Studies on MMA-TBB Resin I. Comparison of TBB and Other Initiators in the Polymerization of PMMA/MMA Resin

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Polymerization characteristics of poly (methyl methacrylate) (PMMA)/(methyl methacrylate) (MMA) resin initiated by tributylborane (TBB) were compared with those by benzoyl peroxide (BPO)/N,N-dimethyl-p-toluidine and camphorquinone (CQ)/N,N-dimethylaminoethyl methacrylate from the aspects of temporal changes of residual MMA and molecular weight up to 4 weeks at 37°C. Residual MMA 30 min after polymerization decreased from 8.15% for TBB resin, 8.39% for the BPO resin, and 9.19% for the CQ resin to 0.48%, 3.54%, and 6.79%, respectively, after 4 weeks. The molecular weights at 30 min and 4 weeks after polymerization were $4.09 \times 10^3$ and $2.47 \times 10^3$ for TBB resin, $2.97 \times 10^3$ and $2.82 \times 10^3$ for the BPO resin, and $2.67 \times 10^3$ and $2.31 \times 10^3$ for the CQ resin, respectively. The present results revealed that the TBB-initiated polymerization had unique and different characteristics compared with those initiated by the other common initiators: (1) The decrease in residual MMA was fast, sustained for a long time and resulted in very low value; (2) high molecular weight PMMA was formed first and then decreased with time.

Key words: PMMA/MMA resin, TBB, Polymerization initiator

INTRODUCTION

The methyl methacrylate (MMA)-based resin catalyzed by tributylborane (TBB) (MMA-TBB resin) (Super-Bond C&B, Sun Medical Co., Moriyama, Japan) has been used clinically for nearly 20 years as a most reliable adhesive resin for dentin. The MMA-TBB resin for an orthodontic bonding system (Orthomite Super-Bond, Sun Medical Co., Moriyama, Japan) was first marketed in 1982 and that for general dental adhesive use (Super-Bond C&B) was introduced the following year (1983). The TBB used in the resin is not a common initiator but is used exclusively in this specific commercial resin. Moreover, the TBB used in the resin is not tributylborane exactly, but is composed mainly of butoxydibutylborane$^1$. Despite this, this special derivative of TBB has generally been called TBB for convenience.

TBB was first introduced to dentistry in 1962 as an initiator of a self-curing resin by Masuhara et al. and they found that TBB was effective for adhesion of resin to wet dentin$^2$-$^4$. In commercial resin, TBB is the key component and its important involvement in the adhesion at the dentin interface has been suggested$^{5,6}$. However, few studies of the polymerization characteristics of the MMA-TBB resin have been reported. Houga found that the amount of residual MMA contained in a polymer-
ized resin decreased markedly after 24 hr storage at 37°C compared with that immediately after polymerization and suggested that this marked reduction in the residual MMA is characteristic of the MMA-TBB resin⁶). According to the suggestion by Hougå, the polymerization, especially postpolymerization, characteristics of the MMA-TBB resin appeared quite unique. However, information was very limited and thus detailed further study was needed.

The purpose of this study was to examine whether the polymerization of PMMA/MMA resin initiated by TBB has any different characteristics compared with that of other more common initiators from the aspects of long term changes of residual MMA and molecular weight during postpolymerization.

MATERIALS AND METHODS

Materials
MMA (Mitsubishi Rayon Co., Tokyo, Japan), stabilized with 50 ppm of hydroquinone, was used without further purification. As TBB, the catalyst used in the commercial MMA-TBB resin (Super-Bond C&B) was employed. N,N-dimethyl-p-toluidine (DMPT), camphorquinone (CQ), and N,N-dimethylaminoethyl methacrylate (DMAEMA) were obtained commercially (Tokyo Kasei Kogyo Co., Tokyo, Japan) and used as received. Benzoyl peroxide (BPO) (Nacalai Tesque, Inc., Kyoto, Japan) was purified from acetone/methanol. PMMA beads (MB-8C, Sekisui Co. Osaka, Japan) were used after modification by γ-irradiation from a ⁶⁰Co source at 30 kGy (dose rate of 10 kGy/hr) at 25°C and had a mean particle diameter of 7μm, with weight average molecular weight of 239×10³, number average molecular weight of 108×10³, a residual MMA of 0.06%, and residual BPO of less than 0.01%.

