Macromolecules **2007,** *40,* 8991−8998

Synthesis, Characterization, and Membrane Properties of Poly(1-trimethylgermyl-1-propyne) and Its Nanocomposite with TiO_2

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Received June 30, 2007; Revised Manuscript Received August 31, 2007

ABSTRACT: The relationship between poly(1-trimethylgermyl-1-propyne) (PTMGP) microstructure and gas permeability property is reported. Controlling the synthesis conditions via $TaCl_5$ and $NbCl_5$ catalyst systems, tailor-made polyacetylenes in a wide range of cis/trans ratio (trans content from 35 to ∼100%) were obtained. According to the cis and trans ratio in the polymeric chain, a two-phase structure was found characterized by the presence of regions with enhanced level of macrochains ordering and with amorphous regions. The polymer microstructure has been related with free-volume, gas permeability, and polymer resistance toward liquid hydrocarbons. PTMGP membranes with high trans content (80−90%) exhibited higher gas permeability than samples with low trans content. Gas permeability of PTMGP membranes decreased with the density of polymer films, i.e., with the free-volume fraction in polymers with different microstructures. Furthermore, it was demonstrated that gas permeability and resistance toward solvents of the PTMGPs are directly defined by their cis/trans microstructure and supramolecular ordering. PTMGP with well-defined microstructure (trans content between 80 and 90%) can be considered as potential membrane material for gas separation, e.g., separation of higher hydrocarbons from natural gas. PTMGP/TiO_2 nanocomposite membranes were also studied for exploring the gas permeability properties and stability of polyacetylene membranes. Gas transport properties were affected slightly by TiO_2 presence; however, the long-term stability was enhanced.

Introduction

Exceptional gas transport properties, particularly high selectivity (condensable hydrocarbons/permanent gas) of 1,2-disubstituted poly(acetylenes), have led to considerable interest in their synthesis and detailed investigation on microstructure−property relationships.[1,2]

Poly(1-trimethylsilyl-1-propyne) (PTMSP), a silicon-containing polymer belonging to the class of 1,2-disubstituted poly(acetylenes), exhibits a record level of gas and vapor permeability.[3−6] This was attributed to a large free volume of PTMSP (around 28%), where the free-volume voids are big enough to be considered as micropores. The properties of PTMSP have been rationalized with its chemical microstructure, particularly the high stiffness of macrochains[5,7−9] and the presence of a bulky substituent which acts as intersegmental spacer are responsible for the unusual morphology of this polymer.

The important feature of PTMSP and some other high-permeable substituted polyacetylenes is their gas and vapor transport properties, which increases with the increase of penetrant molecular size.[4,10−13] Besides, the PTMSP selectivity value for vapor/permanent gas mixture separation is essentially higher than that obtained for pure gas permeation experiments.[14,15] The permanent gas permeability of the PTMSP decreases significantly in the presence of vapor, since the vapor condensates in the free volume voids of the polymer and surface diffusion of condensed component becomes dominant. The selectivity of the *n*-butane/methane mixture separation using the PTMSP membrane is about 30, which is 6 times higher than the pure gas selectivity.[14] This unique property of the PTMSP is attractive for the application in removal of higher hydrocarbons during natural gas conditioning. However, the presence of higher hydrocarbons in the natural gas streams lead to the degradation of the membrane due to the solubility of PTMSP in liquids hydrocarbons. Thus, from a practical point of view, the study and development of new polyacetylenes with well-defined microstructure and good resistance to high hydrocarbons is important.

Our present notions on unusual gas transport behavior of highly permeable glassy polymers are mostly based on data obtained for silicon-containing materials. A detailed investigation of PTMSP synthesis at various conditions and its influence on polymer properties[16] found that gas permeability of PTMSP and its solubility in organic solvents depends on the geometric structure of macromolecules (content of units having cis and trans microstructures) and supramolecular organization (packing of polymer chains). In turn, the geometric structure of macromolecules depends upon synthesis conditions of the polymer, such as catalytic system, solvent, polymerization temperature, etc. Variation of polymerization conditions allows changing the geometry of polyacetylene macromolecules and hence enable us to tailor polymer properties.

Great interest has been noted for the nearest structural analogue of PTMSP, the germanium-containing poly(1-trimethylgermyl-1-propyne) (PTMGP). This polymer differs from PTMSP only by the nature of the heteroatom in the side group. The germanium atom has a higher atomic weight and ionic radius than silicon, the Ge−C bond stability is higher than Si−C,[17] and consequently the Ge containing polymer has higher

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10.1021/ma0714518 CCC: \$37.00

resistance toward corrosive media, particularly toward hydrolysis and oxidation. PTMGP synthesis and properties were first described in a U.S. patent by Langsam and Savoca.[18] This polymer was obtained via polymerization of 1-trimethylgermyl-1-propyne (TMGP) monomer in toluene with $TaCl_5$ as catalyst. The obtained polymer was soluble only in carbon disulfide and was insoluble in other organic solvents. Synthesis of PTMGP soluble not only in carbon disulfide but also in cyclohexane, carbon tetrachloride (CCl_4), and tetrahydrofurane (THF) which were resistant toward aliphatic and aromatic hydrocarbons was reported by Khotimsky et al.[19,20] Various PTMGP samples soluble in aromatic hydrocarbons but having different solubility in aliphatic hydrocarbons were also reported.[21] These differences in polyacetylenes properties were mainly attributed to the different microstructure of polymer samples synthesized in different polymerization conditions.

The present work investigates the PTMGP synthesis under various polymerization conditions and relates polymerization conditions and PTMGP permeability properties. Additionally, synthesis of organic−inorganic nanocomposites based on these polymers and investigation of gas transport properties, especially for hydrocarbons separation such as n-C_4H_{10}/CH_4, were carried out.

