Kinetic Studies on Anaerobic Initiated Polymerization

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SYNOPSIS

Using a model reaction system consisting of cumene hydroperoxide, *N,N*-dimethyl-*p*-toluidine and O-benzoic sulfimide in toluene solvent (without reactive acrylic monomer), attempts have been made to understand the initiation mechanism operating during anaerobic polymerization. In these studies, the instrumental techniques of visible spectroscopy (VS), high performance liquid chromatography (HPLC) and infrared spectroscopy (IR) were employed.

Valuable kinetic data have been obtained using these three instrumental techniques. HPLC studies have shown conclusively that the *N,N*-dimethyl-*p*-toluidine (N,N-DMpT) component is significantly depleted during the initiation step of the anaerobic process. By way of contrast, the benzoic sulfimide (BS) concentration was found to be essentially unchanged during initiation.

Visible spectral changes with the model anaerobic solutions indicate that the initiation mechanism may involve radical-ionic species derived from N,N-DMpT rather than free radical reactive intermediates. Increasing the acidity of the reaction solution, with addition of acetic acid, appears to accelerate the initiation rate under anaerobic conditions.

INTRODUCTION

Anaerobic resins are precatalyzed polymerizable compositions which are inhibited from curing in the presence of oxygen or air, but will cure or gel rapidly when oxygen is excluded.[1]

The earliest commercially acceptable anaerobic compositions were based on precatalyzed acrylate ester monomers.[2] Improvements in these compositions were obtained with the inclusion of certain latent accelerators of free radical polymerization to increase the speed of cure.[3,4] The most successful anaerobic materials[5,6] are available as adhesives for the sealing of threaded and flanged metal joints. These adhesives, available either as low viscosity liquids or thixotropic liquids and pastes, are claimed to have the ability to remain in the uncured state as long as adequate contact is maintained with atmospheric oxygen, but will polymerize rapidly when placed between metal or other impervious surfaces.[7]

These anaerobic compositions are also claimed to possess excellent chemical resistance and thermal stability, and good electrical and tensile properties up to 150°C.[7] However, it may be of significance that the properties of these anaerobic compositions are continually being modified,[8-13] and the cure properties are still being optimized.

Recent work at our laboratories revealed that some of these anaerobic formulations were effectively cured in a N_2 stream of in a pressurized vessel containing N_2. Replacing N_2 with air resulted in total inhibitions of cure.[14]

Although significant progress has been made in utilizing these types of anaerobic resins in various coating and adhesive applications, the mechanism of cure, particularly when an N_2 atmosphere is used, is not very well understood. Also, because of the complex chemistry inherent in the initiation process, some unusual side effects, particularly the loss of gelation reactivity, have been observed during prolonged storage of some of the anaerobic formulations.

Because of the lack of real understanding of the anaerobic cure mechanism, a basic study was initiated to obtain more insight into the various molecular interactions occurring in these anaerobic resin systems with the intent of optimizing their cure characteristics and storage properties.

In these basic investigations, the instrumental

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techniques of visible spectroscopy (VS) and high performance liquid chromatography (HPLC) and infrared spectroscopy (IR) were used.

The present paper also deals with the effects of varying some of the basic parameters in the model initiation system. These variations included such things as:

1. Replacing the toluene solvent with other solvents
2. Replacing the benzoic sulfimide (BS) coaccelerator with other additives
3. Varying the acidity of the solvent by addition of acetic acid.

As will be revealed in this paper, many interesting discoveries were made by employing the various instrumental procedures to make a direct comparison between anaerobic (oxygen-free) and aerobic (oxygen-containing) samples derived from the same model reaction solution. In many instances, this direct comparison revealed striking differences in VS, HPLC, and IR experimental data between the anaerobic and aerobic samples, thereby indicating the important role played by O_2 in the initiation step of these processes.

