

**Highly stable PDMS-PTFPMS/PVDF OSN membranes for hexane recovery during
vegetable oil production**

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1. PVDF supporting membrane preparation

PVDF ultrafiltration support previously prepared using non-solvent-induced phase separation (NIPs) method¹. 20 wt.% of PVDF (PVDF-6020) in triethylphosphate solution was cast on a polyester nonwoven fabric with a 150 μm casting knife, and subsequently immersed in a 25 °C water bath. The membrane was washed with DI water for 2 hours, and stored for three days to remove residual solvent. Finally, as-synthesized membrane was dried in air at 25 °C. All the membrane formation steps were performed in an air conditioned room at 25 °C and with a relative humidity (RH) in the range of 30–40%.






2. Cross-linking time for various PDMS-PTFPMS copolymers

Table S1 Cross-linking time for various polymers at 10 °C

Polymer	PDMS	F15	F25	F100	F50-L	F50-M	F50-H
Cross-linking time (h)	~ 0.5	~ 3	~ 3	~ 24	~ 16	~ 3	~16

3. Stability of cross-linked PDMS-PTFPMS/PVDF membranes

Table S2 Visible surface change from digital photos of membranes suffering from testing experiments

	a. PDMS	b. F15	c. F25	d. F50-M	e. F100
Testing condition	A	A	A	B	A
Testing time (day)	2	2	2	32	15
Visible surface change from digital photo					

Note: A: in 26 \pm 1 wt% soybean oil/hexane at 25 \pm 1 °C; B: in 7 \pm 1 wt% soybean oil/hexane at 25 \pm 1 °C

Comparing these five composite membranes, PDMS, F15 and F15 have visible bubbles on their surfaces, showing weak stability in 26 wt.% soybean oil/hexane mixture. In contrast, F50-M and F100 have excellent stability respectively after 32 days and 15 days testing. Therefore, we believe that F50-M and F100 have the best selection for further study on solvent recovery process.

4. FTIR

Fig. S1. depicts the FTIR spectra of PVDF substrate, PDMS-PTFPMS polymers and cross-linked PDMS-PTFPMS/PVDF composite membranes. Strong, sharp adsorption bands of PVDF substrate appear at 1070 cm^{-1} , 975 cm^{-1} , 853 cm^{-1} and 795 cm^{-1} ; yet they disappear for PDMS-PTFPMS/PVDF composite membranes. New adsorption bands at around 1210 cm^{-1} (Si-CH₂CH₂CF₃) and 2900 cm^{-1} (-CH₃) also emerge. These indicate that the PVDF substrate surface is fully coated by a layer of PDMS-PTFPMS. The characteristic band of Si-OH group in PDMS-PTFPMS polymers disappears or greatly weakens after forming cross-linked membranes. Therefore, cross-linked membranes are successfully prepared from these PDMS-PTFPMS polymers.

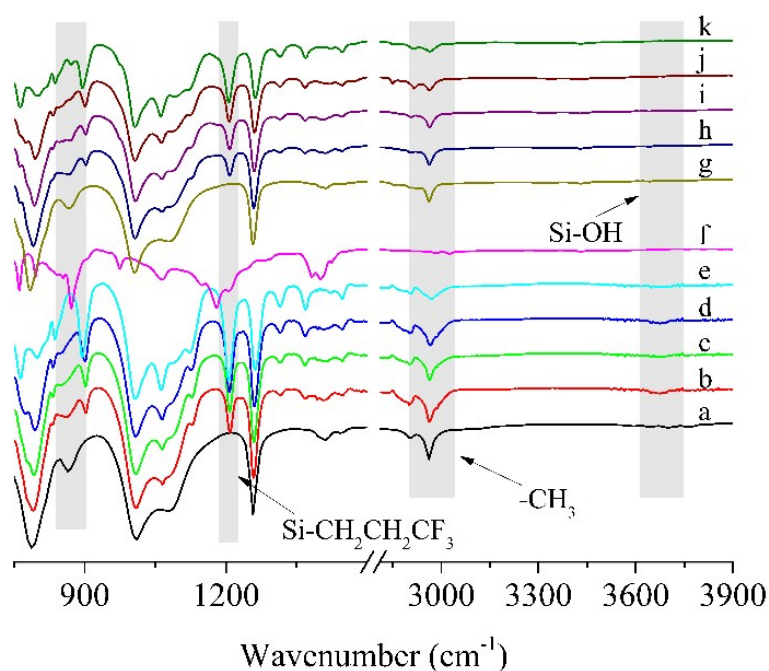


Fig. S1. ATR spectra of origin a) PDMS, b) F15, c) F25, d) F50-M, e) F100 polymer and cross-linked g) PDMS, h) F15, i) F25, j) F50-M, k) F100 on f) PVDF substrate