Experimental Section

Synthesis of the Monomer. TMGP was obtained by a three-step organomagnesium Grignard synthesis, and all steps were conducted in dry THF. The first step, which included the preparation of ethylmagnesium bromide, was performed at a molar ratio of ethyl bromide:magnesium = 1:1 and at 45 °C of temperature. At the second stage, the Jocitsch reagent was synthesized from methylacetylene−allene fraction (70%) at 45−50 °C. The completion of this stage was determined based on the gas liquid chromatography (GLC) data for the composition of the gaseous products. The interaction of methylacetylenylmagnesium bromide with trimethylchlorogermane was carried out at the same temperature. When the reaction was completed, the reaction mixture was hydrolyzed by a saturated solution of ammonium sulfate, the organic layer was dried over calcium chloride over a period of 24 h, the solvent was removed, and the residue was distilled. The yield of TMGP was 75%. The produced product was rectified, and the fraction with a boiling point of 112 °C was taken away until the monomer with a purity of not less than 99.9% was obtained.

Purification of Reagents. Toluene with high-purity grade used as solvent in polymerization experiments was washed with 5% solution of sulfuric acid, then with water and a 10% solution of sodium hydroxide, and at the end with water again. CCl_4 of reagent grade was purified with a 10% solution of potassium hydroxide and washed with water. Toluene and CCl_4 were then dried over $CaCl_2$ for 24 h. Prior polymerization, toluene and cyclohexane were distilled three times over calcium hydride in a high-purity argon atmosphere, and CCl_4 was distilled three times over phosphorus pentoxide in the same atmosphere.

Niobium pentachloride $NbCl_5$ (99.9%) and tantalum pentachloride $TaCl_5$ (99.9%) from Fluka were used as received. Other components of the catalytic systems as cocatalysts, Ph_3Bi (99%, Aldrich), Bu_4Sn (98%, Fluka), Et_3SiH (>97%, Fluka), and Ph_3SiH (>97%, Fluka) were also used as received. Powderlike catalyst was dosed in sealed glass ampoules under argon atmosphere, and then they were unsealed directly before being used.

Polymerization of TMGP. A solution of catalyst ($NbCl_5$ or $TaCl_5$) in solvent was loaded in a glass reactor and stirred at the reaction temperature for 30 min. The monomer was added to the catalyst solution, and the reactor was sealed. After 24 h, the reactor was unsealed and the reaction mixture was treated with a 6-fold (by volume) excess of methanol to deactivate the catalyst. The precipitated polymer was washed with pure methanol, dissolved in CCl_4 (∼2 wt.%), and reprecipitated again with methanol. The produced polymer was filtered on a Schott filter and dried in air for 24 h at room temperature. Then, the polymer was dissolved, reprecipitated and dried once more. The as-obtained polymer was additionally dried in vacuum at room temperature for 8 h until observing constant weight, and then the yield of the polymer was determined.

Scheme 1. Hydrolysis and Condensation Reactions for the Formation of TiO_2-sol Nanoparticles

Hydrolysis:

$$Ti(OPr^i)_4 + nH_2O \longrightarrow Ti(OPr^i)_{4-n}(OH)_n + nHOPr^i$$

Condensation:

$$Ti(OPr^i)_{4-n}(OH)_n + Ti(OPr^i)_{4-n}(OH)_n \longrightarrow Ti(OPr^i)_{4-n}(OH)_{n-1}\text{-}O\text{-}Ti(OPr^i)_{4-n}(OH)_{n-1} + H_2O$$

$$\text{Or: } Ti(OPr^i)_{4-n}(OH)_n + Ti(OPr^i)_4 \longrightarrow Ti(OPr^i)_{4-n}(OH)_{n-1}\text{-}O\text{-}Ti(OPr^i)_3$$

Polymerization of TMGP via catalytic systems based on niobium and tantalum pentachlorides in combination with alkylating agents such as Ph_3Bi, Ph_3SiH, Et_3SiH, and Bu_4Sn were carried out under the same conditions described above. However, in the case of cocatalysts Ph_3SiH and Ph_3Bi, needed amounts of solid cocatalyst were added to the solution of pentachloride (catalyst:cocatalyst = 1:1, mol:mol). Liquid cocatalysts Et_3SiH and Bu_4Sn were added by using a syringe, and the ratio of catalyst:cocatalyst was the same (1:1, mol:mol). The solution of catalyst:cocatalyst system formed as a complex was stirred for 0.5 h, and then the monomer was added.

Characterization of Polymers. The values of molecular weight ($\overline{M}_w$ and $\overline{M}_n$) were determined by gel permeation chromatography (GPC). The measurements were carried out at 50 °C using a Waters chromatograph equipped with a Chrompack microgel-5 mix R-401 column; toluene and THF were used as solvent.

The intrinsic viscosities of polymer solutions in CCl_4 were measured at 25 °C with the aid of an Ostwald−Ubbelohde viscometer.

The chemical structure of the synthesized polymer was studied by FT-IR and ^{13}C NMR spectroscopy. For ^{13}C NMR analysis, PTMGP solutions in $CDCl_3$ were used; the chemical shifts of carbons were determined relative to $CHCl_3$, and the spectra were recorded on a Bruker MSh-300 instrument operated at 75.47 MHz; the solution concentration was 20 wt.% and the acquisition time was 12 h. The infrared (IR) spectra of PTMGP were recorded in the 4000−400 cm^{-1} range by a Specord M-82 spectrophotometer (Carl Zeiss, Jena). The samples were prepared by applying a polymer solution in CCl_4 on KBr plates.

Differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermal gravimetric analysis (TGA) measurements were conducted with a Mettler TA 3000 thermal analysis system; the heating rate was 5 °C/min, and the air or nitrogen flow rate was 0.3×10^{-3} m^3/s.

The mechanical properties of PTMGP films were studied at 20 °C and at a constant stretching rate of 5 mm/min using an Instron Series IX Automated Materials Testing Systems 1.16.

X-ray diffraction analysis was performed at room temperature by a standard DRON-1.5 diffractometer using Ni-filtered Cu Kα radiation ($\lambda = 0.154$ nm) under transmission and reflection modes. Samples used in X-ray experiments (∼100 μm films) were prepared by casting polymer solutions. The samples were composed of a pile of five parallel films with a surface area of 10×10 mm^2.