EXPERIMENTAL

Model Initiation System

To overcome the complications of polymer formation, the monomers were eliminated. In doing so, a basic study of the initiation mechanism is anaerobic curing processes could be performed. This elimination was justified by the knowledge that the anaerobic initiation step would not involve the monomers. Instead, it would involve the interactions among the peroxide and the accelerators (organosulfur and amine).

The components of the basic model initiation system were: Organic peroxide, cumene hydroperoxide (CHP); Tertiary amine, *N,N*-dimethyl-*p*-toludine (N,N-DMpT); Organosulfur, *O*-benzoic sulfimide (BS); Inert solvent, toluene.

These components were selected on the basis of their effectiveness in initiating polymerization under anaerobic conditions. Toluene was chosen as the in-

Table I Calibration Curve Data for CHP* in Toluene at 480 nm (Visible)

Concentration (g/L)		Percentage Transmittance	Absorbance
No. 1	0.094	2.3	1.64
No. 2	0.078	4.1	1.39
No. 3	0.056	10.2	0.971
No. 4	0.039	15.1	0.821
No. 5	0.020	33.5	0.475

* CHP = Cumene hydroperoxide.

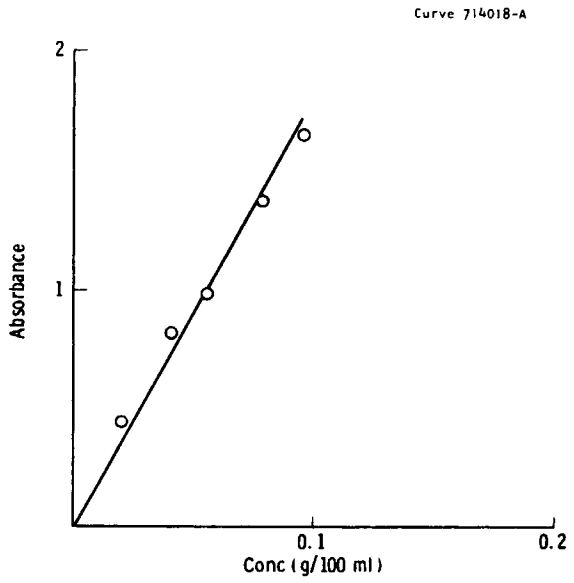

Figure 1 Calibration curve of CHP in toluene at 480 nm from Table I.

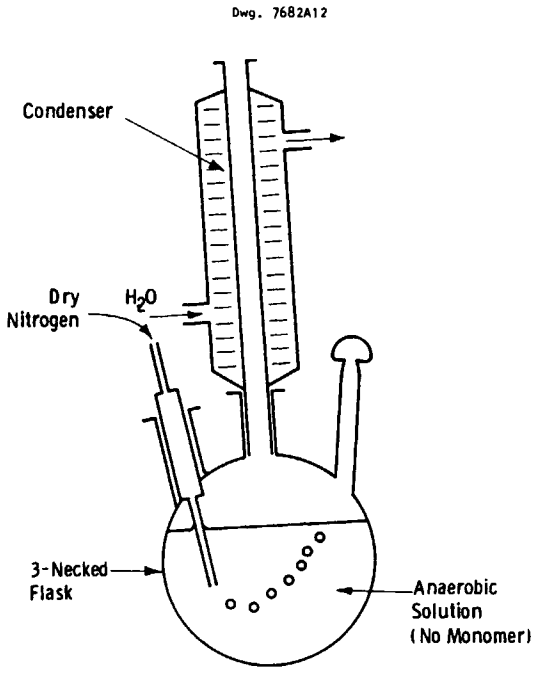

Figure 2 Schematic diagram of set-up used to study anaerobic initiation mechanism.

