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A Novel Imide-Bridged Polysiloxane Membrane Was Prepared via One-Pot Hydrosilylation Reaction for O_2/N_2 Separation

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Cite This: *ACS Omega* 2021, 6, 19553−19558

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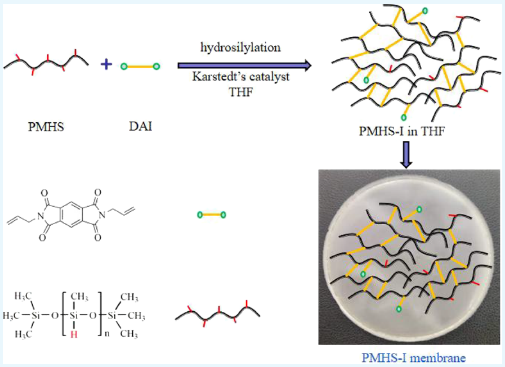
ABSTRACT: The synthesis of poly(methyhydrosiloxane) (PMHS) and *N,N′*-bis(3-allyl)pyromellitic diimide was optimized for O_2/N_2 separation. The membrane exhibits excellent mechanical and thermal properties and shows an O_2/N_2 selectivity of up to 4.44 with an O_2 permeability of 31.0 Barrer; compared with polydimethylsiloxane (PDMS) and pure polyimide (PI) membranes, the separation selectivity shows a 107% increase for PDMS, and the permeation shows a 660% increase for pure PI. The obtained results were well above the ones reported on the literature for similar conditions opening the door for the preparation of a stable polysiloxane (PMHS-I) gas separation membrane with extraordinary O_2/N_2 separation performance.



1. INTRODUCTION

Membrane gas separation technology has been of profound attention in many industrial applications due to the advantages of low energy consumption, high efficiency, and environmental friendliness compared with conventional gas separation processes such as cryogenic distillation and pressure swing adsorption.[1−4] In the membrane gas separation application, the membrane materials play the leading role.[5] Therefore, all kinds of materials have been utilized for these membranes in the last three decades. Among various membrane materials, polymeric membranes have been widely developed and applied according to their low cost, easy processability, and good mechanical property. However, most polymeric membranes follow a trade-off phenomenon where permeability and selectivity are mutually dependent (permeability decreases when selectivity increases and vice versa),[6,7] which would limit their further application in an actual membrane gas separation process.

The polydimethylsiloxane (PDMS) membrane shows high oxygen permeability with the lowest selectivity of O_2/N_2 and poor film forming ability because the Si−O−Si bonds in the polymer are very flexible.[8−14] Polyimide (PI) has a relatively high PO_2/PN_2 (low PO_2) and good film forming ability because of its unique rigid structures with imide rings.[4,15−19] As well known, permeating routes of oxygen through the polymer membranes are hard to control because there are dynamic spaces between their macromolecules. To overcome the two disadvantages, we hope that polymer chain rigidification that would limit the transportation of large gas molecules and facilitate the transportation of small molecules, leading to the enhancement of gas selectivity.[20−27] In this study, we continued our work on predicting gas separation in the ladder polysiloxane,[28] and we will report an imide-bridged polysiloxane by reaction poly(methyhydrosiloxane) (PMHS) with *N,N′*-bis(3-allyl)pyromellitic diimide (DAI) via a one-pot hydrosilylation reaction. In this reaction, the ratios and block length sizes as well as the number of functional groups can be precisely adjusted by reaction conditions, and at the same time, the functionalization via hydrosilylation provides good conversions without notable side reactions.[29] Their membrane is expected to increase the O_2/N_2 separation with high gas permeation. In this experiment, diene-bridged polysiloxanes were used for the first time to make controlled cross-linking reactions of polysiloxanes using more convenient and simple means, with low reaction cost, high efficiency, short time, and high controllability.

