Effect of Siloxane Chain Lengths of Monomers on Characteristics of Pervaporation Membranes Prepared by Plasma Polymerization

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SYNOPSIS

Plasma-polymerized membranes were prepared from a series of monomers with the different siloxane chain lengths, i.e., hexamethyldisiloxane, octamethyltrisiloxane, and decamethyl-tetrasiloxane, and effects of the starting monomers on both the structures of the plasma polymers and the pervaporation characteristics of ethanol/water mixture were investigated. By IR and XPS measurements, it was found that with increase of the siloxane chain lengths of the monomer the siloxane chains in the plasma polymers were linked more continuously and smaller amounts of additional oxygen were newly incorporated into the polymers. All membranes obtained from the three monomers were found to be ethanol-permselective. From the standpoint of obtaining both high selectivity and high permeation rate, the monomer with the longer siloxane chain was profitable. The relations between the results of the analysis of the plasma polymers by IR and XPS measurements and the pervaporation characteristics obtained are discussed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Plasma polymerization is recognized as a unique method to prepare a thin film, and the film obtained thus has been highlighted in terms of characteristics different from those of the film by a conventional polymerization method.[1] The plasma polymers are naturally affected by the molecular structures of the starting monomers as well as the operating parameters such as power input, monomer flow rate, and pressure in the reaction chamber. Moreover, because almost all organic compounds can be polymerized by this technique, many desirable monomers can be used. These factors have given rise to many studies on the effects of a series of monomers such as saturated hydrocarbons[2,3] and unsaturated hydrocarbons[2,4] on plasma-deposition rates or chemical structures of the obtained polymers.

However, little has been reported concerning how a series of monomers influence the functions of

plasma polymers such as separation characteristics. Sakata et al.[5] investigated the effects of starting silicon compounds on gas permeabilities of plasma-polymerized membrane and clarified that the permeability P_{O_2} increased and P_{O_2}/P_{N_2} decreased with increasing oxidation numbers of Si atoms of the monomers.

With respect to pervaporation membranes prepared by plasma polymerization, various monomers such as silicon compounds,[6,7] fluorine compounds,[8,9] and vinyl acetate[10] have been used. However, as far as we know, the systematic studies have been hardly carried out from the standpoint of the clarification of the effects of a series of monomers. The purpose of this work was to elucidate how three monomers with different siloxane chain lengths influence the pervaporation performances on the basis of analyses of the chemical structures of respective plasma polymers.

EXPERIMENTAL

The apparatus and procedures for the glow-discharge polymerization are the same as reported pre-

viously.[11] The apparatus (Samco International Institute Co., BP-1) consisted of a bell-jar-type reaction chamber made of Pyrex glass (bottom diameter: 31.5 cm; height: 35.5 cm) equipped with a pair of parallel electrodes, 13.56 MHz radio-frequency (RF) generator, matching network, and a vessel for the monomer thermostated at 298 K. Substrates were horizontally placed on the lower electrode controlled at 298 K by circulating temperature-controlled water, and the system was evacuated to less than 2.6 Pa. The monomer vapor adjusted to a fixed flow rate at a pressure of 26 Pa was injected into the reaction chamber without any carrier gas such as argon. The RF power was turned on, and glow-discharge polymerization was initiated and continued at a level of 15 W power input for a suitable duration. The monomer flow rates were the operating parameters and were changed.

Hexamethyldisiloxane (HMDSO), octamethyltrisiloxane (OMTSO), and decamethyltetrasiloxane (DMTSO), supplied from Shin-Etsu Chemical Co., were used as monomers without further purification. The substrate on which plasma polymers deposited was a porous membrane made of mixed esters of cellulose (Millipore VS, mean pore diameter: 0.025 μm, supplied by Japan Millipore).

The deposition rates of the polymers were obtained by weighing the deposits on the glass substrates. The deposition rates on glass were confirmed to be almost equal to those on the porous membrane used in the pervaporation experiments.

