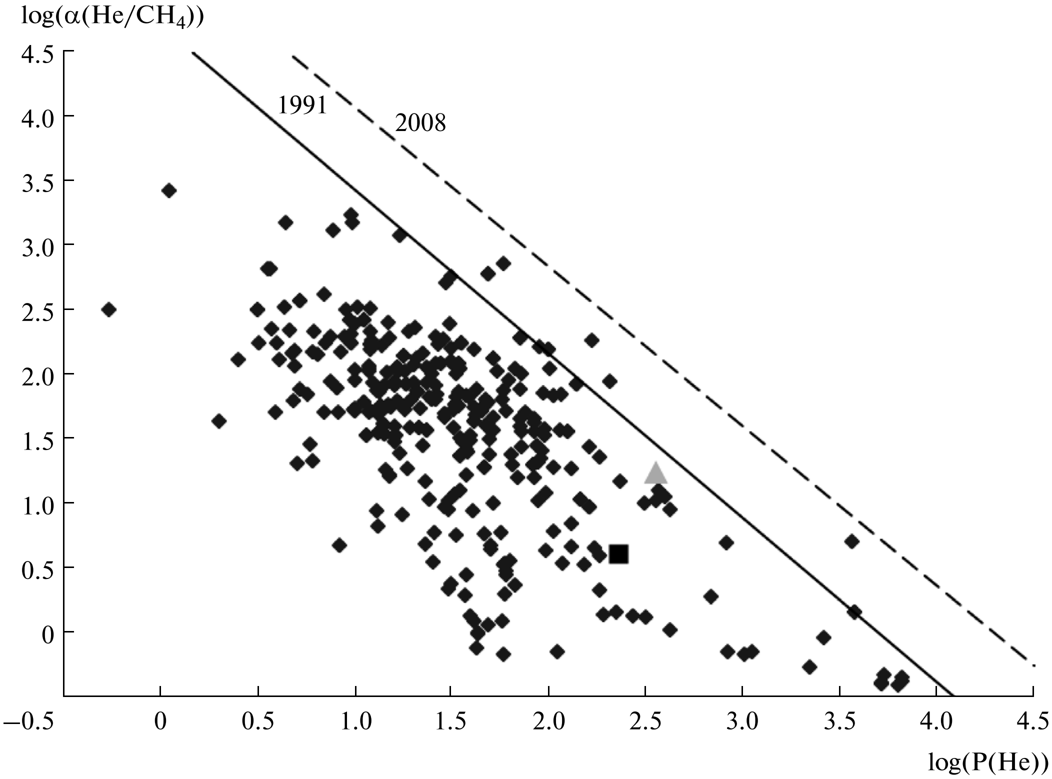


Fig. 3. Robeson diagram [18, 19] for the He/CH_4 pair (green triangle, F-PTCN; black square, silicon-containing polytricyclononene).

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