Adhesive Properties and Kinetic Polymerization Behavior of Resins Containing Adhesion Promoting Monomers for Precious Metals

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Adhesive promoting monomers - 5-(4-vinylbenzyl)-2-thiobarbituric acid (5VS), 9,10-epithiodecyl methacrylate (EP8MA), 9,10-epithiodecyl 4-vinylbenzoate (EP8VB), and 3,4-epithiobuty1 2,2-bis(methacryloyloxyethyl)propionate (EP2BMA) - were added to the MMA liquid of a MMA-PMMA/TBBO resin. Three dental precious metal alloys were butt-jointed together with the MMA-PMMA/TBBO adhesive resin, and tensile bond strength was measured after 2,000 thermocycles in water. Polymerization kinetics of MMA by 2,2'-azobis(isobutyronitrile) at 70°C in the presence of 5VS, EP8MA, EP8VB, or EP2BMA were examined quantitatively using a DSC to clarify the relationship between the adhesive properties of MMA-PMMA/TBBO adhesive resin and the kinetic polymerization behavior thereof.

Obtained kinetic parameters indicated that 5VS was not suitable as an adhesive monomer for adhesive resin formulations and that EP2BMA possessed the latent potential as an adhesive monomer. Further, tensile test results revealed the applicability of EP8MA, EP8VB, and EP2BMA as an adhesive monomer component of adhesive resin formulations.

Key words: Polymerization kinetics, Adhesive monomer, Bond strength

INTRODUCTION

It is generally difficult to obtain stable bonding of resin to precious metals because of the latter's chemical inertness. A number of surface modification methods - such as high-temperature oxidation, electroplating with tin, silica coating, and application of liquid Ga-Sn alloy - have been developed for the surface treatment of dental precious metal alloys. Chemical surface treatments using adhesion promoting monomers for dental precious metal alloys have recently attracted interest as an alternative method to improve the bonding between precious metal alloy and resin, because the application method is simpler, less expensive than other methods, and does not require any proprietary equipment. Several sulfur-containing monomers such as thiol, thiophenol, disulfide, thiophosphoric acid, triazinedithione, sulfide, dithiolane, and thioaracil have been synthesized based on the molecular design of adhesion promoting monomer for precious metals. These monomers consist of a polymerizable double bond, a connecting group, and an adhesion promoting group which interacts with the metal surface to form durable linkages between the interacting molecules. Laboratory evaluations have demonstrated that adhesion promoting monomers adsorbed on precious metals significantly improve the bond strength of resin by their copolymerization with the matrix monomers of resin.

Since adhesion promoting monomers are particularly effective at improving interfacial adhesion, they are used in surface treatment agents of precious metals and in some commercial primers which contain the monomer as the main component. An alternative application of the adhesion promoting monomer is as an adhesive monomer component of adhesive resin formulations. While it is generally easy and simple to handle adhesive resins, the addition of an adhesive monomer may adversely affect their curing behavior. There are two different molecular designs for this type of application: one which utilizes tautomerism in adhesion promoting groups and the other which utilizes the precursor of a mercapto compound. Thiobarbituric acid monomers were prepared based on the former technique, and thirane monomers on the latter. In the present study, some typical adhesion promoting monomers for precious metals of both types were added to the MMA liquid of an MMA-PMMA resin. Tri-n-butylborane oxide (TBBO) was used as a polymerization initiator, and thus experimental MMA-PMMA/TBBO adhesive resins were prepared. The polymerization reactivity of these adhesion promoting monomers was examined quantitatively with a differential scanning calorimeter (DSC), and the relationship between the adhesive properties and kinetic polymerization behavior was discussed by comparing their chemical structures.

