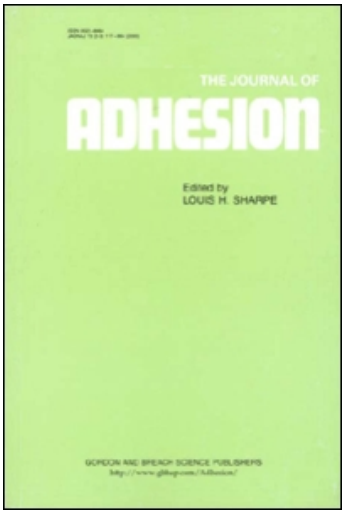

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Anaerobic Adhesive Cure Mechanism-I

Y. Okamoto[a]
[a] Loctite Corporation, Newington, CT, U.S.A.

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NOTE

Anaerobic Adhesive Cure Mechanism—I

Y. OKAMOTO

Loctite Corporation, 705 North Mountain Road, Newington, CT 06111, U.S.A.

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KEY WORDS Anaerobic adhesive; redox polymerization; cure mechanism; acrylics; activation energy; charge-transfer complex.

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.[1]

Anaerobic adhesives were devleoped by Krieble in 1959 and their main ingredients were methacrylate monomers, amines and hydroperoxides.[2] Although many anaerobic adhesive formulations were developed and more than 250 U.S. Patents were issued since then, the majority of anaerobic adhesives still use cure systems based on teritary amines, benzoic sulfimide (saccharin), and/or hydroperoxides.

There is hardly any scientific literature relevant to the cure mechanism of anaerobic ahdesives. One of the few studies reported is that of methyl methacrylate (MMA) polymerization using various amine salts of benzoic sulfimide (BS). Amines examined in the above study were *N,N*-dimethyl-p-toluidine (DMPT), *N,N'*-dimethylaniline, indoline, quinoline, 1,2,3,4-tetrahydroquinoline, 6-methyl-1,2,3,4-tetrahydroquinoline, and triethylamine. The highest polymer conversion was obtained from the DMPT salts of BS. The rate of the polymerization was reported to be dependent on the square root of amine salt concentration, and the activation energy was determined to be 79 kJ/mol.[3]. These results indicate that the polymerization mentioned above proceeded by a radical polymerization mechanism.

Although several other researchers also suggested that anaerobic adhesives are cured by a radical polymerization mechanism, the cure mechanism of anaerobic adhesives is still obscure.[1,4,5] Thus, an anaerobic adhesive cure mechanism study was conducted using MMA as a model monomer, and the role of DMPT, BS, and cumene hydroperoxide (CHP) in anaerobic adhesives was examined.

EXPERIMENTAL

MMA was washed with a sodium hydroxide solution and then distilled under vacuum. BS was recrystallized from methanol, mp 211–212°. DMPT was distilled and stored under nitrogen atmosphere. Cumene hydroperoxide (80%) was used as received from Aldrich.

The kinetic study was conducted by polymerizing MMA in sealed tubes. Into the tubes was charged 10 ml of MMA, 0.137 g (0.75 mmol) of BS, 0.1 g (0.75 mmol) of DMPT, and 0.142 g (0.75 mmol) of CHP. Then the tube was sealed and the MMA solution was deaerated by repeated freezing and thawing under vacuum and under nitrogen atmosphere. The polymerization was carried out at 25°C. The polymerization was terminated at various intervals by pouring the MMA solution into large amounts of methanol to precipitate the polymer. The obtained polymer was washed thoroughly with methanol and dried *in vacuo*, then the polymer conversion was calculated.

The cure speed test was conducted in a test tube in a similar manner to that described above. After deaeration, the atmosphere in the tube was replaced with nitrogen, and a thermocouple was placed in the tube and sealed with minimum air exposure. Then the tube was placed in a 25°C constant temperature bath and the maximum exothermic cure time and temperature was determined using a strip chart recorder.

RESULTS AND DISCUSSION

The model study of anaerobic adhesive cure mechanism was conducted using MMA employing a DMPT–BS–CHP cure system.

