Clinical significance
Soft denture lining materials are required to be minimally contaminated from the viewpoint of oral hygiene. The experimental materials containing fluorinated monomers showed high flexibility and high contamination resistance. The use of monomers with a large number of fluorine atoms could give clinically-useful properties to these materials.

Abstract
Purpose: To develop a new fluorine-containing soft denture lining material, the influences of fluorinated monomers on physical properties and contamination resistance were examined.
Methods: Five experimental materials of different chemical compositions in fluorinated monomer and two plasticized acrylics (Supersoft, VertexSoft) were used to evaluate water sorption, solubility, staining resistance, Shore A hardness, and contact angle. Five specimens for each test were fabricated. The results were analyzed with one-way analysis of variance (ANOVA) and Tukey’s HSD test using statistical software at $p = 0.05$.
Results: The amount of water sorption tended to decrease as the number of the fluorine atoms in fluorinated monomers increased. Similar solubility was shown regardless of the type of fluorinated monomer. The use of fluorinated monomers for immersion in coffee allowed suppression of discoloration. In β-carotene, there were no significant differences in color changes among four experimental materials with fluorinated monomer. Shore A hardness was decreased and the contact angles tended to increase as the number of fluorine atoms in fluorinated monomers increased. When comparing the experimental materials and commercially available materials, the experimental materials containing fluorinated monomers with large numbers of fluorine atoms showed adequate clinical properties except for staining test of β-carotene.
Conclusion: Monomers with a large number of fluorine atoms can be used to develop applicable soft denture lining materials in clinical practice.

Key words: soft denture lining materials, fluorinated monomers, contamination resistance

Introduction
In our rapidly aging society, the number of patients with difficulties in complete denture treatment, including highly absorbed alveolar ridges, is increasing. In the case of an extremely resorbed residual ridge, the overlying mucosa decreases in thickness according to the resorption. As the shock-absorbing effect of the mucosa is diminished and masticatory impact forces are directly transmitted to the underlying tissue, the burden on the residual ridge is increased. In addition, lesions, generalized irritation, or soreness are seen on the basal seat because the thin mucosa is pinched between the hard denture base and the bone during mastication. In such cases, it is necessary to line the inner surface of the denture base with a soft material similar to the mucosa in order to compensate for the lost thickness and viscoelasticity of the mucosa. The pain is relieved by reducing the impact force during mastication and dispersing the force widely over the alveolar ridge to give a cushioning effect. The application of a soft lining material to the mandibular denture can also increase the patient’s masticatory performance and biting force, and moreover improve the chewing rhythm.
Materials made of acrylic and silicon are mainly used for soft denture lining at present.\(^1\), \(^3\), \(^4\) The silicone soft lining materials are chemically stable and thus the elasticity can be maintained, but as they do not directly adhere to acrylic resin, an adhesive is necessary. The bond strength is not yet sufficient.\(^5\), \(^6\) In addition, as the silicone rubber is porous, food debris, which stagnates inside the pores, enhances the growth of fungi such as \textit{Candida albicans}, leading to the formation of fungal colonies.\(^7\) On the other hand, acrylic soft lining materials adhere strongly to the acrylic resin denture base, but the added plasticizer will gradually diffuse onto the surface of the resin and will be leached out by the saliva, resulting in a liner that will gradually harden.\(^8\) Also, there is a problem of bacterial contamination which may be due to the roughness of the surface or water sorption of the material.\(^9\) Thus, since soft denture lining materials are likely to be contaminated, the materials are required to be minimally contaminated from the viewpoint of oral hygiene.

