Permselective silicon-containing vinyl copolymers

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This paper presents the synthesis of copolymers of vinyl *p*-t-butylbenzoate (PTBBA) with 3-methacryloxypropyltris(trimethylsiloxy)silane (Si-1) and their permselective properties for oxygen and nitrogen. Analysis of the glass transition temperature profile by the Kwei equation implied the existence of some interaction between PTBBA and Si-1 moieties. The oxygen permeability of 1.6×10^{-8} cm^3(STP) cm cm^{-2} s^{-1} cmHg^{-1} for the Si-1 homopolymer decreased with decreasing Si-1 content to arrive at 9.1×10^{-10} cm^3(STP) cm cm^{-2} s^{-1} cmHg^{-1} for the PTBBA homopolymer. Oxygen and nitrogen permeabilities were investigated in connection with Si-1 content and the glass transition temperature in the copolymer. Furthermore, the effect of the condition of preparation on gas permeability was studied; that is, we prepared the copolymers of PTBBA and Si-1 with various polymerization times, and investigated their permselective properties for oxygen and nitrogen.

(Keywords: silicon-containing copolymer; oxygen permeability; glass transition temperature)

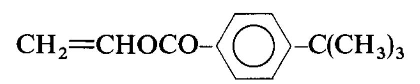
INTRODUCTION

The oxygen permeability of silicon-containing polymers has been extensively investigated for the application of these materials to fuel combustion systems and the purification of air for medical purposes[1]. We have already synthesized the silicon-containing polyamides[2,3], copolyamides[4], polyimides[5], polyesters[3] and network polyamides and copolyamides[6] and have characterized their properties as well as their oxygen permeabilities.

In a previous communication[7], the preparation of new copolymers of vinyl *p*-t-butylbenzoate (PTBBA) and 3-methacryloxypropyltris(trimethylsiloxy)silane (Si-1) was reported and some properties including the oxygen permeability of the copolymers were investigated. In this paper, we make a further investigation of gas permeability in connection with the Si-1 content and the glass transition temperature in the copolymers. We also investigate for the first time the effect of the condition of preparation on gas permeability. To this end, we prepared copolymers of PTBBA and Si-1 with various polymerization times, and investigated their permselective properties for oxygen and nitrogen.

EXPERIMENTAL

Vinyl *p*-t-butylbenzoate monomer (Fuso Chem. Co.) and 3-methacryloxypropyltris(trimethylsiloxy)silane monomer (Chisso Co.) were used as received.



(PTBBA)

$CH_2{=}C(CH_3)COOCH_2CH_2CH_2Si[OSi(CH_3)_3]_3$ (Si-1)

AIBN was recrystallized from methanol. A mixture of PTBBA and Si-1 of a given molar ratio was polymerized with AIBN as the initiator at 60°C for 3 h in a nitrogen atmosphere, after which the mixture was reprecipitated in methanol. When synthesizing copolymers with different compositions, polymerization was carried out for longer times up to 6 h. The polymers obtained were filtered and dried *in vacuo*.

Molecular weight distributions of the polymers were determined on a Toyo Soda HLC-802 gel permeation chromatography (g.p.c.) apparatus with TSK gel G4000H. Infra-red spectra were recorded on a Jasco A-1 spectrophotometer using a KBr pellet or a thin film on a KRS substrate. Differential scanning calorimetry (d.s.c.) was performed in a specific heat measurement mode in the temperature range from -170 to 200°C at a heating rate of 5°C min^{-1} in a helium atmosphere using a Perkin–Elmer 1020 series DSC7 thermal analysis system. Thermomechanical analysis (t.m.a.) was performed in a penetration mode under a pressure of 10 kg cm^{-2} and at a heating rate of 10°C min^{-1} in a nitrogen atmosphere using a Seiko TMA-100; all t.m.a. data were recorded on an SSC-5200H disc station.