Synthesis of TiO_2 Nanoparticles. Metal alkoxides were used in the sol−gel process to obtain nanosized particles in a variety of solvents. The molecular approach is based on well-defined starting molecules and provides good control over purity, composition, homogeneity, and structure of the resulting materials. The work has been focused on the synthesis of titania nanoclusters starting from $Ti(O^iPr)_4$. Basically two reactions, hydrolysis and condensation, govern the formation of sol particles from alkoxide precursors (Scheme 1). When the hydrolysis and condensation procedure is controlled carefully, nanoparticles with a narrow size distribution can easily be obtained. The hydrolysis was performed in the presence of an acid catalyst (HNO_3). $Ti(O^iPr)_4$ has been purified via distillation before use and directly hydrolyzed without modification.

Sols were generally prepared by adding slowly water under inert conditions to the precursors: In order to limit precondensation, the precursor solutions were cooled at 0 °C during the water addition and then aged for 1 h.

Manufacturing of Polymer and Nanocomposite Membranes. In order to control the influence of preparation history on membrane properties, all samples were prepared under the same conditions: controlled solvent evaporation for 72 h at ambient conditions, mechanical membrane removal from PTFE surface, and overnight conditioning in vacuum at 30 °C using an oil-free membrane pump. The polymer solution was prepared in cyclohexane at room temperature (3 wt.% of polymer) by stirring for 24 h.

For nanocomposite membranes, polymeric solutions were prepared using cyclohexane/THF mixture (80/20 wt/wt) and TiO_2 sol received from SINTEF as described above ([Ti] = 0.34 mol/L in THF; $D_{\mathrm{Ti-alcoxo}} = 9.4 \pm 3.6$ nm), and then it was stirred for 20 min. The obtained polymer/TiO_2 solution with TiO_2 content of 5−20 wt.% (in relation to polymer) was used for membrane formation at conditions described for the pure polymer. Membranes with a thickness of 40−70 μm and thickness difference less than 2 μm were obtained and used for gas transport experiments.

Gas Permeation Experiment. Single gas transport properties of H_2, N_2, O_2, CH_4, CO_2, and n-C_4H_{10} in PTMGP and nanocomposite dense membranes were determined with a constant-volume/variable-pressure (time-lag) method at 30 °C.[22,23] The feed pressure was 180 mmHg for all gases, and the permeate pressure as a function of time was obtained. The permeate pressure did not exceed 10 mmHg, and before each gas permeation experiment, the permeation cell with the polymer membrane under study was evacuated for 12 h. Each measurement was repeated at least 3 times for 3 membrane samples of the same composition and history.

n-C_4H_{10} and CH_4 mixed gas permeation experiments were carried out with the experimental setup schematically shown in the Supporting Information. The facility allows studying permeation of binary gas mixtures through flat membranes having a wide range of permeances. The gas mixture was prepared directly before measurement by mixing individual gases as well as beforehand prepared gas mixtures can be used. The gas flow and pressure of the feed and sweep were measured on the entrance to the measurement cell. The compositions of the feed, retentate, and permeate side were analyzed by an Agilent 9890N gas chromatograph. Nitrogen was used as a sweep gas since it has one of the lowest gas permeability coefficients, thus mostly preventing its back diffusion from the permeate side to the feed side of the membrane. The design of the measurement cell provides radial flow of gases on both sides of the membrane and prevents formation of dead zones.

Long-Term Aging Experiment. Several samples of dense membranes made from pure PTMGP as well as nanocomposites were tested during 30 days. This time can be considered as critical to observe the changes on the gas transport properties (aging). Between each measurement, the membranes were stored in air in clean glass desiccators at ambient conditions. No special action was taken to prevent contamination of membrane samples.

Results and Discussion

I. Polymerization and Characterization of Polyacetylenes.

As described in the Experimental Section, TMGP polymerization was carried out with $TaCl_5$ and $NbCl_5$ as catalysts as well as via catalytic systems based on $TaCl_5$ and $NbCl_5$ with various cocatalysts (Ph_3Bi, Ph_3SiH, Et_3SiH, and Bu_4Sn). The polymerization occurred at different temperatures (25−80 °C) and in various solvents. The obtained polymers had high molecular weight (between 105 and 290 kg/mol). Polymerization conditions and characteristics of PTMGP samples are given in the Supporting Information.

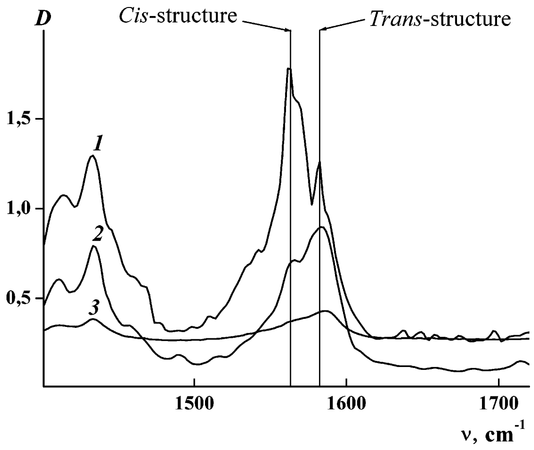

Figure 1. IR spectra of PTMGP samples; (1) 35% trans content (catalyst $NbCl_5$; (2) 90% trans content (catalyst $TaCl_5$); and (3) ~100% trans content, soluble only in CS_2 (catalyst $TaCl_5$).

