

# Preparation and Gas Permeability of Polymer Blend Membranes of Polystyrene and Poly[1,1,1-Tris(trimethylsiloxy)methacrylate Propylsilane]

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## Synopsis

The gas permeability of O<sub>2</sub> and CO<sub>2</sub> was studied for various polymer blend membranes of polystyrene (PSt) and poly[1,1,1-tris(trimethylsiloxy)methacrylate propylsilane (PTMPS)]. In order to improve the compatibility of these polymer blends, the effect of addition of the graft copolymer was also investigated. The gas permeability of various composition polymer-blend membranes increases rapidly with an increasing content of PTMPS in the polymer blend. In the polymer blend membranes containing the graft copolymer, the gas permeability decreases with an increase in the graft copolymer content and then reaches a nearly constant value, when the PTMPS content remains constant. This result is attributed to a decrease in interstices at phase boundaries, owing to improvement in compatibility of the component polymers. This method of membrane preparation is very useful for making membranes with required properties.

## INTRODUCTION

The permeation behaviors of gas through various types of polymer membranes has been widely investigated for the development of the membrane separation process. Silicone rubber membranes show high permeability to various gases, O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, and He.<sup>1</sup> The segmental mobility of poly(dimethylsiloxane) is high, and the cooperative redistribution of the free volume is very easy due to the weak interchain interactions. The diffusion and the sorption of gas in polymer matrixes are largely dependent on the extent of the free volume and the rapid redistribution of the free volume causes the fast transport of gas. Ward and Browall<sup>2</sup> prepared copolymer membranes of poly(dimethylsiloxane) and polycarbonate and measured the permeability of oxygen across the membranes. According to their experiments, the permeability of oxygen increases with an increasing content of the siloxane unit in the copolymer.

In polymer blend membranes, the transport mechanism of penetrant through the membrane differs from that of the homogeneous polymer membrane; that is, the polymer blend membranes are composed of two phases, each of which is mainly composed of either of the polymer components, and the boundaries between different phases contribute largely to the gas permeation process. Recently, Shur and Rånby reported on the transport behavior of gas through the polymer blend membrane made up of poly(vinyl chloride) (PVC) and poly(ethylene-co-vinyl acetate) (PEVA), and investigated the relationship of the compatibility of polymers to the gas permeability. The permeation coefficient decreased with increasing milling temperature and the content of vinyl acetate in PEVA. Moreover, they showed<sup>4,5</sup> that transport behavior of penetrant across

the polymer blend membrane is affected by interpolymer interactions, segmental mobility, and polarity as well as compatibility. Stallings and Hopfenberg<sup>6</sup> reported that polystyrene and 2,6-dimethyl-1,4-phenylene oxide are quite compatible and form a homogeneous blend. However, it is hard to prepare a homogeneous blend of polymer due to their low compatibility.

To improve the homogeneity of polymer blends, the polymer blend is milled at high temperature or an emulsifier is added. Some graft copolymers act as emulsifiers and increase the compatibility of polymers to each other,<sup>7</sup> and, therefore, it could be expected that the homogeneity of low compatible polymers is improved by adding a suitable graft copolymer.

The purpose of the present study is to clarify the gas permeability of polymer blends of polystyrene and the polymer having siloxane bond in the side chain, and to improve the homogeneity of the polymer blend using an appropriate graft copolymer.

## EXPERIMENTAL

### Materials

Trimethylacetoxysilane(1) was prepared according to Etienne's method<sup>8</sup> and 1,1,1-tris(trimethylsiloxy)methacrylate propylsilane(3) (TMPS) was prepared from  $\gamma$ -methacryloxypropylmethoxysilane(2) and (1), as shown in Figure 1,<sup>9</sup> and purified by reduced pressure distillation. Polymerization of TMPS was carried out in benzene solution using benzoylperoxide (BPO) as initiator. The polymer (PTMPS) was purified by reprecipitation from benzene-methanol solutions. The limiting viscosity number of PTMPS was 0.18 in benzene.

The graft copolymer was prepared by the reaction of PTMPS and styrene monomer at 80°C for 48 h. BPO was used as an initiator. Graft ratio was 50% and the content of PTMPS in the graft copolymer was estimated as about 67 wt % by the NMR method. Commercial polystyrene was used without further purification. The degree of polymerization was about 1600–1800.

