# Comparison of the Initial Reactant Structure and Crosslinked Network of Poly(dimethyl siloxane) Membranes from Different Macromonomers

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**ABSTRACT:** Some of the best entities for the removal of volatile organic pollutants from water, poly(dimethyl siloxane) (PDMS) membranes from two types of initial PDMS precursors, were thoroughly investigated. In both the cases, the sizes of the initial macromonomers increased because of the crosslinking in the liquid state, and they exhibited Gaussian chain statistics, which were condensed by further crosslinking to the formation of the membranes. The structures of both the membrane types exhibited large interchain spacing on swelling; this implied a high degree of chain mobility. Their structural properties were corroborated by their separation performances. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41461.

## INTRODUCTION

Membrane-based separation processes are economical, safe, and ecofriendly. Today, membrane processes have acquired a significant position by replacing many conventional unit operation processes. They are becoming powerful tools in solving global problems in both the domestic and industrial sectors for sustainable growth. Among them, pervaporation separation with poly(dimethyl siloxane) (PDMS) membranes is one of the best process for the treatment of polluted water containing volatile organics.[1–3] However, the performance of PDMS membranes is poor when it is applied to the treatment of feeds containing larger amounts of organics.[4,5] Thus, the application of PDMS membranes is limited for petrochemicals and pharmaceuticals effluents containing large amounts of organic solvents, although the PDMS material is organophilic and highly stable in organic solvents.

The development of the PDMS membranes with improved properties for the treatment of the previously discussed industrial harsh effluents will have high socioeconomic relevance in terms of environmental safety and energy savings and in building up a global technology. Global companies, such as GKSS

Germany, MTR USA, GE USA, and Beijing Huaer Co., Ltd., have patents on their proprietary PDMS membranes. Efforts have also been made to prepare PDMS-based membranes by blending with other polymers or inorganic material. Despite these, very limited knowledge is available on the critical synthesis parameters that influence the properties of final PDMS membranes.

In general, PDMS membranes are formed by the crosslinking of the initial reactants (precursors) in a reaction in which the precursors are highly polydispersed viscous liquids with a large distribution of macromolecular masses. The high polydispersity of the precursors occurs because of their tendencies to form cyclic macromolecules during synthesis.[6] Small-angle neutron scattering (SANS) is one of the best techniques for characterizing the structural features of siloxane polymers; these features include the form factor, average radius of gyration ($R_g$), chain aggregation, and Gaussian chain statistics.[7] A hierarchical structure of a multicomponent structural model could suitably fit to polysiloxane chains with large $R_g$ values,[6] whereas the Debye chain model[8] or cyclic chain model[9] was found to be more suited to polymers of smaller mass. In our earlier publication with SANS and performance studies,[10] we reported that the PDMS

membrane structure and properties were affected by the type of solvent used in the preparation, the crosslinking reaction temperature, and the curing conditions, such as degassing before curing and curing at different temperatures. We observed[11] further that the thinner membranes prepared from dilute solutions had a relatively loose structure that was responsible for low selectivity but high flux in the separation of organics from water. This could have been related to the solubility parameters of the reactant and solvent. The dissolution of smaller polymeric macromolecules or the swelling of crosslinked polymer occurred when they were exposed to a solvent with similar solubility parameters.[12] Therefore, the initial reactant precursor in the dilute solution systems could be altered because of the structural changes caused by the interaction between the macromolecular units and the solvent. Controlled crosslinking between the macromolecular chain segments is crucial to the formation of a cohesive thin membrane film without any defects.

Therefore, the identification of the components in the initial reactants of the membrane is of utmost importance in examining their effects on membrane network structure formation. Hitherto, a satisfactory analysis of the initial reactant precursors of the PDMS membrane has not been found in the literature. Herein, a systematic comparison study of two types of PDMS membranes from an initial reactant system to final membrane formation is reported. We studied the initial reactant structures of the liquid macromonomers, the crosslinked structure in the liquid state, and the final crosslinked network of the PDMS membranes. In both membrane types, the polymer crosslinking degree was varied with different amounts of the poly(methyl hydrosiloxane) (PMHS) crosslinker. The performances of the membranes were also compared in the removal of volatile organics from water through the pervaporation separation process.

## EXPERIMENTAL

The first hydroxyl-terminated poly(dimethyl siloxane) (HPDMS1; density = 0.97 g/mL, viscosity = 18,000–22,000 cSt), another hydroxyl-terminated poly(dimethyl siloxane) (HPDMS2; density = 0.97 g/mL density, viscosity = 50,000 cSt), PMHS (density = 1.006 g/mL, viscosity = 12–45 cSt), dibutyl tin dilaurate, and deuterated chloroform (CDCl$_3$) were obtained from Sigma-Aldrich Chemical Co. Other solvents, including acetone, acetonitrile, tetrahydrofuran, hexane, diethyl ether, carbon tetrachloride (CCl$_4$), toluene, benzene, CDCl$_3$, chlorobenzene, and dichloromethane, were obtained from S. D. Fine Chemicals, Ltd. (India). The preparation of the initial polymer solution (20 wt %) was carried out at 25°C through the mixture of the hydroxyl-terminated poly(dimethyl siloxane) (HPDMS) precursor with the PMHS crosslinker in CDCl$_3$. The ratio of the reactants (HPDMS/PMHS) ranged from 100:20 to 100:0.1 w/w. The dibutyl tin dilaurate catalyst was added to the mixed polymer solution. The quantity of the catalyst was 3% of the total mass of HPDMS and PMHS. The polymer mixture was then vigorously stirred for about 1 h to produce a highly viscous solution, which was then cast as a thin film and finally cured at 80°C. More details on the preparation procedures of the PDMS membranes prepared from various solvents and

polymer solution concentrations can be found in other published articles.[4,10,11]

