Abstract

The reactivity of bisphenol A (BPA), diethylstilbestrol (DEST), 2,2'-biphenol (22'BP), 4,4'-biphenol (44'BP) and hydroquinone (HQ) as radical scavengers was examined in 2,2'-azobisisobutyronitrile (AIBN)- and benzoyl peroxide (BPO) - induced methyl methacrylate (MMA) polymerization with respect to kinetic considerations. The initial rate of polymerization (IRP) was found to decrease in the order: 44'BP > BPA, DEST > 22'BP > HQ, while the stoichiometric factor (n) of free radicals trapped by phenolic moiety decreased in the order: 44'BP (2.3) > HQ (2.0) > BPA, DEST (1.8) > 22'BP (0.8).

It was found that BPA was a more highly efficient inhibitor than HQ and that HQ acts as a retarder at higher concentrations in the BPO system. The high activity of BPA indicated that BPA is probably oxidized by a radical interaction in the dental resin system.

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Biomaterials

Kinetic evaluation of reactivity of bisphenol A derivatives as radical scavengers for methacrylate polymerization

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1. Introduction

The release of the chemical BPA from light-activated fissure sealants was recently reported (1, 2). BPA is known to be estrogenic at moderate concentration levels (1, 2). Some studies have shown using HPLC analysis that dental sealants and composite resins may be contaminated with BPA (1-3). BPA from uncured commercial Bis-GMA dental resins is probably found at very low concentration levels using HPLC and/or GC/GM analysis. However, after light-curing sealants, all BPAs have been reported to be undetected as an elute from the tested sealants (4-7).

BPA, a diphenyl compound containing 2 hydroxy groups in para positions (2,2-bis(4-hydroxyphenyl)propane) probably acts as an inhibitor in the polymerization of mono- or dimethacrylates, since compounds such as hydroquinone, which has 2 hydroxy groups in para position, are well-known inhibitors in the polymerization system.

Our studies are based on the hypothesis that the estrogenetic BPA in Bis-GMA monomers may be greatly reduced if this compound scavenges radicals derived from the decomposition of the initiator in the resin system. The compound itself is possibly converted into other BPA derivatives due to its radical scavenging reaction in air. The interaction between phenols and peroxy radicals in the presence of oxygen generally yields phenol derivatives due to oxidation (8). We have previously investigated the kinetics of the polymerization of methyl methacrylate (MMA) by 2,2'-azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO) in the presence of air using differential scanning calorimetry (DSC), demonstrating that this method was highly successful and reliable to elucidate the mechanism of a reaction between phenols as antioxidants and radicals derived from the decomposition of the initiators (9).

The present investigation was undertaken to elucidate the reactivity of BPA and its related compounds such as hydroquinone (HQ), 2,2'-biphenol, 4,4'-biphenol, and diethylstilbestrol (DEST) in the polymerization of MMA by AIBN or BPO in the presence of air using DSC. Activities of BPA are compared with those of its related compounds.

2. Materials and methods

2.1. Materials

Bisphenol A (BPA), hydroquinone (HQ), 2,2'-biphenol and 4,4'-biphenol, diethylstilbestrol (DEST), 2,6-di-t-butyl-4-methoxyphenol (DTBM), 2,6-di-t-buty1-4-methylphenol (butylhydroxytoluene, BHT) were obtained from Tokyo Kasei Chemical Co., Tokyo, Japan. MMA was purchased from Tokyo Kasei Chemical Co. and was purified by distillation. AIBN and BPO were obtained from Wako Pure Chemical Industries Ltd. and recrystallized from methanol and chloroform/methanol, respectively. The chemical structure of BPA-related compounds is shown in Fig. 1.
The heat of polymerization of MMA was indicated initiators and/or inhibitors was loaded into an aluminium sample container and sealed by applying.

Some typical conversion-time curves of BPA, DEST and related compounds of AIBN polymerization are shown in Fig. 4. The linear curves of the values of the IP plots of the first linear line of the conversion rate of polymerization of MMA with the inhibition rate (initial rate of polymerization) and termination, $k_p$ is the rate constant for propagation, $k_i$ is the rate of initiation (2).

The inducation period method was used to determine the inhibition rate (initial rate of polymerization) and $k_i$. The number of moles of peroxy radicals trapped by moles of the relevant inhibitor is $n$.

In the case of polymerizing, the heat of polymerization of MMA was determined graphically from the plot of the conversion versus time, as the point of inersection of the first linear line of the conversion rate of polymerization of MMA with oxygen or BPA and related compounds and following this the polymerization is much more rapid. BPO is known to show an induced decomposition in the initiation period the polymerization is much more rapid. BPO is known to show an induced decomposition in the initiation period.

The kinetics of the polymerization reaction proceeds.