MATERIALS AND METHODS

Materials
One thiobarbituric acid monomer and three kinds of thirane monomer were used as adhesion promoting monomers for precious metals. 5-(4-vinylbenzyl)-2-
thiobarbituric acid (5VS) \(^9\), 9,10-epithiodecyl methacrylate (EP8MA) \(^{20}\), 9,10-epithiodecyl 4-vinylbenzoate (EP8VB) \(^{21}\), and 3,4-epithiobutyl 2,2-bis (methacryloyloxymethyl)propionate (EP2BMA) \(^{22}\) were synthesized according to previously described methods. The chemical structures of the adhesion promoting monomers are shown in Fig. 1. Methyl methacrylate (MMA) (Wako Pure Chemical Industries Ltd., Osaka, Japan) was washed successively with aqueous solutions of 5 wt% sodium hydrogen sulfate, 5 wt% sodium hydroxide and 20 wt% sodium chloride to remove hydroquinone, and distilled under reduced pressure after drying over anhydrous sodium sulfate for one day. 2,2'-azobis(isobutyronitrile) (AIBN) (Wako Pure Chemical Industries Ltd., Osaka, Japan) was recrystallized from methanol solution. Poly(methyl methacrylate) (PMMA) powder and an initiator, tri-n-butylborane (TBBO), were obtained from Sun Medical Co. Ltd. (Kyoto, Japan) as a dental adhesive resin, Super-Bond C&B\(^{23-25}\). Three kinds of dental precious metal alloy — Casting Gold M.C. Type IV (Au alloy, GC Dental Products Corp., Tokyo, Japan), Castwell M.C. (Pd alloy, GC Dental Products Corp., Tokyo, Japan), and Sunsiver CB (Ag alloy, Sankin Kogyo Co. Ltd., Tokyo, Japan) — were selected as adherends and their compositions are given in Table 1.

### Experimental adhesive resins

Adhesion promoting monomers — 5VS, EP8MA, EP8VB, and EP2BMA — were dissolved separately in MMA monomer at a concentration of 1.0 mol%. The MMA solutions were utilized as the liquid component of MMA-PMMA/TBBO adhesive resin. One drop of TBBO was added to MMA liquid in one dappen dish immediately before use, and the concentration of TBBO was about 9.2 wt%. The PMMA powder was placed in another dappen dish, and the resin was applied by the brush-on technique\(^{26}\).

### Surface finishing of metal adherends

Metal adherends were cylindrically shaped ( \(\phi 5 \text{ mm} \times 4 \text{ mm}\) ). Each metal specimen had an exterior screw on one side connected to a jig for the tensile test. In addition, the surface of each metal specimen was lapped to a smooth mirror finish with lapping film (Sumitomo 3M Ltd., Tokyo, Japan) using a sequence of #1,000, #2,000, and #4,000 grit to eliminate mechanical retention due to a surface irregularity. After washing with acetone, the specimen was dried naturally in air.

### Measurement of tensile bond strength to metal adherends

Two specimens of each metal were butt-jointed together with an experimental adhesive resin using the brush-on technique. Excess resin outside the circumference of the cylinder was removed using a double-edged razor blade (FEATHER Safety Razor Co. Ltd., Osaka, Japan), and the assembly was left to stand undisturbed for one hour at room temperature to allow adequate curing of the resin. One hour after cementation, the bonded specimens were stored in water at room temperature until all of the specimens were ready to be thermocycled. The specimens were then thermocycled 2,000 times in water between 4 and 60°C, with a one-minute dwell time at each temperature. Tensile bond strength of five specimens for each condition was determined with a universal testing machine (Autograph AGS-1000A, Shimadzu Co., Kyoto, Japan) at a crosshead speed of 2 mm/min. The mean and standard deviation of five replications were calculated for each condition, and the results analyzed at 95% level of confidence by t-test. The specimens fractured during thermal cycling were excluded from mean and standard deviation calculations.

### Table 1 Compositions of dental precious metal alloys

<table>
<thead>
<tr>
<th>Precious metal alloy</th>
<th>Code</th>
<th>Manufacturer</th>
<th>Composition (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Casting Gold M.C. Type IV</td>
<td>Au alloy</td>
<td>GC</td>
<td>Au: 70, Cu: 14, Ag: 10, Pt: 3, Pd: 3</td>
</tr>
<tr>
<td>Castwell M.C.</td>
<td>Pd alloy</td>
<td>GC</td>
<td>Ag: 45, Pd: 20, Cu: 18, Au: 12, Others: 5</td>
</tr>
<tr>
<td>Sunsilver CB</td>
<td>Ag alloy</td>
<td>Sankin</td>
<td>Ag: 79, Au: 7, Cu: 5, Others: 2</td>
</tr>
</tbody>
</table>

GC: GC Dental Products Corp., Tokyo, Japan; Sankin: Sankin Kogyo Co. Ltd., Tokyo, Japan; Jelenko: Jelenko Dental Health Products, Amonk, USA; Towa Giken: Tokuyama Dental Corp., Tokyo, Japan.