To analyze the chemical structures of the plasma polymers, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were used. FTIR and XPS spectra were measured with a Shimadzu FTIR 4100 spectrometer by the attenuated total reflection method using a KRS-5 element of a 45° reflection angle and with a Shimadzu electron spectrometer 750 employing MgKα exiting radiation, respectively. Contact angles of water against the plasma films were measured with a contact anglemeter (Kyowa Kaimenkagaku Co., CA-A) at about 293 K and about 50% humidity.

In pervaporation, separation of the ethanol/water mixture (ethanol concentration: 5 vol %) was investigated. Pervaporation experiments were carried out by the same apparatus and procedures as reported previously.[11]

RESULTS AND DISCUSSION

Deposition Rate and Membrane Structure

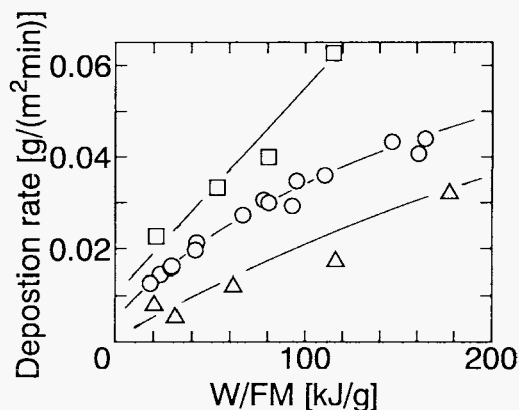Figure 1 shows the relations between the polymer deposition rates from three monomers and the

Figure 1   Relation between deposition rate and W/FM. W = 15 W. ($\triangle$) HMDSO; ($\bigcirc$) OMTSO; ($\square$) DMTSO.

plasma parameter W/FM (W: power input; F: monomer flow rate; M: molecular weight of monomer). In these experiments, the change of F can directly bring about the change of W/FM values because the power input was maintained at the constant value (15 W). The parameter W/FM denotes an input energy per unit mass of monomer and was first presented by Yasuda and Hirotsu[12] to describe the characteristics of the plasma polymerization. In the plasma polymerization from OMTSO, we previously showed that the parameter was useful to describe not only the deposition rates but also pervaporation performances such as the separation coefficient and permeation rates.[11] As can be seen from Figure 1, the deposition rates increased with the increase of the siloxane chain lengths of the monomers at the same W/FM value. Even if the input energies per unit mass of the monomers are the same in the three monomers, as far as the structures of the monomers were not decomposed too much, the longer monomer is presumed to be an advantage in the deposition rate because the depositing unit structure is larger.

Figure 2 shows the IR spectra of the plasma polymers from the three monomers at about the same W/FM value. On three spectra, there were main absorbances at 2960 (CH_3 stretching), 2130 (Si—H stretching), 1410 (CH_3 deformation), 1250 (Si—CH_3 deformation), 1060 (Si—O—R stretching[13]), 1020 (Si—O—Si stretching[13]), and 700–800 cm^{-1} (Si—CH_3 wagging, Si—C stretching, and Si—CH_3 rocking). Si—H groups in the plasma polymers, which are not contained in the monomers, were formed from the cleavages of the Si—CH_3 group or the Si—O group. Although the difference between spectrum of the polymer from OMTSO and that from HMDSO was not clear, the ratio of the absorption at 1020 cm^{-1} to that at 1060 cm^{-1} in the
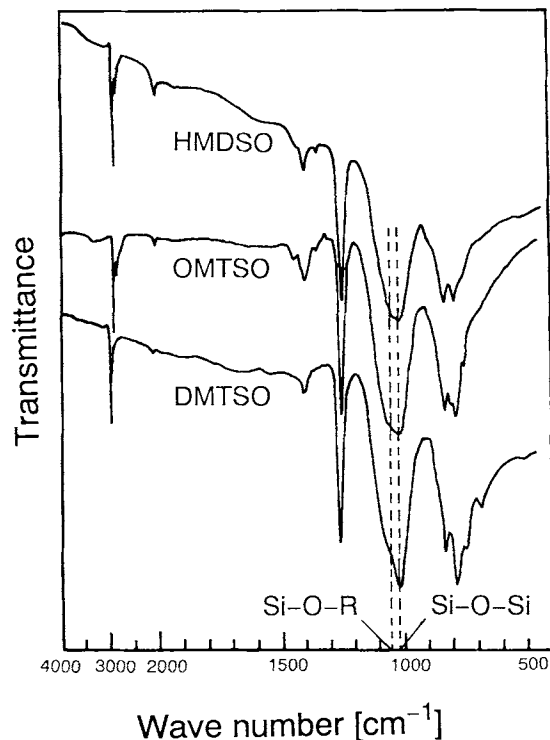
Figure 2 IR spectra of plasma polymers. HMDSO: $W/FM = 55.0$; OMTSO: $W/FM = 57.5$; DMTSO: $W/FM = 54.0$ kJ/g.

