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Anaerobic Adhesive Cure Mechanism-II

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NOTE

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INTRODUCTION

Anaerobic adhesives are single-component acrylic adhesives which cure rapidly at or below room temperature when air is excluded, but they remain in an uncured stage over a long time when they are exposed to an adequate supply of air. Thus, anaerobic adhesives are widely used in retaining compounds for nuts and bolts, in sealants, and for impregnation. Recently, anaerobic adhesives have also been used in electrical and electronic applications because of their fast room temperature cure capability and their convenience.

Anaerobic adhesives were developed by Krieble in 1959,[1] and more than 250 U.S. Patents were issued on anaerobic adhesive formulation since then. However, the anaerobic adhesive curing mechanism is still obscure. Very little technical literature exists. A model study of anaerobic adhesives using salts of benzoic sulfimide (BS) and 6-methyl-1,2,3,4-tetrahydroquinoline was reported.[2] In the above study, the rate of the polymerization was reported to be dependent on the square root of the salt concentration and the activation energy was determined to be 79 kJ/mol. Based on these results, the anaerobic adhesive using the salt mentioned above was speculated to cure by a radical polymerization mechanism. Since the anaerobic adhesives mentioned above did not contain any peroxide in their curing system, an anaerobic adhesive using amines and peroxides in the curing system was examined. In a previous report, the curing mechanism of an anaerobic adhesive was investigated using methyl methacrylate (MMA) as a model monomer and a mixture of N,N-dimethyl-p-toluidine-benzoic sulfimide-cumene hydroperoxide (DMPT–BS–CHP) as a curing system.[3] It was speculated that the polymerization proceeded by a redox radical polymerization

based on its low apparent activation energy, 43 kJ/mole, and also based on a study of the curing system's structure–curing rate relationship.

We have extended our anaerobic curing mechanism study to curing systems other than DMPT–BS–CHP. This report will discuss the polymerization mechanism of the acetyl phenyl hydrazine-BS–CHP (APH–BS–CHP) curing system.

EXPERIMENTAL

Materials were purified by the manner described in the previous study.[3] APH was recrystallized from ethanol.

The kinetic study was conducted by polymerizing MMA in sealed tubes. Into the tubes was charged 10 ml of MMA, 0.075 g (0.5 mmol) of APH, 0.090 g (0.5 mmol) of BS, 0.28 g (1.5 mmol) of CHP and 5 ppm of Cu^{2+} (copper(II) ethyl hexanoate). The polymerization of the MMA solution described above was conducted by a procedure identical to that reported.[3]

RESULTS AND DISCUSSION

The model study of the anaerobic adhesive curing mechanism was investigated using MMA and an APH–BS–CHP curing system.

One major difference between an APH–BS–CHP system and a DMPT–BS–CHP system was that the former produced a slow cure and had a long induction period. Thus, 5 ppm of Cu^{2+} was added to shorten the induction period from over 5 hr to 10–15 min.

Activation energy determination

The effect of polymerization temperature on the polymerization rate, R_p, was examined and the apparent activation energy, E_a, was determined.

As shown in Figures 1 and 2, the polymerization proceeded more rapidly at higher temperature, and the E_a was determined to be 30.1 kJ/mol. The E_a of 30.1 kJ/mol for an APH–BS–CHP curing system was slightly lower than that of 43.5 kJ/mol for a DMPT–BS–CHP system, probably due to the presence of Cu^{2+} used as a catalyst. This low E_a indicates that this polymerization proceeded most likely by a redox radical polymerization.[4]

Determination of Rp

A kinetic study of MMA model polymerization was investigated using an APH–BS–CHP system. First, the effect of APH was examined and the results are summarized in Table I.