TMGP polymerization with Nb-containing catalysts gave high polymer yields (60−95%). Intrinsic viscosities of PTMGP synthesized with individual $NbCl_5$ increase from 0.4 to 0.5 dL/g and to 0.7 dL/g when the cocatalysts system was used. However, Ta-containing catalysts gave less polymer yields (40−85%) than the previous one, but the intrinsic viscosity of PTMGP synthesized with individual $TaCl_5$ is higher than that for PTMGP synthesized with $NbCl_5$ and significantly increase from 0.6 to 1.1 dL/g with solvent polarity (cyclohexane < CCl_4 < toluene). On the other hand, the increase of polymerization temperature up to 80 °C ($TaCl_5$ catalyst system and toluene as solvent) increases the intrinsic viscosity of polymer up to 2.17 dL/g. Polymerization on Ta-based catalytic systems using cocatalysts Ph_3Bi, Et_3SiH, Ph_3SiH, and Bu_4Sn resulted in a decreasing of intrinsic viscosity of polymers which was contrary to $NbCl_5$-based catalytic systems with analogous cocatalysts.

The IR spectra of PTMGP (Figure 1) demonstrates the presence of a double C=C bond in the polymer macromolecule (absorption band at 1600 cm^{-1}). Vibrations of a C−H bond (band at 2900 cm^{-1}), a C−Ge−H bond (band at 900 cm^{-1}), and a C−Ge bond (band at 500 cm^{-1}) were also observed but these are not shown in the figure. No bands corresponding to a triple C≡C bond are seen at 2200 cm^{-1}. Therefore, this result indicates that polymerization proceeds through a triple bond of the monomer to provide a polymer bearing double bonds in the polymer backbone. Consequently, PTMGP macromolecule is composed of $-[C(-Me)=C(-Ge(-Me)_3)]_n-$ as the monomer unit.

The analysis of the PTMGP microstructure was carried out using ^{13}C NMR spectroscopy methods. ^{13}C NMR spectra of PTMGP solutions in $CDCl_3$ demonstrates four characteristic doublets corresponding to four carbons of the monomer unit of PTMGP $-[C(-Me)=C(-Ge(-Me)_3)]_n-$, with chemical shifts of 1.9−5.0 ppm ($-Ge-(\mathit{C}H_3)_3$), 24.0−26.5 ppm ($-\mathit{C}H_3$), 138.5−140.5 ppm ($=\mathit{C}-Ge$), and 147.0−149.0 ppm ($=\mathit{C}-CH_3$). The doublet structure of signals corresponding to the carbons in the monomer units shows the existence of cis and trans units (Figure 2), and the relative intensities of signals in doublets are related to the quantitative ratio of these units in the polymer.

The assignment of signals to cis and trans microstructures in NMR spectra was performed using the method based on combination of NMR and IR spectroscopy with theoretical analysis of normal vibrational spectra of polymers having various geometries.

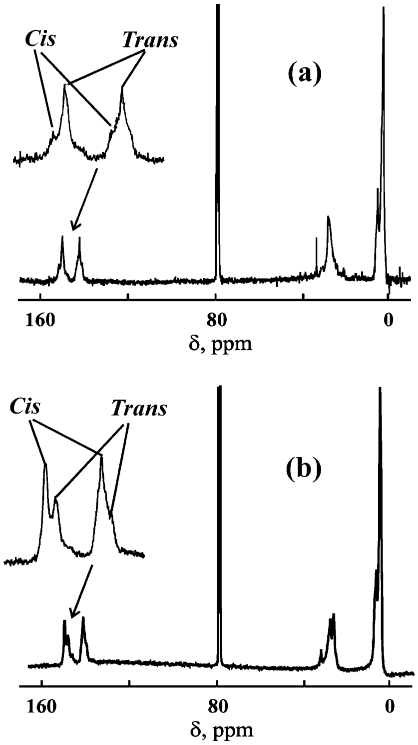

Figure 2. ^{13}**C** NMR spectra of PTMGP and their interpretation; (a) 95% trans microstructure (catalyst TaCl$_5$) and (b) 35% trans microstructure (catalyst NbCl$_5$).

From the comparison of theoretical spectra models of cis and trans microstructures, the majority of bands in vibrational spectra coincide with respect to position and intensity. The differences are only observed in the region of absorption of a long-wave region and in the region of double bonds. The interpretation was performed on the basis of these differences. In the theoretical IR spectrum for the trans microstructure, two very weak absorption bands are seen at 1580 and 1520 cm^{-1}. In the experimental IR spectrum of PTMGP synthesized with TaCl$_5$ (Figure 1 (2)), two weak absorption bands at 1581 and 1517 cm^{-1} are observed, these bands can be interpreted as corresponding to trans microstructures in polymer. Absorption bands corresponding to cis microstructures in the theoretical spectrum of *cis*-PTMGP are shifted in position (1565 and 1540 cm^{-1}) and have a significantly higher intensity. Bands in the experimental IR spectrum of PTMGP synthesized with NbCl$_5$ (Figure 1 (1)) are intensive and located at 1561 and 1548 cm^{-1}, and thus, we can conclude that these bands can be interpreted as corresponding to polymer cis microstructures.

In accordance with ^{13}C NMR spectra, PTMGP synthesized with TaCl$_5$ consists mainly of the trans isomer (Figure 2a). At the same time, PTMGP obtained with NbCl$_5$ contains both cis and trans microstructures (Figure 2b). The comparison of results and interpretation of IR spectra for PTMGP with relative position of peaks in doublets in^{13}**C** NMR spectra have enabled us to interpret signals of cis and trans microstructures spectra. In the^{13}**C** NMR spectrum of PTMGP, peaks at 1.9−2.5 ppm ($-$Ge$-$($\boldsymbol{C}$H$_3$)$_3$), 26.0−26.5 ppm ($-\boldsymbol{C}$H$_3$), 138.5−139.5 ppm ($=\boldsymbol{C}-$Ge), and 147.0−147.5 ppm ($=\boldsymbol{C}-$CH$_3$) correspond to the trans microstructures, whereas peaks at 4.0−5.0 ppm ($-$Ge$-$($\boldsymbol{C}$H$_3$)$_3$), 23.5−24.0 ppm ($-\boldsymbol{C}$H$_3$), 140.0−140.5 ppm ($=C-$Ge), and 148.9−149.0 ppm ($=\boldsymbol{C}-$CH$_3$) are corresponding to cis microstructures.