Some attempts to apply fluorocarbon polymers to the dental field have been made because of their characteristics including water and oil repellency, contamination resistance, and chemical stability.\(^10\), \(^11\) Hayakawa et al developed a fluoropolymer soft denture liner (Kurepeet\(^8\), Kurecha Co., Tokyo, Japan) with extremely low water sorption, excellent adhesion to acrylic resins, and a stable quality.\(^12\) Moreover, Hayakawa et al developed a dough-type fluoropolymer soft denture liner (Kurepeet Dough\(^8\), Kurecha Co., Tokyo, Japan) by improving usability and softness without losing the excellent physical properties of Kurepeet.\(^13\) However, these liners are not available at present, because carbon tetrachloride is used in the production process and this is banned by the Montreal Protocol.

In this study the influences of fluorinated monomers on physical properties and contamination resistance were assessed with the aim of making, on an experimental basis, a new paste to be used as a fluorinated heat-polymerized soft denture lining material.

### Materials and Methods

#### 1. Materials and preparation of test specimens

The composition of the five experimental soft lining materials used in this study are listed in Table 1. The details of each fluorinated monomer are listed in Table 2. The value of 3F indicates 1 as a standard value in the relative amount of fluorine.

### Table 1. Constituents of experimental soft denture lining materials (weight %)

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Code</th>
<th>Code</th>
<th>Code</th>
<th>Code</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trifluoroethyl methacrylate (3F)</td>
<td>0</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Octafluoroethyl methacrylate (8F)</td>
<td>0</td>
<td>0</td>
<td>12</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Dodecafluoroheptyl methacrylate (12F)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>Heptadecafluorodecy methacrylate (17F)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>Fluorinated soft resin</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
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<tr>
<td>Acrylic monomers</td>
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<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
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<td>Acrylic polymers</td>
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<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Hydrophobic silica</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Benzoyl peroxide</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
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</tr>
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</table>

### Table 2. Fluorinated monomers

<table>
<thead>
<tr>
<th></th>
<th>The number of fluorides in 1 molecule</th>
<th>Molecular weight</th>
<th>Molarity (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trifluoroethyl methacrylate (3F)</td>
<td>3</td>
<td>168.12</td>
<td>71.38</td>
</tr>
<tr>
<td>Octafluoroethyl methacrylate (8F)</td>
<td>8</td>
<td>300.14</td>
<td>39.98</td>
</tr>
<tr>
<td>Dodecafluoroheptyl methacrylate (12F)</td>
<td>12</td>
<td>400.15</td>
<td>29.99</td>
</tr>
<tr>
<td>Heptadecafluorodecyl methacrylate (17F)</td>
<td>17</td>
<td>532.19</td>
<td>22.55</td>
</tr>
</tbody>
</table>

Materials and Methods

1. Materials and preparation of test specimens

The composition of the five experimental soft lining materials used in this study are listed in Table 1. The details of each fluorinated monomer are listed in Table 2. The value of 3F indicates 1 as a standard value in the relative amount of fluorine.
and the length of carbon side chain. The materials used as controls were commercially available acryl-
ic soft lining materials, Supersoft (SS) and Vertex-
Soft (VS) (Table 3). The experimental soft lining materials described herein were polymerized by mooring at 20°C to 100°C (the temperature was raised within 60 minutes), and then polymerized at 100°C for 30 minutes. The commercially avail-
able soft lining materials were polymerized accord-
ging to the manufacturer’s instructions.

A water sorption and solubility test, staining test, hardness test, and contact angle measurement were conducted.

2. Water sorption and solubility test
The measurements of amount of water sorption and solubility conformed to those specified by the ISO 1567-1997. Each test specimen was a disc of 20 mm in diameter and 1 mm in thickness, prepared with a stainless steel mold. Each specimen was stored in drying mode with a desiccator until reaching constant weight, and then weighed on a chemical balance (AE240; Mettler Toledo, Tokyo, Japan). After the specimens had reached constant weight, they were immersed in purified water at 37°C for 7 days, then taken out of the water, weighed, and stored in drying mode with a desiccator until reaching constant weight again.

