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POLYMERIC MEMBRANES

Copolymers of 1,2-Disubstituted Acetylenes Containing Trifluoropropyl Groups Synthesized in the Presence of $NbCl_5$-Based Catalyst Systems: Structure and Gas-Transport Behavior

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Abstract—Using a $NbCl_5$-based catalyst system, random copolymers of 1-(3,3,3-trifluoropropyldimethylsilyl)-1-propyne and 1-trimethylsilyl-1-propyne are synthesized in a wide range of comonomer contents. The dependences of gas-transport behavior on the composition and supramolecular organization of the copolymer are studied. Composition regions and conditions of preparing copolymers combining high permeability coefficients with resistance against nonpolar organic solvents are ascertained. The copolymers demonstrate a high selectivity in the separation of butane from a methane–butane mixture.

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The presence of a rigid polyacetylene chain in 1,2-disubstituted polyacetylenes shielded by bulky substituents provides high free volumes and, as a consequence, high parameters of gas and vapor transfer of this class of polymers. This makes them potentially attractive materials for various membrane-separation processes [1]. The best-investigated polymer of this class is poly(1-trimethylsilyl-1-propyne) (PTMSP), which possesses the highest gas-permeability coefficients among the studied polymers. Moreover, PTMSP and a number of its analogs, such as poly(trimethylgermyl-1-propyne) and poly(4-methyl-2-pentyne), manifest properties unique for glassy polymers: the permeability of hydrocarbons grows with an increase in the molecular mass of a penetrant. It is believed that this specific feature of the given polymers is provided by their supramolecular organization, in particular, by the presence of a system of interconnecting channels passing through the polymer matrix [2]. These properties of PTMSP and its several analogs may be of considerable interest for gas-separation processes (e.g., conditioning of natural gas and separation of hydrocarbons C_{3+} from the associated gas), during the employment of PTMSP-based membranes in high-pressure contactors applied to isolate CO_2 from various industrial gas mixtures (including waste gases of the chemical industry), in the processes of purification of syngas and biogas, and during pervaporation (evaporation through membrane) of diverse organic and aqueous–organic mixtures.

Nevertheless, a wide application of PTMSP in real separation processes is hampered by its poor resistance against various nonpolar organic compounds which are contained as a rule in the form of vapors or in the liquid state in real industrial mixtures. On one hand, this problem may be solved by controlling the microstructure of the polymer at the stage of synthesis using certain catalyst systems. For example, as was shown in the case of PTMSP, a change in the content of units in the cis or trans configuration in polyacetylene may considerably influence the resistance of the polymer against various classes of solvents. Specifically, it was found that PTMSP of the mixed microstructure (60% trans units) is soluble in aromatic and aliphatic hydrocarbons. While the cis-enriched polymer (<35% trans units) is resistant against *n*-alkanes C_5–C_7 [3], it is still soluble in alicyclic and aromatic hydrocarbons. However, even stereoregular PTMSP (containing predominantly cis or trans units) preserves the ability to swell in higher alkanes and other hydrocarbons. This feature may worsen the membrane parameters of the polymer. On the other hand, the resistance of the polymer may be improved via introduction of various functional groups into polyacetylene. For example, fluoro-containing homo- and copolymers based on 1,2-disubstituted acetylenes may be of considerable interest as new membrane materials.

As was shown in [4], fluoro-containing 1,2-disubstituted acetylene—1-(3,3,3-trifluoropropyldimethylsilyl)-1-propyne (TFPS)—efficiently polymerizes in toluene in the presence of catalysts systems $TaCl_5$–Ph_3Bi and $NbCl_5$–Ph_3SiH [4]. However, the polymer formed with catalysts based on $TaCl_5$ is fully insoluble. Whereas the polymer formed in the presence of the system $NbCl_5$–Ph_3SiH shows solubility predominantly in polar solvents (ketones, chloroform, ethers), it albeit preserves resistance against aliphatic and aromatic hydrocarbons, as is inherent in fluoro-containing polymers. Thus, the synthesis of TFPS–TMSP copolymers is of importance from the viewpoint of obtaining new membrane materials combining high transport parameters of PTMSP with resistance against hydrocarbons typical of PTFPS. In accordance with [5, 6], the copolymers of TFPS and TMSP may be synthesized by the random copolymerization of monomers in the presence of catalysts based on tantalum(V) chloride. However, these copolymers preserve solubility only in a limited composition range, because the PTFPS homopolymer and copolymers with a high content of TFPS units synthesized using this system are insoluble. Therefore, it is impossible to manufacture polymeric membranes of their basis. In this regard, the synthesis of copolymers of TFPS and TMSP in the presence of the catalyst system $NbCl_5$–Ph_3SiH may be of interest, because these copolymers should preserve solubility and film-forming properties throughout the whole composition range.