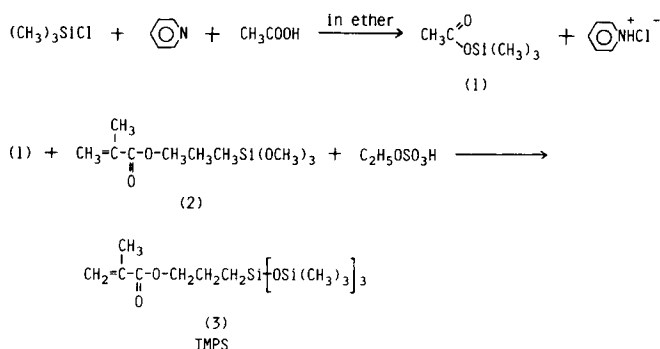


Fig. 1. Synthesis of 1,1,1-tris(trimethylsiloxy) methacrylate propylsilane (TMPS).

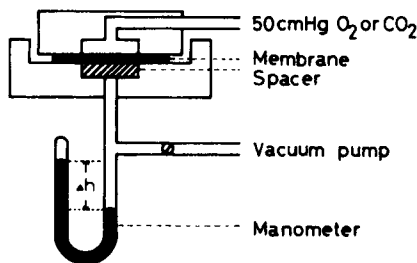


Fig. 2. Apparatus for gas permeability measurement.

### Membrane Preparation

The polymer blend membranes, approximately 0.1 mm thick, were made by the casting method from benzene solutions. The weight ratio(PSt/PTMPS) were 100, 90/10, 80/20, 70/30, and 60/40. The polymer blend membranes containing the graft copolymer were prepared by addition of varying amounts of the graft copolymer into the polymer blend. The total content of PTMPS in the blend was set at 30 wt %, and the content of the graft copolymer was about 5, 10, 16.7, 20, and 26.7 wt %. The membranes were prepared by casting from benzene solution onto the glass surface and were stripped off the glass after drying under reduced pressure at room temperature for 24 h.

### Gas Permeability Measurement

The gas permeability through various polymer blend membranes was determined in a permeation cell (Rikaseiki, K-315) (Fig. 2). The penetrants used were CO<sub>2</sub> and O<sub>2</sub>. The permeation coefficient *P* was calculated from the following equation:

$$P = \frac{1}{p_0} \cdot \frac{dp}{dt} \cdot \frac{V \cdot 273 \cdot l}{76 \cdot T \cdot A}$$

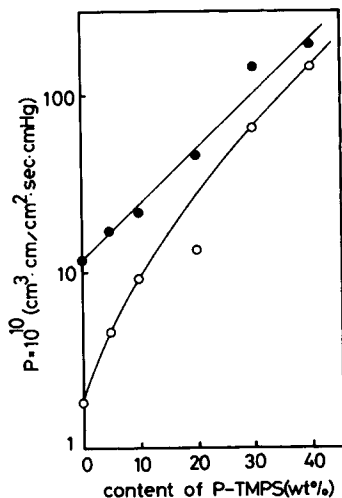
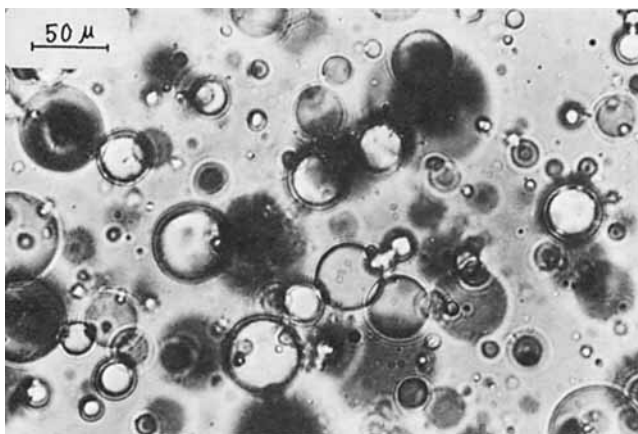
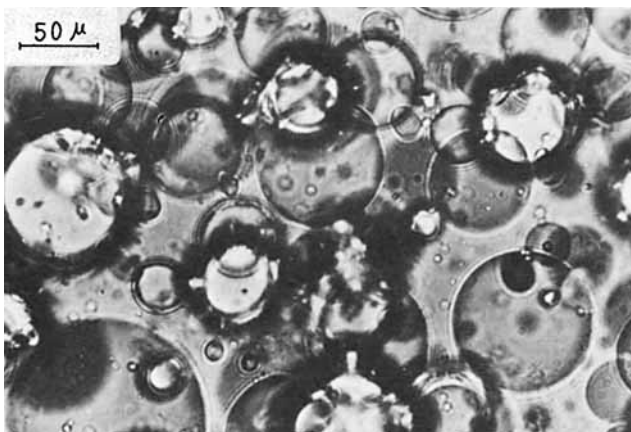


Fig. 3. Relationship between permeation coefficients and the content of PTMPS in polymer blends. (○) O<sub>2</sub>; (●) CO<sub>2</sub>.