Table II Components Used in the Evaluation of the Initiation Mechanism of Anaerobic Resins

	BS[a] (.0016 mole)	N,N-DmpT[b] (.003 mole)	CHP[c] (.013 mole)
Solution 1a	+[d]	+	−
Solution 2a	−[e]	+	+
Solution 3a	+	−	+
Solution 4a	−	−	+

[a] CHP = Cumene hydroperoxide.
[b] N,N-DmpT = *N,N*-dimethyl-*p*-Toluidine.
[c] BS = *O*-benzoic sulfimide.
[d] (+) = Components present.
[e] (−) = Components absent.

ert solvent for this initiating system because it exhibits low transfer constant with peroxy-free radicals. Nitrogen gas was used to promote anaerobic cure. The gas was bubbled through the system at a constant flow rate of 4 L/min. Because the above system was a model, it was used in evaluating other organosulfurs, organometallics, inert solvents, and the effect of changing the acidity of the system.

Visible Spectrophotometric Analysis

The relationship between absorption of a particular wavelength of radiation and the number of molecules absorbing is known as the Beer–Lambert Law, which can be written as

$$A = -abc = \log_{10} \frac{100}{\%T}$$

where A = absorbance; a = absorptivity coefficient; b = cell path length (cm); c = molar concentration; and T = transmittance.

The visible spectrum of CHP in toluene at varying wavelengths was obtained in the range 380–600 nm using the procedure described by Banerjee and Bukde.[15] The concentration of the sample used was 10 g/L, and the cell path length was 2.50 cm. The strongest absorption band obtainable through scanning the visible spectral range was at 480 nm.

In collecting data to construct the calibration curve (Fig. 1), five different concentrations of CHP in toluene were used (Table I). The data were collected as percent transmittance (% T) and converted to absorbance. This conversion was made because absorbance is a linear function of concentration, whereas transmittance is not. The calibration curve in Figure 1 could then be used to monitor the change in CHP concentrations for the various experimental runs, thereby providing decomposition rate data.

High Performance Liquid Chromatography (HPLC)

As with all chromatographic techniques, HPLC works on the principle that two components can be separated by the preferential retention of one of the components on the column.[16] This preferential retention is possible because all substances are not the same size, shape, weight, solubility, or polarity. In the case of HPLC, the components are separated on a stationary column of silica gel (10 μ) using isooctane containing 10% dioxane as the carrier solvent.

Procedure for Obtaining Kinetic Data

The apparatus used in obtaining kinetic data is schematically shown in Figure 2. Typical experimental runs with the various modifications of components are shown in Tables II–IV.

The procedure used for obtaining the kinetic data was as follows: predetermined weights of CHP, N,N-DMpT and BS (Table II) were added to 150 mL of toluene, and mixing was performed until almost complete dissolution of the BS was achieved. This mixture was diluted to 250 mL in a volumetric flask

Table III Components Used in the Evaluation of Organosulfur Accelerators

Run	CHP (.07 mole)	Organosulfur (1 mole)	N,N-DmpT (.006 mole)	Toluene
1b	+[a]	BS	+	+
2b	+	Thiate-E	+	+
3b	+	1,4-Thioxane	+	+

[a] (+) = Components present.

Table IV Components Used in the Evaluation of Solvent Systems

Run	CHP (.07 mole)	N,N-DmpT (.006 mole)	BS (.003 mole)	Solvent (~1000 mL)
1c	+	+	+	Toluene
2c	+	+	+	Diacetone Alcohol
3c	+	+	+	Ethyl Cellosolve Acetate
4c	+	+	+	Methyl Cellosolve Acetate
5c	+	.06 mole	+	Toluene
6c	+	.06 mole	+	1:99 Acetic Acid Toluene
7c	+	.06 mole	+	10:90 Acetic Acid Toluene
8c	+	+	+	50:50 Acetic Acid Toluene

and mixed until the BS has completely dissolved. An aliquot of 100 mL was placed in the 200 mL three-necked flask. The extra 150 mL of solution was poured into a glass bottle, capped, and stored in the dark. Nitrogen was bubbled through the solution for 6 h at a flow rate of 4 L/min. To perform visible spectral studies, 0.5 mL samples were removed from both the flask and the stored bottle. Each sample was diluted to 10 mL with toluene. One milliliter was removed from each sample and placed in a 25 mL volumetric flask. These samples were then diluted to 25 mL with a 2 : 1 acetic acid–chloroform mixture. Each sample was poured into a cuvette and sparged with nitrogen for 1 min. A 1 mL addition of 50% potassium iodide solution was made to the cuvettes and the sample was then sparged for an additional 1.5 min with nitrogen gas. The samples were capped and stored in the dark for 10 min. Each sample was then placed in the sample chamber of a calibrated visible spectrophotometer. The meter gave a readout of $\%T$ for the sample. Typical visible spectral data are shown in Figure 3.