The goals of this study are to synthesize random copolymers of TFPS and TMSP in the presence of the system $NbCl_5$–Ph_3SiH in a wide composition range and to gain insight into the effect of supramolecular organization of the copolymers on resistance against hydrocarbons and transport parameters of F-containing polyacethylenes.

EXPERIMENTAL

Initial Compounds and Their Purification

In this study, monomers TFPS and TMSP used in homo- and copolymerization were synthesized by organomagnesium synthesis, as described in [3]. Purity was analyzed on a Thermo Focus DSQ II chromatograph-mass spectrometer (capillary column Varian VF-5ms; length, 30 m; inner diameter, 0.25 mm; immobile phase thickness, 0.25 μm; carrier gas, helium; heating rate, 15 K/min; ionization energy, 70 eV). The components were identified using the mass spectra presented in the database NIST/EPA/NIH 11.

Before polymerization, monomers and toluene used as a solvent (99.9%, Merck) were distilled three times over calcium hydride under high-purity argon.

Catalysts tantalum pentachloride $TaCl_5$ (99.9%) and niobium pentachloride $NbCl_5$ (99.9%) (both from Fluka) and cocatalysts triphenyl bismuth Ph_3Bi (99%) and triphenylsilane Ph_3SiH (97%) (both from Aldrich) were used as received.

Powdery catalysts $NbCl_5$ and $TaCl_5$ were dosed under argon in sealed glass ampoules that were opened directly before use.

Copolymerization

The copolymers were synthesized as follows. The solution of the calculated amount of catalyst $NbCl_5$ in toluene was stirred at 25°C for 30 min in a glass reactor in a flow of high-purity argon, and a mixture of monomers TFPS and TMSP was added. Polymerization was performed at 25°C in a sealed 150-mL reactor under continuous stirring for 24 h. In all of the samples, the catalyst-to-cocatalyst ratio was 1 : 1, and the total initial concentration of the monomers and the catalyst was 1 and 0.02 mol/L, respectively. Before isolation of the polymer, the reaction mixture was treated with methanol to deactivate the catalyst. Then the polymer was dissolved in acetone or toluene (depending on solubility). The solution was precipitated in a 5-fold (by volume) excess of methanol. The precipitated polymer was separated on a funnel with a glass filtering bottom and dried in air at room temperature for 24 h. For better purification, the polymer was redissolved, precipitated in methanol, and dried in vacuum until a constant weight. The yield of the product was determined gravimetrically.

Study of the Structure and Properties of the Polymers

The intrinsic viscosity of the polymer samples was measured in toluene at 25°C in an Ostwald–Ubbelohde viscometer. The molecular-mass characteristics of the polymers were determined by GPC. Measurements were conducted in THF at 30°C on a VWR/Hitachi_L2130_21E37-024 chromatograph equipped with a refractometric detector. Molecular masses were calculated proceeding from the calibration curve obtained using PTMSP samples with known molecular masses (GPC data obtained using light-scattering detector and refractometer). The accuracy of determination was 10%.

The chemical structure of the polymers was studied by IR spectroscopy and ^{13}C and ^{1}H NMR spectroscopy using polymer solutions in $CDCl_3$ (solution concentration, 4 wt %). ^{13}C and ^{1}H NMR spectra were registered on Bruker MSh-300 instruments with operating frequencies of 75.47 and 300 MHz, respectively. The content of cis and trans units in the samples of homo- and copolymers was quantified from the ^{13}C NMR spectra using the software ACD/CNMR processor applicable to treatment of poorly resolved spectra.

The composition of polymerization products was determined from the results of IR studies and elemental analysis.