Gas permeability was measured by the vacuum method using a Rikaseiki K-315-N equipped with a an MKS baratron pressure transducer. Sample films were cast on a porous SiC substrate (1 mm thick, 700–2200 Å pore

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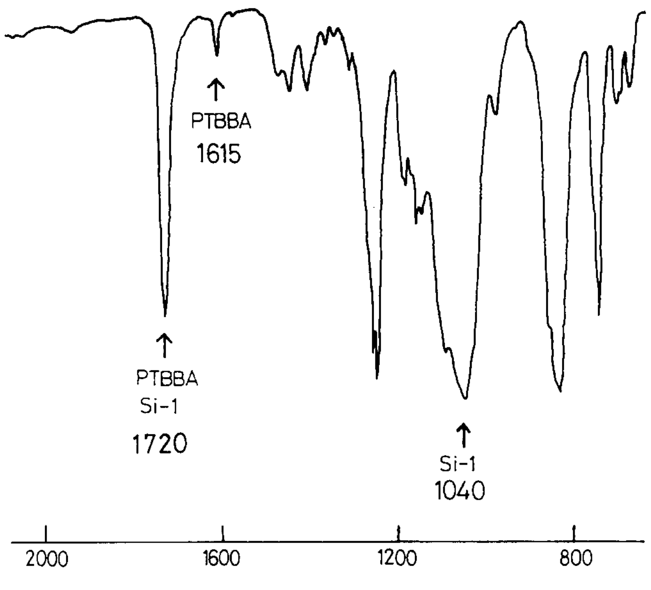

Figure 1 Infra-red spectrum of the PTBBA/Si-1 34/66 mol% copolymer

size, 33% porosity; Nippon Soda Co.), and this substrate with the polymer film was directly attached to the gas permeation cell. The film thickness L was determined using the equation $L=W/(A\rho)$, where W, A and ρ are the weight, surface area and density of the polymer film, respectively. The density of the polymer film was measured using a sink-and-float test in a zinc sulfate solution. The film thickness was in the range 20–40 μm. The volume of gas permeating through a polymer film from upstream to downstream in a vacuum of 0.1 mmHg was measured on a pressure transducer. The permeability coefficient P was calculated from the slope of the steady state in a time–pressure curve (dp/dt).

RESULTS AND DISCUSSION

Preparation of PTBBA/Si-1 copolymers

Molecular weights of the copolymers measured by g.p.c. were of the order of 10^5. The copolymers were easily processable by casting from benzene solution.

Figure 1 shows the infra-red spectrum of the copolymer with 34 mol% PTBBA and 66 mol% Si-1. The infra-red spectra of all the copolymers showed characteristic absorption peaks at 1040, 1615 and 1720 cm^{-1} for the Si–O band, carbon–carbon stretching within the benzene ring and the C=O stretching vibration, respectively. The absorption intensity at 1615 cm^{-1} decreased and that at 1040 cm^{-1} increased with increasing Si-1 content. The absorption intensity at 1720 cm^{-1} was constant irrespective of Si-1 content. The molar fraction of Si-1 in the copolymer was calculated from the change in the absorbance ratio of the peaks at 1615 and 1720 cm^{-1}

$$\frac{C_{\text{Si-1}}}{C_{\text{PTBBA}}+C_{\text{Si-1}}}=1-\left(\frac{A_{1720}}{A_{1615}}\right)^{\text{PTBBA}}\times\left(\frac{A_{1615}}{A_{1720}}\right)^{\text{copolymer}} \tag{1}$$

where C_{PTBBA} and $C_{\text{Si-1}}$ are the molar concentrations of PTBBA and Si-1 units in the copolymer, respectively, and A_{1720} and A_{1615} are the infra-red absorbances at 1720 and 1615 cm^{-1}, respectively. The molar fraction of Si-1 in the obtained copolymer is plotted against that in the feed in *Figure 2*. The result shows that the reactivity of Si-1 is considerably greater than that of PTBBA. Since the reaction yield of the copolymerization is between 5 and 20%, the plot in *Figure 2* can be analysed using the Mayo–Lewis equation[8]

$$F_1=\frac{r_1f_1^2+f_1f_2}{r_1f_1^2+2f_1f_2+r_2f_2^2} \tag{2}$$

where $F_1=\text{d[Si-1]}/\text{d([Si-1]+[PTBBA])}$, $f_1=\text{[Si-1]}/\text{([Si-1]+[PTBBA])}$, $f_2=\text{[PTBBA]}/\text{([Si-1]+PTBBA])}$, and r_1 and r_2 are the Si-1 and PTBBA monomer reactivity ratios, respectively. The solid curve in *Figure 2* is the theoretical Mayo–Lewis curve with $r_1=10$ and $r_2=0.1$. Since the product of r_1 and r_2 is equal to unity or may be less than unity when best fitting, it is adequate that the overall copolymerization proceeds randomly.