### SANS Study

SANS measurements of the samples were carried out over the wave vector range ($Q$) of 0.018–0.35 Å$^{-1}$ at 25°C on a SANS instrument at the Dhruva Reactor, BARC, Mumbai, India. Dilute solution samples were made with a CDCl$_3$ solvent for measurements from solutions with different polymer concentrations. The solutions were clear and homogeneous. In case of the solid film samples, a film of a desired quantity was cut into small pieces and was fully swelled in the CDCl$_3$ solvent, with the amount of the solvent being 80% w/w. The measurements were carried out at 25°C with a 2-mm path length quartz cell purchased from Starna Cells, Inc. We observed that the polymer pieces were indistinguishable from the CDCl$_3$ solvent as a result of the homogeneously swollen polymer mass in the solvent. The details of the sample preparations and measurement procedures were published in our earlier articles.[10,11]

The scattering intensity, $I(Q)$ of a chain conformation is related by the following expression of the polymer chain Debye form factor of Gaussian statistics:[8,13,14]

$$I(Q) = \varphi(\rho_p - \rho_s)^2 V^2 \frac{2}{u^2} [\exp(-u) - 1 + u]$$

$$u = Q^2 R_{g(D)}^2$$

where $\phi$ is the number density; $\rho_p$ and $\rho_s$ are the scattering densities of the polymer and solvent, respectively; $(\rho_p - \rho_s)^2$ is referred as the scattering contrast; and $V$ and $R_{g(D)}$ are the volume and radius of gyration of the polymer chain, respectively.

For dilute solution and in the low-$Q$ region ($QR_g < 1$), $I(Q)$ is a spherical particle form factor, given here as the first approximation with the Guinier relation:[13]

$$I(Q) = I(0)\exp(-Q^2 R_g^2/3)$$

where $I(0)$ is the scattering intensity from $Q = 0$, $R_g$ is the radius of gyration of the spherical particle form.

Furthermore, the correlation length ($\xi$), which is an average width of the correlation function of the polymer chain in a dilute solution system, was obtained with a Zimm plot of $1/I(Q)$ versus $Q^2$ with the assumption of a Lorentzian form for the $Q$-dependence of the scattering intensity as follows:[13,14]

$$I(Q) = \frac{I(0)}{1 + Q^2 \xi^2}$$

It gives an estimate of the average distance between the chain entanglements.

The previous expressions are for dilute systems in which the scattering units are well separated from one another so that the $I(Q)$ receives contributions only from the form factor, as the structure factor is considered unity. When there are correlations of position or orientation between the scattering units, $I(Q)$ receives contributions from both the form factor and structure factor. The analysis of the structure factor provides information on the nature of the interaction. In such system, the Ornstein–Zernike approach can be applied to describe the correlation from direct interactions between the pair of interacting particles
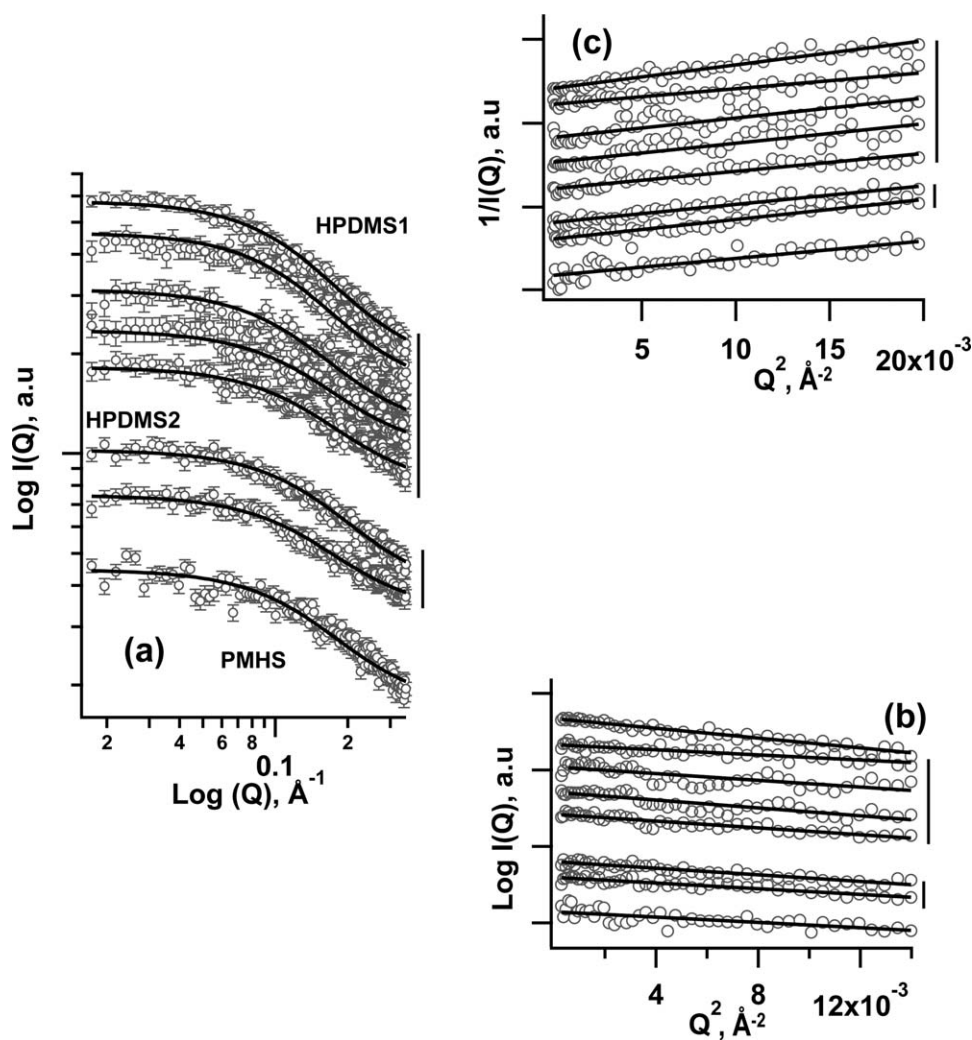
**Figure 1.** SANS profiles for the dilute CDCl$_3$ solutions of initial polymer reactants: (a) log $I$ versus log $Q$ profiles along with the Debye chain model fits, (b) Guinier plot log $I(Q)$ versus $Q^2$, and (c) Zimm plot: $1/I(Q)$ versus $Q^2$. The plots were shifted in the vertical direction by arbitrary units to present each of them distinctly.

and interactions through other particles with the Lorentzian form of the scattering intensity to estimate the average distance between the interacting macromolecular segmental units of a crosslinked polymer. Another model to describe a mixture of polymer macromolecules in the homogeneous phase is the random phase approximation (RPA) model, which is based on mean field theory, in which the functions of polymer units are described by the Debye form factor of the Gaussian statistics.

