Polymer Membranes Containing 4-Trimethylsilylmethylstyrene Units

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Membranes of enzyme sensors are in general composed of three layers.[1] For examples, the oxygen electrode in glucose biosensors is covered with an oxygen-permeable membrane which protects the electrolyte solution and prevents an interference from nonvolatile electroactive components in the samples. The middle layer contains glucose oxidases in a polymer gel or on a filter pad. The outer layer such as a cellophane dialysis membrane protects the enzymes from the substrate environments. If enzymes can be immobilized at a surface of oxygen-permeable polymer membrane, the biocatalyst support materials may not be necessary.[2,3]

Poly(dimethylsiloxane) (PDMS) is one of the highest gas-permeable polymers among the industrial membrane materials, but exhibits the lowest oxygen/nitrogen permeation selectivity and insufficient self-supporting characteristics. One of many possible strategies to overcome the shortcomings of PDMS is to combine the advantages of both PDMS and its partner component with properties opposite to those of PDMS. Block or graft copolymers containing PDMS were used for this purpose.[4-6]

The gas permeability of organosilicone-containing polystyrenes was also reported.[7,8] The membranes usually showed a high oxygen permeability and a reasonably high permselectivity of oxygen against nitrogen. The permeability behavior was attributed to a high affinity of oxygen molecules to Si atoms and the relatively large free volumes between the polymers, resulting from the restricted mobility of the side chains in the repeat units.[9,10] Thus this type of polymers may be applicable to the biosensor electrode membranes as lng as their chemical and physical properties are appropriate, but which were not reported in detail.

The ultimate purpose of this research was to investigate a gas-permeable and enzyme-immobilizable polymeric material that can be utilized as the oxygen electrode membranes in biosensors. In this study, the organosilicone-containing styrene was chosen as a comonomer for the preparation of terpolymers, as shown in Scheme 1. The -COOH groups in the polymers can be employed for immobilization of enzymes via covalent bonding when necessary. This paper describes the thermal and mechanical property in addition to the gas permeability of the new polymer membranes.

Experimental Section

Instruments. The FT-IR spectra were obtained with a JASCO FT-infrared spectrophotometer. The ¹H-NMR spectra were obtained with a JEOL-JMN 400 (500MHz) spectrometer. The differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) experiment were performed using a DuPont 2000 differential scanning calorimeter. Gel permeation chromatography (GPC) data were obtained with a Waters 440 HPLC calibrated with polystyrene standard samples. The tensile test of polymer films was performed by using an United STM-10 at room temperature with a crosshead speed of 2 mm/min.

Synthesis. 4-Trimethylsilylmethylstyrene (TMS) was prepared according to the procedure of Nagasaki and Tsuruta[11] (40-60%). Mixtures of TMS, methyl methacrylate (MMA), and methacrylic acid (MAA) in three different molar ratios containing 2.2'-azobisisobutymitrile (0.5 mol%) in ampoules were frozen and degassed under vacuum. The freezing and degassing procedure was repeated three times, and the ampoules were sealed. The solutions were polymerized at 60 °C for 5 h. The product was precipitated into methanol (75-85%).