Glass transition temperature

Glass transition temperatures T_g measured by d.s.c. are plotted against Si-1 content in *Figure 3*. PTBBA and Si-1 homopolymers have T_g values at 127 and −111°C, respectively. The T_g value decreases with increasing Si-1 content in the copolymer. In *Figure 3*, the dashed line is the theoretical plot based on the Gordon–Taylor equation[9] (with $k=1$)

$$T_g=\frac{w_1T_{g1}+kw_2T_{g2}}{w_1+kw_2} \tag{3}$$

where T_g, T_{g1} and T_{g2} are the glass transition temperatures for the copolymer, PTBBA homopolymer and Si-1 homopolymer, respectively; w_1 and w_2 are the weight fractions of PTBBA and Si-1 in the copolymer, respectively; and k represents the ratio of the volume expansion coefficients of the components at the glass transition temperature[9]. Deviation of the T_g plot from the Gordon–Taylor equation can be compensated by the introduction of a specific interaction term into equation (3), which has been developed by Kwei[10,11]. The solid curve in *Figure 3* is the theoretical fitting to the Kwei equation[10,11], including the interaction term (with $k=4.5$

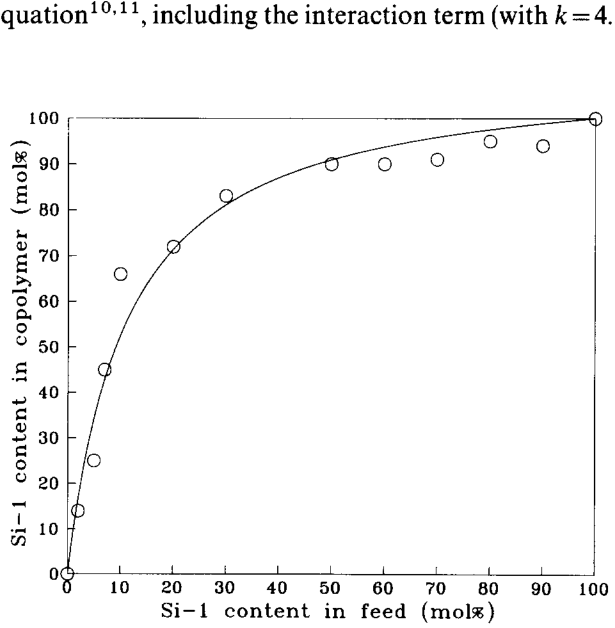

Figure 2 Plots of Si-1 content in the copolymer against that in the feed. The solid curve is the Mayo–Lewis relationship with $r_1=10$ and $r_2=0.1$

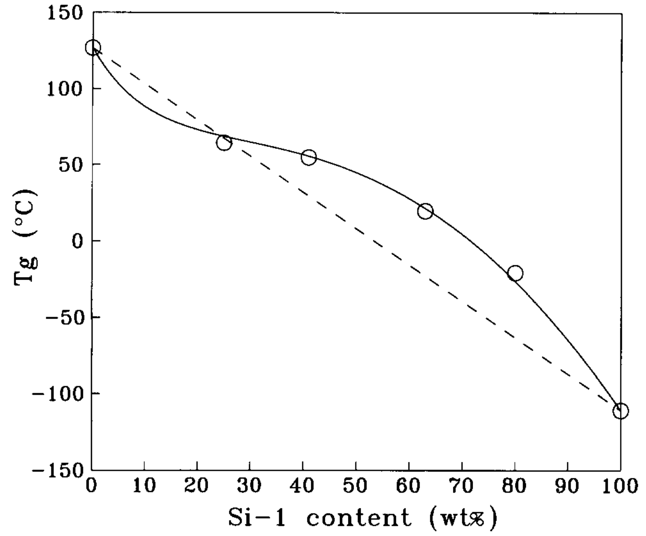

Figure 3 Plots of T_g *versus* Si-1 content in the copolymer. The dashed line is the theoretical plot according to the Gordon–Taylor equation (equation (3)). The solid curve is the theoretical fitting to the Kwei equation (equation (4))

and $q=450$)

$$T_g=\frac{w_1T_{g1}+kw_2T_{g2}}{w_1+kw_2}+qw_1w_2 \qquad (4)$$

where q is a parameter considered as a measure of the strength of a specific interaction between components 1 and 2 in the copolymer. The hydrophobic–hydrophobic interaction between methyl groups of PTBBA and Si-1 can be considered for this specific interaction. *Figure 4* shows the infra-red absorption spectra in the range 2000–4000 cm^{-1} for PTBBA and Si-1 homopolymers and the PTBBA/Si-1 37/63 wt% copolymer. Absorption bands around 2960–2970 and 2880–2900 cm^{-1} are assigned to asymmetric and symmetric stretching vibrations of methyl groups, respectively[12]. The absorption band around 2880–2990 cm^{-1} for the copolymer is a shoulder, whereas those bands for both homopolymers are distinct and sharp peaks. This result implies that some interaction between methyl groups may affect this absorption band for the copolymer, and its intensity decreases to a shoulder.