First, the effect of polymerization temperature on the polymerization rate, R_p, was examined at various temperatures.

As shown in Figure 1, the polymerization proceeded faster at higher temperature. The apparent activation energy, E_a, of this polymerization system was determined to be 43.5 KJ/mol from the slope of the straight line obtained by plotting the logarithm of R_p against $1/T$ as shown in Figure 2.

This activation energy is roughly half the typical thermally initiated radical polymerization of approximately 90 KJ/mol. This low activation energy indicates

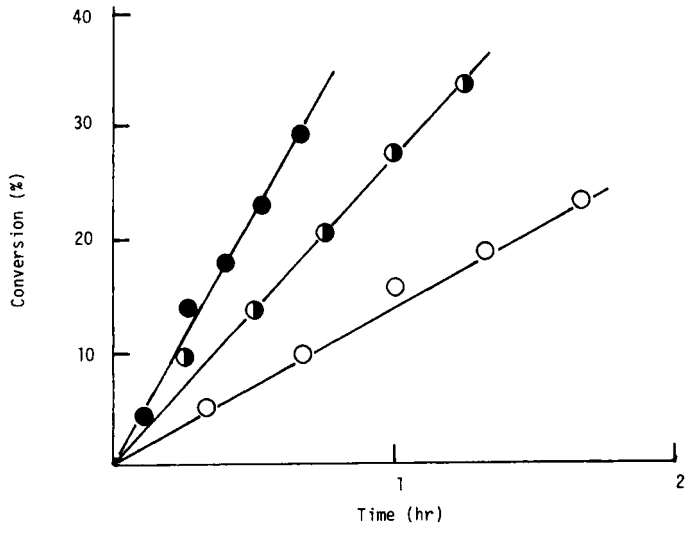


FIGURE 1 Polymerization rate at various temperatures. ○ = 25°C, ◑ = 35°C, ● = 45°C.

that this polymerization proceeds, most likely, by a redox radical polymerization.[6]

This low activation energy of methacrylate polymerization initiated by a DMPT-BS-CHP system enables an anaerobic adhesive to cure at or below room temperature.

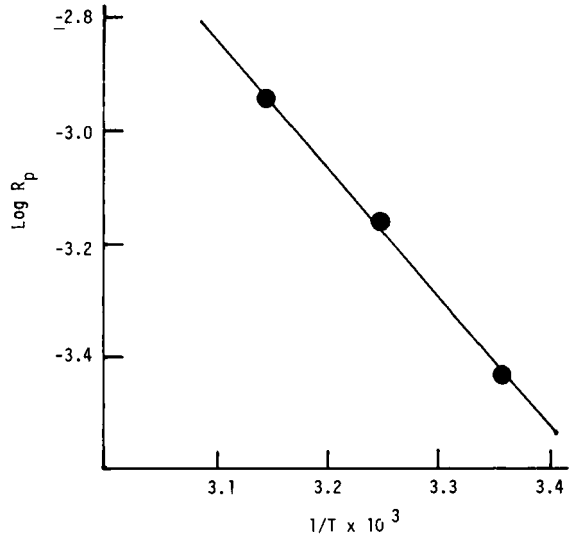


FIGURE 2 Determination of activation energy.

KINETIC STUDY

Next, a kinetic study of MMA polymerization initiated by a DMPT-BS-CHP system was conducted to determine the effect of DMPT. As shown in Figure 3, the polymerization proceeded faster with the higher concentration of DMPT, and no polymerization took place without DMPT. The R_p was then calculated from the slope of each line in Figure 3, and plotting $\log R_p$ *vs.* $\log$ [DMPT] gave a straight line with slope of 0.34. Thus, the R_p is directly related to 0.34 power of DMPT concentration.