Table 1. Pressure of gas mixture, concentration of *n*-butane, partial pressure, and activity of components in measurements of gas-separation properties of polymeric membranes

Total pressure, bar	Concentration, vol %	Pressure, bar	Activity p/p_0
10.0	4.67	0.468	0.20
20.2	4.59	0.927	0.39
30.0	4.65	1.40	0.58

IR spectra were measured in the range of 500–3500 cm^{-1} on an IFS-Bruker-113V spectrometer. Samples were prepared in the form of films cast from $CHCl_3$ or toluene solution (depending on polymer solubility). In order to determine the composition of copolymers TFPS–TMSP, bands at 687 and 1069 cm^{-1} corresponding to vibrations of three Si–C bonds in TMSP and bonds of the CF_3 group in TFPS, respectively, were used as analytical bands.

Elemental analysis was performed by pyrolytic chromatography on a Carlo Erba (Italy) instrument. The IR spectra of the samples were interpreted proceeding from the theoretical analysis of normal vibrations in PTMSP of the regular microstructure (cis or trans), as described in [3]. The main absorption bands in the IR spectrum of PTFPS correspond to the absorption bands of PTMSP. This fact makes it possible to interpret these spectra in a similar manner.

In extraction with the selective solvent, the polymer was placed in toluene (acetone) and stirred for 24 h, the solution was filtered, and the filtrate was precipitated in methanol. The solubility of the polymer was estimated from the gravimetry data.

The DSC studies of the samples were conducted on a Mettler Toledo DSC-823e instrument in the temperature range of 20–350°C; thermogravimetric analysis was performed in air on a Mettler Toledo TGA/DSC-1 instrument in the range of 20–1000°C.

The X-ray diffraction analysis of the polymers was conducted on an apparatus based on a 12-kW generator equipped with a RU-200 Rotaflex rotating copper anode (Rigaku, Japan). Measurements were performed in the transmission mode (40 kV, 140 mA) using CuK_α radiation (λ = 0.1542 nm). The sample was a tablet with a thickness of 1 mm and an area of 10 mm^2. The position and half-width of reflections were determined using the software EVA Diffrac plus (Bruker AXS).

The mechanical properties of polymer films were investigated at a constant stretching rate of 10 mm/min on an Instron-1122 tensile testing machine at 20°C. Polymer films were cast from 1 wt % solution in toluene or methyl ethyl ketone (depending on solubility) on a Cellophane substrate. The films were dried first in air for 7 days and then under vacuum for 48 h. The thickness of the films was 25–50 μm.

The permeability parameters of the polymer films with respect to individual gases were determined at 25°C on a laboratory apparatus operating according to the constant volume–variable pressure principle [7] and intended for measuring the permeability of planar polymeric membranes for individual gases. The permeability in the mixture methane–*n*-butane was measured at 20°C on an apparatus intended for permeability studies of binary gas mixtures and operating according to the constant pressure–variable volume principle. The composition of the feed mixture, permeate, and retentate was determined using a Variant 3400 gas chromatograph equipped with a Chromosorb 107 column.[1] Measurements were conducted at 25°C and pressures of 10, 20, and 30 bar. In order to avoid concentration polarization on the membrane surface, the flow velocity was not less than 10 nm^3/h. In the course of measurements, the composition of the gas mixture containing 4.6 ± 0.1 vol % *n*-butane was kept constant. The permeate pressure was maintained at the level of 20 Mbar with the aid of a membrane vacuum pump (Vacuubrand, Germany). The flow was measured using sensors mounted on the back side of the membrane. The pressure of permeate and retentate was selected in accordance with the technique described in [8]. Measurements performed at three different pressure values revealed no marked differences in the permeability and selectivity of the samples. All conditions of gas-separation studies of the copolymers for the hydrocarbon mixture are presented in Table 1.

RESULTS AND DISCUSSION

The synthesis of TFPS–TMSP copolymers may be of interest from the viewpoint of obtaining new materials combining high transport parameters of PTMSP with resistance against nonpolar organic substances which is inherent in PTFPS. Previously, fluoro-containing polyacetylenes resistant against various classes of organic compounds were prepared by the copolymerization of TFPS and TMSP catalyzed by the system $TaCl_5$–Ph_3Bi. However, the resulting copolymers preserve solubility and film-forming behavior only in a limited composition range, because the copolymers with a high content of fluorine are insoluble like homopolymer PTFPS synthesized using this system. X-ray diffraction studies showed that their insolubility is associated with the presence of regions of increased ordering playing the role of crosslinks in the amorphous matrix of the polymer. It may be anticipated that the use of catalysts based on niobium(V) chloride may bring about formation of fully amorphous copolymers preserving selective solubility at any content of TFPS units. Therefore, in this study, the copolymer-

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[1] Measurements were conducted at the Helmholtz-Zentrum Geesthacht Centre for Materials and Coastal Research, Institute of Polymer Research (Germany).