Metal specimens were cylindrically shaped ( \(\phi 5 \text{ mm} \times 4 \text{ mm}\) ). Each had an exterior screw on one side which was connected to a jig for tensile test.
DSC measurement of the polymerization of MMA in the presence of an adhesion promoting monomer

The adhesion promoting monomer and AIBN were dissolved in MMA at a concentration of 1.0 mol% for each. Approximately 10 mg of the MMA solution was loaded into an aluminum sample container and sealed by applying pressure. The container was placed on a sample holder of a DSC (model DSC 3100, MAC Science Co., Tokyo, Japan) kept at 70°C, and PMMA was employed as a thermally neutral sample (reference material). Heat evolution induced by polymerization was recorded for up to about 140 minutes. The heat of polymerization of MMA was 13.0 kcal/mole in this experimental condition. Polymerization curves (time-conversion curves) were derived from DSC thermograms (time-exotherm curves) using the value of 13.0 kcal/mole as the integrated heat evolved by the polymerization of MMA. Values of peak height and peak time were determined from the time-exotherm curves. Time-conversion curves broke when a polymerization inhibitor was consumed, and tangents were drawn to the polymerization curves at these breaks. Induction period was determined from the length of time (min) between the zero point on the abscissa and the point of intersection of tangents, and the initial rate of polymerization was calculated from the slopes of tangents.

RESULTS

The polymerization kinetics of MMA in the presence of four adhesion promoting monomers for precious metals were determined to clarify the additive effects of adhesive monomer. This is because the copolymerization of MMA with an additive monomer would affect both the curing process and adhesion mechanism of adhesive resins, since the amount of additive monomer in the adhesive resin formulation could not be disregarded when compared to that of MMA. It is well known that DSC quantitative analysis of polymerization reaction provides a reliable measure of the reaction's kinetic parameters. As such, the copolymerization of MMA (98 mol%) with adhesive monomer (1 mol%) was carried out in DSC at 70°C using AIBN (1 mol%) as a polymerization initiator. DSC thermograms for the copolymerization of MMA with 5VS, EP8MA, EP8VB, and EP2BMA are exhibited graphically as time-exotherm curves in Fig. 2. Fig. 3 shows their time-conversion curves derived from the time-exotherm curves by using the value of the heat of polymerization for MMA (13.0 kcal/mole). Peak time and peak height were read off from time-exotherm curves, and induction period and initial rate of polymerization were determined from time-conversion curves as mentioned before. The conversion of all samples, as calculated from the peak area of DSC thermograms, was 94.3-95.2%. Kinetic parameters of the polymerization are listed in Table 2.

The adhesion promoting monomers for precious

![Fig. 2 Time-exotherm curves for copolymerization of MMA with 1 mol% adhesion promoting monomer.](image)

![Fig. 3 Time-conversion curves for copolymerization of MMA with 1 mol% adhesion promoting monomer.](image)

<table>
<thead>
<tr>
<th>Additive monomer</th>
<th>Peak time (min)</th>
<th>Peak height (mcal/min)</th>
<th>Induction period (min)</th>
<th>Initial rate of polymerization (%/min)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None (control)</td>
<td>41.47</td>
<td>228.80</td>
<td>3.09</td>
<td>1.554</td>
<td>94.9</td>
</tr>
<tr>
<td>5VS</td>
<td>42.33</td>
<td>219.61</td>
<td>9.20</td>
<td>1.334</td>
<td>95.2</td>
</tr>
<tr>
<td>EP8MA</td>
<td>41.77</td>
<td>205.02</td>
<td>3.63</td>
<td>1.600</td>
<td>94.3</td>
</tr>
<tr>
<td>EP8VB</td>
<td>46.32</td>
<td>210.23</td>
<td>3.93</td>
<td>1.280</td>
<td>95.0</td>
</tr>
<tr>
<td>EP2BMA</td>
<td>30.68</td>
<td>235.45</td>
<td>4.02</td>
<td>1.561</td>
<td>95.2</td>
</tr>
</tbody>
</table>

Table 2 Kinetic parameters of the copolymerization of MMA with 1 mol% additive monomer

Copolymerization was carried out in DSC at 70°C using AIBN as a polymerization initiator.
Table 3  Tensile bond strength (MPa) to dental precious metal alloys of MMA-PMMA/TBBO adhesive resin containing an adhesion promoting monomer

<table>
<thead>
<tr>
<th>Adherend</th>
<th>Adhesion promoting monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>None</td>
</tr>
<tr>
<td>Au alloy</td>
<td>0.7 (0.5) [2]⁴</td>
</tr>
<tr>
<td>Pd alloy</td>
<td>1.1 (0.4) [1]⁴</td>
</tr>
<tr>
<td>Ag alloy</td>
<td>0.2 (0.2) [3]⁴</td>
</tr>
</tbody>
</table>

Adhesion promoting monomer was added to MMA monomer liquid at a concentration of 1.0 mol%. Tensile bond strength after 2,000 thermocycles in water at temperatures of 4 and 60°C. Values in square brackets are the number of specimens fractured during thermal cycling, and these specimens were excluded from the mean and standard deviation calculations. Same superscript after square brackets denotes insignificant difference between adhesion promoting monomers at p<0.05.