The amounts of cis and trans microstructures in polymers were calculated on ^{13}C NMR spectra using a WinNMR1d program (Bruker) helpful for calculating poorly resolved spectra. This allowed us to determine the content of cis and trans microstructures in polymers synthesized under different polymerization conditions.

Table 1. Solubility (Resistance) of PTMGP in Hydrocarbons: *T* = 25 °C, Test Duration 1 Week

		solvents				
PTMGP samples[a]	trans content [%]	pentane hexane	heptane octane	toluene	benzene	CCl$_4$, CHCl$_3$ THF
33CM[b]	≈100	−	−	−	−	−
9CM, 10CM 16CM, 19CM 21CM, 22CM 33CM,[c] 29CM	85−95	−	−	−	−	+
14CM, 17CM 28CM	75−80	+	+	+	+	+
18CM,24CM 26CM,27CM	35−40	−	+	+	+	+

[a] All samples are soluble in CS$_2$. [b] Insoluble fraction. − Insoluble. [c] Soluble fraction. + Soluble.

The microstructure of polymer strongly depends on polymerization conditions (see the Supporting Information), which is influenced by catalyst nature and polarity of solvents. Ta-based catalytic systems give more trans microstructures (75−100% of trans content), whereas polymers obtained with Nb-based catalysts are enriched with cis microstructures (35−40% trans content). According to IR spectroscopy (Figure 1), PTMGP fraction soluble only in CS$_2$ was practically composed of trans microstructures. The change of solvent polarity (toluene > CCl$_4$ > cyclohexane) during polymerization decreased the polymer trans content from 90 to 80%. Thus, varying synthesis conditions, we have managed to change the microstructure of polymers in a wide range of cis/trans ratio: the content of trans microstructures varies from 35% in polymer samples of mixed microstructure to 90−100% in samples enriched with trans-structure.

Obtained polymers are colorless (or slightly creamy). During TGA experiments, the decomposition of PTMGP in inert atmosphere begins at 330 °C (5% weight loss) and in air at 295 °C. These data show high thermal and thermo-oxidative stability of PTMGP. It was also found that PTMGP is an amorphous glassy polymer and its glass transition temperature (T_g) is >300 °C (DSC data). In the same way, it was found that PTMGP has high film-forming properties. Mechanical properties of PTMGP films (strength, $\sigma = 23.2$ MPa for PTMGP synthesized with TaCl$_5$; 22.8 MPa for PTMGP synthesized with NbCl$_5$; strain break, ϵ = 8% and 23%, respectively; Young's modulus, E = 633.1 and 802.1 MPa) are similar to those of PTMSP (strength, $\sigma = 23.0$ MPa for PTMSP synthesized with TaCl$_5$ and 33.8 MPa for PTMSP synthesized with NbCl$_5$; strain break, ϵ = 42% and 24%, correspondingly; Young's modulus, E = 447.4 and 701.9 MPa).

PTMGP resistance toward organic solvents was investigated (Table 1). The resistance of polymers to hydrocarbons depends on their microstructure, and all polymer samples can be divided into four groups: (1) PTMGP, predominantly composed of trans microstructures (∼100%) which is soluble only in CS$_2$; (2) PTMGP highly enriched with trans microstructures (85−95%) soluble only in CCl$_4$, CHCl$_3$, THF and cyclohexane; (3) PTMGP which contains less amount of trans microstructures (up to 75%) soluble in a wide range of organic solvents; and (4) PTMGP which contains mainly cis microstructures (35−40% trans) soluble in halogenated hydrocarbon (CCl$_4$ and CHCl$_3$), THF, and aromatic hydrocarbons (benzene and toluene) and insoluble in *n*-alkanes C$_5$−C$_6$. It supposes that the reason for different

Table 2. X-ray Data for PTMGP Samples with Different Microstructure

samples	trans content [%]	d (Å) 1 reflex	2 reflex	3 reflex	4 reflex	$\Delta_{1/2}$ main reflex
PTMGP 9CM	95	9.40	4.75	3.35	2.10	1.60
PTMGP 26CM	35	9.00	4.70	3.30	2.10	2.00

Table 3. Pure Gas Permeability of Different PTMGP Membranes as a Function of Trans Content

			permeability [barrer][a]					
samples	trans content [%]	thickness [μm]	H_2	N_2	O_2	CH_4	CO_2	n-C_4H_{10}
PTMGP 10CM	90	40	5520	2030	3130	5070	13100	19950
PTMGP 29CM	85	40	6930	2200	3830	8450	16600	15000
PTMGP 17CM	80	35	7900	2780	4140	6300	18600	17000
PTMGP 24CM	40	37	5740	1640	2800	3870	13300	6520

[a] [barrer] = 1×10^{-10} [cm^3 cm/cm^2 s cmHg].

solubility of PTMGP with different microstructure is due to different supramolecular organization of PTMGP with different microstructures such as it will be discussed in X-ray analysis.

The supramolecular structure of PTMGP was studied by X-ray diffraction analysis (see Table 2). The scattering profile shows an amorphous-like pattern and displays three diffuse maxima with angular positions of $2\Theta \sim 10$, 20, and 28° and an additional halo with the angular position $2\Theta \sim 43°$, which is likely the reflection order of one of the previous diffuse maxima. The half-widths of corresponding reflections are 1.6 and 2.0° for PTMGP synthesized with $TaCl_5$ and $NbCl_5$, correspondently. This indicates that, although the coherent scattering region is small, it is larger than in the case of amorphous polymers, for which the reflection half-width is usually 5−8°. In terms of supramolecular ordering, the structure of PTMGP can be defined as a certain state intermediate between liquid-like truly amorphous and ordered states (crystalline or liquid-crystalline). The X-ray data testified that PTMGP possess a two-phase structure characterized by the presence of regions with an increased level of ordering dispersed in amorphous polymer matrix. On the basis of the reflection half-width and, consequently, on the basis of the size of coherent scattering regions, one may distinguish a more regular polymer, which is strongly enriched with trans microstructures and a less ordered groups of polymers with a mixed microstructure.