(A)



(B)

Fig. 4. Microphotographs of the polymer blends. (A) 5 wt % PTMPS; (B) 20 wt % PTMPS.

where  $p_0$  is the pressure of penetrant gas in the reservoir (about 50 cmHg),  $dp/dt$  is the rate of pressure change measured by a manometer connected to the low pressure chamber,  $V$  is the volume of this chamber,  $l$  is the membrane thickness,  $A$  is the effective membrane area, and  $T$  is the measurement temperature (at 25°C), respectively. The permeation coefficient is expressed by a common unit  $\text{cm}^3\cdot\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{cmHg}$ .

### DSC and Density Measurements

Thermal properties of the polymer blends were measured by a differential scanning calorimeter (Daini Seicōsha, SSC 560) in the range of temperature, 30–350°C.

The density of the blends was determined by finding the concentration of NaCl solution at which the density of the solution equals that of the blend.

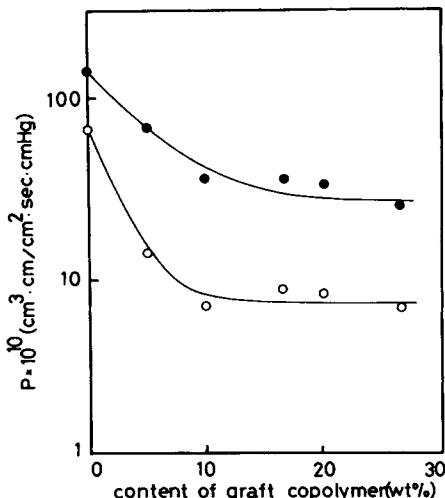


Fig. 5. Effect of the graft copolymer content on permeation coefficient. (○) O<sub>2</sub>; (●) CO<sub>2</sub>.

RESULTS AND DISCUSSION

The values of permeation coefficients of O<sub>2</sub> and CO<sub>2</sub> through the polymer blend membranes of various compositions are shown in Figure 3, where the permeation coefficients of O<sub>2</sub> and CO<sub>2</sub> increase rapidly with an increasing content of PTMPS in the blend. When the PTMPS content in the polymer blend is about 30 wt %, the permeation coefficients are about 40 times larger than that of PSt membranes. This rapid increase was due to the existence of interstices at phase boundaries as a result of low compatibility of the component polymers.

This is deduced from observations with a microscope. In Figure 4, (A) is a microphotograph of the polymer blend containing 5 wt % PTMPS, and (B) is that of the blend of 20 wt % PTMPS content. The spherical island is the phase of PTMPS, while the sea is the phase of PSt. The island particles of PTMPS grow larger as the PTMPS content increases (Fig. 4). Around these particles the interstices are formed, resulting in an increment of the gas permeability through the membrane.

The total permeability  $P_t$  through the polymer blend membrane consisting of these incompatible polymers is affected largely by the presence of the interstices at the phase boundaries. It could be expressed as

$$P_t = (1 - \alpha)P_1 + \alpha P_2 + P_h$$

where  $P_1$  and  $P_2$  are the permeation coefficients through the phases of PSt and

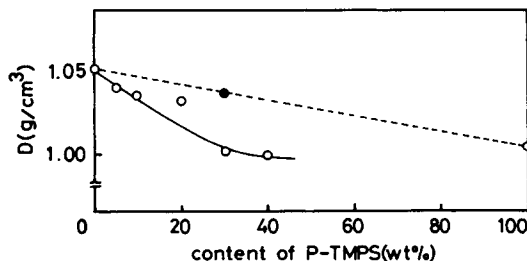


Fig. 6. (○) Density of the blend polymer at 25°C; (●) density of the polymer blend containing graft copolymer of 26.7 wt %.

