Studies on the Behavior of Partially Oxidized Tributylborane as a Radical Initiator for Methyl Methacrylate (MMA) Polymerization

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The structure of the catalyst and the influences of oxygen and water on the activity for MMA polymerization were investigated. The main component of partially oxidized tributylborane was found to be butoxydibutylborane. Higher oxygen concentrations in the atmospheric gas tended to result in higher levels of polymerization activity within the oxygen concentration range of 0.1 to 0.2 mole percent relative to the catalyst. The presence of 0.3 to 0.5 mole, per mole of the catalyst, of water resulted in improvements in activity. The above results suggest that the catalyst contains some active species such as peroxides, or butyl radicals as a precursor and that oxygen and water promote both the formation and elimination of such active species.

Tributylborane (TBB), which is used as a polymerization initiator in the production of dental adhesives, shows polymerization catalyzing activity in the presence of water or oxygen[1-3] and has remarkable properties in that it provides good adhesion to the tooth.[4-6]

It is generally accepted that the mechanisms of initiation involve the following:[7]

$$\mathrm{Bu_3B + O_2 \rightarrow Bu_2BOOBu} \quad (1)$$

$$\mathrm{Bu_2BOOBu + Bu_3B \rightarrow Bu_3BBuO\cdot + Bu_2BO\cdot} \quad (2)$$

$$\mathrm{BuO\cdot + Bu_3B \rightarrow BuOBBu_2 + Bu\cdot} \quad (3)$$

$$\mathrm{Bu_2BO\cdot + Bu_3B \rightarrow Bu_2BOBBu_2 + Bu\cdot} \quad (4)$$

Tributylborane has a very high affinity for oxygen, hence it is unstable and ready to fume and ignite in the air. This is disadvantageous in handling it. Therefore, for improved stability and ease of handling, air is blown into TBB and the resulting partially oxidized tributylborane (TBB-O) is now in use. However, the details of its structure and behavior as a polymerization initiator remain unknown.

In this paper, investigations were made to characterize the structure of TBB-O and unravel the influences of oxygen and water on the polymerization reaction .

Polymerization reactions were carried out at 37 ℃ with 50 ml (47 g, 0.47 mol) of MMA . The catalyst (0.7 ml, about 550 mg), which was produced by Sun Medical, was added (time: zero min) and samples (4 ml, 3.76 g) were collected at 10, 20, 40 and 60 min. Each sample was poured in 50 ml of methanol and the precipitated polymer was recovered and dried in vacuo. The percent conversion was determined by the gravimetric method. The water content was determined with a Karl-Fischer type analyzer, and the oxygen concentration with a polarographic analyzer. The components contained in the catalyst prior to use were analyzed by GC and GC-MS.

It was found that the main component is butoxydibutylborane with a purity of about 75%. The results of GC analysis indicate that the reaction of formula (4) is slow, suggesting that the reaction of formula (3) and the coupling reaction between the butyl radical formed and the boron oxy radical take place.

Influences of dissolved oxygen were investigated under argon, air, or oxygen gas. As seen in Figure 1, the polymerization proceeded even in argon with a very low dissolved oxygen level. In air, the activity of polymerization catalyst was further improved. In oxygen, however, the initial rate of polymerization was low and the polymerization ceased to proceed on the way. The relationship between the oxygen content and the rate of polymerization as determined from the data shown in Figure 1 revealed decreases in initial rate at the oxygen concentrations, relative to the catalyst, of 1 mole percent and above. The extent of consumption of actual oxygen in the polymerization reaction was studied. The time-conversion curve of the polymerization reaction as constructed by varying the oxygen concentration in atmospheric gas from 0 to 20% is shown in Figure 2. The results indicate that the polymerization reaction proceeded even in the oxygen-free system, although slowly. Within the range studied, the activity of polymerization catalyst increased with the increase of the oxygen concentration. Within this range, the higher the oxygen concentration in atmospheric gas was, the higher was the initial activity as a tendency.

The oxygen concentrations in atmospheric gas before and after reaction were measured. The results are shown in Table 1. The data shown indicate that the oxygen consumption amounted only to 0.1 to 0.2 mole percent with respect to the catalyst.

It is presumed that the amount of active species depends on that of catalysts and the activity of catalyst depends on oxygen concentrations in gas phase. Also, we supposed that occurence of polymerization under oxygen gas 0% in Figure 2. is due to the remaining oxygen gas in fresh catalyst.

