# New copolymer of vinyl *p*-tert-butylbenzoate with 3-methacryloxypropyltris(trimethylsiloxy)silane and oxygen permeability

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The synthesis of copolymers of vinyl *p*-tert-butylbenzoate (PTBBA) with 3-methacryloxypropyltris(trimethylsiloxy)silane (Si-1) and their properties including oxygen permeability are presented. All copolymers had molecular weights above $10^5$ and were easily processable by casting from benzene solution. The Si-1 comonomer content in the obtained copolymer was estimated from the change in the characteristic infra-red absorption due to the carbonyl group of PTBBA and Si-1 units and the benzene ring of the PTBBA unit. The oxygen permeability $P_{O_2}$ increases from $9.1 \times 10^{-10}$ cm$^3$ (STP) cm(cm$^2$ s cmHg)$^{-1}$ for the PTBBA homopolymer to $1.6 \times 10^{-8}$ cm$^3$(STP) cm(cm$^2$ s cmHg)$^{-1}$ for the Si-1 homopolymer, whereas the corresponding ratio of $P_{O_2}/P_{N_2}$ decreases from 2.7 to 2.2. $P_{O_2}$ and $P_{O_2}/P_{N_2}$ for the copolymer reach a plateau around 25–65 Si-1 mol%, where the values are $0.9 \times 10^{-8}$–$1 \times 10^{-8}$ cm$^3$(STP) cm(cm$^2$ s cmHg)$^{-1}$ and 2.4–2.5, respectively. The logarithmic value of $P_{O_2}$ linearly increases with decreasing glass transition temperature.

**(Keywords: copolymer; 3-methacryloxypropyltris(trimethylsiloxy)silane; vinyl *p*-tert-butylbenzoate; oxygen permeability)**

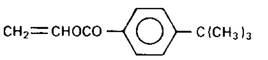
## *Introduction*

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

In this study, we synthesized a new copolymer of vinyl *p*-tert-butylbenzoate whose homopolymer has relatively high oxygen permeability[7], using a silicon-containing vinyl monomer of 3-methacryloxypropyltris(trimethylsiloxy)silane, and characterized the oxygen permeability.

## *Experimental*

Vinyl *p*-tert-butylbenzoate monomer supplied from Fuso Chemical Co. Ltd, Japan and 3-methacryloxypropyltris(trimethylsiloxy)silane monomer donated by Chisso Co., Japan, 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. The mixture of PTBBA and Si-1 of a given molar ratio was polymerized with AIBN as an initiator at 60°C for 3–5 h in the nitrogen atmosphere, and then reprecipitated in methanol. The obtained polymers were filtered and dried *in vacuo*.

The molecular weight distribution of the polymers was determined by a Toyo Soda HLC-802 gel permeation chromatograph with TSK gel G4000H. Infra-red (i.r.) spectra were recorded on a Jasco model i.r. A-1 spectrophotometer using a KBr pellet or a thin film on a KRS substrate. Thermomechanical analysis (t.m.a.) was performed in a penetration mode under a pressure of 10 kg cm$^{-2}$ and a heating rate of 10°C min$^{-1}$ in a nitrogen atmosphere, using Seiko Instruments model TMA-100 and all t.m.a. data were recorded on a model SSC-5200H disc station.

Gas permeability was measured by the vacuum method using Rikaseiki model K-315-N equipped with a MKS baratron pressure transducer. Sample film was cast on porous SiC substrate (1 mm thick, 700–2200 Å pore size and 33% porosity) provided by Nippon Soda Co. Ltd, Japan, and this substrate with 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 $\rho$ 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 method in zinc sulphate solution. The film thickness was in the range of 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 pressure–time curve, $dp/dt$.

## *Results and discussion*

All copolymers had molecular weights above $10^5$ and were easily processable by casting from benzene solution.