2. EXPERIMENTAL SECTION

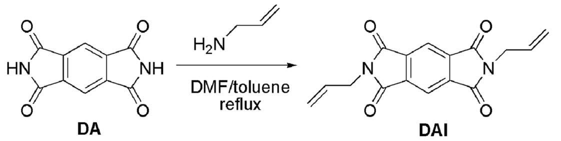
2.1. Materials. All the solvents used for monomer synthesis and polymerization were distilled as usual. Poly(methyhydrosiloxane) (PMHS) with an average molecular weight that ranged from 3000 was purchased from Wuhan Hanxiang Biotechnology Co. 1,2,4,5-Benzenetetracarboxylic

Received: April 13, 2021
Accepted: July 8, 2021
Published: July 23, 2021

anhydride (PMDA) and 3-aminopropene were purchased from Aladdin, Karstedt's catalyst was purchased from KeJunchi, and acetone and chloroform were purchased from Thermo Fisher Scientific. Tetrahydrofuran (THF) was purchased from Kaitong Chemical Reagent Co., Ltd. (Tianjin). The composition of mixed gas used in this work was made of O_2/N_2 (50/50, v/v %). Purity (99.999%) was purchased from Xuelong Petrochemical Technology Development Co., Ltd. (Daqing). DA was synthesized according to ref 28.

2.2. Synthesis Method of *N,N′*-Bis(3-allyl)pyromellitic Diimide (DAI). As shown in Scheme 1, *N,N′*-bis(3-allyl)-pyromellitic diimide (DAI) was synthesized through a transimidation from DA reaction with 3-aminopropene, where DA was synthesized according to ref 28.

Scheme 1. Synthesis of *N,N′*-Bis(3-allyl)pyromellitic Diimide (DAI)



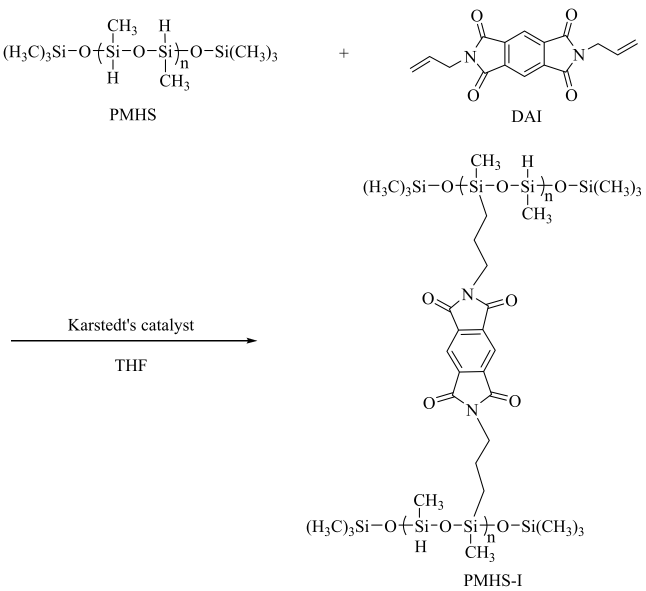
Pyromellitic diimide (DAI, 2.16 g) was added into a three-necked flask with a condenser and magnetic stirring bar, and then it was evacuated and purged with nitrogen five times. DMF (5.00 mL) and 50.0 mL of toluene were added, then the mixture was heated to 70 °C for 0.5 h, and 1.5 mL of 3-aminopropene was added and stirred at 130 °C for 48 h. After cooling to room temperature, filtration was applied to remove the solid. Then, the solution was concentrated under reduced pressure to about 5 mL. The residual solution was poured into a large amount of MeOH, and the precipitation was filtrated and dried in vacuo to give a white solid.

2.3. Synthesis and Membrane Fabrication of PMHS-I. Imide-bridged polysiloxane (PMHS-I) was synthesized via a hydrosilylation reaction, according to Scheme 2. Then, the solution was poured directly into a poly(tetrafluoroethylene) dish and dried to give a self-standing membrane.

Pyromellitic diimide (DAI, 6.87 g) and 10 mg of Karstedt's catalyst were added into a three-necked flask with a condenser and magnetic stirring bar, and then it was evacuated and purged with nitrogen five times; 30 mL of THF was added and stirred at 85 °C for 1 h, and then 11.6 mL of polymethylhydrogensiloxane (PMHS) was added and stirred for 4 h. After cooling to room temperature, the solution was poured into a 10 cm diameter Teflon (PTFE) dish. After the solvent was evaporated for 12 h at 25 °C, the membranes were detached from the dish and dried in vacuo at 25 °C for 24 h. The thickness (L) of the membranes was between 150 and 152 μm, and the mechanical properties of the membranes were tested five times, as shown in Table S1.