3. Staining test
Staining test specimens were immersed in two solu-
tion types: color differences before versus after immersion were determined. Each specimen was a disc 20 mm in diameter and 1 mm in thickness. The two solution types for immersion were a 2% coffee solution (Nestle Philippines Co., Philippines) and a 0.1% β-carotene/olive oil solution (Nacalai Tesque Co., Kyoto Japan / The Nisshin OilliO Group Co., Italia). Each specimen was immersed in each solution at 37°C for 1 week. According to the CIE regulations, L*ab values before and after immersion were determined with a spectro-differential colorimeter (Minolta CR-13, Konica Minolta Co., Tokyo, Japan). Prior to measurements, these specimens were washed with a neutral detergent for 5 minutes. A white background was used during measurements, and the values were determined three times for each specimen to obtain the L* value (brightness), a* value (red-green proportion) and b* value (yellow-blue proportion). From the following formula, ΔE (color change) is obtained:

\[ \Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \]

4. Hardness test
Each specimen was cylindrical, being 10 mm in diameter and 10 mm in thickness, and Shore A hardness was determined with a durometer (Model DD2-A, Kobunshi Keiki CO., Kyoto, Japan) according to the ISO 7619-2004. After immersion of the specimens in purified water at 37°C for 24 hours, the specimens were subjected to the test.

5. Contact angle
Each specimen was a disc of 20 mm in diameter and 1 mm in thickness. 5 µl of purified water at 20°C were dropped onto the surface of the speci-
men, and a contact angle was then determined, for 30 seconds, at a room temperature of 20°C by means of a contact angle measurement device (PTA125, First Ten Angstroms USA).

6. Statistical analysis
The data were analyzed with one-way analysis of variance (ANOVA) and Tukey’s HSD test using statistical software (JMP 5J, SAS, Tokyo, Japan). The significance level was set at 0.05.

Results
Table 4 shows the water sorption and solubility, the color change, using two types of coloring solu-
tions, Shore A hardness, and contact angles. SR0F decreased physical properties more than SS or VS except Shore A hardness. The experimental soft lining materials replacing acrylic monomers by fluorinated monomers showed better physical properties than SS or VS. There was a significant difference only in contact angle between SR12F and SR17F.

Table 3. Commercially available materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>Code</th>
<th>Manufacturer</th>
<th>Lot no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylic soft lining materials</td>
<td>SS</td>
<td>GC America, Inc.</td>
<td>507091</td>
</tr>
<tr>
<td></td>
<td>VS</td>
<td>Vertex Dental B.V.</td>
<td>Powder YR271P06, Fluid YR364L01</td>
</tr>
</tbody>
</table>
Table 4. Mean (SD) of water sorption, solubility, color change, shore A hardness and contact angle of lining materials (n = 5 for each test group)

<table>
<thead>
<tr>
<th>Materials</th>
<th>Water sorption (µg/mm²)</th>
<th>Solubility (µg/mm²)</th>
<th>Color change (ΔE) Coffee</th>
<th>Color change (ΔE) β-carotene</th>
<th>Shore A hardness</th>
<th>Contact angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SR0F</td>
<td>49.99(3.24)</td>
<td>6.280(0.59)</td>
<td>35.28(2.37)</td>
<td>2.660(0.40)</td>
<td>39.2(12)</td>
<td>74.12(1.78)</td>
</tr>
<tr>
<td>SR3F</td>
<td>19.48(1.23)</td>
<td>3.970(0.34)</td>
<td>17.97(2.47)</td>
<td>0.670(0.23)</td>
<td>57.16(1.37)</td>
<td>92.99(2.89)</td>
</tr>
<tr>
<td>SR8F</td>
<td>15.260(0.86)</td>
<td>3.930(0.64)</td>
<td>3.330(0.26)</td>
<td>1.020(0.30)</td>
<td>50.280(0.99)</td>
<td>94.82(2.14)</td>
</tr>
<tr>
<td>SR12F</td>
<td>12.310(0.72)</td>
<td>3.870(0.78)</td>
<td>3.140(0.31)</td>
<td>1.000(0.53)</td>
<td>41.04(1.77)</td>
<td>94.55(3.38)</td>
</tr>
<tr>
<td>SR17F</td>
<td>11.990(0.80)</td>
<td>3.960(0.50)</td>
<td>4.170(0.27)</td>
<td>1.050(0.31)</td>
<td>37.320(1.63)</td>
<td>100.62(2.35)</td>
</tr>
<tr>
<td>SS</td>
<td>15.940(1.30)</td>
<td>8.080(1.16)</td>
<td>26.460(3.46)</td>
<td>1.560(3.4)</td>
<td>43.680(2.34)</td>
<td>86.09(2.21)</td>
</tr>
<tr>
<td>VS</td>
<td>18.440(1.19)</td>
<td>5.010(1.17)</td>
<td>14.940(1.80)</td>
<td>1.900(0.33)</td>
<td>46.640(2.86)</td>
<td>83.65(2.20)</td>
</tr>
</tbody>
</table>