Preparation of membranes. The polymer was dissolved in THF (4 wt%) and the solution was cast on a flat glass plate. The solvent was evaporated slowly at room temperature and the membrane was completely dried in a vacuum oven at 60 °C and 300 torr for 24 h. The thickness of the membranes was in the range of 100-140 μm.
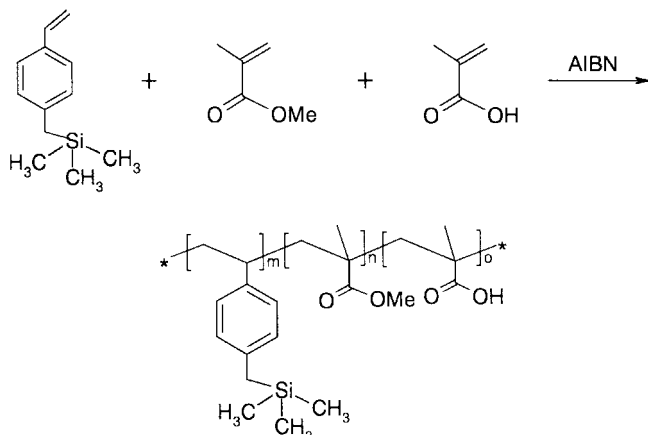
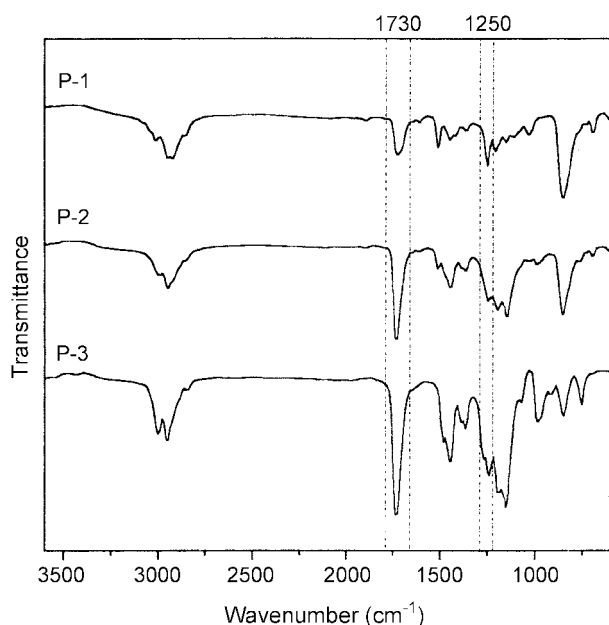Scheme 1. Radical polymerization of TMS, MMA, and MAA.
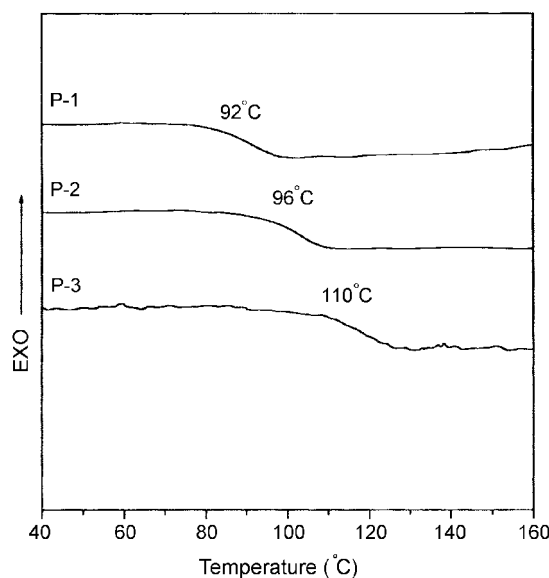
Figure 1. FT-IR spectra of P-1, P-2, and P-3 (KBr).

Figure 2. DSC thermograms of P-1, P-2, and P-3. All of the thermograms were obtained from the second heating scans and the scan rate was 10 °C/min.

Results and Discussion

The FT-IR spectra of the purified polymers showed the characteristic peaks at 1730 and 1250 cm^{-1} which are corresponding to the ester bonds in the MMA units and Si-C bonds in the TMS units, respectively (Figure 1). The relative intensity of the two peaks was dependent on the relative contents of MMA and TMS units in the polymers. The ^{1}H-NMR data indicated that the molar compositions of the three different repeat units in the polymers were pretty close to those of the comonomers in feed (Table 1). The number- (M_n) and weight-average molecular weight (M_w) of the polymers were in the range of 50700-68900, and 103000-197000, respectively.