2.4. Measurements. Fourier transform infrared spectroscopy was used to record functional group information (Spectrum Two, PE Company, Waltham, Massachusetts, USA). The thickness gauge was used to test the membrane thickness (CH-1-B hand-type millimeter thickness gauge, graduation value: 0.001 mm, measurement range: 0−1 mm, and error range: ≤0.007 mm, Shanghai Liuling Instrument Factory, China). A film tensile testing machine was used to record the mechanical property at 25 °C (XLW(PC)-500 N, Sumspring, Jinan, China). The thermal performance of the membranes was recorded by a thermogravimetric analyzer (Q5000IRS type, American TA Co., Ltd., USA). A gas transmission instrument was used to test permeation under different pressures (GTR-11MH type, GTR TEC Corporation, Kyoto, Japan; test area: 0.785 cm^2; test temperature: 34 °C; test pressure: 49 KPa; gas mixture pressure: 0.1 MPa; carrier gas (H_2) pressure: 0.5 MPa).

Scheme 2. Synthesis of Imido-Bridged Polysiloxane (PMHS-I)



2.5. Calculations. The gas permeability coefficient P was calculated by the following relation (eq 1):

$$P = \frac{q \times K \times L}{a \times p \times t}(\text{mL}\cdot\text{cm}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}\cdot\text{cmHg}^{-1}) \tag{1}$$

where q is the transmission volume (mL), K is the auxiliary positive coefficient (the fixed value is 2), it is the setting point instrument by factory, L is the film thickness (cm), p is the permeability pressure (cmHg), t is the measurement time (s), and a is the area of the gas permeation film (the fixed value is 0.785 cm^2).

In this experiment, the gas separation factor was calculated by the following relation (eq 2):

$$\alpha = \frac{PO_2}{PN_2} \tag{2}$$

where PO_2 and PN_2 attributed to gas pressure (O_2 and N_2, respectively), which can be calculated in eq 1. Pure gas permeation property tests were performed with a fixed-volume pressure increase instrument time-lag apparatus (VAC-V2 type, Labthink Instrument Co., Ltd., Jinan, China) at 34 °C. The membranes were first placed in a stainless-steel cell, and the disk was sealed with rubber O-rings to avoid leakage. Then, both the upstream and downstream sides of the system were degassed at ambient temperature to ensure that the system was not disturbed. Next, pure gases (O_2 and N_2) were fed into the membrane individually, and the permeance of each pure gas was measured at a feed pressure of 2 bar. The gas permeance P was calculated by the following relation (eq 3):

$$P_g = \left(\frac{\text{d}p}{\text{d}t}\right)\frac{V\cdot T_0}{A\cdot\Delta p\cdot P_0\cdot T}(\text{mL}\cdot\text{cm}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}\cdot\text{cmHg}^{-1}) \tag{3}$$