Two-phase morphology of PTMGP with different geometric structures can be due to different molecular characteristics of these PTMGPs. The study of equilibrium rigidity of PTMGP macrochains with various microstructures has been established. Kuhn segment length for PTMGP decreases with increase of cis content in polymer and it is around $80-100 \times 10^{-8}$ cm (∼38 units) for PTMGP containing 95% of trans- microstructures, and 50×10^{-8} cm (∼19 units) for PTMGP containing 65% of cis- microstructures.[24−26] So, PTMGP macromolecules probably consist of a rigid trans and a more flexible cis sequences.

PTMGP enriched with trans microstructures (85−95% trans) has a high density of packing of macrochains in the ordered regions, because it has high stereoregularity, and consequently, it is stable toward C5−C7, octane, decane, and toluene and it is soluble only in CCl_4, $CHCl_3$, and THF. The insoluble PTMGP fraction (sample 33 CM) containing only a trans unit (∼100% according to IR spectra) has the densest packing of macrochains in the ordered regions. This is a completely stereoregular polymer, and its stability toward pentane, hexane, octane, decane, toluene, CCl_4, and THF demonstrated the highest resistance to organic solvents (soluble only in CS_2).

When the trans content of PTMGP is between 75−80%, trans blocks cannot be densely packed, and it does not form ordered regions due to the flexibility of macrochains. Therefore, it is an irregular amorphous polymer and soluble in a wide range of solvents. With a decrease in the trans content, the stability of the polymer toward hydrocarbons is unexpectedly enhanced. PTMGP with a mixed microstructure containing 35−40% trans microstructures, which have ordered regions formed by a rigid trans blocks packed owing to presence of enough amounts of flexible cis blocks shows stability toward hydrocarbons (insoluble in C5−C6).

Therefore, from these analyses, we suppose that high content of trans- microstructures is needed for high resistance of PTMGP toward organic solvents, the ability to tailor the resistance of polymers toward solvents is also very important for the creation of polymeric membranes on the basis of 1,2-disubstituted polyacetylenes.

II. Gas Permeability Properties. *Effect of the Polyacetylene Microstructure on Membrane Properties.* In order to obtain polymers with specific properties for the preparation of membranes and their application in hydrocarbon separation, four poly(1-trimethylgermyl-1-propyne) samples with different microstructures were selected for membrane preparation and characterized according to gas separation properties.

Pure Gas Permeation. H_2, N_2, O_2, CH_4, CO_2, and n-C_4H_{10} pure gas permeability through the PTMGP membrane at 30 °C as a function of trans- content are shown in Table 3. Almost all gas permeabilities increased when the trans content in the polymer chain is decreased from 90 to 80%; however, when the trans content is lower (40%) the gas permeability dropped unexpectedly.

These results can be directly related to the cis/trans ratio present in the polymer sample. As it is known, the polymer microstructure is responsible for many properties of a dense membrane. In disubstituted polyacetylenes, the high permeability to large organic vapors is attributed to the high fractional free-volume. Therefore, an alteration in the polymer packing by ordering of the polymeric chains induces changes in the total free-volume of the polymer as well as the structure of free-volume. PTMGP sample with 90% of trans content presents low permeability, it has lower free-volume and maybe the free-volume-elements are less interconnected due to the packing of macrochains in long trans regular sequences. Decreasing of trans content up to 80% induce an increase of gas permeability. It may be related with the breaking of regularity in the macrochains and, consequently more loose packing is realized. PTMGP membranes with lower content of trans microstructure (40%)

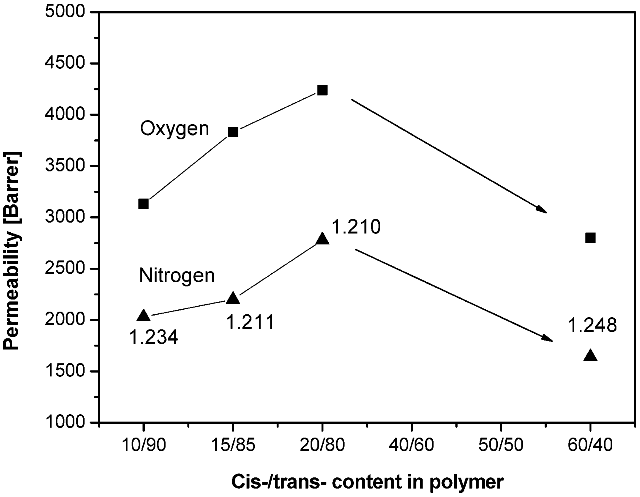

Figure 3. Oxygen and nitrogen permeability and geometric density of PTMGP membranes as function of cis/trans unit ratio (density is the numbers next to experimental points).

showed lower permeabilities than PTMGP with high trans content in the range of 90 to 80% (see Figure 3 permeability as function of cis/trans ratio). This behavior can be attributed to a mutual ordering of the chains because a more flexible cis microstructure promotes more dense packing of trans sequence and thus a decreasing of the free-volume could have happened.

Different geometric densities of PTMSP have been reported depending on membrane preparation history.[10,27−29] This has been directly related to the polyacetylene microstructure (ratio of cis-/trans-) and to the free-volume. In PTMGP, the density depends on the polymer microstructure and the film preparation history. A small change of the microstructure in the PTMGP can induce changes to the free-volume. The permeability of PTMGP samples is in good correlation with the values of geometric density (Figure 3, numbers next to experimental points), i.e., changes in PTMGP microstructure induce to changes of geometric density and consequently of the free-volume of the polymer. As discussed, the cis microstructure is more flexible, thus one could speculate that PTMGP samples with trans content of 80−90% would have the free-volume-elements continuously increased according to increase of cis content. The data reported in the literature[10,28] and the data demonstrated in Figure 3, show that PTMGP with higher cis content (40% of trans unit) has lower gas permeability. Khotimsky et al.[16] found low permeability (oxygen) in membranes prepared from PTMGP with 65% of cis content, and it was attributed to high geometric density of polymer. Freeman et al.[10] also reported similar results for PTMGP as well as for PTMSP.