Within column, groups having similar lowercase letters are not statistically different (p > 0.05).

Discussion

Desirable properties for soft denture lining materials should include low water sorption, color stability, permanent softness or resilience, high bond strength to the denture base, dimensional stability, ease of processing, and biocompatibility. The Kurepeet Dough®, the fluorinated soft denture liner developed by Hayakawa et al in our department, satisfied these properties, but is not commercially available at present.12,13 Softness of SR0F was high, as compared to that of commercially available materials, but SR0F was inferior to commercially available materials in terms of other physical properties. The reason for the inferiority of SR0F appears to be that the characteristics of fluorinated soft resin as a chief ingredient are suppressed by acrylic monomers necessary for allowance of the material form. Therefore, it takes replacement of acrylic monomers by fluorinated ones to improve the physical properties of experimental materials.

High water sorption and solubility of lining materials cause dimensional change, loss of resilience, discoloration, bad odor, and separation from the denture base. Water sorption depends on the degree of hydrophobicity and porosity of the material.20 The gradual leaching of plasticizers and residual monomers out of the plasticized acrylic also causes clinical problems. The electro-negativity of the fluorine atom is highest. When the surface of a solid is covered with fluorine atoms, surface energy is decreased. The surface of the material containing fluorine atoms is therefore considered to be minimally permeable to liquids with high intermolecular cohesion and is thus water-repellent, leading to decreased water sorption. The results of the present study indicated that the use of fluorinated monomers instead of acrylic monomers with the introduction of a fluorine atom which alters the characteristics of the surface considerably decreases the amount of water sorption, and that the use of monomers with a large number of fluorine atoms further decreases the amount of water sorption. However, there was no significant difference between SR12F and SR17F in terms of the amount of water sorption. The use of fluorinated monomers with a large number of fluorine atoms is therefore considered to decrease the number of fluorine atoms in the paste and the relative amount of fluorine becomes increasingly convergent, because the molecular weight of fluorinated monomers is increased simultaneously with the increase in the number of fluorine atoms in one molecule of fluorinated monomer. For this reason, it is considered to be impossible for the amount of water sorption to further decrease. The reasons for the same amounts of solubility among SR3F, SR8F, SR12F, and SR17F and for the fact that the amounts for these materials were smaller than that for SR0F appear to be that fluorinated monomers are barely eluted in water, i.e. even less than acrylic monomers. It is also predicted that deterioration of the materials by the eluted constituents and stimulation of the oral mucosa would be minimal.