5. DSC and TG analysis

To qualitatively estimate the flexibility of polymer chains, T_g of PDMS-PTFPMS samples are determined with a deviation of about 1 °C in Fig. S2. T_g is -123 °C for PDMS polymer and it increases when the ratio of the PTFPMS segment increases, showing a T_g of -121 °C, -117 °C and -78 °C for F15, F25 and F100, respectively. We also compare cross-linked F25 membrane with F25 polymer, showing a higher T_g of -115 °C. Similar results are obtained from the other comparisons.

We believe that cross-linked microstructure and larger side groups (e.g. trifluoropropyl groups) can raise T_g and then reduce polymer chain mobility^{2,3}. Interestingly, F50 polymer differ from the linear PDMS, in their level of T_g and viscosity⁴. T_g is $-96\text{ }^\circ\text{C}$ for F50-L polymer and it decreases slightly to $-107\text{ }^\circ\text{C}$ for F50-M polymer, then dramatically increases to $-79\text{ }^\circ\text{C}$ for F50-H polymer. In contrast, the T_g of linear PDMS grows with increasing polymer viscosity until it reaches around $-123\text{ }^\circ\text{C}$. This fact indicates that unique microstructure and composition derived from the PTFPMS segment reduce polymer mobility.

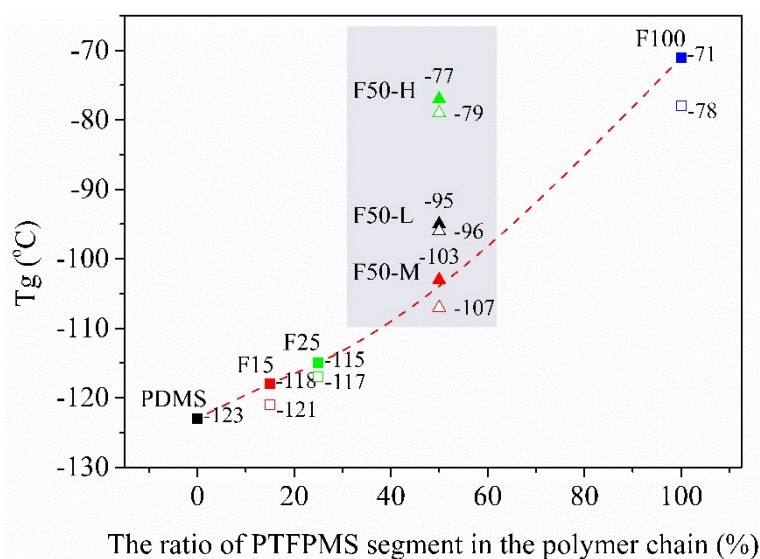


Fig. S2. T_g of cross-linked PDMS-PTFPMS film samples (solid) and PDMS-PTFPMS polymer (open)

Thermal stability and degradation behaviors of cross-linked PDMS-PTFPMS film samples are shown in Fig. S3. Fig S3(a) shows that the initial resolution temperature is around $324\text{ }^\circ\text{C}$ for the PDMS sample and it successively decreases when the ratio of PTFPMS segment increases, showing weaker thermal stability. This is because of the decomposition to low-molecular cyclic products which can be highly volatile, as well as possible oxidation or free radical attack^{5,6}. The degradation rate of $\text{PDMS} < \text{F15} < \text{F25} < \text{F100}$ is further evidence of this phenomenon. Additionally, Fig. S3(b) shows that the initial resolution temperature of F50-M is $321\text{ }^\circ\text{C}$ higher than F50-L and F50-H, showing better thermal stability. This should be attributed to the poor cross-linking of F50-L and F50-H as shown in Section 3.2⁷. Nevertheless, F15, F25 and F50-M membranes still have high thermal stability close to the PDMS membrane.