Mixed Gas Permeation. It is well-known that permeation of mixed gases (condensable gas mixed with permanent gas) through membranes made of polyacetylenes and other polymers with high free volume are significantly different to those experimental results obtained with single gases.[14,15] A mixture of methane and *n*-butane (98.4/1.6 mol/mol) was used as a test gas; this *n*-butane/methane ratio is typical for many natural gas streams. The data presented in Table 4 show the effect of the trans content on polyacetylene membrane permeability when mixed gas is used. Membranes made from PTMGP with high trans content fraction show the highest permeability. PTMGP samples with trans content of 80−85% presented higher selectivity than PTMGP with 40% of trans content. This result shows the importance of polyacetylene microstructure on the gas selectivity, especially when the feed gas mixture contains a condensable gas. Samples with high trans content (80−85%) have high free-volume and the chain packing could be more stable preventing mutual ordering of the chains.

Table 4. Mixed Gas Permeation Properties of Polyacetylene Membranes as Function of Trans Content (Feed Composition; 98.4 mol % Methane and 1.6 mol % *n*-Butane)

		permeability [barrer]		selectivity
samples	trans content [%]	CH_4	n-C_4H_{10}	n-C_4H_{10}/CH_4
PTMGP 10CM	90	2640	62830	24.8
PTMGP 29CM	85	2130	66190	31.1
PTMGP 17CM	80	1980	70900	35.8
PTMGP 24CM	40	1340	32370	24.2

Molecular transport through a dense polymeric membrane strongly depends on the amount of free-volume or space not occupied by polymer chains and the structure of the free-volume-elements.[28−30] In general, in dense size-selective polymer membranes, small molecules preferentially permeate relative to larger one. However, in membranes with reverse-selective properties, the larger one preferentially permeates in a gas mixture. The high n-C_4H_{10}/CH_4 selectivity in polyacetylene membranes has been studied and discussed by many authors and it can be represented either by extended dual-mode sorption mechanism introduced by Koros et al.[30] or by selective surface sorption, where the methane permeability depression is caused by pore blocking due to the capillary condensation of *n*-butane on the inner surface of microcavities.

Due to the facts discussed above, PTMGP 29CM and PTMGP 17CM samples with high trans- content which present high resistance toward hydrocarbon solvents can be considered as membrane material for natural gas hydrocarbon dewpointing and similar applications. PTMGP 10CM presents the highest resistance to solvents, but it has lower permeability and selectivity. Thus, we consider that PTMGP 29CM and 17CM samples are the best for membrane preparation and, due to their high selectivity and resistance toward organic solvents, nanocomposite membranes based on these polymers were prepared.

PTMGP/TiO_2 Nanocomposite Membranes. Nanocomposite membranes are considered as a promising alternative to conventional polymeric membranes. According to theoretical and experimental works of a number of research groups around the world, the use of inorganic inert or active fillers dispersed in the matrix of the selective polymer can lead to membranes with improved separation properties, stability, and durability.[31−33] As reported, in PTMSP and PMP with high free-volume, the permeability increased with filler content,[34−36] since inorganic nanoparticles disrupt polymer chain packing.

Pure Gas Permeation. Table 5 presents pure gas permeability coefficients of H_2, N_2, O_2, CH_4, CO_2, and n-C_4H_{10} for PTMGP and polymer/TiO_2 nanocomposite membranes as a function of filler content. As it can be seen, the permeability for all single gases slightly increased when filler was added to the polymer. The membrane based on PTMGP 29CM sample with 20% wt of TiO_2 filler was brittle and it was not possible to measure the single gas permeability. However, the PTMGP 17CM sample presented a good mechanical stability, and thus membranes with 5, 10, and 20 wt % of TiO_2 filler were prepared.

For both nanocomposites with PTMGP 29CM and PTMGP 17CM, the permeability was slightly enhanced (10−20%, approximately). Due to the fact that PTMGP has analogous characteristics to PTMSP,[10,16,21] these results can be considered consistent with previous reports related to PTMSP.[28,34,37,38] In addition, the systematic increase of permeability shown by the

Table 5. Pure Gas Permeability for PTMGP and Their Polymer/TiO_2 Nanocomposite Membranes

			permeability [barrer]					
samples	TiO_2 content [wt. %]	thickness [μ**m**]	H_2	N_2	O_2	CH_4	CO_2	n-C_4H_{10}
PTMGP 29CM		40	6930	2200	3830	8450	16600	15000
	10	57	8320	3120	4190	7490	19100	14300
	20[a]	72						
PTMGP 17CM		37	7900	2780	4240	6300	18600	17000
	5	60	8450	3260	4680	8240	20000	17700
	10	50	8160	3110	4830	8120	24900	18300
	20	56	8450	3140	4700	7990	20400	17000

[a] Sample was broken.

Table 6. Mixed Gas Permeability for PTMGP and Nanocomposite Membranes (Feed Composition; 98.4% Methane and 1.6% Butane)

		permeability [barrer]		selectivity
samples	TiO_2 content [wt %]	CH_4	n-C_4H_{10}	n-C_4H_{10}/CH_4
PTMGP 29CM		2130	66190	31.1
	10	1840	56280	30.6
	20	1210	36350	30.0
PTMGP 17CM		1980	70900	35.8
	5	2130	66890	31.4
	10	1990	62280	31.3
	20	1250	36010	28.8

PTMGP/TiO_2 nanocomposite can be qualitatively compared to PTMSP nanocomposite membranes. Therefore, the TiO_2 filler addition into the polymer matrix would also produce even more permeable material.

Mixed Gas Permeation. Methane and *n*-butane mixed gas permeability and selectivity is shown in Table 6. The permeability of *n*-butane and methane decreased with filler content up to fifty percent with 20% of filler content. The *n*-butane/methane selectivity in membranes based on PTMGP 29CM sample stayed nearly constant; however, for PTMGP/TiO_2 based on the PTMGP 17CM sample, the selectivity dropped from 35.8 to 29.0.