Figure 3 Effect of W/FM on O/Si and C/Si; 15 W. ($\triangle$) HMDSO; ($\bigcirc$) OMTSO; ($\square$) DMTSO.

spectrum of the polymer from DMTSO was larger than the ratio in the spectrum of the polymer from OMTSO or HMDSO. This suggested that the siloxane chains were linked more continuously in the polymer from the monomer with the longer siloxane chain. This result is probably attributable to the considerable preservation of the monomer structures in these plasma-polymerization conditions.

Ratios of carbon or oxygen to silicon in the polymer surfaces detected by XPS measurements are plotted against W/FM in Figure 3. There were no considerable differences in the ratios of C/Si of three kind of polymers because the respective C/Si ratios of the starting monomers are similar (HMDSO: 3.0; OMTSO: 2.67; DMTSO: 2.50). All the C/Si ratios of the polymers were smaller than those of the monomers. This may be because hydrocarbon fragments are less reactive than are silicon-containing fragments.[11,14] Previously, we reported that in the plasma polymerization from OMTSO the C/Si ratio decreased first and later increased with increasing W/FM.[11] Such a minimum of the C/Si against W/FM was not observed in these experiments, probably because the W/FM regions in these experiments are large and correspond to the regions where the C/Si ratio increases monotonously.
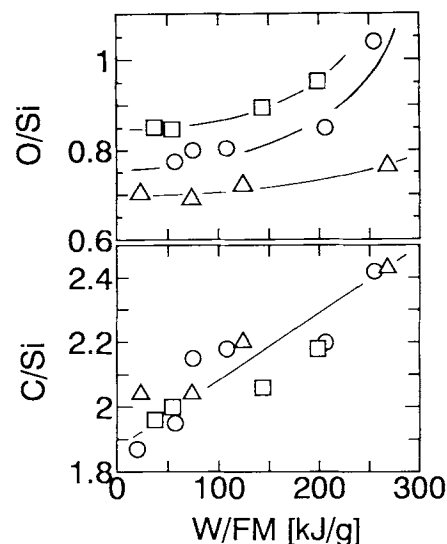
The ratios of O/Si of three kind of polymers were larger than the respective values of monomers (HMDSO: 0.5; OMTSO: 0.66; DMTSO: 0.75), and as recognized widely, the ratios increased with increase of W/FM due to increase of residual radicals that can react with oxygen or water vapor in the atmosphere.[14] The O/Si ratio of the polymer from DMTSO was the largest and that from HMDSO was the smallest at the same W/FM value due to the influence of the monomer composition.