I.r. spectra showed the characteristic absorption peaks

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at 1040, 1615 and 1720 cm$^{-1}$ due to Si–O, benzene ring and C=O absorptions, 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 the Si-1 unit in the copolymer was calculated from the change in the absorbance ratio between 1615 cm$^{-1}$ and 1720 cm$^{-1}$:

$$C_{\mathrm{Si-1}}/(C_{\mathrm{PTBBA}}+C_{\mathrm{Si-1}})=1-(A_{1720}/A_{1615})^{\mathrm{PTBBA}} \times (A_{1615}/A_{1720})^{\mathrm{copolymer}}$$

where $C_{\mathrm{PTBBA}}$ and $C_{\mathrm{Si-1}}$ are the molar concentrations of PTBBA and Si-1 units in the copolymer, respectively, and $A_{1720}$ and $A_{1615}$ are the i.r. absorbance at 1720 and 1615 cm$^{-1}$, respectively. The molar fraction of Si-1 unit in the obtained copolymer is plotted against that in the monomer mixture in *Figure 1*. The result shows that the reactivity of the Si-1 monomer is considerably larger than that of the PTBBA monomer. Since the reaction yield of copolymerization is between 5% and 20%, the plot in the figure can be analysed by the Mayo–Lewis equation[8]:

$$F_1=(r_1f_1^2+f_1f_2)/(r_1f_1^2+2f_1f_2+r_2f_2^2)$$

where $F_1=\mathrm{d[Si\text{-}1]/d([Si\text{-}1]+[PTBBA])}$, $f_1=\mathrm{[Si\text{-}1]/([Si\text{-}1]+[PTBBA])}$, $f_2=\mathrm{[PTBBA]/([Si\text{-}1]+[PTBBA])}$ and $r_1$ and $r_2$ are the Si-1 and PTBBA monomer reactivity ratios, respectively. The solid curve in *Figure 1* is the theoretical Mayo–Lewis expression for $r_1=10$ 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.

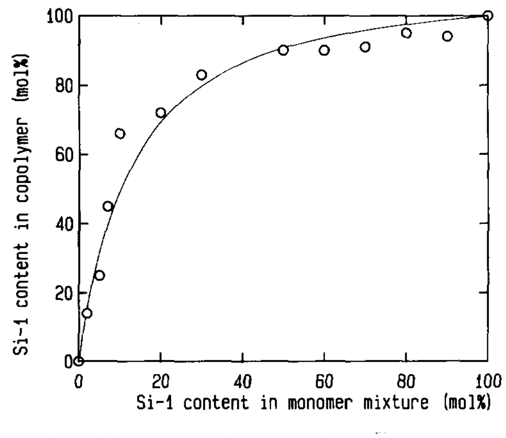

**Figure 1** Plot of Si-1 content in the obtained copolymer against that in the monomer mixture

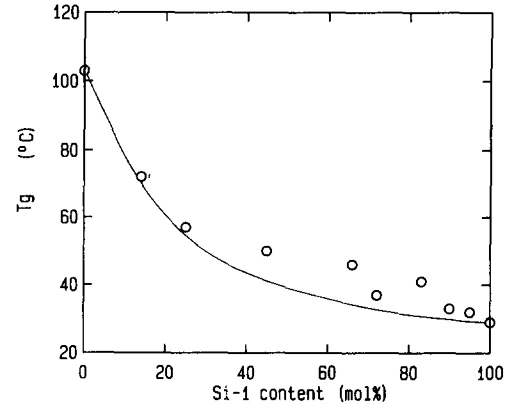

**Figure 2** $T_g$ *versus* Si-1 monomer content in the obtained copolymer

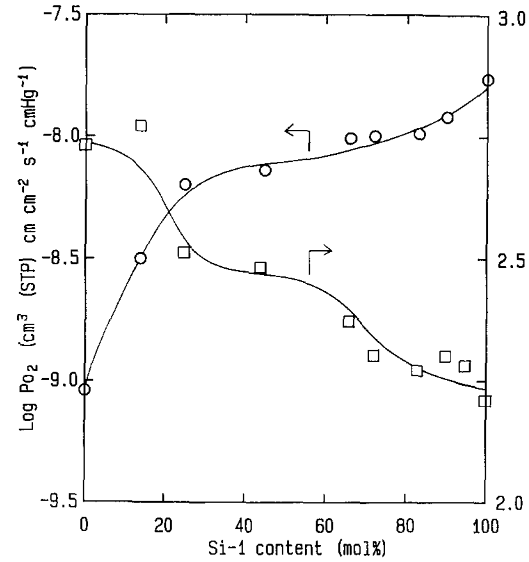

**Figure 3** Plots of log $P_{O_2}$ and $P_{O_2}/P_{N_2}$ *versus* Si-1 monomer content in the obtained copolymer. Temperature: 60°C