**Table I.** $R_g$, $I(0)$, and $\xi$ Values for the Initial Reactants Given by the Debye Fits and Guinier and Zimm Plots

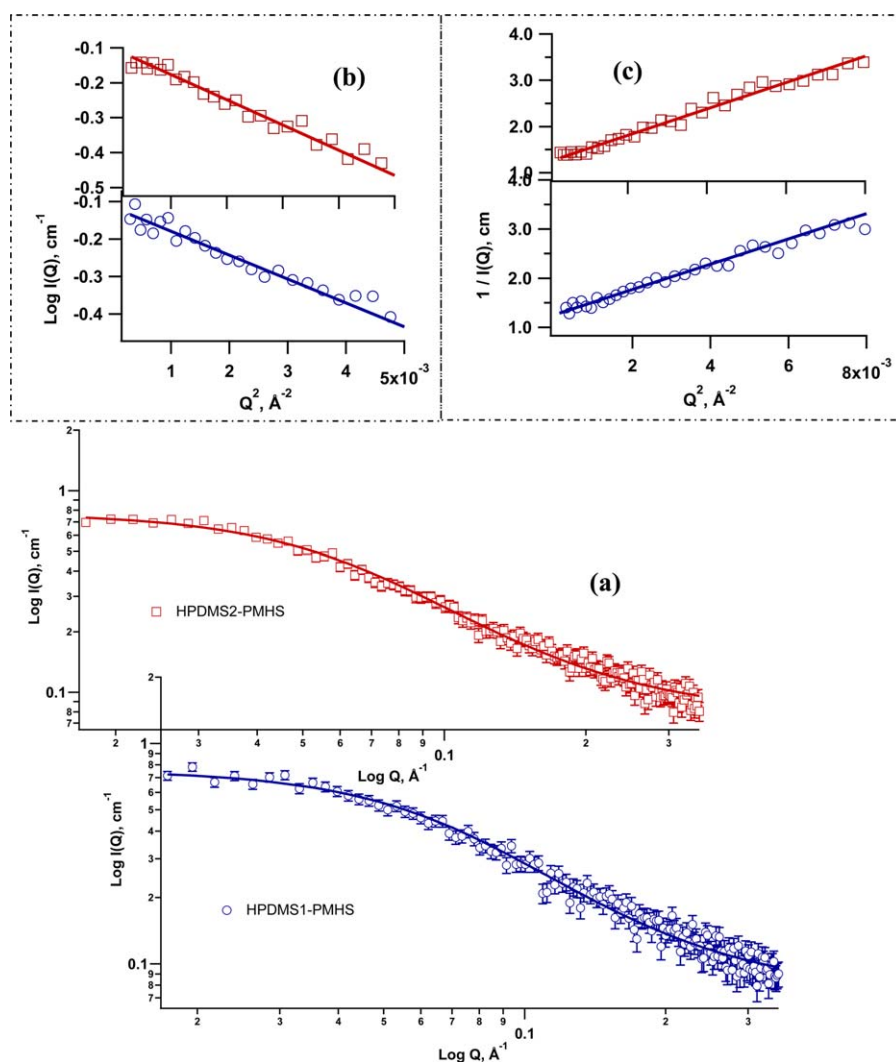| Macromonomer | Weight percentage in CDCl$_3$ | Debye | | Guinier | | Zimm |
|---|---|---|---|---|---|---|
| | | $I(0)$ (cm$^{-1}$) | $R_g$ (Å) | $I(0)$ (cm$^{-1}$) | $R_g$ (Å) | $\xi$ (Å) |
| PMHS | 20 | 0.27 | 11.1 | 0.22 | 7.3 | 4.2 |
| HPDMS1 | 20 | 0.26 | 10.9 | 0.25 | 7.9 | 4.4 |
| HPDMS1 | 23 | 0.27 | 11.2 | 0.26 | 8.1 | 4.6 |
| HPDMS1 | 25 | 0.33 | 12.0 | 0.28 | 7.7 | 4.8 |
| HPDMS1 | 27 | 0.36 | 11.3 | 0.33 | 7.2 | 4.9 |
| HPDMS1 | 30 | 0.40 | 11.5 | 0.34 | 7.9 | 5.8 |
| HPDMS2 | 20 | 0.25 | 11.0 | 0.25 | 7.8 | 4.7 |
| HPDMS2 | 25 | 0.31 | 10.1 | 0.30 | 8.0 | 4.7 |

**Figure 2.** (a) SANS profiles along with the (b) Guinier and (c) Zimm plots for the crosslinked HPDMS1–PMHS and HPDMS2–PMHS oligomers in CDCl₃. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The Gaussian characteristic for the scattering chains can be observed with a Kratky plot [$Q^2I(Q)$ vs $Q$]. The plot tends to a horizontal asymptote at high $Q$ for Gaussian polymer chain conformation as its structure factor varies like $I(Q) \approx 1/Q^2$ at high $Q$. The $Q$ value at which the plateau value is reached is directly related to the statistical segment of the Gaussian chain.