The resin formulations were as follows: powder was PMMA alone or with 1% BPO added, liquid was MMA added 1% DMPT or 0.5% CQ and 0.5% DMAEMA, or 8% TBB (which was added immediately before mixing), and a powder/liquid ratio of 150 mg powder per 75 mg liquid. The resin codes and compositions are presented in Table 1. All percentages are presented as a mass/mass ratio unless stated otherwise.

<table>
<thead>
<tr>
<th>Resin code</th>
<th>Composition (mass%)</th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Powder</td>
<td>Additive</td>
<td>MMA</td>
</tr>
<tr>
<td>BPO</td>
<td>99</td>
<td>BPO 1</td>
<td>99</td>
</tr>
<tr>
<td>CQ</td>
<td>100</td>
<td>0</td>
<td>99</td>
</tr>
<tr>
<td>TBB</td>
<td>100</td>
<td>0</td>
<td>92</td>
</tr>
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Table 1 Code and composition of the initiator system of the resins studied

Powder: liquid ratio=2:1 in mass
BPO, benzoyl peroxide; DMPT, N, N-dimethyl-p-toluidine
CQ, camphorquinone; DMAEMA, N, N-dimethylaminoethyl methacrylate
TBB, tributylborane, which was added immediately before mixing the two components.
The initiator compositions and polymerization condition were established, based on preliminary experiments, for the residual MMA immediately after polymerization to be about 8-9% on the basis of the values obtained from 8% TBB resin (8% TBB is the standard composition used in the commercial MMA-TBB resin).

Preparation of specimens
A dough obtained by mixing the powder and the liquid 2:1 was placed on a Teflon plate with a 0.2 mm spacer, covered by a glass plate on which a 5 kg weight was placed, and was polymerized for 30 min at room temperature (25°C). For CQ resin, the dough was sandwiched between two plates, held by binder clips, placed in close contact with a projector lens, and polymerized for 5 min using a slide projector (Custom 860H, 120 V/300 W tungsten halogen lamp, 30 mW/cm², Eastman Kodak Co., Rochester, NY, USA). The projector was used instead of a dental curing light because the specimen size (approximately 4 cm in diameter) was so large that it was impossible for the dental light with a small light probe (less than 13 mm) to irradiate all the specimen area at the same time.

Each specimen obtained was divided into 4 pieces. One piece was subjected to measurements by HPLC and SEC immediately after preparation. The remaining 3 pieces were each put into a small heat-sealable aluminum pack, heat-sealed, and then stored in an incubator at 37°C for 24 hr, 1 and 4 weeks. The mass loss by volatization of MMA during the storage was negligible because the mass remained practically unchanged. Three specimens for each resin were prepared and subjected to the same procedure described above and the means and standard deviations were calculated.

High performance liquid chromatography (HPLC)
A 50 mg sample of the polymerized resin was dissolved in 1 ml acetone and then 10 ml methanol was added to the solution to precipitate PMMA. The supernatant of the solution was filtered through a 0.45μm pore size filter (Nihon Millipore Kogyo Co., Yonezawa, Japan). Reversed-phase HPLC analysis was performed using an HPLC system (GULLIVER 1500, JASCO, Tokyo, Japan), equipped with a column (CAPCELL PAK C18, UG120, 4.6 mm × 250 mm, Shiseido, Tokyo, Japan) and a diode array detector (MD-1510) (detection at λ = 230 nm). Ten microliters of the sample solution was injected and analyzed at 40°C with a flow rate of 1.0 ml/min with acetonitrile:water (50:50) for the determination of the MMA monomer. Residual MMA (RM) (%) was calculated from: \[ \text{(mass of MMA contained in polymerized resin)/(mass of polymerized resin)} \times 100. \]