The previous paper[7] reported T_g values estimated from the heat distortion temperature T_h using a penetration mode of t.m.a. which requires loading of the probe. All T_g values estimated from t.m.a. in the previous paper[7] were above room temperature even when sample heating started from −170°C, because the sample film was cooled down as the probe tip was loaded. In the case where the sample film was cooled down to −170°C with the probe tip unloaded and then t.m.a. started with the probe tip loaded, a clear T_h correspondence to T_g measured by d.s.c. was observed. T_h was −106°C for Si-1 homopolymer.

Gas permeability

Logarithmic plots of P_{O_2} and P_{N_2} *versus* reciprocal temperature show a linear relationship. No significant hysteresis of the permeabilities was observed upon heating and cooling through T_g. The permeability coefficients of oxygen (P_{O_2}) and nitrogen (P_{N_2}) for all films increased with increasing temperature. Activation of the segmental motion with increasing temperature makes the free volume larger, and thus the permeation of oxygen and nitrogen is enhanced with increasing temperature.

P_{O_2} values at 60°C are plotted against the weight fraction of Si-1 in the copolymer in *Figure 5*. The P_{O_2} values of PTBBA and Si-1 homopolymers are 9.1×10^{-10} and 1.6×10^{-8} cm^3(STP) cm cm^{-2} s^{-1} cmHg^{-1}, respectively. Incorporation of a small amount of PTBBA up to 10 wt% (major portion the Si-1 component) gives a large decrease in P_{O_2} and a subsequent reduction in Si-1 content yields a further decrease in P_{O_2}. The deviated T_g profile from a linear relationship in *Figure 3* implies a specific interaction between Si-1 and PTBBA moieties in the range of Si-1 contents from 40 to 80 wt%. In other words, in this region the specific interaction reduces the free volume and increases T_g. Thus the large decrease in P_{O_2} in this region is reasonably related to the reduction in free volume due to a specific interaction between the PTBBA and Si-1 components.

Regarding the effect of molecular motion on gas

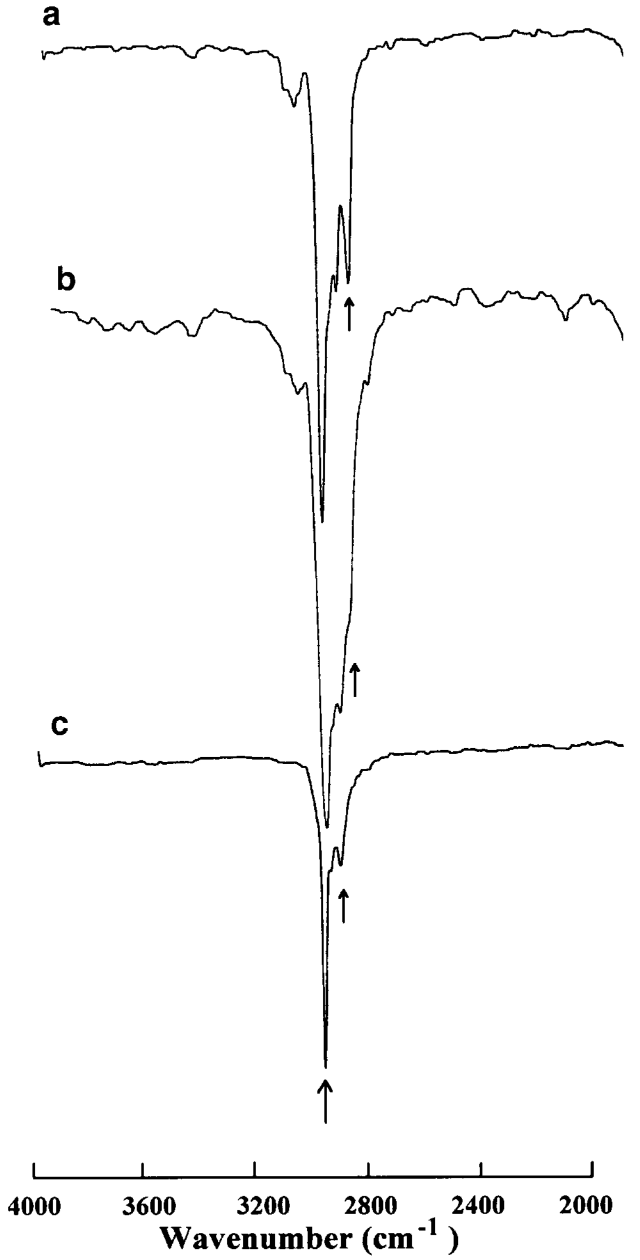

Figure 4 Infra-red absorption spectra for (a) PTBBA homopolymer, (b) Si-1 homopolymer and (c) the PTBBA-Si-1 37/63 wt% copolymer