The thermal transitions of the polymers were studied with DSC (Figure 2). The glass transition temperature (T_g) of P-1, P-2, and P-3 were measured to be about 92, 96, and 110 °C, respectively. The melting transitions of the polymers were not observed in the experimental temperature range. The T_gs of the terpolymers may be predicted from the Fox equation: $1/T_g = W_1/T_{g1} + W_2/T_{g2} + W_3/T_{g3}$. The W_1, W_2 and W_3 represent the weight fraction of component 1 (TMS unit), 2 (MMA unit), and 3 (MAA unit), respectively. The T_g of poly(TMS) (M_w 9400).[11] poly(methyl methacrylate) (PMMA, Aldrich, M_w 120000), poly(methacrylic acid) (PMAA) is about 85, 114, and 228 °C[12], respectively. The calculated T_g of P-1, P-

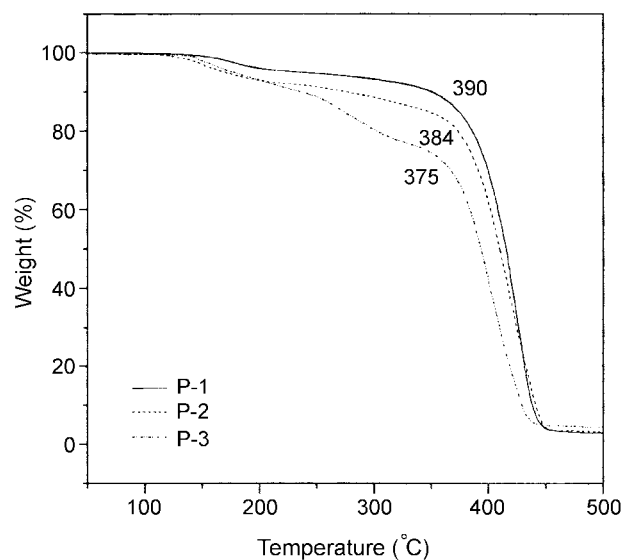Figure 3. TGA thermograms of P-1, P-2, and P-3. The heating rate was 20 °C/min under a nitrogen atmosphere.

2, and P-3 is 97, 106, and 111 °C, respectively. This result indicates that the terpolymers are essentially random copolymers.

The thermal stability of the polymers was studied with TGA (Figure 3). The initial weight loss occurred in one step

Table 1. The average molecular weights (M_n and M_w) of P-1, P-2, and P-3

Polymer	Molar compositions of monomers in the feed (%)			Molar compositions of repeat units in the polymer (%)			M_n	M_w	M_w/M_n
	TMS	MMA	MAA	TMS	MMA	MAA			
P-1	68	22	10	63	30	7.0	68,900	103,000	1.49
P-2	32	61	7.0	27	69	4.0	67,600	197,000	2.91
P-3	5.0	91	4.0	12	85	3.0	50,700	186,000	3.66
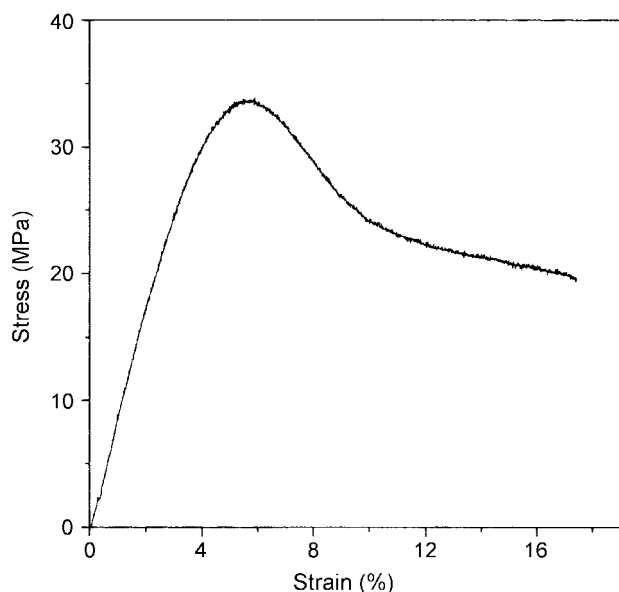
Figure 4. Strain-stress curve of P-3 membrane (thickness ~100 μm).

Figure 5. Po_2 as a function of upstream oxygen gas pressure.