( ): SD

metals, 5VS, EP8MA, EP8VB, and EP2BMA, were dissolved separately in MMA monomer of MMA-PMMA/TBBO resin at a concentration of 1.0 mol%. Thus, four kinds of experimental adhesive resin for precious metals were prepared. Au alloy, Pd alloy, and Ag alloy with a mirror-like finish were butt-jointed together with each experimental adhesive resin. After 2,000 thermocycles in water at temperatures of 4 and 60°C, tensile bond strength was measured. The mean and standard deviation of tensile bond strength with five replications are summarized in Table 3. When compared with the control resin, the tensile bond strength — of MMA-PMMA/TBBO adhesive resin containing an adhesion monomer — to precious metal alloys was significantly enhanced by the addition of an adhesive monomer without any spontaneous failures during thermal cycling. Among the evaluated adhesion promoting monomers, tensile bond strength of the adhesive resin with 5VS was significantly lower than that of the other three with all precious metal alloys (p<0.01). Among the thirane monomers — EP8MA, EP8VB, and EP2BMA, the differences in bond strength were statistically insignificant in all cases (p>0.05). The average tensile bond strength to precious metal alloys of adhesive resins with a thirane monomer generally decreased in the order of Au alloy>Pd alloy>Ag alloy.

**DISCUSSION**

Copolymerization kinetics of MMA with various adhesion promoting monomers were analyzed quantitatively using several parameters shown in Table 2. Peak height indicates the maximum rate of polymerization, and peak time corresponds to the time required to reach the maximum rate. An accelerated polymerization at late stage is attributable to the increased viscosity of reaction media as seen with MMA-PMMA type resins. Peak time is, therefore, closely related to the curing time of resins, since the curing reaction reaches completion rapidly after exhibiting the Trommsdorff effect (or gel effect). Induction period is the initial period during which polymerization is completely suppressed by polymerization inhibitors³⁸. The presence of oxygen inhibits polymerization because oxygen reacts with MMA radicals activated by the initiator. Thus, polymerization of the control was slightly inhibited even though the reaction was carried out in a sealed DSC pan. This is because the pan still contained a small amount of oxygen as it had been sealed in air. The time difference between the induction period of control and one in the presence of a comonomer was considered to indicate the actual inhibitory effect caused by an additive monomer. Following this induction period, propagation reaction of growing polymer radicals reaches a steady-state concentration of radicals and the rate of polymerization is kept almost constant — of which is called the initial rate of polymerization. The initial rate of polymerization highly depends on the polymerization reactivity of comonomers under the same experimental condition. Conversion, i.e. yield of polymer, was determined from the total heat evolved using the value of 13.0 kcal/mol for transformation.

As seen in Table 2, induction period was slightly increased when a precursor type of adhesion promoting monomer, EP8MA, EP8VB, or EP2BMA, was added to MMA. On the other hand, a tautomer type of 5VS significantly lengthened the induction period and was considered to exhibit an inhibitory action against free radicals. Thiols compounds are known to interfere with polymerization reaction in a complicated way, and they often act as an inhibitor to polymerization. Although no thiol groups exist in the chemical structure of 5VS, the stable structure with a thione type (—NH—CS—) is tautomerized to the reactive tautomer with a thiol type (—N=C(SH)—) in the tautomerization process²⁸,⁴⁰. This is in sharp contrast to the thirane monomers which are chemically stable in an MMA solution. Thus, the inhibitory effect of 5VS could be ascribed to the thione-
thiol type tautomerism in an MMA solution.

For the initial rate of polymerization, the adhesion promoting monomers did not differ much with the exception of EP8VB. The polymerizable double bond of EP8MA, EP2BMA, or MMA is a methacryloyl group, while 5VS and EP8VB possess styrene structure as a double bond. Since methacrylate monomers generally show a higher polymerization reactivity than styrene monomers, the results given in Table 2 indicate that the reactivity of styrene moiety in 5VS was considerably enhanced. This might have been caused by a thiobarbituric acid substituent at para-position of the styrene ring in 5VS, although details of the mechanism are unknown at present.