Effects of BS and CHP concentration were then examined in a similar manner as shown in Figures 5 and 6, and the overall rate of polymerization was expressed by

$$R_p = k[\text{DMPT}]^{0.34}[\text{BS}]^{0.36}[\text{CHP}]^0$$

One surprise from the above rate of polymerization study is that polymerization took place without CHP. Although the polymerization took place without CHP, the rate of polymerization was approximately 20–50% faster in the presence of CHP. It also seems that the rate of polymerization was independent of the CHP concentration as shown in Figure 6.

The effect of MMA concentration was also examined using cyclohexane and ethyl acetate as solvents and R_p was expressed by

$$R_p = k[\text{MMA}]^{3.3} \text{ in cyclohexane, and}$$

$$R_p = k[\text{MMA}]^{1.2} \text{ in ethyl acetate.}$$

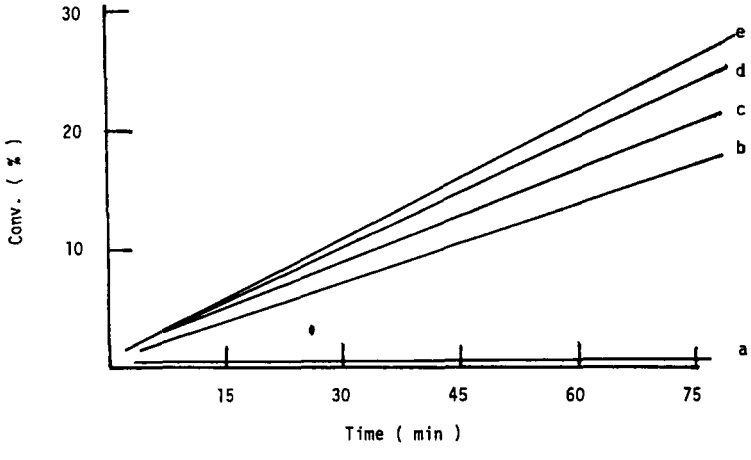


FIGURE 3 Polymerization rate at various DMPT concentrations. MMA = 9.36 mol/l; BS = 0.075 mol/l; CHP = 0.075 mol/l; DMPT a = 0, b = 0.018, c = 0.037, d = 0.056, e = 0.075 mol/l.

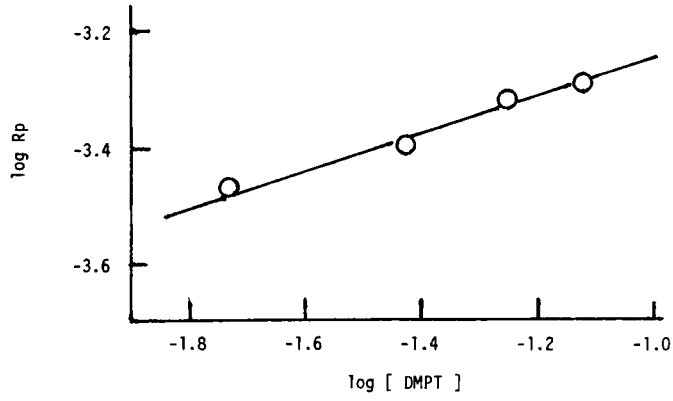


FIGURE 4. Determination of polymerization rate.

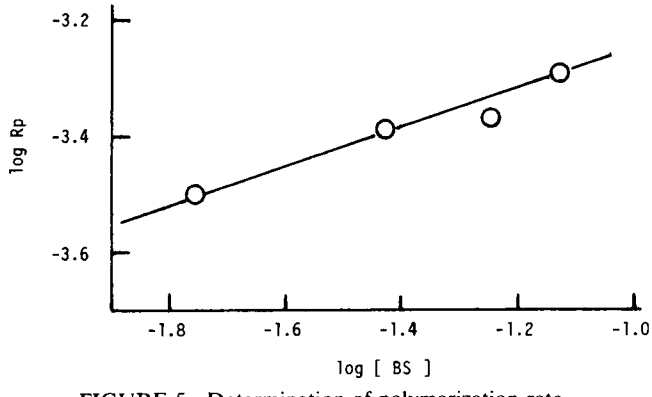


FIGURE 5 Determination of polymerization rate.