The reduction of n-C_4H_{10}/CH_4 selectivity suggest that TiO_2 filler increased the free-volume more than required for selective n-C_4H_{10} separation. This result demonstrates that the filler creates free-volume elements large enough permitting permanent gas to pass (no-blocking).

Long-Term Aging Analysis. As it is known, the density and other properties are sensitive to physical aging in polyacetylene such as PMP, PTMSP, and PTMGP; it is because the enormous free- volume of these polymers provides a large driving force for relaxation of nonequilibrium excess volume.[4,21,39,40] The gas permeability reduction during storage was attributed to the physical aging, chemical aging, and contamination or a combination of all them. Nagai et al.[4] reported that probably contamination is the dominant factor when polymer is stored for a long time in air.

In Figure 4, the PTMGP and PTMGP/TiO_2 (10 and 20 wt %) membrane aging is presented. The permeability decrease is clearly observed when the membranes were stored at room temperature. The aging behavior in this polymer is similar to that presented for the PMP system; first a rapid decreasing of permeability and then a slower and gradually decrease.[39] For the PTMGP/TiO_2 nanocomposite, the permeability decreases less than that observed in the pure PTMGP polymer membrane.

It can be concluded that the addition of TiO_2 nanoparticles in PTMGP slows down the aging and consequently contributes to the stability of the membranes during its application. For future works, a study of TiO_2 addition to PTMGP is recommended for discussing stability (aging) of the nanocomposite membranes.

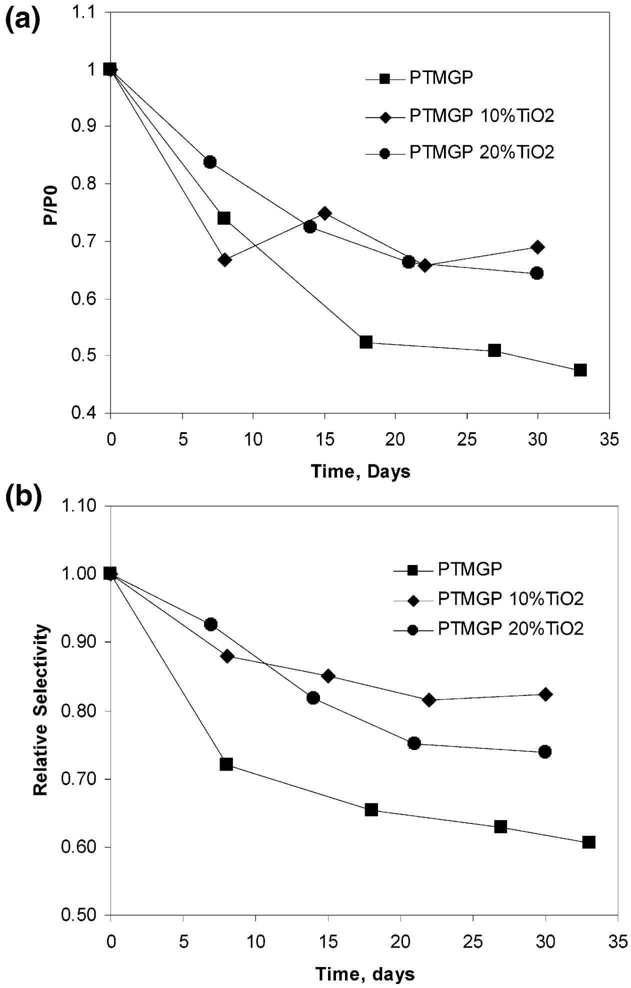

Figure 4. Aging of PTMGP and nanocomposite (10 and 20 wt % of TiO_2) membranes stored at room temperature: (a) Relative permeability of *n*-butane and (b) relative selectivity of *n*-butane/methane to day "0".

Conclusion

Tailor-made poly(1-trimethylgermyl-1-propyne) with different microstructures was synthesized via $TaCl_5$ and $NbCl_5$ catalysts. Varying the synthesis conditions such as catalyst systems, solvents, monomer/catalyst ratio, temperature, etc., we obtained polymers with specific properties and in a wide range of cis/trans ratio (cis:trans from 5:95 to 65:35%). X-ray diffraction data testified that PTMGP possess a two-phase structure characterized by the presence of regions with an enhanced level of ordering of macrochains dispersed in an amorphous polymer matrix. Therefore, and on the basis of resistance experiments toward organic solvents, we conclude that a high content of trans microstructures (content of trans- unit >85) is needed for high resistance of PTMGP toward hydrocarbons.

The cis/trans microstructure ratio significantly affected the permeability properties of the membranes. Sample with 40% of trans content (sample 24CM) showed lower pure-gas permeability. However, samples with high trans content changed in a form not expected; a slightly increase of permeability was observed when the trans content is changed from 90 to 80% (samples 10CM, 29CM, and 17CM).

The *n*-butane/methane mixed gas experiment showed that the polyacetylene microstructure is very important for membrane preparation, because the resistance of membranes toward organic solvents depends on the polyacetylene microstructure. These results were related to cis and trans microstructure properties, and consequently to the free-volume of the polymers.

The TiO_2 nanoparticles addition to selected polyacetylenes did not show an improvement of permeability and selectivity of the membranes what shows that PTMGP can be used without filler as potential membrane material. However, samples with 10−20 wt % of TiO_2 as filler stored for a long time in air presented a good stability, thus it is suggested to carry out a detailed study about aging.

Acknowledgment. Partial funding for this research was provided by the European Commission (Project COMPOSE, Project Number NMP3-CT-2003-505633). The authors thank G. N. Bondarenko for assistance in carrying out IR-spectroscopy and to A. I. Rebrov for assistance in carrying out NMR analyses.

Supporting Information Available: Experimental conditions and device used for mixed gas measurements; polymerization conditions and characteristics fo PTMGP samples. This information is available free of charge via the Internet at http://pubs.acs.org.

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MA0714518