Table 2. Random copolymerization of TMSP–TFPS catalyzed by $NbCl_5$–Ph_3SiH in toluene (the total initial concentrations of monomers $[M]_0$ = 1 mol/L and catalyst of 0.02 mol/L, respectively; catalyst : cocatalyst = 1 : 1 (mol/mol); T = 25°C; 24 h)

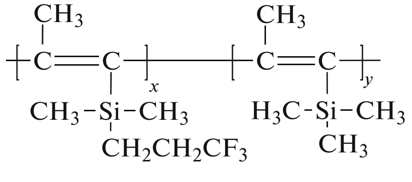
Content of TFPS in the monomer mixture (mol %)	Copolymer yield, %	Content of TFPS units in copolymer, mol %	[η], dL/g (measured in toluene)	$M_w \times 10^3$	$M_n \times 10^3$
20	68	16	0.3	120	90
36	75	33	0.49	180	120
50	50	39	0.63	260	170
50	70	51	0.4	150	100
80	30	68	0.5	180	110
80	71	87	0.74*	160	110

*Measured in THF.

ization of TFPS and TMSP was investigated using the catalyst system $NbCl_5$–Ph_3SiH. A number of copolymer samples with different content of TFPS units were synthesized. The conditions and results of copolymerization are listed in Table 2.

The chemical structure of the copolymers was studied by IR and ^1H NMR spectroscopy. The typical ^1H NMR spectrum of PTMSP contains two singlet peaks with chemical shifts of 1.83 and 0.23 ppm, respectively, which corresponds to hydrogen atoms of groups $–C(CH_3)=$ and $–Si(CH_3)_3$. The spectrum of PTFPS is composed of three singlets with chemical shifts of 1.77, 1.03, and 0.07 ppm corresponding to protons of groups $=C(CH_3)–$, $–CH_2–$, and $Si(CH_3)_3$. The typical spectrum of the copolymer shows all peaks typical of both comonomers, suggesting the absence of isomerization in the course of synthesis.

In the IR spectrum of the copolymer, absorption bands are seen in the range of 1500–1600 cm^{-1}. This fact indicates the presence of alternating double bonds in a macromolecule. The intense absorption bands at 1264, 1212, 1200, 1130, and 1067 cm^{-1} provide evidence for the presence of trifluoropropyl groups. Note that bands characteristic of the triple bond of monomers (1980 and 2200 cm^{-1} for TMSP and TFPS, respectively) are absent in the spectrum. Thus, the results of spectral studies fully confirm the proposed structure of the copolymers:



The true character of copolymerization is confirmed by the extraction of polymer samples by toluene (or acetone), which is a selective solvent for the mixture of PTFPS and PTMSP homopolymers. The latter polymer is soluble in toluene, as opposed to PTFPS. For the samples with a high content of fluorine which are insoluble in toluene, acetone, which is a solvent for PTFPS rather than for PTMSP, was used as a selective solvent. The absence of the insoluble fraction in solutions of copolymerization products and the content of both TFPS and TMSP units in them, as confirmed by IR spectroscopy, suggest that the test samples are true copolymers rather the mixtures of PTFPS and PTMSP homopolymers. The quantitative composition of the copolymers was studied by IR spectroscopy using calibration obtained on the basis of the elemental analysis of fluoro-containing polyacetylenes containing different amounts of fluorine. The content of each component in the copolymer was calculated from the ratio of intensities of analytical bands at 687 and 1069 cm^{-1} corresponding to vibrations of three Si–C bonds in TMSP and bonds of the CF3 group in TFPS.