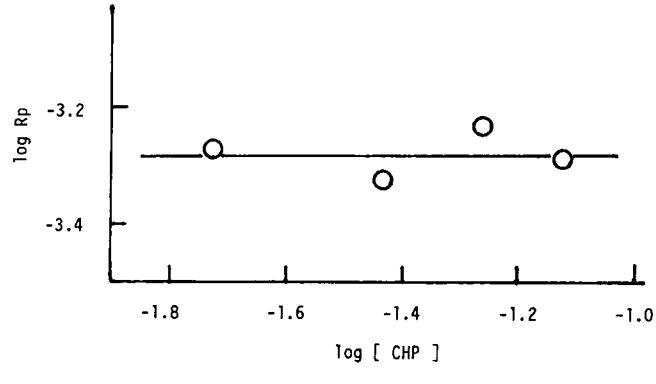


FIGURE 6 Determination of polymerization rate.

STRUCTURE–CURE SPEED RELATIONSHIP STUDY

The structure–cure speed relationship study was conducted using DMPT, BS and their derivatives and the results are summarized in Tables I and II.

As shown in Table I, the cure speed was increased by an electron-donating methyl group on the para position of *N,N*-dimethylaniline, but it was decreased by the presence of the same group in the ortho position. The monomers were polymerized slightly more slowly when DMPT was replaced by the secondary amines, indoline and 1,2,3,4-tetrahydroquinoline.

BS showed the fastest cure speed and the cure speed was decreased by an electron-donating group in BS and by any substituents on the nitrogen atom in BS. The polymerization speed was also decreased by open chain analogs of BS, such as *N*-benzenesulfonylbenzamide.

POLYMERIZATION MECHANISM

Based on the kinetic study and the structure-cure speed relationship study, this polymerization most likely proceeded by a redox radical polymerization. The reducing agent of this redox initiation system is speculated to be a charge transfer

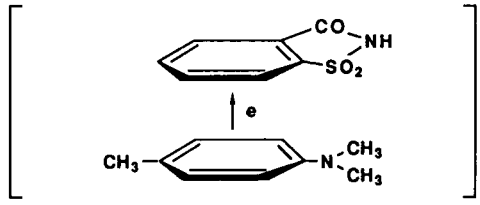
TABLE I
Effect of amine structure on cure speed

Amines	Max. exotherm time (hr.)	Max. exotherm temp (°C)
N,N-Dimethylaniline	>4.5	—
N,N-Dimethyl-p-toluidine	1.4	103
N,N-Dimethyl-o-toluidine	>8	32
N,N-Diethyl-p-toluidine	2.8	75
Indoline	2.2	70
1,2,3,4-Tetrahydroquinoline	2.2	82

TABLE II
Effect of sulfimide structure on cure speed

Sulfimides	Max. exotherm time (hr.)	Max. exotherm temp (°C)
Benzoic Sulfimide	1.4	103
4-Cyclohexylbenzoic Sulfimide	4.7	33
4-*t*-butylbenzoic Sulfimide	4.7	31
N-Acetylbenzoic Sulfimide	>72	25
N-Benzoylbenzoic Sulfimide	4.2	34
N-Methylbenzoic Sulfimide	<24	25
N-Benzenesulfonylbenzamide	11	30

complex of DMPT and BS, shown below, by the following observations.



Charge-Transfer Complex

Firstly, the kinetic study revealed that the rate of polymerization was expressed by

$$R_p = k[\text{DMPT}]^{0.34}[\text{BS}]^{0.36}[\text{MMA}]^{3.3}$$

R_p depends on the almost identical orders of DMPT and BS concentrations, 0.34 and 0.36, respectively. R_p also depends on the 3.3 order of MMA concentration and this result may indicate that the charge transfer complex could be solvated by MMA monomer. If MMA does not participate in the charge transfer complex solvation, R_p should depend on the first order of MMA concentration, $R_p = k[\text{MMA}]^{1.0}$.