(P-1 and P-2) or two steps (P-3) before the significant weight loss in the temperature range of 375-390 °C. It was reported that the thermal degradation of PMMA occurred in three steps at 150-200, 250-300, and 350 °C respectively.[13] and PMAA was degraded in two steps at 250-280 and 300-400 °C. respectively.[14] The initial weight loss of the polymers increased in the following order: P-1 < P-2 < P-3. The total molar composition of MMA and MAA units in the polymers increased in the same order: P-1 (37%) < P-2 (73%) < P-3 (88%) (Table 1). This result suggests that the initial weight loss may be mainly due to the thermal degradation of MMA and MAA units in these polymers.

The membranes of P-1 and P-2 were somewhat brittle. while those of P-3 were not brittle and showed some mechanical strength with a certain flexibility. Thus the tensile strength of P-3 membranes (thickness ~100 μm) was tested. Figure 4 shows the stress-strain curve of P-3 membrane. The yield stress and yield point were lowered compared to those of PMMA membrane which were reported to be about 45 MPa and 10%, respectively.[15] However, the overall tendency of the stress-strain curve of P-3 is very similar to that of PMMA. indicating that the high content of MMA unit (85 mol%) dominates the mechanical property of P-3 membrane. The P-3 membranes which were thinner than ~60 μm were more flexible but easily torn on handling.

The oxygen permeability of the polymeric membranes was measured as reported in our previous paper.[16] The oxygen permeability coefficient (Po_2) was calculated employing the equation derived from the Fick's first law. and expressed in a unit of Barrer. corresponding to 10^{-10} cm^3 (STP)·cm/ cm^2·sec·cmHg. The Po_2 values were plotted as a function of the upstream oxygen pressure, as shown in Figure 5.

Nagasaki *et al.* reported that the Po_2 of the organosilicone-containing polymer membranes increased with the Si content.[11] The increased oxygen permeability was attributed to the empty d-orbital of Si atom which interacts with oxygen
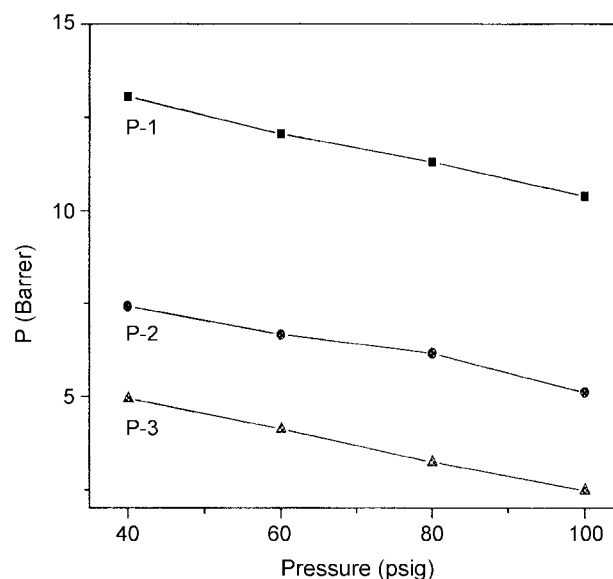
molecule. They found that the mobility of the side chains at the α-position also strongly influenced the gas permeability of the polymer membranes since the restricted movements in the side chains increased the free volume.

A similar behavior was observed here. The Po_2 values at the equal upstream pressure of oxygen decreased in the following order: P-1 > P-2 > P-3. The molar percentage of TMS unit in the membranes decreased in the same order: P-1 (63) > P-2 (27) > P-3 (12) (Table 1). This permeability behavior is also probably due to the TMS contents which are expected to affect significantly the gas solubility and free volume of the membranes. The Po_2 values are very high in all of the three different membranes. Especially, it is noticeable that the only 12 mol% TMS units in the P-3 membranes, played an important role in enhancing the Po_2 of the resulting membranes since the Po_2 of pure PMMA membranes was about 0.086 Barrer at 35 °C.[17]

In summary. the polymers with relatively high TMS contents were somewhat brittle, while the polymers which consists of mainly MMA units. were pretty flexible and showed a mechanical property similar to that of PMMA. The Po_2 in the membranes was dependent on the TMS content. but high enough. However, for a practical application as the oxygen electrode membranes, the mechanical strength of the membranes may need to be improved.

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