The plot of $\ln R_p$ vs $\ln [APH]$ shown in Figure 3 gives a straight line having a slope of 0.55, thus $R_p = [APH]^{0.55}$.
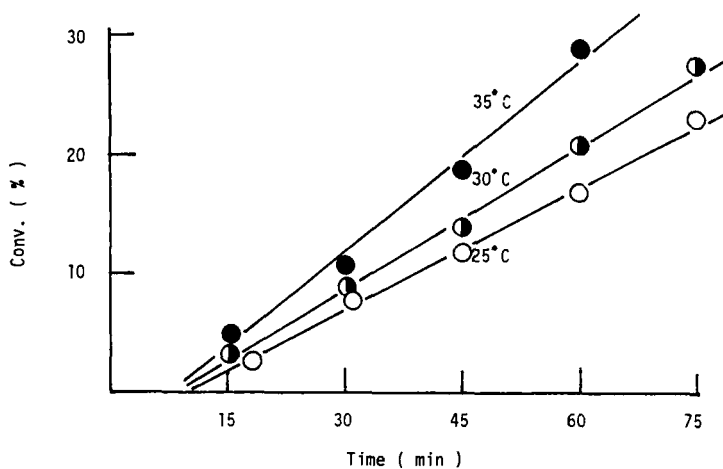
FIGURE 1   Polymerization rate at various polymerization temperature. MMA = 9.36 mol/l; APH = 0.05 mol/l; BS = 0.05 mol/l; CHP = 0.15 mol/l.
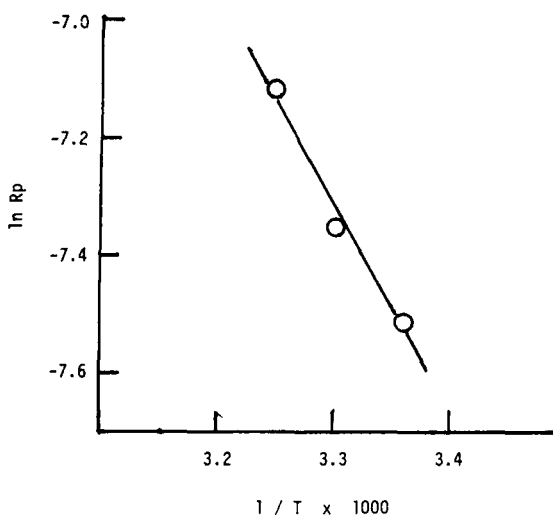
FIGURE 2   Determination of activation energy.

TABLE I
Effect of APH on R_p

[APH], mol/L	R_p mol/L sec
0.050	5.44×10^{-4}
0.038	5.64×10^{-4}
0.025	3.86×10^{-4}
0.013	2.17×10^{-4}
0	0

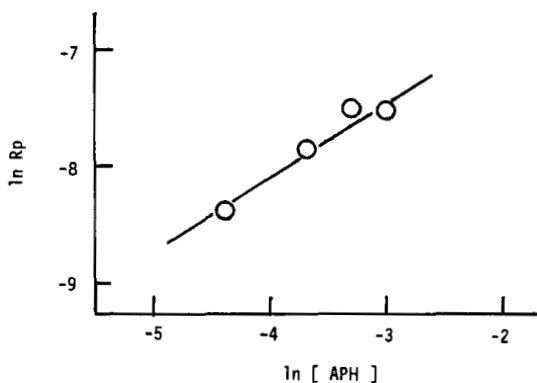[MMA] = 9.36, [BS] = 0.05, and [CHP] = 0.15 mol/L.

FIGURE 3   Determination of polymerization rate.

Next, the effect of BS was examined and the results were as shown in Figure 4. The polymerization took place even without BS, and the rate of polymerization seemed to be identical with and without BS, although a slightly longer induction period was observed without BS. These results indicate that the rate of polymerization seems to be independent of BS concentration, $R_p = [BS]^0$, and BS behaves as a catalyst to shorten the induction period slightly from 30–40 min to ~10 min.

The effect of CHP on R_p is summarized in Table II.

The R_p was extremely low when the [CHP]/[APH] molar ratio was below 0.75, but R_p increased when the [CHP]/[APH] molar ratio was increased to 1.0 as shown in Figure 5. When the [CHP]/[APH] molar ratio exceeded 1.0, the R_p became constant as shown in Figures 5 and 6. The above results suggest that some kind of interaction between CHP and APH exists, but we do not know at this moment what interaction or reaction took place.
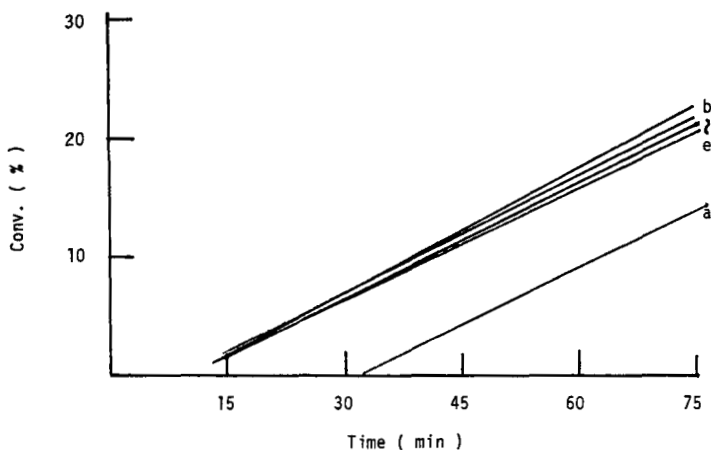

FIGURE 4   Polymerization rate at various BS concentrations.   MMA = 9.36 mol/l;   APH = 0.05 mol/l; CHP = 0.15 mol/l; BS a = 0, b = 0.013, c = 0.025, d = 0.038, e = 0.05 mol/l.