By proceeding from linearization of the data on the composition of copolymers isolated at incomplete conversions (≤50%) from the reaction mixture with different initial content of the monomers, the relative activity of the monomers in copolymerization was estimated. The reactivity ratios were calculated in accordance with the Kelen–Tüdõs method, which is applicable to calculating reactivity ratios at both low and high (up to 60%) monomer conversions [9]. The as-calculated values are $r_1 = 1.0 \pm 0.2$ for TFPS and $r_2 = 3.2 \pm 1$ for TMSP. Within the measurement error, these values correspond to reactivity ratios found for copolymerization performed with the $TaCl_5$–Ph_3Bi system [5]. These data suggest that the relative reactivities of both TFPS and TMSP in their copolymerization with two different catalyst systems are similar. This proportion between reactivity ratios testifies to the random character of copolymerization showing the tendency to the microblockiness of TMSP units owing to its much higher activity.

The X-ray diffraction study of the morphology of copolymer samples showed that they possess a fully amorphous structure throughout the studied composition range. The typical spectrum of the copolymer

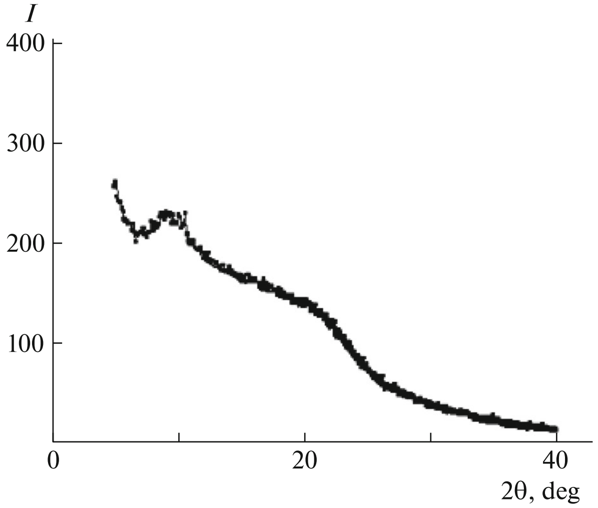


Fig. 1. X-ray pattern of TFPS–TMSP copolymer (80 : 20, mol %) measured in the transmission mode. Catalyst $NbCl_5$–Ph_3SiH.

synthesized in the presence of $NbCl_5$–Ph_3SiH (Fig. 1) contains one amorphous halo with a maximum at $2\theta = 9°$.

The copolymers with a high content of fluorine which were synthesized in the presence of the $TaCl_5$-based catalyst, as was shown in [5], contain regions of enhanced ordering probably formed by homogeneous sequences of units in the trans configuration in trans-enriched copolymers. The fully amorphous structure of the copolymers synthesized in the presence of $NbCl_5$–Ph_3SiH is apparently related to their irregular cis and trans composition. The detailed comparison of the IR spectra of the copolymers with the same comonomer composition which were prepared using various catalyst systems (Fig. 2) revealed that there are differences in the region of absorption of double bonds (1500–1600 cm^{-1}). The typical IR spectrum of the copolymer prepared using the catalyst $NbCl_5$–Ph_3SiH shows the absorption band at 1562 cm^{-1} corresponding to the substituted double bond of the trans configuration and the band at 1545 cm^{-1} corresponding to the stretching vibrations of the cis-substituted double bond (Fig. 2, spectrum *1*). This finding suggests the mixed microstructure of this copolymer containing not only trans but also cis units. In the spectrum of the copolymer synthesized using the catalyst based on $TaCl_5$ (spectrum *2*), the band due to the C=C bond in the cis configuration is absent while the presence of a well-defined signal at 1562 cm^{-1} indicates the microstructure of the copolymer enriched in trans units.