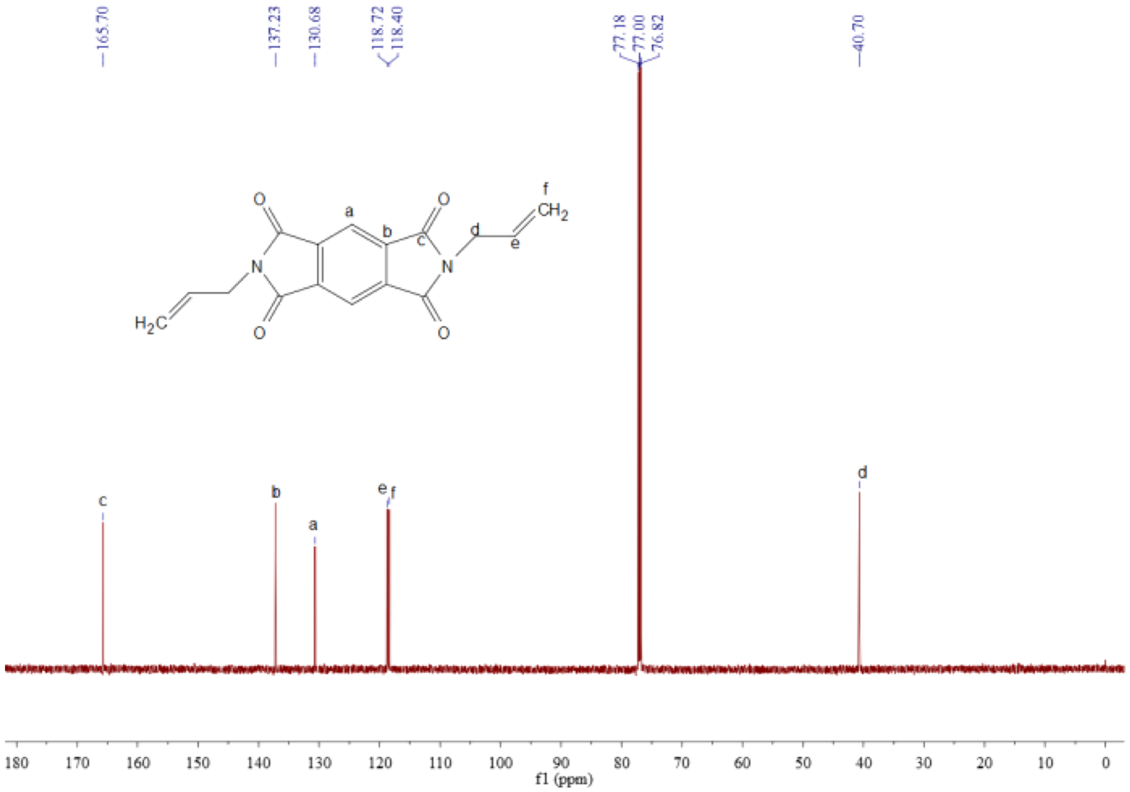


Figure 1. ^{13}C NMR spectra of *N,N′*-bis(3-allyl)pyromellitic diimide in $CDCl_3$.

where dp/dt is the slope (cmHg/s) of the pressure against time in the pseudo-steady state, V is the downstream volume (cm^3) of gas permeation, Δp (cmHg) is the difference in the pressure between the two sides of the membrane, A is the effective membrane area (3.14 cm^2), P_0 is 76 cmHg, T_0 is 273 K, and T is the measured temperature of 307 K. The ideal selectivity coefficients of gases A and B are reported as the ratio of the permeance of P_A and P_B, respectively. The conversion of hydrosilylation (degree of cross-linking) is calculated using the flow equation:[31]

$$\text{convention} = \frac{A_{(\text{PMHS},2168)}/A_{(\text{PMHS},1261)} - A_{(\text{PMHS-I},2168)}/A_{(\text{PMHS-I},1261)}}{A_{(\text{PMHS},2168)}/A_{(\text{PMHS},1261)}} \times 100$$

where $A_{(\text{PMHS},2168)}$ and $A_{(\text{PMHS},1261)}$ represented integral absorption intensities at 2168 and 1261 cm^{-1} PMHS, respectively. $A_{(\text{PMHS-I},2168)}$ and $A_{(\text{PMHS-I},1261)}$ represented integral absorption intensities at 2168 and 1261 cm^{-1} PMHS-I, respectively. In addition, the characteristic peak existing at 1705 cm^{-1} attributed to the C═C group in PMHS-I, which suggested that a small part of butadiene reacted with Si–H and the generated C═C group only.[31]

3. RESULTS AND DISCUSSION

3.1. Characterization. DAI was accomplished by introducing 3-aminopropene through a transimidation from diimide (DA) rather than the reaction of 1,2,4,5-benzenetetracarboxylic anhydride (PMDA) with 3-aminopropene. Because the above-mentioned transamination leads to the almost exclusive formation of the target product, because the byproduct is NH_3 in the formation of DAI, it will promote the reaction. This can be found from the ^{1}H NMR data of DAI (Figure S1), and ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm: 165.70, 137.23, 130.68, 118.72, 118.40, and 40.70.) (Figure 1) shows similar results where there is only DAI resonating without any other byproduct.

The IR spectra of PMHS-I, PMHS, and DAI are shown in Figure 2. The peak around 2168 cm^{-1} was credited to the Si–H bond stretching vibration from PMHS; the absorption peak at 1705 cm^{-1} attributed to the C═C bond stretching vibration in DAI correspondingly. However, these two peaks from the spectrum of PMHS-I have disappeared, indicating the hydrosilylation process between PMHS and DAI. In addition, the peak observed at 1380 cm^{-1} corresponded to the characteristic peak of the imide structure and the absorption peak at 1023 cm^{-1} can be ascribed to the Si–O–Si bond stretching vibration, which verified the successful synthesis of PMHS-I.