Size exclusion chromatography (SEC)
SEC analysis of the polymerized resin was performed after dissolution of the resin in tetrahydrofuran (THF) (Kanto Chemical Co., Tokyo, Japan) and filtering insoluble substances on a GPC system (SC-8020, Tosoh, Tokyo, Japan) using two GPC columns (Asahipak GSM-700 7E, 7.6 mm × 250 mm, Showa Denko Co., Tokyo, Japan) at 40
°C with THF as the eluent at a flow rate of 0.8 ml/min. Weight average molecular weight (Mw) was calculated using the calibration data of polystyrene standards.

Statistical analysis
Data were subjected to one-way ANOVA and means were compared by Fisher's PLSD multiple comparison test at the significance level of 0.05 and grouped.

RESULTS AND DISCUSSION

Fig. 1 shows the results of residual MMA (RM) measurements. RM immediately after polymerization (30 min) was similar for the three resins (8.15-9.19%), although RM for the CQ resin was significantly higher than those for the other two. However, the amounts of RM after 24 hr, 1 and 4 weeks were always highest in the CQ resin and always lowest in the TBB resin.

The pattern of the temporal change of RM had high similarity among the three resins; RM decreased significantly during the 30 min - 24 hr period and remained significantly unchanged during 1-4 weeks, although the amounts of RM tended to decrease with time after polymerization time. However, the temporal change of RM values was completely different among the resins. RM after 30 min, 24 hr, 1 and 4

![Fig. 1](image-url)
Fig. 2 Log-log plots of residual MMA against time after polymerization. The plots produced linear lines and residual MMA decreasing rate constants \( (k) \) were calculated from the slope of the lines.

weeks decreased from 8.39% to 4.50%, 3.67%, and 3.54% for BPO resin, from 9.19% to 7.99%, 7.28%, and 6.79% for CQ resin, and from 8.15% to 1.96%, 0.84%, and 0.48% for TBB resin, respectively. Fig. 2 shows log-log plots of RM against time after polymerization, demonstrating a good linear relation between the two parameters. From the slope of the line, the RM decreasing rate constant \( (k) \) was calculated and is given in Fig. 2. The rate constant for TBB resin was about 3- and 10-fold larger than that for BPO and CQ resins, respectively. It was natural that the rate constant for CQ resin was lowest because the resin was not exposed to light during postpolymeriation.

RM was not significantly different between the value after 1 week and 4 weeks within each resin. This suggested that the polymerization of MMA ceased similarly during the 1-4 weeks period, independent of the type of resins. However, this was not the case. It appears that the polymerization of TBB resin, different from those of the other two resins, remained significantly during the 1-4 weeks period, as judged from the extent of the decrease of RM; the extent of the decrease of RM at 4 weeks calculated on the basis of RM at 1 week was 3.5% for BPO, 6.7% for CQ, and 42.9% for TBB resin, indicating that RM for TBB resin decreased approximately by 6- to 12-fold more.

The RM of 0.48% at 4 weeks was comparable with that reported for the typical heat cured PMMA/MMA resin (0.4-0.6%)\(^7\). This is surprising in that TBB was able to promote the polymerization of MMA to very high conversion even at the lower temperature of 37°C. It is expected that RM will decrease further by extending the polymerization time. The long term sustained postpolymerization of TBB resin found first in this study was unexpected from the short term study of Houga\(^6\).

Fig. 3 shows the results of molecular weight measurements. The Mw for BPO resin decreased from \( 297 \times 10^3 \) to \( 235 \times 10^3 \) and then increased significantly to \( 255 \times \)
Fig. 3 Comparison of weight average molecular weight \( (\text{Mw}) \) among the three resins at different times after polymerization. The different lower-case letters above the bars indicate that the mean values are significantly different between the three resins at different times after polymerization (a, b for 30 min, d, e for 24 hr, h, i, j for 1 week, and l, m, n for 4 weeks). The different upper-case letters above the bars indicate that the mean values are significantly different between the times after polymerization within each resin (O, P, Q, R for BPO, T, U for CQ, and X, Y, Z for TBB resin).