Secondly, development of a purple color and a new broad UV absorption around 500–600 nm when DMPT and BS were mixed may indicate the formation of the charge transfer complex. The charge transfer complex is formed by a weak force, thus it could easily be destroyed by a strong external force such as heat. Indeed, the purple color disappeared when the DMPT-BS solution was heated around 70°C, and it reappeared when the solution was cooled again.

Thirdly, the relationship study among DMPT, BS structures and cure rates supports the formation of the charge transfer complex. The cure rate was accelerated by introducing electron-donating substituent groups on the aromatic amine, while it was retarded by introducing electron-donating groups on the BS molecule. The cure rate was also retarded by introducing bulky substituent groups which could prevent the formation of the charge transfer complex due to destruction of the plane molecular structure.

Unexpectedly, CHP appeared not to be the oxidizing agent for this redox system. The kinetic study revealed that the redox polymerization took place without CHP. Thus, the oxidizing agent in this redox system could be a trace of air (oxygen) in the system.

TABLE III
Effect of air

	As is	Purged with nitrogen	Deaerated twice	Deaerated six times
Cure time, hr.	2.3	3.1	3.1	3.6

(MMA = 9.4, DMPT = 7.5×10^{-2}, BS = 7.5×10^{-2}, CHP = 0 mol/l.

A cursory study of the effect of air indicated that the cure speed is retarded by the more careful deaeration process shown in Table III.

The literature also indicated that the polymerization is faster in the presence of air.[3,5] Establishing the relationship between residual oxygen dissolved in the monomer and cure time was unsuccessful due to the difficulty involved with quantitative measurement of residual oxygen in the monomer. Molecular oxygen in air could be the oxidizing agent for this system. Hydrogen peroxide, however, is another candidate for the oxidizing agent and it could formed by the following reaction in the presence of DMPT, BS and a trace of metal,[7]

$$O_2 + 2e + 2H^+ \longrightarrow H_2O_2$$

or in the presence of reducing agents such as ascorbic acid and diphenylhydrazine.[8]

$$O_2 + 2e \longrightarrow O_2^{-\cdot} \xrightarrow[\text{agent}]{\text{reducing}} H_2O_2$$

Presently, it is clear that the presence of a trace of oxygen is the important factor in the DMPT–BS–CHP redox system, but it is still uncertain whether molecular oxygen itself and/or hydrogen peroxide are the oxidizing agents in this redox system.

Although the redox polymerization took place without CHP, the presence of a small amount of CHP clearly showed an acceleration effect on the polymerization. At this time, we do not know the exact role of CHP in this polymerization and we will leave this subject for future study.

Overall, the curing mechanism of anaerobic adhesives is as follows. As soon as DMPT, BS and CHP are mixed into MMA monomer, the redox reaction starts taking place to generate radicals continuously. When a sufficient amount of air is present in the adhesives, oxygen reacts with the continuously generated radicals to form less reactive ROO$^{\cdot}$ radicals which are not able to initiate the methacrylate polymerization. Thus, the adhesives remain in the uncured stage. However, when the supply of air is shut off, the continuously generated radicals consume all oxygen and then start reacting with methacrylate monomer to initiate the polymerization. Thus anaerobic adhesives start curing.

Anaerobic adhesives are, therefore, exploiting the slight difference between the rate of polymerization and the rate of oxygen inhibition. When the rate of polymerization is too fast, the adhesives cure faster but show poor shelf stability. On the other hand, if the rate of inhibition is too fast, the adhesive cures very slowly. The true art of anaerobic adhesives is balancing these rates of polymerization and inhibition.

CONCLUSIONS

Anaerobic adhesives appeared to cure by a redox radical polymerization mechanism. The activation energy of this redox polymerization was so low that

anaerobic adhesives could be cured at or below room temperature. The reducing agent of this polymerization system seems to be a charge transfer complex of DMPT and BS, and the oxidizing agent is most likely the residual oxygen in the monomer.

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