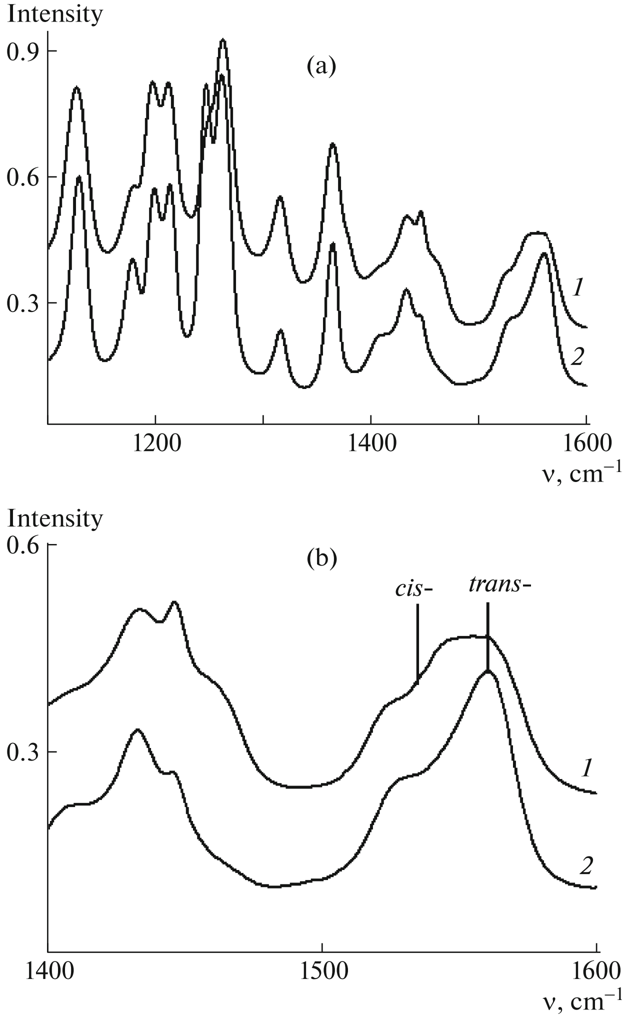


Fig. 2. (a) IR spectra of TFPS–*co*-TMSP synthesized in the presence of (*1*) $NbCl_5$–Ph_3SiH and (*2*) $TaCl_5$–Ph_3Bi and (b) absorption bands due to double bonds in cis and trans units in the copolymers. Copolymer composition is 23 mol % TFPS and 77 mol % TMSP.

A greater content of cis units in polyacetylenes synthesized in the presence of $NbCl_5$-based catalysts compared with the analogous polymers prepared in the presence of $TaCl_5$, as was noted for PTMSP and PTMGP [3, 10] as well as PTFPS [4], may be explained by different sizes of the coordination sphere of the metal ion in the catalyst system. A large coordination radius of the Ta ion provides steric hindrances in coordination of the metal to the substituted double bond, thereby promoting formation of a less strained trans configuration. The catalyst based on Nb(V) with a smaller radius causes lower steric hindrances; therefore, other conditions being the same, the probability of formation of both cis- and trans-substituted double bonds is fairly high. As a result, the formed polymer has a mixed microstructure containing a considerable amount of both types of units.

In accordance with the DSC study of the copolymer, there are no signs of glass transition or flowability in the temperature range of 25–300°C. The onset temperature of polymer weight loss in air, as evidenced by the TGA data, is in the range of 260–300°C. This

Table 3. Permeability coefficients with respect to individual gases for films of TFPS–TMSP copolymers of various composition

TFPS, mol %	Catalyst	*P*, barrer			
		O_2	N_2	CO_2	H_2
0	$NbCl_5$–Ph_3SiH	7000	4500	25000	13000
23	$NbCl_5$–Ph_3SiH	2700	1500	11400	5400
23	$TaCl_5$–Ph_3Bi	2500	1400	9900	6600
39	$NbCl_5$–Ph_3SiH	1900	1000	8700	4000
41	$TaCl_5$–Ph_3Bi	1100	500	3700	2000
51	$NbCl_5$–Ph_3SiH	1500	780	6000	3400
46	$TaCl_5$–Ph_3Bi	500	200	2300	1300
87	$NbCl_5$–Ph_3SiH	370	150	1000	700
100	$NbCl_5$–Ph_3SiH	170	55	760	350

Table 4. Resistance of the copolymers of TFPS and TMSP against solvents at room temperature

TFPS, mol %	Toluene	CCl_4	$CHCl_3$	Cyclohexane	Acetone	THF	*n*-Alkanes C_6–C_{12}
100	–	–	+	–	+	+	–
87	–	–	+	–	+	+	–
50	+	+	+	–	–	+	–
39	+	+	+	±	–	+	–
23	+	+	+	+	–	+	–
0	+	+	+	+	–	+	+

"+" implies soluble; "–" implies insoluble; and "±" implies contains the insoluble fraction.

parameter increases with the content of TFPS probably owing to the shielding of the polymer chain by bulky trifluoropropyl substituents. Thus, the glass-transition temperature of all of the copolymer samples is higher than the onset temperature of thermo-oxidative degradation.