Infrared spectral curves were obtained by weighing out 10 g of both the stored and nitrogen samples in separate aluminum dishes. The samples were exposed to an air current to drive off the inert solvent. A smear was prepared from each residue on sodium chloride sample cells, and the infrared spectrum of each sample was recorded. Typical infrared spectral curves for some of the reaction products obtained in this way are shown in Figures 4–7 and Figures 13–16.

Only in the cases of Runs 1c and 5c (Table 4) were HPLC evaluations performed. The sample solutions were prepared in the same way as the initial

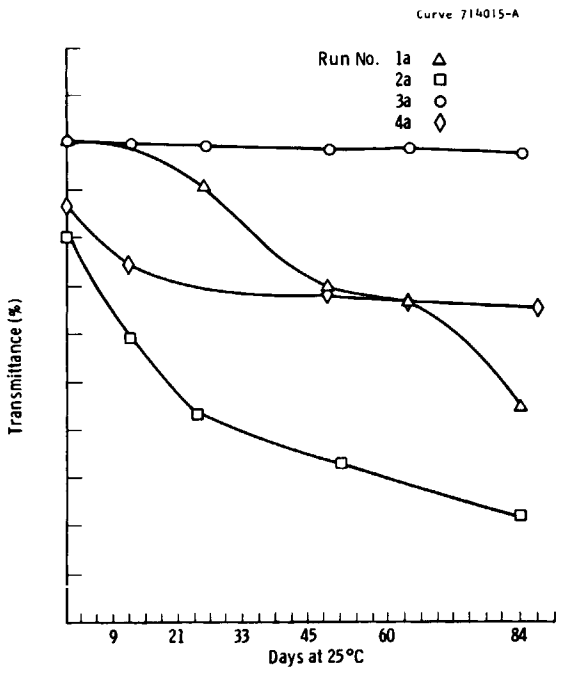

Figure 3 Visible spectrum of reaction products (at 610 nm) from Table II (Runs 1–4a).