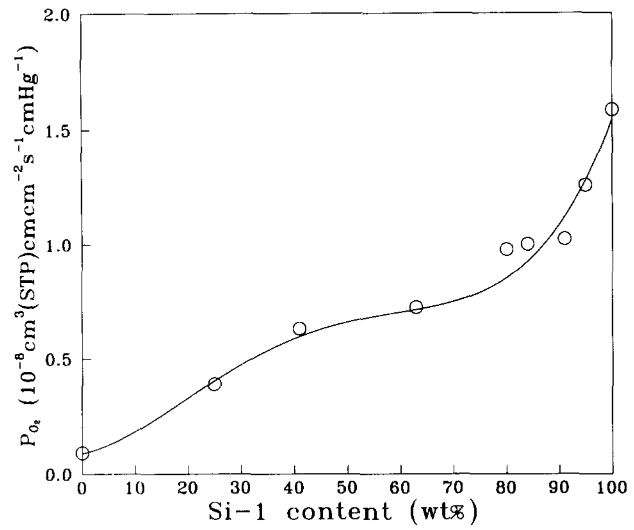

Figure 5 Plots of P_{O_2} at 60°C *versus* Si-1 content in the copolymer

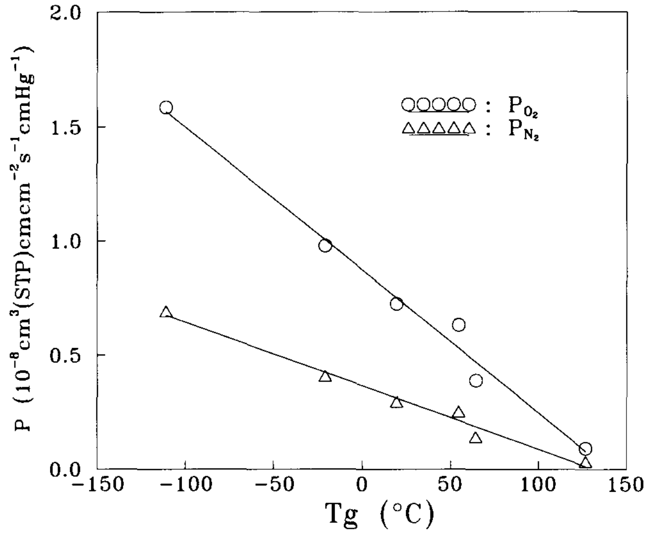

Figure 6 Plots of P_{O_2} and P_{N_2} at 60°C *versus* T_g for the copolymer

permeation, the values of P_{O_2} and P_{N_2} at 60°C are replotted against copolymer T_g (as a measure of molecular motion) in *Figure 6*. In this figure, the permeability–T_g profiles show an almost linear relationship. This result implies that the segmental mobility as estimated by T_g dominates the oxygen and nitrogen permeabilities. A higher Si-1 fraction in the copolymer makes T_g lower and leads to greater segmental mobility, hence the higher P_{O_2} value. A similar type of relationship between P_{O_2} and T_g has been obtained for polyamides and polyesters with siloxane moieties in their side chains[3] and for network copolyamides with siloxane moieties in their main chains[6].

Effect of copolymer composition distribution on gas permeability in the copolymer

Table 1 shows the results of the yield and Si-1 content for the sample films prepared with increasing PTBBA/Si-1 copolymer polymerization times. The PTBBA/Si-1 molar ratio in the feed was 90/10. Increasing polymerization time increases the yield and decreases the Si-1 content in the copolymer, which corresponds well to the decrease in P_{O_2}.