The Mw for CQ resin decreased significantly from \( 267 \times 10^3 \) to \( 233 \times 10^3 \), \( 224 \times 10^3 \), and \( 231 \times 10^3 \). The Mw for TBB resin decreased significantly from \( 409 \times 10^3 \) to \( 351 \times 10^3 \) and \( 306 \times 10^3 \) and further to \( 247 \times 10^3 \) with a significant difference.

Molecular weights at 24 hr decreased significantly compared with those at 30 min for all the resins. A possible explanation for this could be as follows: The postpolymerization of MMA proceeded significantly during a 24 hr period, as is clear from Fig. 1, demonstrating that residual MMA decreased significantly. However, the molecular weight of the polymer formed during a 24 hr period will be low because the diffusion of MMA is limited within the resin matrix and the chain propagation of the growing polymer radical is therefore limited, which results in the formation of a low molecular weight polymer.

The pattern of the temporal change of the Mw after 24 hr was significantly different among the resins. The Mw increased with time for the BPO resin, remained unchanged for the CQ resin, and decreased markedly for TBB resin. The increase in Mw for the BPO resin could be the result of a slow termination reaction due to increasing viscosity of the resin matrix. In general, the molecular weight of the polymer produced by radical polymerization is determined by the ratio of (rate of propagation)/(rate of termination) and the rate of termination depends on the viscosity of the polymerization medium\(^8\). The small change in the Mw for the CQ resin
may be the result of the balance between the propagation and termination reaction within the less viscous resin matrix containing relatively large amounts of MMA.

In contrast to BPO and CQ resins, TBB resin showed an entirely different temporal change in Mw. The Mw was very high during the initial period and decreased with time over the long term. The different characteristics of TBB resin in the change of Mw were exhibited further in the molecular weight distribution curves. Fig. 4 shows the changes in the molecular weight distribution curves with time for TBB resin (Fig. 4a) and BPO resin (Fig. 4b). Fig. 4a shows that the curve was a two-peak pattern for TBB resin at 30 min, deformed to that with a shoulder at 24 hr and changed into one-peak patterns at 1 and 4 weeks. In contrast, four curves for BPO resin, shown in Fig. 4b, were always similar one-peak patterns. The patterns of the molecular weight distribution curves for CQ resin were also similar to those for BPO resin (not shown in the figure). Fig. 4a demonstrates that the high molecular weight PMMA formed during the initial period disappeared later, suggesting the decomposition of the PMMA formed.

This unique and unexpected feature of molecular weight change in TBB resin was found for the first time in this study. The mechanism of the formation of the high molecular weight PMMA and its decomposition is entirely unclear and should be investigated in the future. It may be too early to propose the mechanism, but on the basis of previous findings related to oxidation of trialkylboranes and polymerization by them\(^{9,10}\), a possible mechanism is as follows: the TBB used in this study was actually butoxydibutylborane\(^1\), which has two active boron-carbon bonds capable of producing initiating radicals. Therefore, the two polymer chains may be combined to one TBB molecule. However, when one polymer chain is combined through a weak bond like a peroxy bond, the weak bond will be cleaved by the spontaneous decomposition or the radical chain transfer reaction during the course of postpolymerization, resulting in the reduction of the molecular weight of the polymer.
CONCLUSIONS

The present study revealed for the first time the unique and different characteristics of the TBB-initiated polymerization of PMMA/MMA resin compared with the resins initiated by other common initiators during the course of postpolymerization: (1) the decrease in residual MMA was fast, sustained for a long time and resulted in very low residual MMA; (2) high molecular weight PMMA was formed first and then decreased rapidly with time. It is conceivable that the long-term sustained polymerization of MMA may correlate with the long-term sustained molecular weight decrease. However, the mechanism of these phenomena is entirely unknown at present and needs to be investigated in future studies.

REFERENCES