The synthesized glassy polymers possess good film-forming and mechanical properties. For the copolymer films, breaking strength σ is in the range of 30–40 MPa, elongation at break is $\varepsilon = 35$–60%, and Young's modulus is $E = 500$–1000 MPa depending on composition. The gas-permeability parameters of the copolymers are typical of disubstituted polyacetylenes. They grows with an increase in the content of TMSP units (Table 3).

It is interesting that the test samples show higher permeability coefficients with respect to individual gases compared with previously studied copolymers having similar compositions which were prepared using the catalyst system $TaCl_5$–Ph_3Bi [5].

Different permeabilities of the polymers synthesized using different catalysts may be due to their different geometries. Specifically, as was shown for PTMSP and its Ge-containing analog—poly(1-trimethylgermyl-1-propyne)—[11], even small changes in the microstructure of polyacetylene may exert a strong effect on the value of free volume in the polymer and the character of its distribution in the polymer matrix; as a result, polyacetylenes of different geometry demonstrate different transport properties [11].

The solubility of the synthesized copolymers is determined by their composition. The data on the resistance of the samples against organic solvents are summarized in Table 4.

It is seen that, as the content of TFPS or TMSP units in the copolymers grows, the sample begins to demonstrate solubility typical of the corresponding homopolymer. For example, the copolymers with a low content of TFPS show solubility predominantly in nonpolar media, like PTMSP [3]. With an increase in the content of fluorine, the copolymer, like homopolymer PTFPS, exhibits solubility in more polar solvents [4]. The solubility of all of the copolymers in tetrahydrofuran and chloroform allows polymeric membranes to be prepared via casting.

The above data make it possible to reveal the composition regions of the copolymers combining high permeability coefficients with resistance against ali-

Table 5. Transport behavior of copolymers TFPS–TMSP in the separation of the mixture *n*-butane–methane (95 mol % CH_4, 5 mol % n-C_4H_{10})

TFPS, mol %	Mixture n-C_4H_{10}–CH_4			Individual gases		
	Permeability, barrer		α n-C_4H_{10}–CH_4	Permeability, barrer		α n-C_4H_{10}–CH_4
	n-C_4H_{10}	CH_4		n-C_4H_{10}	CH_4	
51	4900	300	17	1600	500	3.3
33	17700	800	22	8400	2200	3.8
0*	28500	1500	19	25000	10000	2.5

* PTMSP synthesized in the presence of $NbCl_5$ [10].

phatic hydrocarbons C_6–C_{12} and showing promise for use as materials for membrane separation of hydrocarbon-containing organic media, specifically for natural gas conditioning and separation of “heavy” hydrocarbons from the associated petroleum gas. The permeability coefficients of the copolymers for methane and *n*-butane are listed in Table 5.

It is seen that the selectivity of *n*-butane separation from the mixture (α n-C_4H_{10}–CH_4) modeling the composition of the natural gas for copolymers TFPS–*co*-TMSP is much higher than the value calculated from the permeability coefficients of individual hydrocarbons. This phenomenon, which is inherent in PTMSP and other highly permeable disubstituted polyacetylenes [2, 11], is explained by the predominant sorption of the condensable gas (*n*-butane) inside microvoids of the polymer matrix and this hinders the transport of molecules of the constant gas (methane). For polymers of disubstituted acetylenes with different microstructure, the permeability coefficients for condensable hydrocarbons and selectivity α (n-C_4H_{10}–CH_4) depend on the value of total free volume of the polymer [10, 12, 13]. Thus, the observed increase in the permeability of butane with the content of TMSP units in the copolymer (Table 5) is caused by a gain in free volume with the increasing content of high-permeability polymer (PTMSP) units. This promotes a better sorbability of the organic vapor (*n*-butane) and leads to the growth of permeability and selectivity of its separation from the hydrocarbon mixture.

In this study, the random copolymerization of TFPS and TMSP is studied for the first time in the presence of catalyst system $NbCl_5$–Ph_3SiH possessing other stereoregular properties compared with the previously used catalysts. Research into the behavior of the copolymers containing 15–80 mol % TFPS units made it possible to determine conditions for preparing soluble film-forming polymers combining high gas-transport parameters with resistance against hydrocarbons and high selectivity in the separation of the methane–butane mixture. Owing to the combination of these properties, the fluoro-containing copolymers of TFPS and TMSP show promise as materials for the separation of various liquid and gaseous carbon-containing organic media.

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