### Other Characterization and Performance Studies of the Membranes

The crosslinking density of the polymer ($v$) from the degree of swelling could be measured experimentally[15,16] with the Flory–Rehner equation:[17]

$$v = \frac{d}{M_c} = -\frac{\ln\left(1-\varphi_p\right)+\varphi_p+\chi\varphi_p^2}{V_s\left(\varphi_p^{1/3}-\frac{1}{2}\varphi_p\right)}$$

where $d$ is the density of the polymer, $M_c$ is the molecular weight between crosslinks, $\phi_p$ is the volume fraction of polymer in the swollen polymer, $V_s$ is the molar volume of the swelling agent, and $\chi$ is the Flory–Huggins solvent interaction parameter

estimated from the Bristow and Watson equation[18,19] with a lattice constant value of 0.35 for PDMS.[20]

The solid-state ²⁹Si-NMR measurements were carried out on a Bruker Avance-II 500-MHz instrument. Mass spectrometric study was performed on Waters Micromass Q-Tof micro mass spectrometer equipped with an electrospray ionization source and atmospheric-pressure chemical ionization, a time-of-flight analyzer, and a microchannel plate detector. The mass spectra

**Table II.** Structural Parameters for the Crosslinked Units in CDCl₃

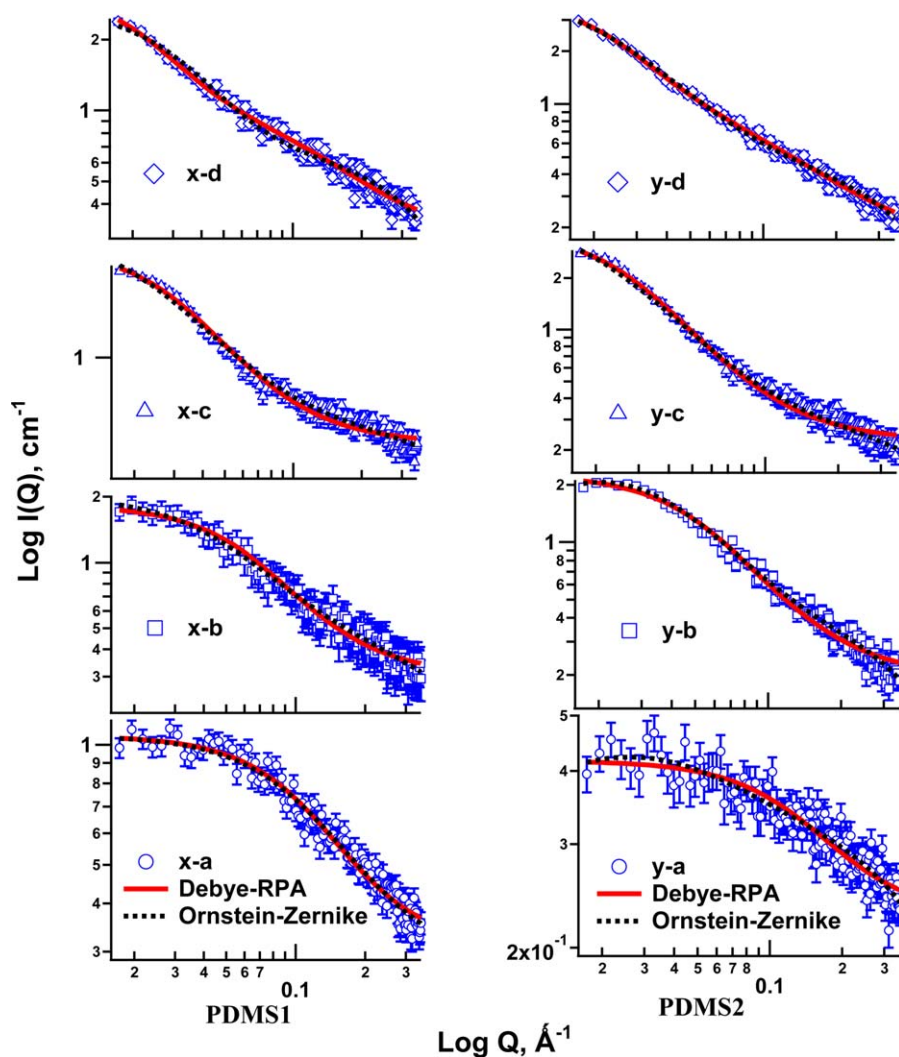| Structural parameter | | HPDMS1–PMHS | HPDMS2–PMHS |
|---|---|---|---|
| Debye | $R_{g(D)}$ (Å) | 22.9 | 25.1 |
| | $I(0)$ (cm⁻¹) | 0.72 | 0.70 |
| Guinier | $R_g$ (Å) | 18.8 | 19.7 |
| | $I(0)$ (cm⁻¹) | 0.66 | 0.69 |
| Zimm | $R_g$ (Å) | 14.3 | 15.2 |
| | $I(0)$ (cm⁻¹) | 0.70 | 0.71 |

**Figure 3.** SANS profiles along with the Ornstein–Zernike and Debye–RPA model fits of the PDMS1 and PDMS2 membranes prepared with different amounts of the PMHS crosslinker: x-a = 0.1%, x-b = 2%, x-c = 10%, x-d = 20% w/w, y-a = 0.1%, y-b = 3%, y-c = 8%, and y-d = 16% w/w PMHS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

data was generated with Masslynx 4.0 software. The separation performance of the membranes was evaluated in the removal of volatile organics from aqueous solutions by a pervaporation separation process. The experiments were carried out with

laboratory-fabricated unit described elsewhere.[10] Benzene (200 ppm) and dichloromethane (150 ppm) were dissolved together in water to make the aqueous feed for the separation experiment. The experiments were carried out at 25°C on a