In general, peak time varies inversely with peak height. However, the latter highly depends on the initial monomer load in a DSC sample pan, hence making the former a more reliable measure of curing time in polymerization, i.e., the overall rate of polymerization. Table 2 demonstrates that the minimum peak time was recorded for EP2BMA and the maximum for EP8VB. EP2BMA is a bifunctional monomer, which inevitably resulted in accelerated curing, and hence a shorter curing time. Taking into consideration the time difference between peak time and induction period, 5VS also demonstrated a shortened curing time in a sense when compared with control. The discrepancy in curing behavior between 5VS and EP8VB — with the same styrene structure — could also be due to the existence of thiobarbituric acid substituent at para-position as mentioned above.

For an adhesion promoting monomer to be applied as an adhesive monomer component in adhesive resins, a requisite quality is to possess excellent solubility in a base monomer such as MMA. The concentration of an adhesive monomer in an adhesive resin is generally higher than that in a precious metal primer. Thus, there have been extremely few reports about adhesive monomers contained in adhesive resins for precious metals. Thiobarbituric acid monomer and thirane monomer are considered to be promising candidates. However, in this current study, the adhesive resin with 5VS showed unexpectedly lower tensile bond strength when compared to those with thirane monomers. There seemed to be two major reasons for the poor performance of 5VS adhesive resin. The chiefest cause could be attributed to the effect of solvent on tautomerization of thione-thiol type. It was reported that the adhesive properties of 5VS significantly depended on solvent species when it was used as a primer for precious metals. The bond strengths to precious metal alloys decreased in the order of acetone > N,N-dimethylformamide > ethanol > 1,4-dioxane > MMA. Thus, MMA provided an unfavorable environment for tautomerization from thione to thiol. The other factor was the inhibitory interaction of 5VS with free radicals. Although thiol-type tautomer of 5VS is an essential constituent of the adhesive system for precious metals, it reacts readily with free radicals — thereby inhibiting the activation of the adhesive species as described above. Therefore, it appeared to be disadvantageous to add a tautomer-type adhesion promoting monomer to adhesive resin formulations.

The adhesion mechanism of thirane monomers for precious metals was analyzed based on SERS study and it took the steps described as follows. The episulfide ring of thirane is cleaved on the surface of a precious metal, and a structure analogous to the mercapto group adsorbed on a precious metal is produced. Then the formation of self-assembled layers by adsorbed molecules occurs on the precious metal surface. It takes time to achieve a stable adhesion at precious metal-resin interface when a thirane monomer is utilized as an adhesive monomer component in adhesive resin. The thirane monomer with both short peak time and long induction period is, therefore, ideal from the point of view of polymerization kinetics. In Table 2, this ideal example is found in EP2BMA — although the differences in bond strength among the thirane monomers were statistically insignificant. EP2BMA is a bifunctional monomer and forms a cross-linked copolymer, while EP8MA and EP8VB provide a linear copolymer. Adhesive properties of a cured resin with linear polymers are generally superior to those with cross-linked copolymers because of the relaxation of residual stress at the adhesion interface. This might be the reason why EP2BMA did not demonstrate outstanding results in tensile bond strength. Therefore, these findings suggested that the most suitable thirane monomer would be EP2BMA, when an adhesive monomer is to be added to bifunctional base monomers as is the case of a composite resin.

Thirane monomers were previously utilized in primers for the same precious metal alloys. The primer with 1 mol% thirane in ethanol was placed on an adherent surface and allowed to stand for one day. The surface was washed with acetone to remove excessive monomer, and the specimens were butt-jointed together with MMA-PMMMA/TPBO resin. When the results after 2,000 thermocycles were compared with those in Table 3, the bond strength of MMA-PMMMA/TPBO adhesive resins to Au alloy was almost the same as those of MMA-PMMMA/TPBO resin with primer treatment. However, the bond strength of MMA-PMMMA/TPBO adhesive resins to Pd alloy or Ag alloy was 14 to 21% less than that with primer treatment. The application method employed here was simpler without one day of standing and washing prior to bonding. Nevertheless, the bond strength to Pd alloy or Ag alloy by this method was sufficiently high — although it was inferior to that with primer treatment. Thus,
thiirane monomers are well poised for a wide variety of applications, and clinical application will be further promoted in the near future.

In conclusion, the polymerization kinetics of MMA in the presence of an adhesion promoting monomer for precious metals – 5VS, EP8MA, EP8VB, or EP2BMA – were examined quantitatively using DSC to clarify the curing behavior of adhesive resin containing one of the above four adhesion promoting monomers. Obtained kinetic parameters theoretically indicated that 5VS was not suitable as an adhesive monomer for adhesive resin formulations and that EP2BMA possessed the latent potential as an adhesion promoting monomer. Tensile bond strength results revealed the applicability of thiirane monomers as an adhesive monomer component of adhesive resin formulations.

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