An optimal soft lining material should not be easily stained or discolored. Several factors may contribute to the discoloration of denture base materials after long-term use. They include stain accumulation, water sorption, dissolution of ingredients, and degradation of intrinsic pigments. It is
well known that beverages such as tea, coffee, wine, and some artificial dyes used in food rapidly increase the discoloration of restorative materials. Two staining solutions were chosen for this staining test, β-carotene/olive oil solution and coffee/water solution. β-carotene (C40H56) is a popular water-insoluble colorant, abundant in many kinds of foods. Another one is tannic acid (C76H52O46), which is present in coffee and tea. It is water-soluble and usually causes the brown dental stain. The use of fluorinated monomers for immersion in coffee induced manifestation of water repellency and allowed suppression of pigmentation, in a manner similar to the test for the amount of water sorption. Color differences among SR8F, SR12F, and SR17F were slight and the SR3F differed significantly in color from SR8F, SR12F, and SR17F. The relative amounts of fluorine also account for these results (1.5, 1.7, and 1.8 for SR8F, SR12F, and SR17F, respectively). When monomers with large numbers of fluorine atoms were used, water repellency was increased and the color difference was decreased. The use of fluorinated monomers of 8F or more showed high contamination resistance. When comparing these compounds and commercially available materials as well, SR8F, SR12F, and SR17F showed high contamination resistance. After immersion in β-carotene, the use of fluorinated monomers induced less color change than for SR0F, and the introduction of fluorine to monomer constituents allowed more remarkable manifestation of the oil repellency of fluorine. There were no significant differences in oil repellency among SR3F, SR8F, SR12F, and SR17F, suggesting the number of fluorine atoms not to be involved in oil repellency and some efficiency is obtained by introduction of a constant number of fluorine. When comparing these experimental materials and commercially available materials, the materials described here showed less color change and adequate contamination resistance.

With regard to hardness, the degree of hardness which is clinically appropriate for denture lining materials has not yet been clarified. Ohe et al., who have made photopolymerized soft lining materials on an experimental basis by using fluorinated monomers (the number of fluorine atoms in 1 molecule is at most 8), have reported that Shore A hardness was decreased as the side chain of the fluorinated monomers was increased and that Shore A hardness was approximately 50. For some patients, however, softer materials may be required. SR0F was soft, showing Shore A hardness of 39.30, but when fluorinated monomers are used, SR3F showed a value as high as 57.16. These observations indicated that the material becomes increasingly softer when the number of the fluorine atoms is increased. Considering that a carbon chain is short and that the intermolecular distance is short in SR3F, which becomes hard, when the length of a carbon chain is increased as in SR8F, SR12F, and SR17F, in that order, the intermolecular distance is increased and thereby contributes to ever greater softness.

It was confirmed that the contact angle is increased by the use of monomers with large numbers of fluorine atoms, leading to remarkable manifestation of water repellency. When comparing the materials made on an experimental basis and commercially available materials, all those made with fluorinated monomers on an experimental basis showed significantly higher contact angles. These results strongly suggest water repellency. Plaque is considered to barely adhere to such materials with low surface energy. Taking into consideration oral contamination, these materials are expected to be quite efficient. On the other hand, wetting of the materials themselves with saliva, etc. results in deterioration, showing that there is apprehension about the materials in terms of their fit to the oral mucosa. However, the protein in the saliva is considered to be adsorbed on the material’s surface in the oral cavity, and the possibility of the materials being in direct contact with the water is low. Retention and stabilization of dentures are included among the various clinical factors. From these findings and observations, the fit to the oral mucosa may be essentially free of problems in clinical cases.

Stability and durability of physical properties are required for soft denture lining materials. In this study we used fluorinated monomers, focusing on water sorption, solubility, and contamination resistance, and obtained favorable results. Further studies are needed to assess bonding strength to the denture base and long-term viscoelasticity.

Conclusion
As the number of fluorine atoms was increased, the feature of softness improved markedly, and...
this feature could be controlled by changes in the number of fluorine atoms. Furthermore, contamination resistance is considered to be decreased with the increase in flexibility. In the present soft denture lining materials, made on an experimental basis, water sorption, solubility, and discoloration were suppressed. The present results indicate SR12F and SR17F particularly to show high flexibility and high contamination resistance, suggesting that these materials will be clinically applicable as soft denture lining materials in the future.

References