**Table III.** Structural Parameters for the Crosslinked PDMS Membranes

|  | PDMS1 | | | | PDMS2 | | | |
|---|---|---|---|---|---|---|---|---|
| Membrane | x-a | x-b | x-c | x-d | y-a | y-b | y-c | y-d |
| Average macromolecular segmental unit (Debye function) | | | | | | | | |
| $R_{g(D)}$ (Å) | 14.4 | 27.6 | 56.1 | 58.6 | 11.7 | 30.5 | 58.1 | 59.1 |
| $I(0)$ (cm$^{-1}$) | 0.4 | 0.5 | 1.2 | 1.2 | 0.2 | 1.3 | 2.0 | 2.8 |
| Polymer chain $\xi$ | | | | | | | | |
| $\xi$ (Å) | 8.5 | 19.9 | 44.7 | 40.8 | 16.4 | 25.6 | 46.0 | 41.6 |
| $I(0)$ | 0.5 | 0.5 | 1.5 | 1.3 | 0.1 | 2.2 | 2.4 | 3.1 |
| Integral structural (macromolecular) parameter | | | | | | | | |
| $R_g$(Å), Guinier | 12.1 | 20.2 | 40.2 | 49.4 | 10.2 | 21.9 | 38.1 | 46.2 |

Descriptions of the amounts of the PMHS crosslinker in the different membranes are given in the legend of Figure 3.
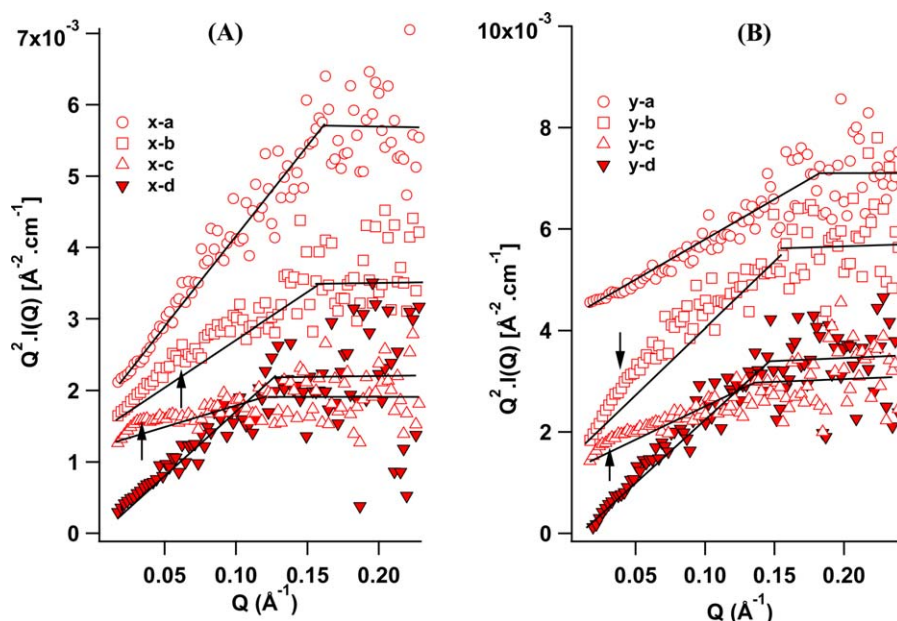
**Figure 4.** Kratky plots for the (A) PDMS1 (x-a, x-b, x-c, and x-d) and (B) PDMS2 (y-a, y-b, y-c, and y-d) membranes formed by different amounts of PMHS crosslinker. Descriptions of the amounts of the PMHS crosslinker in the different membranes are given in the legend of Figure 3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

circular membrane with an area of 18.86 $cm^2$ at a downstream pressure of 2 Torr. The feed and permeate concentrations were measured by an offline gas chromatograph (GC), Trace GC Ultra (Thermo) equipped with an HP-5 fused silica column with a length of 15 m, an inside diameter of 0.5 mm, and a thickness of 1.5 μm. Methanol was used as an internal standard. The separation factor (α) of the mixture was expressed as follows:

$$\alpha = \frac{P_0/F_0}{P_w/F_w}$$

where $P_0$ and $P_w$ represent the organic and water concentrations in the permeate (wt %), respectively, and $F_0$ and $F_w$ represent the organic and water concentrations in the feed (wt %), respectively.

## RESULTS AND DISCUSSION

### Structure of the Initial Reactants

The SANS profiles of the dilute $CDCl_3$ solutions of the initial reactants precursors and crosslinker are shown in Figure 1. The absolute scattering intensity of the chain conformation according to the Debye model fit well to the data, as shown in Figure 1(a). The SANS data were collected from five dilute solutions of the HPDMS1 precursor and two dilute solutions of the HPDMS2 precursor with different concentrations to check the reliability of the results. The $R_g$ values obtained by the fitting of the Debye model to the SANS data collected from the dilute polymer precursor solutions with different concentrations were similar. There was an increase in the scattering intensity with increasing polymer concentration; this was expected, as the scattering intensity was directly proportional to $\phi$ of the scattering unit. The $R_{g(D)}$ values given by the Debye model fit for HPDMS1, HPDMS2, and PMHS were about 10–12 Å. The $R_g$

values were also calculated on the basis of the Guinier approximation with linear plots of $\log[I(Q)]$ versus $Q^2$, as shown in Figure 1(b). Figure 1(c) shows Zimm plots from the SANS data of the dilute solutions of HPDMS1, HPDMS2, and PMHS. The $\xi$ values for the dilute solutions calculated from the Zimm plots were 4–6 Å. Details of the $R_{g(D)}$, $R_g$, $I(0)$, and $\xi$ values given by the Debye fit and Guinier and Zimm plots are given in Table I. As shown in Table I, the structural parameters of the precursors and the crosslinker in dilute solution systems were found to be similar, although there were some differences observed in their size values by the different model fits. The $R_{g(D)}$ value given by the Debye fit was somewhat larger than the value given by the Guinier approximation. This could have been due to different reasons. The Debye model of a dilute solution system is a polymer chain form factor with an intermolecular distance given by the Gaussian distribution, which is not characterized by uniform density, whereas the $I(Q)$ is used as a first approximation for the Guinier relation.