The rate constants for propagation, $k_p$, are defined by the reactions $M*+M* \rightarrow M+M$, $k_i$, $k_p$, $k_t$, and for

$$R_i = \frac{[\text{MMA}]}{[\text{AIBN}]} \times \frac{[\text{IH}]}{[\text{IP}]}$$

where $\text{MMA}$, $\text{AIBN}$, $\text{IH}$, and $\text{IP}$ represent the concentration of MMA, AIBN, inhibitor, and IP, respectively. The value of induction period, $\text{IP}$, was 2 and 3, respectively.

The polymerization curves show a break when the inhibitor was completely consumed. The polymerization reaction proceeds.

The initial rate of polymerization inhibited by BPA and related compounds based on kinetic studies, namely to measure the inhibitive activity of BPA-related compounds was calculated from the slope of the initial rate of polymerization (IRP) of BPA and related compounds in the AIBN- and related compounds initiated with AIBN and BPO in air are shown in Figs. 2 and 3. The IRP of BPA, DEST, and 44' BP were parabolic and were not

$$\text{IRP} \times [\text{MMA}] \times [\text{AIBN}] = k_{\text{IP}}$$

The relative inhibitive activity was calculated from the slope of the plots of first linear line of the conversion rate of polymerization of MMA shown in Figs. 2 and 3. The polymerization curves show a break when the inhibitor was completely consumed. The polymerization reaction proceeds.

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4. Discussion

Activity was significantly higher than that of HQ. Also, the stoichiometric factor (n) for BPA and related compounds at 0.05 mol% was calculated from the findings of AIBN polymerization. In particular, BPA was an efficient inhibitor in both AIBN and BPO-induced MMA polymerization systems. However, the present findings indicated that even though BPA in the AIBN system was close to 2.0 and was almost a similar value to that of HQ, the relative value of n for 22'BP, 0.82, was found to be considerably lower than that for 44'BP, 2.33, indicating an activity difference in the polymerization system.

Comparing IRP of BPA, DEST and HQ in the AIBN polymerization system, their IRP became markedly reduced as their concentration increased. However, the present findings indicated that even though the relative activity of BPA in the AIBN system was close to 2.0 and was almost a similar value to that of HQ, the relative value of n for 22'BP, 0.82, was found to be considerably lower than that for 44'BP, 2.33, indicating an activity difference in the polymerization system.

The relative factor (n) for BPA and related compounds at 0.05 mol% was calculated from the findings of AIBN polymerization. Whereas, IRP of HQ was more strongly reduced than that of other compounds at concentrations >0.05 mol%.

From the findings mentioned above, BPA clearly acted as an inhibitor in both AIBN and BPO-induced MMA polymerization reactions in the clinical dental setting, the depth of cure, intensity of light and curing time would all affect the BPA elution [11]. Our findings suggested a particular inhibitory effect of the inhibitor radical may start a chain by a reaction between inhibitor radicals and growing radicals. One can calculate the relative factor (n) for BPA and related compounds its derivatives due to the reaction between BPA and polymerization initiators. This suggests that human infertility, genital tract malformation might not be linked with BPA eluted from Bis-GMA sealants and composite resins [1].

It has previously been shown that BQ (benzoquinone) is a widely known inhibitor. The relative factor of BPA and related compounds at 0.05 mol% was calculated from the findings of AIBN polymerization. Whereas, IRP of HQ was markedly smaller than that of other compounds. The IRP of HQ was more strongly reduced than that of other compounds at concentrations >0.05 mol%.

IP of Dest and BPA was larger than that of butylhydroxytoluene (BHT), a generally known inhibitor. The relative factor of BPA and related compounds of BPO polymerization are shown in Fig. 7. The IRP of HQ acted as a retarder in MMA polymerization. This was consistent with the generally known kinetic inhibitory effect of BQ [13,14]. Also, it was previously demonstrated that eugenol in BPO-induced MMA polymerization showed a decrease in IRP. Therefore, a decrease in IRP appears to be linked to a reaction between inhibitor radicals and growing radicals. One can calculate the relative factor of BPA and related compounds in the presence of the very reactive MMA radicals derived from the decomposition of initiators in the polymerization system. This implies that one or more HQ oxidation products (i.e. SQ) can also react with peroxy radicals and semiquinone (SQ) radicals derived from the decomposition of the polymerization initiators. These radicals can also react with peroxy radicals and semiquinone radicals derived from the decomposition of the polymerization initiators. One can calculate the relative factor of BPA and related compounds in the presence of the very reactive MMA radicals derived from the decomposition of initiators in the polymerization system. This implies that one or more HQ oxidation products (i.e. SQ) can also react with peroxy radicals and semiquinone radicals derived from the decomposition of the polymerization initiators. These radicals can also react with peroxy radicals and semiquinone radicals derived from the decomposition of the polymerization initiators.