Figure 4 shows the values subtracting the O/Si ratios of the monomers from those of the plasma polymers shown in Figure 3. It was already confirmed by solid-state NMR measurements that the plasma polymer from OMTSO considerably pre-
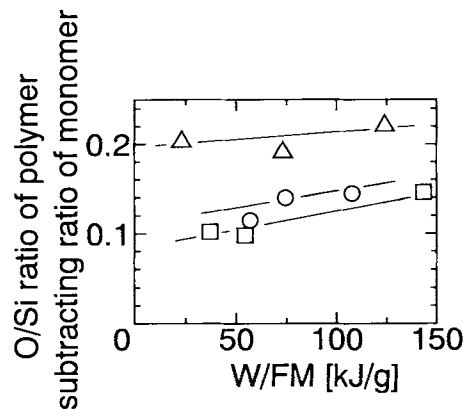

Figure 4 Relation between the Si/O ratio of the polymer subtracting the ratio of the monomer and W/FM: ($\triangle$) HMDSO; ($\bigcirc$) OMTSO; ($\square$) DMTSO.

served the monomeric structure in the low W/FM region.[11] In Figure 4, only the data in the low W/FM region were plotted. Therefore, oxygen in this figure roughly corresponds to the ratio of additional oxygen newly incorporated into the polymer by plasma polymerization, although the values may contain some errors. With the decrease of the siloxane chain lengths of the monomers, the amounts of oxygen incorporated into the polymers increased. This is probably because in the plasma polymer from the smaller monomer there exist more residual radicals per unit mass of the deposit layer, which can react with oxygen, owing to the smaller depositing fragment.

Pervaporation Performances

Figure 5 shows the effects of W/FM on the separation coefficient, α_{EtOH}, and total permeation rate, Q. α_{EtOH} is defined as $(X_P^{Et}/X_P^{W})/(X_F^{Et}/X_F^{W})$, where X_P and X_F are weight fractions in the permeate and feed solution, respectively, and superscripts Et and W denote ethanol and water, respectively. As shown in this figure, all membranes obtained were found ethanol-permselective. The value of α_{EtOH} of the plasma polymer from DMTSO was nearly equal to that from OMTSO, whereas the
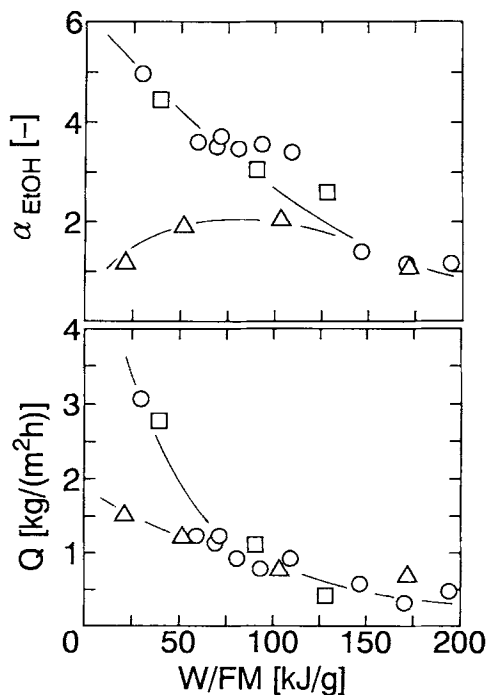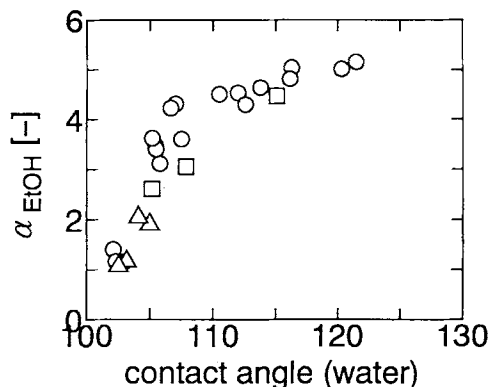

Figure 6 Relation between α_{EtOH} and contact angle of water. Deposition time: 60 min. (○) OMTSO (5, 15, 30 W), reported previously[11]; (△) HMDSO (15 W); (□) DMTSO (15 W).

plasma polymer from HMDSO showed fairly low selectivity. There was no remarkable difference in Q in the cases of three monomers except for the lower Q value of the polymer from HMDSO in the low W/FM region.