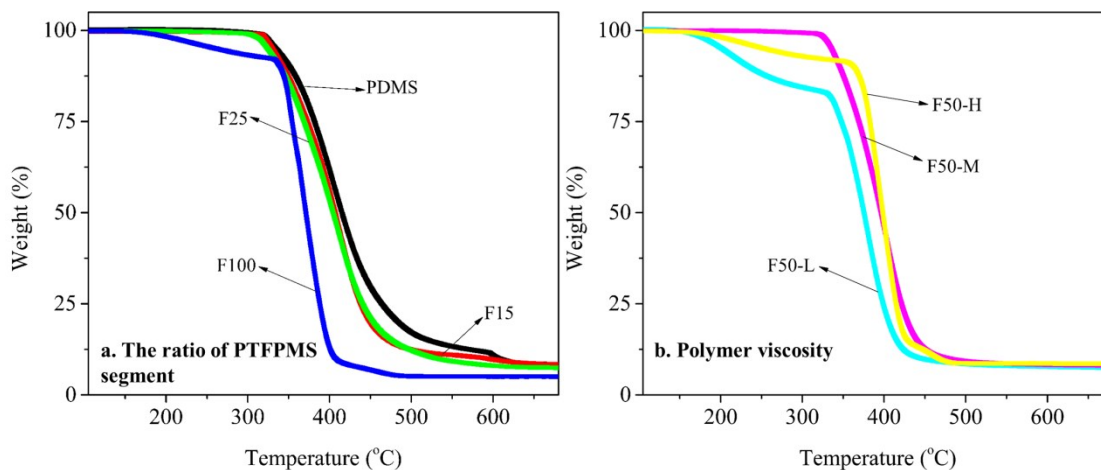


Fig. S3. TG curves of cross-linked PDMS-PTFPMS film samples

6. Pure hexane permeability and dye rejections

Permeation experiments of pure hexane and dye rejection tests are in the custom-made apparatus as shown in Section 2.5. Experiments are performed at 2.0 MPa of transmembrane pressure and $T = 25\text{ }^{\circ}\text{C}$ using pure hexane or 30 mg/l Rose Bengal (RB) feed solution in methanol. Dye concentrations are determined by absorption spectrometry using UV-1 800PC Spectrophotometer at 556 nm. RB rejections are calculated according to Eq. (4). Results are listed below as Table S3 and Table S4.

Table S3 shows that pure hexane permeability of various PDMS-PTFPMS membranes at 2.0 MPa. This is used to explain the effect of the ratio of PTFPMS segment (PDMS, F15, F25 and F100). Compared to PDMS membrane, more hydrophobic surface of F15 membrane enhances the adsorption of non-polar hexane and onto its surface and hexane diffusion through the membrane. Further increasing the ratio of PTFPMS segment from 15% to 100% would reduce pure hexane permeability. Also, it is verified that F50-M has highest hexane permeability when comparing F50-L, F50-M and F50-H.

Table S3 Pure hexane permeability of various PDMS-PTFPMS membranes

Membrane	PDMS	F15	F25	F100	F50-L	F50-M	F50-H
Pure hexane permeability ($\text{kg m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$)	0.59	0.73	0.43	0.07	0.26	0.38	0.02

Table S4 shows that RB rejections and molecular weight cut-off of various PDMS-PTFPMS membranes. Most of them (F15, F25, F100, F50-L, F50-M and F50-H) have smaller effective pore size than PDMS as shown by the RB dye rejection experiments. They should have lower MWCO values than 1000 Da. The average molecular weight of soybean oil is 862.7 Da.⁸ Thus, it is inferred that these membranes would be possible to separate soybean oil/hexane mixture.

Table S4 RB rejections and molecular weight cut-off of various PDMS-PTFPMS membranes

Membrane	R% (RB)	MWCO (Da)
PDMS	80.5	> 1000
F15	97.7	< 1000
F25	97.7	< 1000
F100	99.2	< 1000
F50-L	90.5	~ 1000
F50-M	88.5	> 1000
F50-H	99.5	< 1000

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