We now compare the samples (no. 1, no. 2 and no. 3) whose features are summarized in *Table 2*. These samples were prepared from different comonomer ratios in the feed and in different polymerization times to obtain quite different polymerization yields but almost the same Si-1 contents. The P_{O_2} values for the samples with the higher yields (no. 2 and no. 3) are lower than the P_{O_2} for the sample with the lowest yield (no. 1). The copolymer with the lowest yield and the shortest polymerization time has a random sequence of comonomer units. However, a longer polymerization time (giving a higher yield) will give rise to a polymer with a block-type chain sequence or one almost completely occupied by PTBBA units, because in the later stages of polymerization the PTBBA monomer with the lower reactivity ratio must make the major contribution towards the chain sequence. D.s.c. scanning of sample no. 2 shows a clear T_g at 123°C, and sample no. 3 exhibits clear T_gs at −32 and 123°C. The higher T_g at 123°C is close to that of PTBBA homopolymer at 127°C. These d.s.c. results therefore confirm that samples no. 2 and no. 3 are block copolymers with long PTBBA sequences. *Figure 7* shows the infra-red absorption spectra in the range 2000–4000 cm^{-1} for samples no. 1, no. 2 and no. 3. As discussed above, the infra-red absorption band due to a symmetric stretching vibration around 2880–2900 cm^{-1} is a measure of the interaction between methyl groups of PTBBA and Si-1 units. The absorption band around 2880–2900 cm^{-1} for sample no. 1 is a shoulder, whereas those bands for samples no. 2 and no. 3 are sharp peaks similar to the peak observed for the PTBBA homopolymer shown in *Figure 4a*. These results suggest that the specific interactions between PTBBA and Si-1 units are small for samples no. 2 and no. 3, thus supporting the idea that these samples have long PTBBA sequences. Therefore, a copolymer synthesized over a longer polymerization time has a characteristic copolymer composition distribution different from a copolymer prepared over a shorter polymerization time.

In *Figure 8* the P_{O_2} values of the copolymers prepared over the longer polymerization time (6 h) are plotted against Si-1 content (filled circles). In this figure the P_{O_2} values of the copolymers prepared over the shorter

Table 1 Effect of increasing polymerization time on the yield, Si-1 content, P_{O_2} and P_{O_2}/P_{N_2}

Polymerization time (h)	3	4	5	6
Yield (%)	11	30	63	71
Si-1 content (mol%)	66	37	22	23
P_{O_2} at 60°C[a]	0.98	0.71	0.25	0.22
P_{O_2}/P_{N_2} at 60°C	2.37	2.36	2.62	2.90

[a] Units: 10^{-8} cm^3(STP) cm cm^{-2} s^{-1} cmHg^{-1}

Table 2 Summary of yield, polymerization time, P_{O_2} and P_{O_2}/P_{N_2} for samples with similar Si-1 content

	Sample no. 1	Sample no. 2	Sample no. 3
Si-1 content (mol%) in feed	5	10	10
Si-1 content (mol%) in copolymer	25	22	23
Polymerization time (h)	3	5	6
Yield (%)	9	63	71
P_{O_2} at 60°C[a]	0.63	0.25	0.22
P_{O_2}/P_{N_2} at 60°C	2.51	2.62	2.90