The mass spectroscopy analysis[21] indicated that both the HPDMS1 and HPDMS2 precursors contained cyclic dimethyl siloxane $\{[OSi(CH_3)_2]_n\}$, cyclic dimethyl siloxane oligomers $\{-[OSi(CH_3)_2]_nOSiCH_3-\}$, and linear dimethyl siloxane $\{-[OSi(CH_3)_2]_n-\}$, where $n$ is the degree of polymerization and was about 3–40. This indicated a polydisperse nature of the initial precursors containing a mixture of linear and cyclic macromolecules; this was in agreement with results observed for similar polymer types.[22–24]

### Crosslinked Structure in the Liquid Phase

The crosslinking networks formed by a reaction between the precursors and the crosslinker in the $CDCl_3$ solvent were probed by solution scattering data. Caution was taken for the comparison between samples because the crosslinking reaction forming
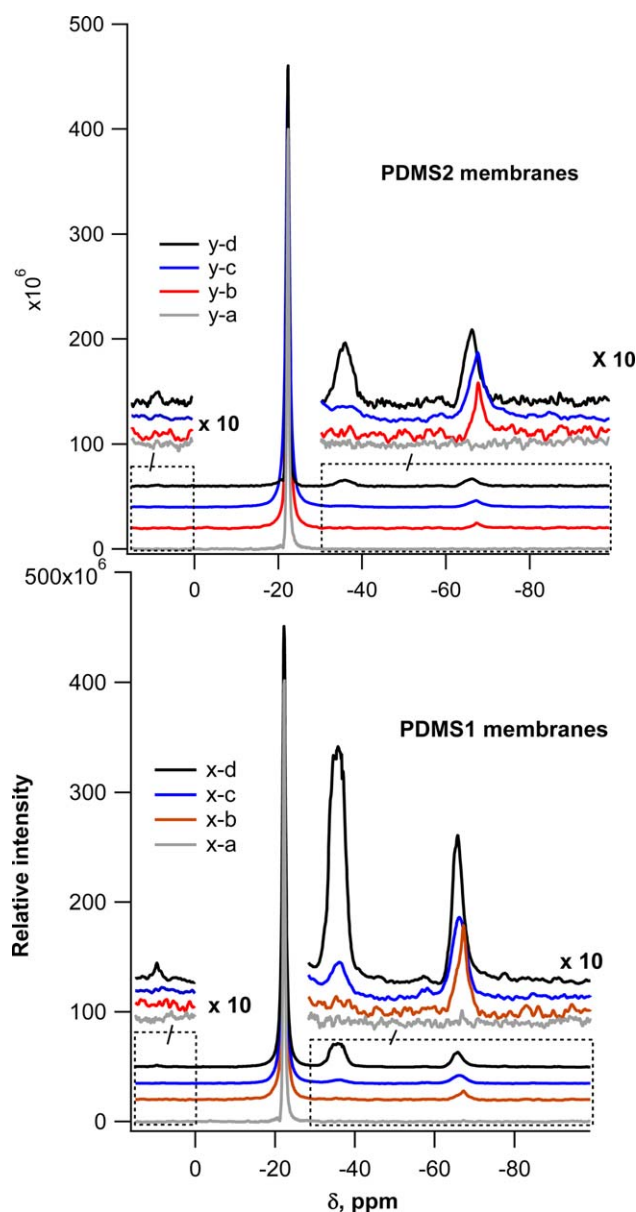
**Figure 5.** $^{29}$Si-NMR spectra of the PDMS1 and PDMS2 membranes prepared with different amounts of the PMHS. Descriptions of the amounts of the PMHS crosslinker in the different membranes are given in the legend of Figure 3. The plots were shifted in the vertical direction by arbitrary units to present each of them distinctly. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the membranes was affected by type and amount of solvent used.[10] The SANS profiles, along with the Guinier and Zimm plots, for the crosslinked HPDMS1–PMHS and HPDMS2–PMHS structures in CDCl$_3$ are shown in Figure 2. The $R_{g(D)}$ values obtained by the fitting of the Debye model to the SANS data collected from the crosslinked HPDMS1–PMHS and HPDMS2–PMHS structures in CDCl$_3$ were 22.9 and 25.1 Å, respectively. This implied that the size of the structural units increased with crosslinking by about twofold compared to their initial size. Similar results on the increase of the structural size during crosslinking was also observed by the analysis of the

Guinier and Zimm plots. The details of the structural parameters of the crosslinked units in solution are given in Table II. The $I(0)$ values obtained from both solutions were about 0.7 cm$^{-1}$; this was about three times the $I(0)$ value of the starting precursor. The change in the intensity observed with the increase in size was not compatible with $I(0) \propto R^6$, where $R^6$ is the radius of the scattering component for a constant scattering contrast. The incompatibility, in terms of the scattering intensity and the size, indicated that the crosslinked oligomers had different scattering contrasts. The change in the scattering contrast was expected because of different scattering length densities for the crosslinked structures having different macromolecular segmental units.

**Structure of the Final Membranes**

We obtained PDMS1 membranes from the HPDMS1 precursor and PDMS2 membranes from the HPDMS2 precursor by crosslinking the precursor with different amounts (% w/w) of the PMHS crosslinker. The SANS profiles of the membranes were similar, as shown in Figure 3. This indicated that both membrane types were a similar nanostructure, and their membrane nanostructures were affected by the degree of crosslinking. The fits to the SANS data with the Ornstein–Zernike model of the Lorentzian form of the scattering intensity and the RPA model of the Debye polymer chain function were excellent.