TABLE II
Effect of CHP on R_p

[CHP], mol/L	[CHP]/[APH]	R_p, mol/L sec
0.010	2.00/1	5.08×10^{-4}
0.068	1.25/1	5.03×10^{-4}
0.050	1.00/1	3.03×10^{-4}
0.047	0.94/1	4.44×10^{-4}
0.044	0.90/1	4.15×10^{-4}
0.041	0.81/1	3.27×10^{-4}
0.038	0.75/1	1.04×10^{-4}
0.025	0.50/1	~ 0

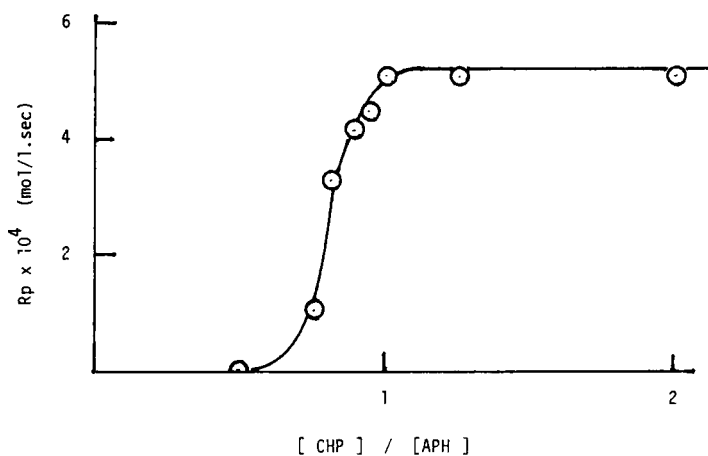[MMA] = 9.36, [APH] = 0.05, [BS] = 0.05 mol/L.

FIGURE 5 Effect of CHP/APH on polymerization rate. MMA = 9.36 mol/l; APH = 0.05 mol/l; BS = 0.05 mol/l.
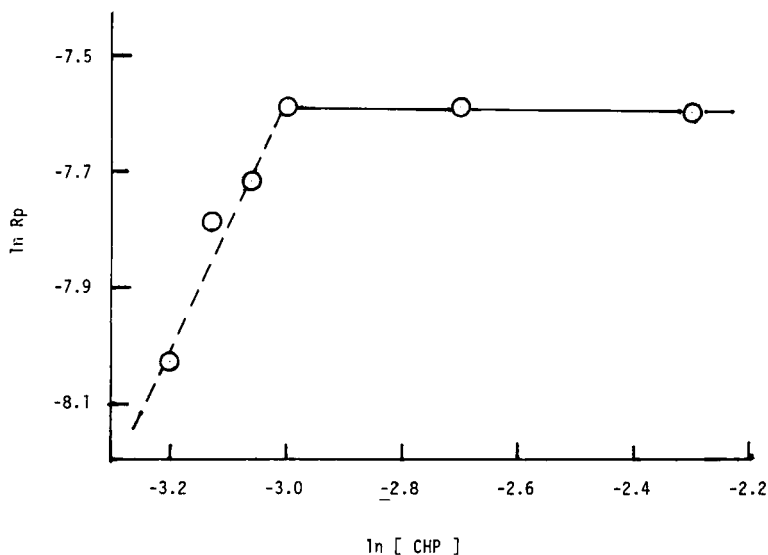

FIGURE 6 Determination of polymerization rate.

TABLE III
Effect of MMA on R_p

[MMA], mol/L	Rp, mol/L sec
9.36	4.19×10^{-4}
8.42	3.60×10^{-4}
7.49	3.22×10^{-4}
6.55	3.07×10^{-4}
5.62	1.72×10^{-4}
4.68	1.38×10^{-4}

[APH] = 0.05,   [BS] = 0.05,   and
[CHP] = 0.15 mol/L.

The effect of MMA concentration was determined using cyclohexane as a solvent and the results are summarized in Table III.

The plot of [MMA] *vs* ln R_p shown in Figure 7 indicates that $R_p = [MMA]^{1.1}$, *i.e.* MMA monomer does not participate in the initiation step of a redox polymerization.