[a] Units: 10^{-8} cm^3(STP) cm cm^{-2} s^{-1} cmHg^{-1}

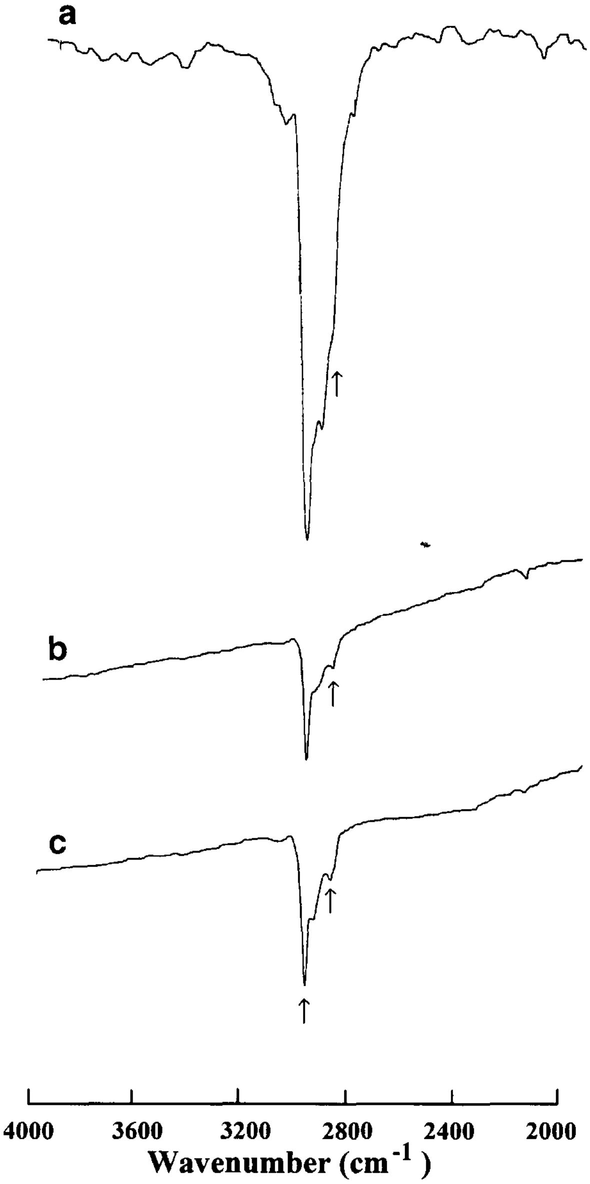

Figure 7 Infra-red absorption spectra for (a) sample no. 1, (b) sample no. 2 and (c) sample no. 3

polymerization time (see *Figure 5*) are replotted (open circles). The results shown in *Figure 8* indicate that the copolymers prepared over the longer polymerization time are the poorer in terms of oxygen permeability. These lower oxygen permeabilities are attributed to the formation of large PTBBA sequence domains, which was experimentally indicated by the d.s.c. scans and infra-red spectra mentioned above. In other words, the large PTBBA sequence domains could form a continuous phase, and thus disturb the oxygen transport.

As shown in *Figure 8*, the largest difference in P_{O_2} between the two plots is obtained in the vicinity of a 40 wt% Si-1 content. Upon increasing the Si-1 content, the P_{O_2} value of the sample prepared over the longer polymerization time approaches that of the sample prepared over the shorter polymerization time. The PTBBA/Si-1 40/60 wt% copolymer still has a distinct absorption peak due to the symmetric stretching vibration of methyl groups around 2880–2900 cm^{-1}, whereas the PTBBA/Si-1 27/73 wt% copolymer has only a shoulder, as shown in *Figure 9*. These infra-red absorption data also support the idea that the PTBBA sequence is shorter for the sample with the higher Si-1 content. Thus, for a high Si-1 content, the total amount of Si-1 in the copolymer will contribute most to the oxygen permeability, and a small contribution from the difference in the copolymer composition distributions can be expected.

Figure 10 shows the relationship between P_{O_2} and the separation ratio P_{O_2}/P_{N_2} for the copolymer samples prepared over the different polymerization times. In each case an increase in P_{O_2} is accompanied by a decrease in P_{O_2}/P_{N_2}. The sample whose plot between P_{O_2} and P_{O_2}/P_{N_2} moves towards the upper right corner (i.e. higher P_{O_2} and greater P_{O_2}/P_{N_2}) in *Figure 10* is the more desirable for use in oxygen and nitrogen membranes. Thus the result

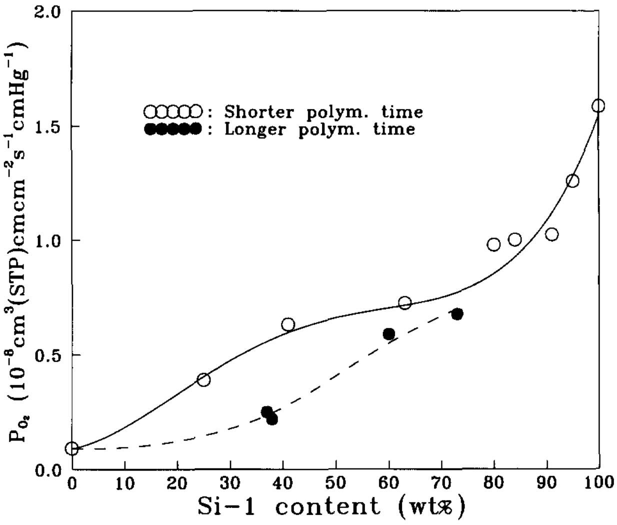

Figure 8 Plots of P_{O_2} at 60°C *versus* Si-1 content for samples prepared with different polymerization times