Table 1. Oxygen consumption

Oxygen concentration <before reaction>(%)	18.9	10.7	5.7	1.0	0.0
Oxygen concentration <after reaction>(%)	18.7	10.4	5.5	0.8	0.0
Change in oxygen concentration (%)	0.2	0.3	0.2	0.2	0.0
Oxygen concentration (μmol)	81.8	122.7	81.8	81.8	0.0
O_2/cat x10^3	1.4	2.1	1.4	1.4	0.0

The polymerization reaction was carried out under air while varying the water content of MMA from zero to an equimolar amount with respect to the catalyst. The polymerization catalyst activity increased with the increase in water content up to about 5 mmol/liter. When the water content increased further, the activity decreased, however. The relationship between the water content relative to the catalyst and the initial rate of polymerization reaction is shown in Figure 3. The initial rate of polymerization was maximal when the water content was about 0.3 mole per mole of the catalyst.The polymerization reaction was performed in a nitrogen atmosphere while varying the water content of MMA from zero to an equimolar amount with respect to the catalyst.

Until the water content had reached about 500 ppm, the polymerization catalyst activity increased with the increase in water content, but decreased as the water content exceeded 500 ppm. The relationship between the water content relative to the catalyst and the initial rate of polymerization reaction is shown in Figure 4. The initial rate of polymerization reaction was maximal when the water content was about 0.5 mole per mole of the catalyst.

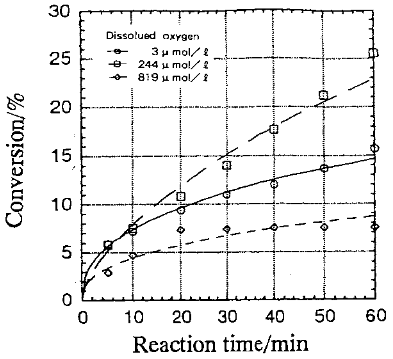

Figure 1. Influence of dissolved oxygen in MMA.

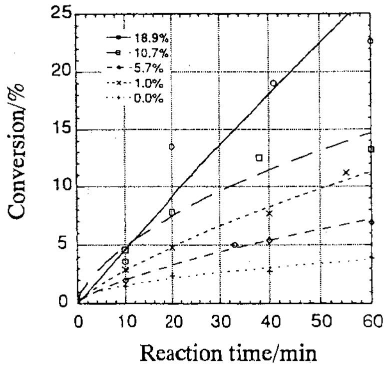

Figure 2. Influence of oxygen in atmospheric gas.

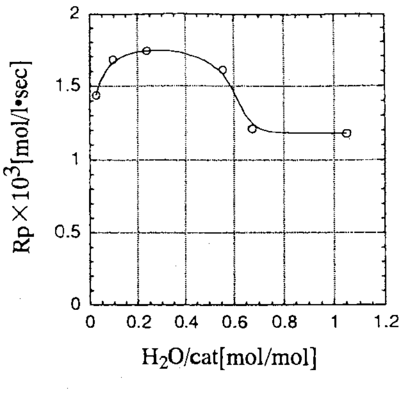

Figure 3. Influence of water (under air).

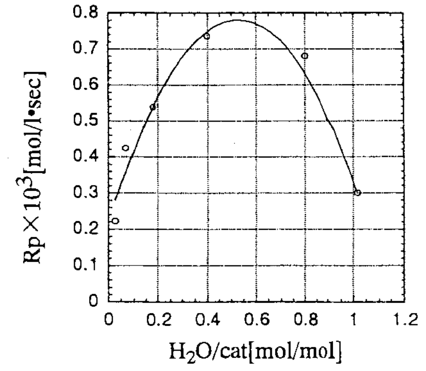

Figure 4. Influence of water (under nitrogen).

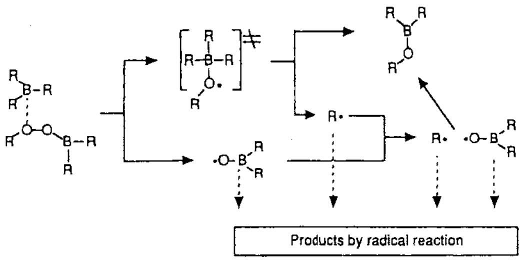

Figure 5. Oxidation reactions of TBB.

It is supposed that water assists the formation of active species from partially oxidized tributylborane.

It is probable that, as shown in Figure 5, various reactions occur concurrently on the occasion of catalyst formation. TBB-O is formed as the main product. On the way of its formation, a peroxide and radicals (butyl radical, oxy radical, etc.) are generated. If it is presumed that these active substances partly remain in the catalyst, the phenomenon that polymerization catalyzing activity is available even under nitrogen may be explained.

From the facts that oxygen and water caused an improvement in polymerization catalyst activity up to a certain concentration level but conversely inhibit the activity at higher levels, it is presumed that they promote both the formation and elimination of such active species.

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