In an early work,[11] it was found that α_{EtOH} in the plasma polymer from OMTSO were well correlated to contact angles of water, which is one of the indications of a hydrophobicity of the membrane surface. Therefore, we mentioned that the separation coefficients might depend on the difference in the solubility based on the difference of the affinity to the polymers rather than on the difference in the diffusivity.

For the plasma polymers in this work, the relations between α_{EtOH} and the contact angles of water are shown in Figure 6. The data from HMDSO and DMTSO were approximately located on the characteristic correlation curve of the plasma polymer from OMTSO reported previously.[11] This suggests that the separation characteristics of the plasma polymers from these three monomers were almost identical in spite of the different monomer structures. In other words, the plasma polymer with the same contact angle showed the same α_{EtOH} regardless of the kind of monomer.

The decrease of α_{EtOH} of the plasma polymer from DMTSO with the increase of W/FM, shown in Figure 5, is attributable to the decrease of the contact angles, i.e., the decrease of a hydrophobicity of the membrane surface as pointed out in the case of the plasma polymer from OMTSO.[11] The plasma polymer from HMDSO was more hydrophilic and showed the lower contact angle of water because of the greater amounts of oxygen incorporated into the polymer, as shown in Figure 4. This is the reason
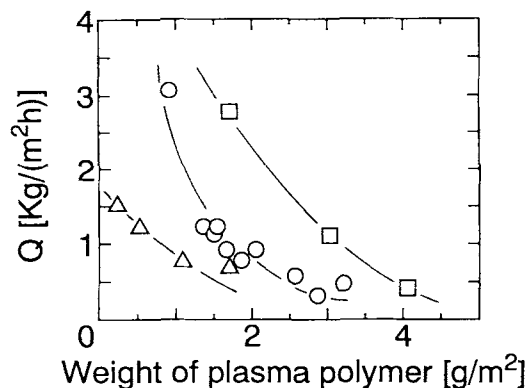

Figure 5 Effect of W/FM on α_{EtOH} and Q; 15 W; deposition time: 60 min. (△) HMDSO; (○) OMTSO; (□) DMTSO.

Figure 7 Relation between Q and weight of the plasma polymer. Deposition time: 60 min. ($\triangle$) HMDSO; ($\bigcirc$) OMTSO; ($\square$) DMTSO.

that α_{EtOH} of the polymer from HMDSO was much smaller. Thus, the monomer with the long siloxane chain must be selected in order to obtain the high selectivity.

Figure 7 shows the relation between Q and weights of the plasma polymer layer per unit area. The deposion time was 60 min. The longer the siloxane chain length of the monomer, the larger was Q at the same weight of the plasma layer. As clarified by IR analysis, when the monomer with the longer siloxane chain was used, the flexible siloxane chains were probably linked more continuously in the plasma polymer. Therefore, the plasma polymer prepared from the monomer with the larger siloxane chain showed the higher permeation rate. Moreover, this may be also the reason for the high permeability in that the plasma polymer from the larger monomer will be less rigid because of less cross-linking brought about by the larger depositing fragment. With respect to the permeation rate, the use of the monomer with the long siloxane chain was also found to be profitable.

However, when the siloxane chain is very long, the boiling point of the monomer is high so that it is difficult to perform the plasma polymerization. In the selection of the monomer, this effect must be taken into account.

CONCLUSION

1. Plasma polymers were prepared from three kinds of monomers having different siloxane

chain lengths, and the structures of the polymers were analyzed by IR and XPS measurements. With increase of the siloxane chain lengths of the monomers, the siloxane chains in the plasma polymers were linked more continuously and smaller amounts of additional oxygen were incorporated into the polymers.

2. Pervaporation performances of the plasma polymers prepared from three monomers were investigated. It was found that in order to obtain both high selectivity and high permeation rate the monomer with the longer siloxane chain should be used.

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