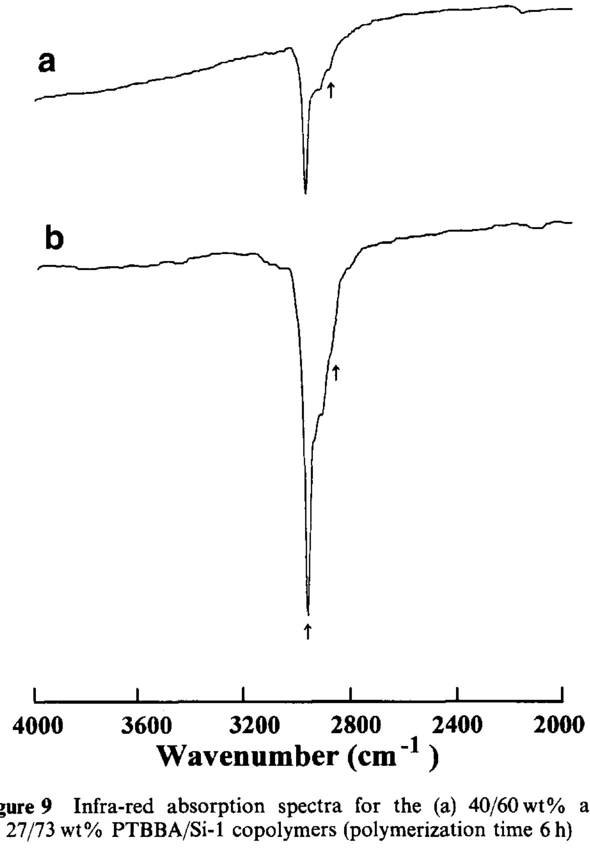

Figure 9 Infra-red absorption spectra for the (a) 40/60 wt% and (b) 27/73 wt% PTBBA/Si-1 copolymers (polymerization time 6 h)

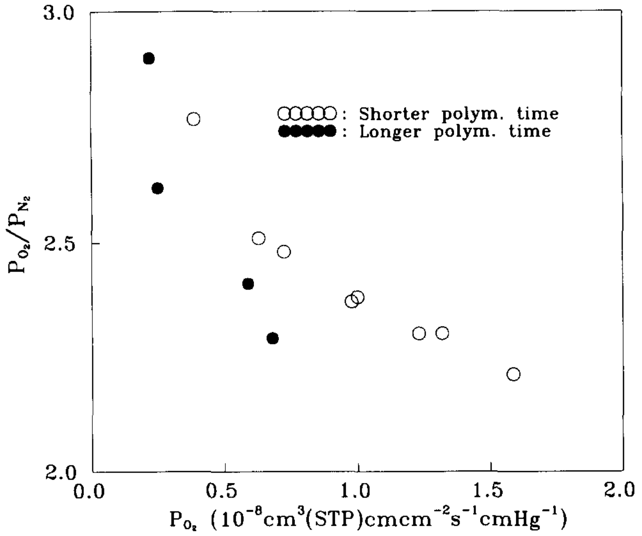

Figure 10 Plots of separation ratio of P_{O_2}/P_{N_2} *versus* P_{O_2} at 60°C for copolymers with different polymerization times

shown in *Figure 10* implies that the copolymers prepared over the shorter polymerization time have the superior permselective properties.

CONCLUSIONS

Silicon-containing vinyl copolymers of PTBBA and Si-1 were prepared and the oxygen and nitrogen permeabilities of the copolymers were investigated in connection with the Si-1 contents and the glass transition temperatures. Analysis of the T_g profile using the Kwei equation, which incorporates a specific interaction parameter, implies the existence of significant hydrophobic–hydrophobic interaction between the methyl groups of PTBBA and Si-1 units, which is also confirmed by the variation with composition in the infra-red absorption band for the symmetric stretching vibration of the methyl group. The large decrease in P_{O_2} upon incorporation of a small amount of PTBBA and the following significant decrease in P_{O_2} with a reduction in Si-1 content reasonably relate to the reduction in free volume due to the specific interaction between PTBBA and Si-1 components. The P_{O_2} and P_{N_2} values show a linear relationship with T_g. This result implies that the degree of segmental mobility, as estimated by the T_g of the copolymer, could significantly affect the P_{O_2} and P_{N_2} values.

Since the reactivity ratio of PTBBA is much smaller than that of Si-1, the copolymer composition distribution can be controlled by changing the polymerization time for the PTBBA/Si-1 copolymer. Copolymer samples with similar Si-1 contents could have quite different copolymer composition distributions depending on the comonomer ratio in the feed and the polymerization time. The P_{O_2} of the sample prepared over the shorter polymerization time is larger than that of the sample prepared over the longer polymerization time. D.s.c. scans and infra-red absorption data show that the samples prepared over the longer polymerization time have long PTBBA sequences. These large PTBBA sequence domains can make a continuous phase, which is unfavourable for oxygen permeability.

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