The average macromolecular segmental unit [$R_{g(D)}$], obtained by the RPA–Debye function model fit; the average distance (or $\xi$) between the interacting macromolecular segmental units of the crosslinked polymer membranes obtained by the Ornstein–Zernike model fit; and the integral structural parameters of the macromolecular segment size ($R_g$, Guinier) approximated by the Guinier and Zimm plots are given in Table III. The average size of the macromolecular segment for both membrane types with the lowest amount of the PMHS crosslinker (0.1% w/w) was found to be only slightly larger than the initial sizes of 10–12 Å $R_{g(D)}$ of the starting precursors. A denser membrane structure for the membrane prepared from the crosslinking of the precursor with a higher amount of the crosslinker was evident, as their scattering profiles fit well with the models of larger $R_g$ and $\xi$ values. The $R_{g(D)}$ and $\xi$ values increased to 28 Å in the case of the PDMS1 type membranes with 2% w/w PMHS and to 56 Å with 10% w/w PMHS. A similar trend in the increases in the $R_{g(D)}$, $R_g$, $\xi$, and $I(0)$ values for the PDMS2 membranes with the PMHS amount (1–10% w/w) was observed; this indicated similar types of structural changes in the PDMS2 membranes. For both membrane types, small changes in the $I(0)$ value were observed, despite large differences in the $R_g$ values; this indicated changes in both the scattering contrast and the size of the structural units as discussed previously.

In both membranes prepared with excess amounts of PMHS (16–20% w/w), there were further increases in the $R_g$ values, even though the polymer chain characteristics, in terms of correlation and segmental lengths, remained nearly the same. This could have been due to changes in the nature of polymer crosslinking for the membranes with excess PMHS contents. To identify the structural differences in the Gaussian characteristics of the scattering chains, Kratky plots [$Q^2I(Q)$ vs $Q$] for the membranes were compared, as shown in Figure 4. All of the

**Table IV.** *S* Values of the PDMS Membranes in Various Solvents

| Solvent | PDMS1 | | | | PDMS2 | | | |
|---|---|---|---|---|---|---|---|---|
| | x-a | x-b | x-c | x-d | y-a | y-b | y-c | y-d |
| Hexane | 12.0 | 8.8 | 7.5 | 3.0 | 11.6 | 9.5 | 6.7 | 2.3 |
| Diethyl ether | 12.5 | 11.9 | 8.2 | 4.2 | 10.9 | 8.6 | 6.5 | 2.3 |
| CCl$_4$ | 16.3 | 12.8 | 8.4 | 7.2 | 15.4 | 12.9 | 7.2 | 5.2 |
| Toluene | 11.3 | 8.0 | 7.1 | 3.7 | 10.9 | 8.4 | 6.1 | 1.9 |
| Benzene | 9.6 | 6.5 | 6.2 | 1.2 | 9.1 | 6.7 | 5.2 | 1.1 |
| CDCl$_3$ | 12.3 | 9.4 | 8.0 | 5.4 | 12.2 | 9.4 | 6.5 | 2.2 |
| Chlorobenzene | 11.3 | 8.1 | 5.5 | 3.9 | 10.7 | 8.3 | 4.9 | 2.5 |
| Dichloromethane | 11.5 | 8.0 | 5.9 | 2.7 | 10.7 | 8.3 | 5.2 | 1.8 |
| Acetone | 8.1 | 5.1 | 2.5 | 0.4 | 7.8 | 5.1 | 2.5 | 0.0 |

$S$ = (Swollen weight − Dry weight)/(Dry weight × Density of the solvent). Descriptions of the amounts of the PMHS crosslinker in the different membranes are given in the legend of Figure 3.

plots were inclined to a horizontal asymptote at high *Q;* this implied Gaussian statistics of the polymer chain. The *Q* value at which the plateau value was reached was about 0.16–0.17 Å$^{-1}$ for both the PDMS1 and PDMS2 membranes with a low PMHS content of 0.1% w/w. This plateau value for the membranes decreased with increasing PMHS content and finally reached about 0.12 Å$^{-1}$ with a PMHS content of 10% w/w. The plateau *Q* value was related (inversely proportional) to the statistical segment length (*l*) of the Gaussian chain (*l* ∝ 1/*Q*); therefore, the decrease in the plateau value implied that the Gaussian segmental length of the polymer chain networks was increased with increasing amount of crosslinker (PMHS). A broad peak at low *Q* (∼0.03–0.06 Å$^{-1}$) was clearly observed for both membranes with 2–10% PMHS, whereas the peak was absent for the membranes with low PMHS contents. Such a peak was also seen in the PDMS membranes prepared from other systems[10,11] and polymer nanocomposites[25] and was interpreted as polymer mesh size or a cluster of chains formed by the highly crosslinked structure (branched networks) of the polymer membrane. Further increases in polymer crosslinking in terms of increases in the Gaussian segmental length and branched networks were not observed in the Kratky plots for both the PDMS1 and PDMS2 membranes with excess loadings of 16–20% PMHS.

The densification of the membrane structure, depending on the degree of crosslinking, was also observed by the $^{29}$Si-NMR study. Figure 5 shows the $^{29}$Si-NMR spectra of the PDMS1 and PDMS2 membranes prepared with different amounts of PMHS. The $^{29}$Si-NMR peaks at −22 and −33 ppm were attributed to the shorter and longer chain [(CH$_3$)$_2$Si(O—)$_2$]$_n$ structures, respectively, whereas the peak at −63 ppm was due to [(CH$_3$)Si(O—)$_3$]$_n$.[26,27] The intensities of the $^{29}$Si peaks at −33 and −63 ppm increased for both membrane types with increasing PMHS amount as a result of the increase in the chain length due to crosslinking. Slightly increased intensities of the $^{29}$Si peaks at −33 and −63 ppm were observed for the PDMS1 membranes compared to the PDMS2 membranes. We noted that a slight shift in the $^{29}$Si peaks of the siloxane chains was observed in case of the membranes prepared from dilute solu-

tion system.[28] A small presence of the $^{29}$Si peak at 8 ppm, attributed to terminal (CH$_3$)$_3$SiO—, was observed in the membranes with a highly crosslinked structure.

**v and Performance Studies of the Membranes**

The extent of membrane swelling in different solvents was compared between the PDMS1 and PDMS2 membranes of different crosslinked densities. The swelling coefficient (*S*) values, calculated from $S$ = (Swollen weight − Dry weight)/(Dry weight × Density of the solvent), for the membranes are given in Table IV. As shown in Table IV, the extent of membrane swelling decreased for both membrane types prepared with increases in the PMHS crosslinker amount, whereas the swelling degree was quite similar between membranes having similar amounts of PMHS.