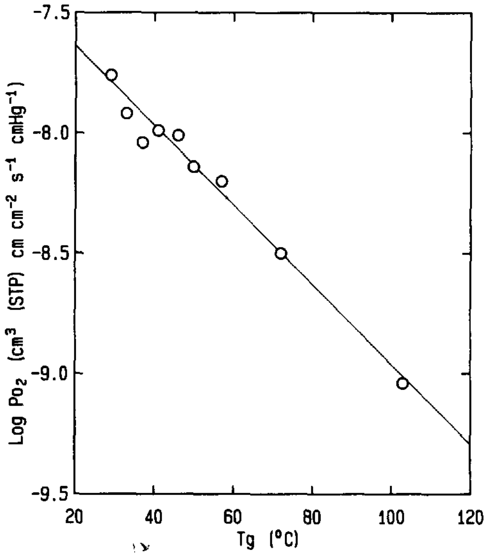

**Figure 4** Plot of log $P_{O_2}$ *versus* $T_g$ of the corresponding copolymer

The t.m.a. results showed that the copolymer obtained has a single glass transition estimated from the heat distortion temperature. The glass transition temperature $T_g$ is plotted against Si-1 content in the obtained copolymer in *Figure 2*. The solid curve in *Figure 2* exhibits the curve predicted from Fox's equation[9] of $1/T_g=W_1/T_{g1}+W_2/T_{g2}$, where $W_1$ and $W_2$ are the weight fractions of the Si-1 and PTBBA monomer units, respectively, and $T_{g1}$ and $T_{g2}$ are the glass transition temperatures of Si-1 and PTBBA homopolymers, respectively.

The values of $P_{O_2}$ and $P_{N_2}$ for all films increased with increasing temperature. The activation of the segmental motion with increasing temperature makes the free volume larger, thus the permeation of oxygen and nitrogen is enhanced by increasing temperature. Both $P_{O_2}$ and $P_{O_2}/P_{N_2}$ at 60°C are plotted against the Si-1 content in *Figure 3*. $P_{O_2}$ increases from $9.1\times10^{-10}$ cm$^3$(STP) cm(cm$^2$ s cmHg)$^{-1}$ for PTBBA homopolymer to 1.6 × 10$^{-8}$ cm$^3$(STP) cm(cm$^2$ s cmHg)$^{-1}$ for Si-1 homopolymer, whereas the corresponding $P_{O_2}/P_{N_2}$ decreases from 2.7 to 2.2. It is noted that $P_{O_2}$ and $P_{O_2}/P_{N_2}$ reach a plateau around 25–65 Si-1 mol%, where their values are 0.9 × 10$^{-8}$–1 × 10$^{-8}$ cm$^3$(STP) cm(cm$^2$ s cmHg)$^{-1}$ and 2.4–2.5, respectively. The logarithmic value of $P_{O_2}$ is replotted against $T_g$ of the copolymer in *Figure 4*. Log $P_{O_2}$ linearly increases with decreasing $T_g$. This result shows that the segmental mobility estimated by $T_g$ dominates the oxygen and nitrogen permeabilities. The same type of linear relationship between log $P_{O_2}$ and $T_g$ has been obtained for polyamides and polyesters with siloxane moieties in their side chains[3] as well as network copolyamides with siloxane moieties in their main chains[6]. As mentioned above, $P_{O_2}$ and $P_{O_2}/P_{N_2}$ reach a plateau region at around 25–65 Si-1 mol%, which corresponds well to the plateau region for $T_g$ values around the same compositions as shown in *Figure 2*.

## *Acknowledgement*

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