



# Poly(vinyl trimethylsilane) and block copolymers of vinyl trimethylsilane with isoprene: Anionic polymerization, morphology and gas transport properties

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## ABSTRACT

Poly(vinyl trimethylsilane) (PVTMS) and block copolymers of vinyl trimethylsilane with isoprene were synthesized by anionic polymerization and characterized. The synthesized pure PVTMS has properties similar to a reference material produced about two decades ago and can be used for thin film composite membrane formation. Even at low isoprene content the block copolymers have improved film forming properties compared to the pure PVTMS. However, the presence of the isoprene units in the block copolymers leads to a decrease of the gas permeability but does not affect the selectivity of the membranes ( $\alpha(\text{O}_2/\text{N}_2) = 3.9$ ).

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## 1. Introduction

Processes involving polymeric membranes for separation of air components meet much attention from industry. The development of new types of membranes can open an opportunity of membrane based process implementation in the areas where it was not considered to be used before.

Most of the processes of air separation do not require extreme selectivities or permeances. For example, shift of the oxygen concentration from 21% to 50% or nitrogen concentration from 78% to 85% are sufficient for such applications as controlled burning, food storage etc.

Poly(vinyl trimethylsilane) (PVTMS) is known for more than 40 years as a polymer with a reasonable  $\text{O}_2$  permeability (40–44 Barrer) and good  $\text{O}_2/\text{N}_2$  selectivity ( $\alpha(\text{O}_2/\text{N}_2) = 4.0$ ) [1]. Integral asymmetric membranes made of PVTMS were industrially produced and used in the Soviet Union and France [2–4]. As far as we know PVTMS was

so far the only polymer produced solely as a membrane material. Unfortunately the production of PVTMS was stopped with the collapse of the USSR.

The PVTMS integral asymmetric membrane has had several drawbacks related to the polymer properties as well as the membrane structure. Its small elongation at break ( $\varepsilon = 5\%$ ) [2–4] has led to brittleness of the membrane; both selective top layer and porous supporting structure were formed from the same polymer leading to a high consumption of PVTMS. The thickness of the selective layer was too large providing  $\text{O}_2$  permeance not more than  $P(\text{O}_2) = 0.4 \text{ Nm}^3 \text{ m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  with the  $\text{O}_2/\text{N}_2$  selectivity slightly lower than the intrinsic one.

The modern state of membrane technology provides one with the possibility to form defect free selective layers having thicknesses below 100 nm for both integral asymmetric and thin film composite (TFC) membranes. TFC membranes give the advantage to use expensive selective layer materials since the consumption of the material will usually not exceed  $0.2 \text{ g m}^{-2}$ . It opens the possibility to use experimental or tailor made polymers for membranes produced in industrial scale. [5].

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The current work has pursued the aim to restart the PVTMS synthesis and bring it again into praxis as gas separation membrane material. Homopolymer as well as block copolymers with polyisoprene were synthesized and characterized for various properties.

Several attempts have been made so far to improve the poor mechanical properties of the PVTMS. Gladkova et al. have synthesized copolymers of poly(vinylmethyl trivinylsilane) with poly(dimethyl siloxane) (PVTMS-*b*-PDMS) since they were considered the most promising membrane materials with enhanced gas permeability and separation selectivity. The technique followed was sequential anionic polymerization in tetrahydrofuran (THF) using *sec*-Butyllithium (BuLi) as initiator. [6].

A further study of this combination of polymeric chains reports the successful synthesis of triblock copolymers of the ABA type (PDMS-*b*-PVTMS-*b*-PDMS) in THF using as initiator for the PVTMS difunctional block, dilithium naphthalene. [7].

Statistical and sequential copolymers consisting of styrene and vinyl trimethylsilane units were investigated as well. The synthesis of such polymeric materials was conducted in heptane with *n*-BuLi as initiator. From this study the much faster polymerization of styrene was concluded since the constant of the copolymerization parameter is  $5.7 \pm 0.03$ , while that of vinyl trimethylsilane is  $0.06 \pm 0.01$  [8].

An additional attempt to improve the mechanical properties of PVTMS homopolymer was done by the sequential copolymerization of VTMS with butadiene (PB-*b*-PVTMS) by anionic polymerization induced by mono- and dilithium compounds. [9].