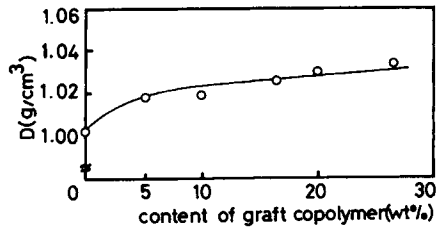
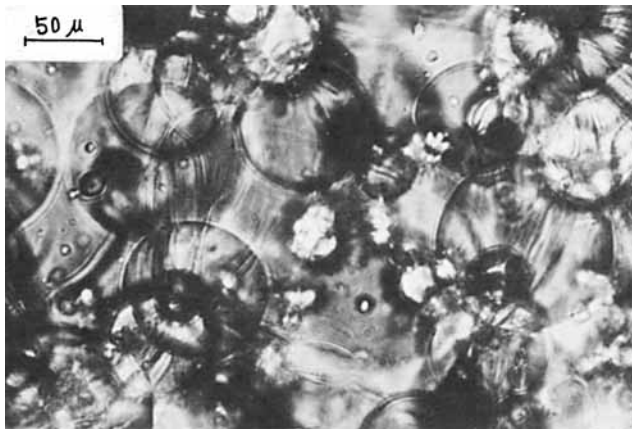


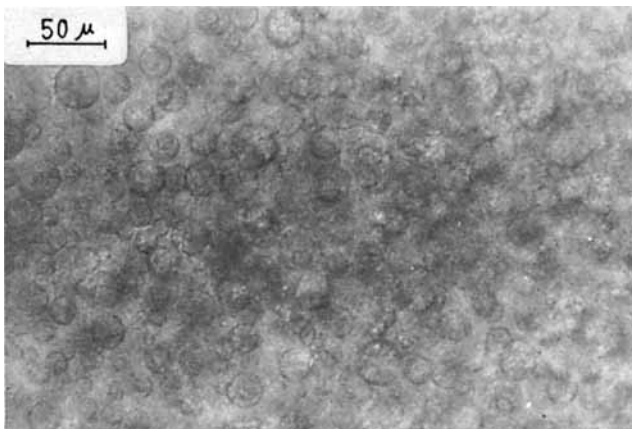
Fig. 7. Effect of the graft copolymer content on density of the polymer blend at 25°C.

PTMPS, respectively, and  $\alpha$  is the ratio of the PTMPS phase.  $P_h$  represents the permeation through the interstices and depends on the composition  $\alpha$ .

These considerations lead to the investigation of the effect of addition of the graft copolymer, PTMPS onto PSt, on the gas permeability of the polymer blend membrane. The addition of the graft copolymer which is compatible to both components should improve the homogeneity of the polymer blend. The plot of the gas permeability of the polymer blend membranes vs. the content of the



(A)



(B)

Fig. 8. Microphotographs of the polymer blends. (A) the polymer blend of PTMPS content of 30 wt %; (B) the polymer blend containing graft copolymer of 26.7 wt %.

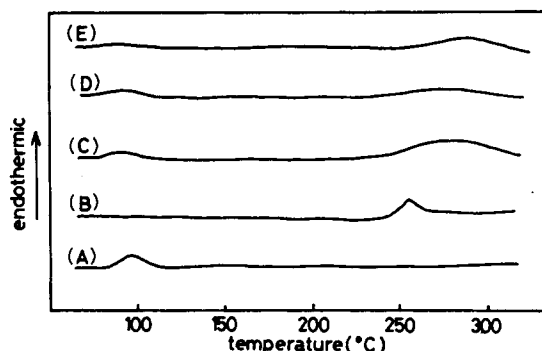


Fig. 9. DSC thermograms of related polymers. (A) PSt; (B) PTMPS; (C) polymer blend of PSt and PTMPS; (D) polymer blend containing the graft copolymer (26.7 wt %); and (E) graft copolymer (PSt on PTMPS).

graft copolymer in the blend is shown in Figure 5. The content of the graft copolymer in the blends ranged from 5, 10, 16.7, 20 to 26.7 wt %, while the total PTMPS content in the blends was fixed at 30 wt %. The gas permeability through the membrane decreases at first with an increase in the graft copolymer content, and then reaches a nearly constant value in the range above 10 wt % of the graft copolymer content.

Expectedly, the addition of the graft copolymer to the blend considerably improves the compatibility of PTMPS and PSt. This is exhibited by the density measurement. The density of the blends with no added graft copolymer is shown in Figure 6. The density decreases with an increasing content of PTMPS. In the same figure, the dotted line represents the line connecting the densities of PTMPS and PSt. The density of the blends having no graft copolymer is below this line. This indicates that boundary interstices in the polymer blend increase with an increasing content of PTMPS.