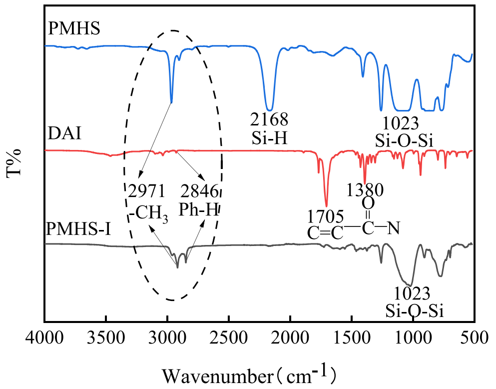


Figure 2. IR spectra of PMHS, DAI, and PMHS-I in KBr.

Table 1. Mechanical Properties of PMHS-I Membranes Compared with PDMS and PI Membranes[a]

sample	THK[b] (μm)	σs[c] (MPa)	Eb[d] (%)	TS[e] (MPa)	E[f] (MPa)	reference
PMHS-I	151.0 ± 1.00	12.5 ± 0.20	9.0 ± 0.14	24.5 ± 0.20	271.0 ± 1.00	this work
PDMS			0.7 ± 0.01	1.8 ± 0.50	89.0 ± 5.10	30

[a] Tested at 5.00 mm/min speed. The standard spline had a length of 40 mm and a width of 10 mm. [b] Thickness (THK). [c] Yield strength (σs). [d] Elongation at break (Eb). [e] Tensile strength (TS). [f] Modulus of elasticity (E).

It is obvious from Figure 2 that the absorption intensity of Si−CH_3 is much higher than that of Si−H in PMHS-I after the completion of hydrosilylation. Because Si−CH_3 does not participate in the hydrosilylation reaction, we can conclude that most Si−H groups reacted with C═C groups, and the conversion of hydrosilylation (degree of cross-linking) was about 97.52%.

3.2. Mechanical and Thermal Properties of PMHS-I Membranes. Tensile stress strain tests were carried out to investigate the mechanical properties of the PMHS-I membrane. The average values of the yield strength, tensile strength, elongation at break, and tensile modulus of samples are determined and shown in Table 1. The PMHS-I membrane shows better mechanical properties than PDMS, and the results indicated that PMHS-I is a cross-linked polysiloxane.

As shown in Table 1, we can see that the elongation at break of the unmodified pure polysiloxane film is 0.70%, the tensile strength is 1.80 MPa, and the elastic modulus is 89.0 MPa. In this work, the elongation at break of the modified polysiloxane increased 11.9 times (9.00%), the tensile strength increased 12.6 times (24.5 MPa), and the modulus of elasticity increased 2.04 times (271.0 MPa). This huge improvement is because the imide group is a rigid group, while the polysiloxane is a flexible chain-like group. The rigid group is introduced into the polysiloxane, and a cross-linked network structure is synthesized. The amplitude improves the mechanical properties of the membrane.[32]

As shown in Figure 3, thermogravimetric analysis (TG) was performed on PMHS-I and the experimental results showed a 5% weight loss at 339 °C and a 50% temperature loss at 462 °C. The structure of the imide chain in the molecule has good thermal stability. This can further indicate the successful preparation of PMHS-1.

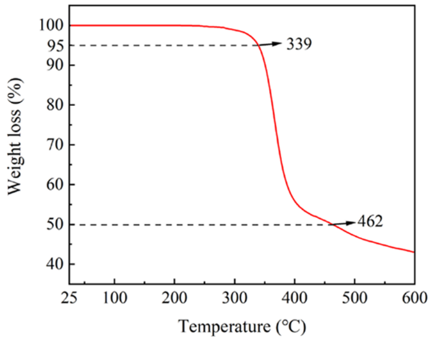


Figure 3. TG analysis of the PMHS-I membrane.

The self-supporting films obtained in this work all start to lose weight after 300 °C and lose weight rapidly in a very short period of time compared to ref 31. While the weight loss of the separation membranes in the references reached more than 90% when the temperature reached about 500 °C,[33] the present work resulted in a final weight loss of only 60% due to the introduction of a rigid structural imide.