Thus the overall rate of MMA polymerization initiated by an APH–BS–CHP system is

$$R_p = k_1[MMA]^{1.1}[APH]^{0.55} \quad \text{when} \quad [CHP]/[APH] > 1.0$$

and

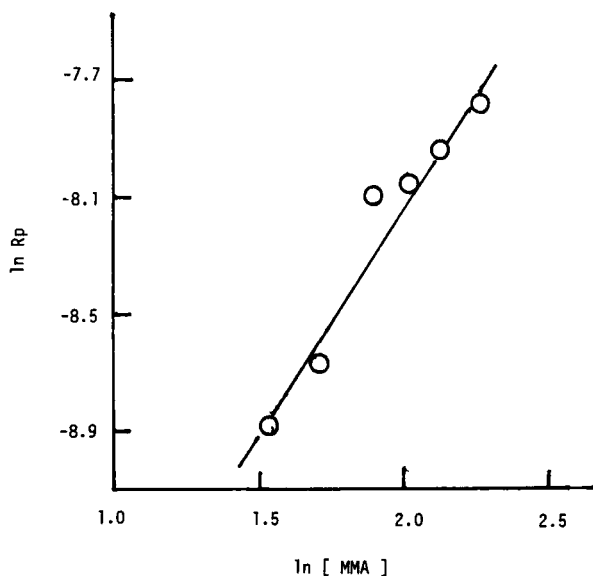$$R_p = k_2[MMA]^{1.1}[APH]^{0.55}[CHP]^{2.2} \quad \text{when} \quad [CHP]/[APH] = 0.75 - 1.0$$

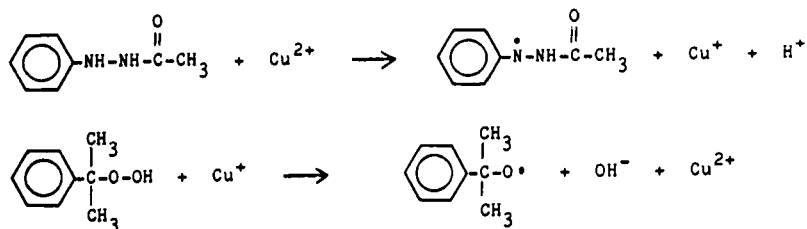

FIGURE 7 Determination of polymerization rate. APH = 0.05 mol/l; BS = 0.05 mol/l; CHP = 0.05 mol/l; MMA = 4.68 ~ 9.36 mol/l.

POLYMERIZATION MECHANISM

Based on these kinetic studies, this polymerization most likely proceeded by a redox radical polymerization.

The following redox initiation mechanism was postulated to generate a cumyloxy radical which initiates the MMA polymerization.

APH and CHP behave as a reducing and an oxidizing agent, respectively, and copper acts as a catalyst.

BS was found to behave as a catalyst to shorten the induction period. One possible explanation is that BS behaves as a mild acid catalyst in the following reaction:
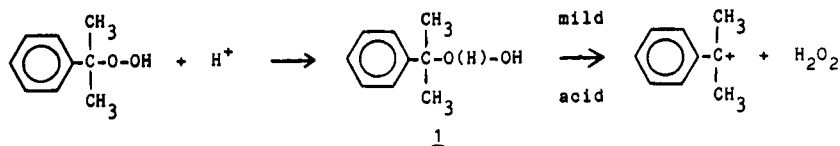
An acid may attack the oxygen of CHP to form the intermediate, **1**. The intermediate, **1**, may form cumyl cation and hydrogen peroxide. This reaction is an equilibrium reaction and the equilibrium can often be forced toward the formation of hydrogen peroxide under mildly acidic conditions.[5]

As mentioned earlier, the APH–BS–CHP system shows a long induction period. This long induction could be due to formation of compound **2** by the following reaction.
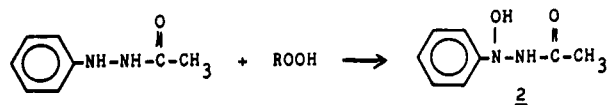
Since the compound **2**, which has a hydroxyamine structure, could behave as a good radical inhibitor, the APH–BS–CHP system showed a long induction period during the MMA polymerization.[6]

CONCLUSIONS

Anaerobic adhesives appeared to cure by a redox radical polymerization mechanism. The APH–BS–CHP initiation system was found to be much slower

than a DMPT–BS–CHP initiation system, and the slow initiation of the APH–BS–CHP system could be accelerated by copper metal catalyst. The activation energy of this APH–BS–CHP system with copper metal catalyst was 30.1 kJ/mol which is slightly lower than that of the DMPT–BS–CHP system. It is speculated that the presence of an induction period during the MMA polymerization using the APH–BS–CHP system is due to APH or an APH reaction product(s) which behaves as a radical inhibitor.

References

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3. Y. Okamoto, *J. Adhesion,* this issue.
4. R. W.Lenz, *Organic Chemistry of Synthetic High Polymers* (Interscience Publishers, New York, 1968), pp 273–276.
5. R. Hiatt, *Organic Peroxides,* **II,** D. Swern, Ed. (Wiley-Interscience, New York, 1971), pp 65–70.
6. R. G. Leonard, private communication.

Acknowledgment