The swelling data of the membranes in the CDCl$_3$ solvent and the Flory–Rehner equation were used to calculate $\phi_p$, *v*, and $M_c$, which are summarized in Table V.

The $\phi_p$, *v*, and $M_c$ values were found to increase for the membranes with increasing PMHS content; this was expected for the membranes with increased densification. The calculated $\phi_p$ and

**Table V.** Calculated *v*, $\phi_p$, and $M_c$ Values of the Membranes Obtained from Swelling Measurements with a CDCl$_3$ Solvent

| Membrane | | $v \times 10^{-4}$ (mol/cm$^3$) | $\phi_p$ | $M_c$ (kg/mol) |
|---|---|---|---|---|
| PDMS1 | x-a | 0.7 | 0.21 | 12.8 |
| | x-b | 0.9 | 0.21 | 10.8 |
| | x-c | 1.2 | 0.26 | 8.0 |
| | x-d | 2.3 | 0.30 | 3.5 |
| PDMS2 | y-a | 0.5 | 0.18 | 18.3 |
| | y-b | 0.5 | 0.21 | 18.0 |
| | y-c | 0.6 | 0.23 | 16.6 |
| | y-d | 4.2 | 0.34 | 2.3 |

Descriptions of the amounts of the PMHS crosslinker in the different membranes are given in the legend of Figure 3.
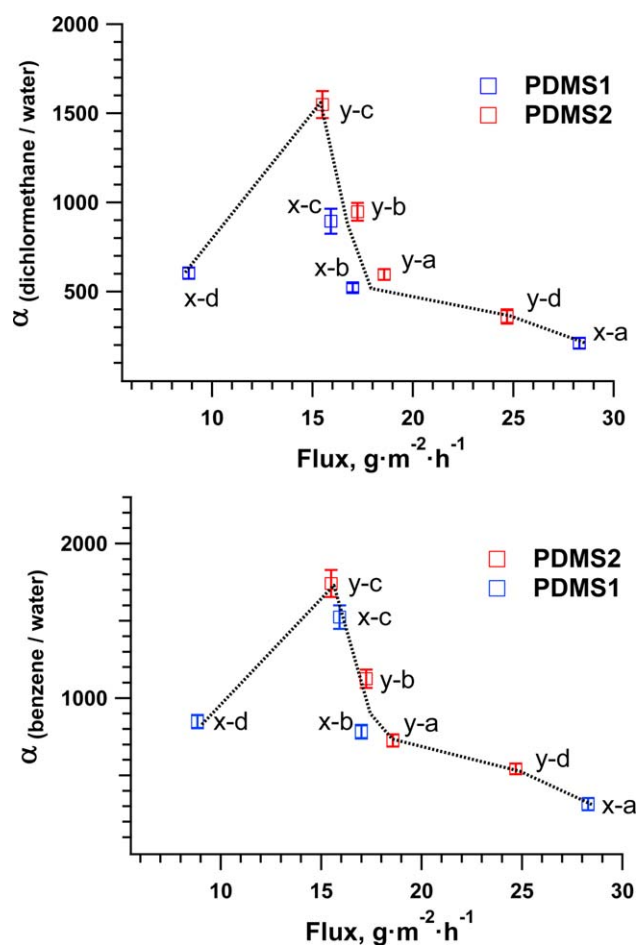
**Figure 6.** Comparison of the performances in terms of α (benzene over water and dichloromethane over water) and flux for the PDMS1 and PDMS2 membranes. Descriptions of the amounts of the PMHS crosslinker in the different membranes are given in the legend of Figure 3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$M_c$ values were, respectively, 0.21–0.30 and 3.5–12.8 kg/mol for PDMS1, whereas the $\phi_p$ and $M_c$ values were 0.18–0.34 and 2.3–18.3 kg/mol, respectively, for the PDMS2. The performances of the PDMS1 and PDMS2 membranes in the separation of volatile organics (benzene and dichloromethane) from water by pervaporation were studied. The α value of the organic (benzene or dichloromethane) over water versus the permeate flux for the membranes of different crosslinked densities (x-a, x-b, x-c, and x-d in case of PDMS1 and y-a, y-b, y-c, and y-d in case of PDMS2) are plotted as shown in Figure 6. A common trend observed from the plots was that the α value increased to a maximum value of about 1600 with a decrease in the flux from 28 to 15 g m$^{-2}$ h$^{-1}$. The membranes with a less dense structure (x-a and y-a) and the membranes with excess crosslinking having aggregates (x-d and y-d) showed inferior performance in terms of either the α value or the flux.

## CONCLUSIONS

PDMS membranes prepared by the crosslinking of two types of HPDMS with PMHS were studied. Membranes with different

amounts of crosslinker were prepared. The structural formation from the initial crosslinking in the liquid state to the final membrane was probed. In both cases, the initial macromolecular sizes were found to be increased because of crosslinking in the liquid state; on evaporation of the solvent, these sizes were condensed by further crosslinking to the formation of the membranes. Both membranes exhibited large interchain spacing on swelling; this implied a high degree of chain mobility. The structural similarities between the membranes were further confirmed by similar performances in the separation of volatile organics from water.

Thus, the PDMS membranes formed from the different starting PDMS precursors were found to be similar in terms of their nanostructures and separation properties. This could have been due to the following reasons. First, the starting precursors in the solution system of membrane preparation were observed to be composed of similar macromolecular units. Second, a similar nature of crosslinking between the precursor and crosslinker in the solution system and the final membrane structure in terms of size and structure was observed for both membranes.

Although an increase in ν of the membrane was obtained with an increased amount of crosslinker, the membrane still exhibited a high degree of chain mobility and high swelling in volatile organic solvents. This implied a limitation of the neat PDMS membrane for applications in the treatment of feeds containing large organics. Components added either by chemical modification or the incorporation of inorganic particles or blending with other polymers may be required to limit the chain mobility and swelling.

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