3.3. Gas Separation Properties. The single-gas permeability coefficient and selectivity of the obtained PMHS-I membrane are shown in Table 2. The PMHS-I membrane yielded permeances of 35.2 and 9.52 Barrer for O_2 and N_2, respectively, and a selectivity of 3.70 for O_2/N_2. Compared with PDMS and pure PI membranes, PMHS-I membranes exhibited higher permeances of O_2 and N_2 for the pure PI membrane and better selectivity of O_2/N_2 for the PDMS membrane. Accordingly, the ideal selectivity of oxygen and nitrogen is contributed from both solubility selectivity (SO_2/SN_2) and diffusivity selectivity (DO_2/DN_2), and from the experimental results, the diffusivity selectivity plays a leading role compared to solubility selectivity. As demonstrated above, PMHS-I is a rigid imide chain-bridged polysiloxane with a restricted network structure; the smaller O_2 molecules can directly diffuse through the network, while larger N_2 molecules are forced to take more tortuous diffusion transportation pathways, leading to the improvement of gas selectivity.

To obtain the true membrane permselectivity in practical applications, we tested the permselectivity of the obtained PMHS-I membrane for mixed gas. The results are compared to the pure gas performance, as shown in Table 2. Both O_2 and N_2 permeabilities have decreased compared with the pure gas permeation properties, but the decrease in N_2 permeability is more pronounced; as a result, the selectivity of O_2/N_2 has increased. In the final analysis, the transportation of a component is slightly different due to the effect of sorption competition between the gas molecules in the binary gas mixture. Overall, the agreement between the mixed gas selectivity and the pure gas selectivity for O_2/N_2 was good.

Compared with ref 28, Xu et al. reported a flexible self-standing membrane from the imido-bridged ladder polysilox-

Table 2. Gas Permeability, Solubility, and Diffusivity Coefficients of Membranes Measured at 34 °C

	pure gas									mixed gas			
	P		S		D								
samples	O_2	N_2	O_2	N_2	O_2	N_2	PO_2/PN_2	SO/SN_2	DO_2/DN_2	PO_2	PN_2	PO_2/PN_2	reference
PMHS-I	35.20	9.52	1.24	1.01	2.84	0.94	3.70	1.23	3.01	31.00	6.98	4.44	this work
PDMS										600.00	280.00	2.14	34
pure PI	0.46	0.09					5.11						35

ane with a high molecular weight; the membrane achieves an oxygen permeation of 1.67 Barrer and an oxygen-nitrogen separation of 4.44. This study simplified the synthesis steps while maintaining the separation ability of oxygen and nitrogen and increased the oxygen transmission rate 17.56 times, which is a simpler and more effective method with good scientific prospects.

The cross-linking degree of polysiloxane obtained in this work is calculated by the above formula to reach 97.52%. A higher degree of cross-linking means that the imide structure is fully introduced into the polysiloxane. Because PI has a high PO_2/PN_2,[28] the acyl full introduction of the imine structure greatly improves the PO_2/PN_2 of the PMHS-I film.

4. CONCLUSIONS

In conclusion, a novel imide-bridged polysiloxane was successfully synthesized by poly(methyhydrosiloxane) reacting to *N,N′*-bis(3-allyl)pyromellitic diimide with Karstedt's catalyst via one-pot hydrosilylation. The obtained self-standing membranes showed excellent mechanical and thermal properties. The membrane showed better O_2 permselectivity (PO_2/PN_2 = 4.44) than PDMS (2.14) and a higher O_2 permeability (31.0 Barrer) than pure PI (0.46). The high selectivity was provided by the enhancement of diffusion selectivity by the network structure, creating small pores (ultramicropores) based on imido linkages.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01964.

> Mechanical properties of PMHS-I membranes, gas separation of PMHS-I membranes, and ^1H NMR spectra of *N,N′*-bis(3-allyl)pyromellitic diimide (DAI) in $CDCl_3$ (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Fundamental Research Funds in Heilongjiang Provincial Universities (YSTSXK201867), the Natural Science Foundation of Heilongjiang Province, China (LH2019B032), and the Graduate Innovative Research Project of Qiqihar University (YJSCX2020058).

■ ABBREVIATIONS

THF, tetrahydrofuran; DAI, *N,N′*-bis(3-allyl)pyromellitic diimide; PMHS, polymethylhydrogensiloxane; PMHS-I, imide-bridged polysiloxane; PTFE, Teflon; DA, diimide; *S*, solubility selectivity; *D*, diffusivity selectivity

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https://doi.org/10.1021/acsomega.1c01964
ACS Omega 2021, 6, 19553−19558