On the other hand, the density increases by addition of the graft copolymer into the blend and the density becomes approximately constant when the graft copolymer content is more than 10 wt %, (Fig. 7). These blends contain about 30 wt % PTMPS and this constant value falls on the dotted straight line (Fig. 6), and is shown as a full circle. With the addition of the graft copolymer, the interstices decrease distinguishably, resulting in the formation of a homogeneous polymer blend.

In Figure 8, (A) is a microphotograph of the polymer blend containing 30 wt % PTMPS with no added graft copolymer. We can observe the existence of many interstices at the phase boundaries. On the other hand, (B) illustrates the polymer blend containing the graft copolymer 26.7 wt %, where small PTMPS particles distribute uniformly in the PSt matrix and the phase boundaries cannot be clearly observed; i.e., the interstices in the phase boundaries disappear.

Figure 9 shows DSC thermograms of the related polymers and polymer blends. The softening point (about 100°C) of PSt and the decomposition point (about 260°C) of PTMPS is only slightly broadened in polymer blends without the graft copolymer. But, in the polymer blend containing the graft copolymer, these peaks become much broader and resemble those of the graft copolymer.

The addition of the graft copolymer remarkably improves the compatibility of PTMPS and PSt, resulting in the formation of practically homogeneous polymer blends having no interstices at phase boundaries.

TABLE I  
Permeation Coefficients  $P$  ( $\text{cm}^3\cdot\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{cmHg}$ ) of  $\text{O}_2$  and  $\text{CO}_2$  and the Permeation Ratio  $P_{\text{CO}_2}/P_{\text{O}_2}$  of Polymer Blend Membranes of PSt and PTMPS

Polymer blend membranes with no added graft copolymer							
PTMPS (wt %)	0	5	10	20	30	40	
$P_{\text{O}_2} \times 10^{10}$	1.83	3.76	9.13	13.1	66.0	143	
$P_{\text{CO}_2} \times 10^{10}$	11.7	15.7	21.5	45.4	142	190	
Polymer blend membranes of 30 wt % PTMPS content with graft copolymer							
Graft copolymer (wt %)	0	5	10	16.7	20	26.7	
$P_{\text{O}_2} \times 10^{10}$	66.0	13.5	6.77	8.45	7.97	6.61	
$P_{\text{CO}_2} \times 10^{10}$	142	66.0	35.2	34.7	33.3	25.0	
Permeation ratio $P_{\text{CO}_2}/P_{\text{O}_2}$ of polymer blend with and without graft copolymer							
Polymer blend	PTMPS (wt %)	0	5	10	20	30	40
	$P_{\text{CO}_2}/P_{\text{O}_2}$	6.4	4.2	2.4	3.5	2.2	1.3
With graft copolymer	graft copolymer (wt %)	0	5	10	16.7	20	26.7
	$P_{\text{CO}_2}/P_{\text{O}_2}$	2.2	4.9	5.2	4.1	4.2	3.8

The addition of the graft copolymer affects the gas permeability. The gas permeability through the polymer blend membranes of PSt and PTMPS shows large values, owing to the contribution of permeation across the interstices at phase boundaries. The selectivity of  $\text{CO}_2$  vs.  $\text{O}_2$  permeation,  $P_{\text{CO}_2}/P_{\text{O}_2}$ , approaches unity as the content of PTMPS increases (Table I). The addition of the graft copolymer increases this selectivity. The permselectivity value through the polymer blend membrane containing the graft copolymer reflects the intrinsic properties of the membrane material. For such homogeneous polymer blend membranes, the membrane containing about 30 wt % PTMPS shows the oxygen permeability coefficient  $P_{\text{O}_2}$  of about  $8 \times 10^{-10}(\text{cm}^3\cdot\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{cm Hg})$  and the selectivity  $P_{\text{CO}_2}/P_{\text{O}_2}$  of about 4. By comparison with the oxygen permeability ( $P_{\text{O}_2} = 1.83 \times 10^{-10}\text{cm}^3\cdot\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{cm Hg}$ ) and the selectivity ( $P_{\text{CO}_2}/P_{\text{O}_2} = 6.4$ ) of PSt membrane, the permselectivity as well as the permeability of oxygen is improved by the blend of PTMPS with PSt using the graft copolymer as an emulsifier. This method of membrane preparation is very useful in the development of membranes with required properties.

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