In the current work isoprene was chosen as a comonomer since it is a purely organic polymer with excellent film forming properties and rather high gas permeability as well as O<sub>2</sub>/N<sub>2</sub> selectivity. It was expected that the resulting block copolymers will lead to less brittle films due to the mechanical properties of polyisoprene. Thus film formation should be improved without significant drop in gas permeability and selectivity.

## 2. Experimental part

### 2.1. Materials

Vinyl trimethylsilane (99% pure) was purchased from ABCR GmbH. Isoprene and cyclohexane both of 99% purity was purchased from Sigma–Aldrich International. All monomers and solvents were further purified to the standards required for anionic polymerization. The initiator *n*-BuLi 1.6 M in hexane was purchased from Acros Organics and used without further purification.

Oxygen and nitrogen with purity 99.999% were purchased from Linde AG and used as received.

### 2.2. Polymer synthesis and purification

In order to achieve the synthesis of both homo- and copolymers all materials were purified to anionic polymerization standards [10,11]. In the case of copolymerization of isoprene and VTMS the procedure followed is given in

details: 40 ml (27.6 g) of vinyl trimethylsilane were dried first over calcium hydride for 24 h at reduced temperature under vacuum. After two freeze-degas cycles it was condensed in a flask containing sodium mirror, made from 1 g of sodium by warming the sodium in the evacuated vessel, and left for 1 h to react. 4 ml (2.68 g) of isoprene were dried to anionic standards as previously referred in the literature [11]. Cyclohexane was used as solvent in all polymerizations and was purified by redistillation in the presence of liquid sodium under inert atmosphere, and after freezing and degassing, transferred under vacuum in a flask containing oligomers of polystyryllithium where it was kept. The red color of living polystyryllithium oligomers in cyclohexane was indicative for the purity of the solvent. It is important at this point to mention that the homopolymerization of VTMS or copolymerization of VTMS with isoprene was successful only in the case of high vacuum conditions. First the initiator ( $0.08 \times 10^{-3}$  moles *n*-BuLi 1.6 M in hexane) was inserted into the vacuum dried polymerization reactor under inert atmosphere followed by thorough drying of the solvent. Then it was rediluted with cyclohexane used for the polymerization. The amount of solvent used in all polymerization reactions was equal to the volume of the VTMS monomer since, as it was observed during our very first attempts and also reported in the literature; a high monomer concentration is required for this slowly polymerizing system.

Isoprene was inserted into the polymerization reactor and left to complete conversion according to the kinetics proposed by Bywater for the polymerization of isoprene with *n*-BuLi in cyclohexane.[12] The addition of VTMS was achieved by distillation into the reactor, and the reaction was left to complete for six days at 35 °C [13]. During the polymerization reaction there were no samples removed and after the completion the polymer was precipitated into excess of methanol only once. Previous works describe the dilution and precipitation at least three times to separate all lower molecular weight fractions, but in this way the cost of production rises and our goal was to follow a procedure as close as possible to industrial production.

In another approach, both monomers were added to the reactor before initiation. The procedure of drying the initiator and purification of materials was exactly the same as before and the amounts of monomers and solvents were kept the same in order to have a comparison between the conversions of the two monomers.

### 2.3. Polymer characterization

Gel permeation chromatography (GPC) measurements were performed at room temperature in THF using 5 μ PSS SDV gel columns (10<sup>2</sup>, 10<sup>3</sup>, 10<sup>4</sup>, 10<sup>5</sup> Å, 8-300 mm each, PSS GmbH, Mainz, Germany) at a flow rate of 1.0 ml/min (VWR-Hitachi 2130 pump). A Waters 2410 refractive index detector ( $\lambda = 930$  nm) and a Waters UV-photometer (typically operated at  $\lambda = 254$  nm) were used for concentration detection. Samples were injected employing a Waters 717 autosampler (injection volume 50 μL). To compensate for flow-rate fluctuations 20 ppm 2,6-di-tert-butyl-hydroxytoluene (BHT) was added as internal standard to each sample. Raw data were processed using PSS WinGPC Unity

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