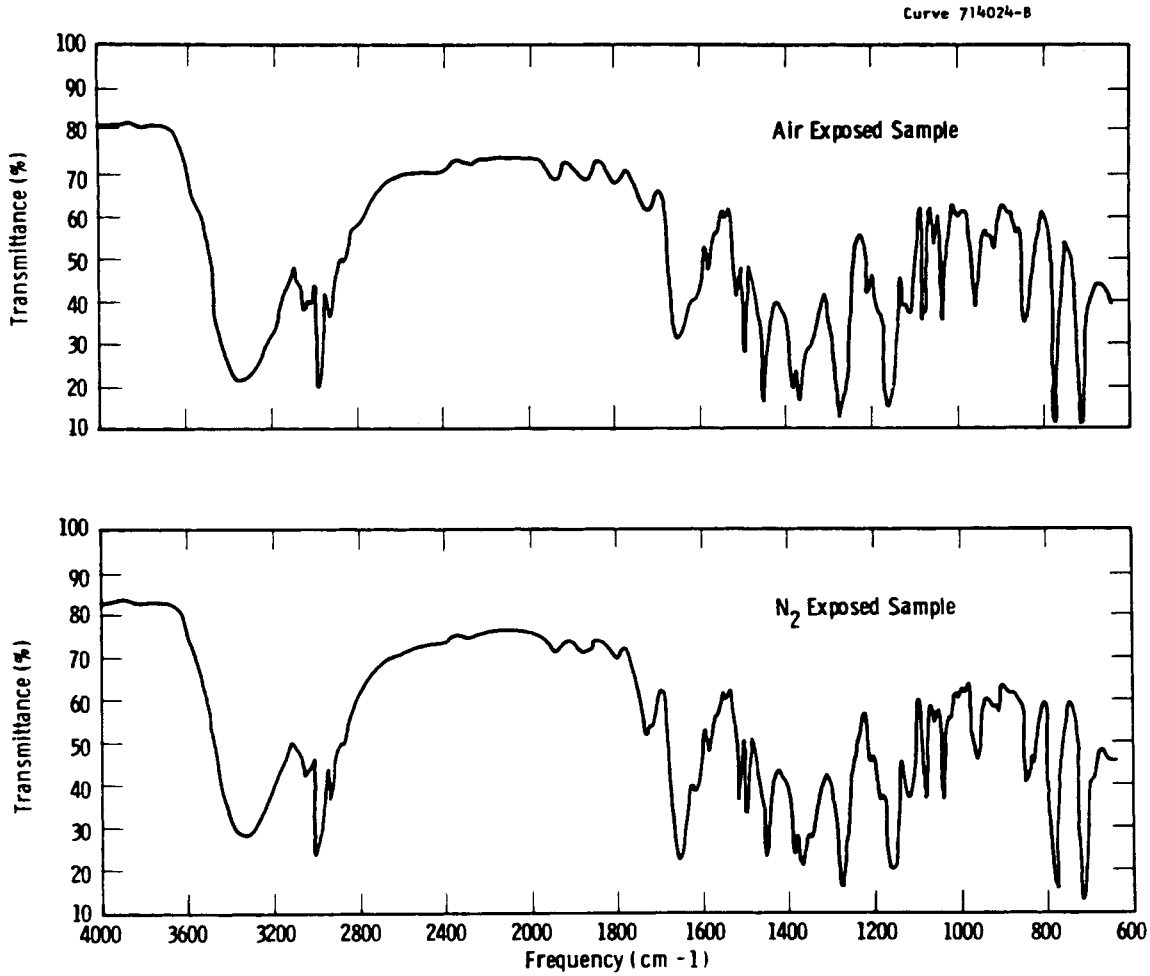

Figure 4 Infrared spectra of reaction products from Table IV (Run 1c) after 9 days: top—air sample; bottom—N_2 sample.

ones. The difference in these two solutions was that one contained 10% more N,N-DMpT than the other. An evaluation was made to determine the solubility and the degree of polarity of each component for the purpose of choosing a solvent system that would yield the maximum separation of all components. HPLC was performed using iso-octane with 10% dioxane as the mobile phase and 10 μ silica gel as the stationary phase. The chromatograph was run several times before it was decided to perform the analysis at wavelengths of 254 and 320 nm. The HPLC experimental data are summarized in Table V and Figures 8–12.

The use of an organic acid (acetic acid) was incorporated into Runs 6c, 7c and 8c (Table IV) to evaluate the effect of increased acidity on the CHP decomposition rates. The acid was introduced as various percentages of the amount of inert solvent being used as shown in Table IV. This system was the same as the model initiation system except for the addition of the acetic acid. This "model" solution (150 mL) was stored in the dark, while another 100 mL was being sparged with nitrogen. Twenty-five milliliters of both the air and nitrogen samples were poured into separate glass cuvettes for comparative visible spectroscopy studies. Later, 10 gm aliquots of the air and nitrogen samples were transferred to aluminum dishes and placed in the hood to evaporate the inert solvent. Smears for infrared studies were prepared from the residues of each.

Infrared spectra were also obtained for several experimental runs evaluating storage time, inert solvents, and organosulfur materials in air and nitrogen environments. All the data collected were evaluated with reference to the rate of decomposition of CHP. In the infrared range, the most significant absorptions for CHP occur at 3450 cm^{-1} and 1200 cm^{-1}. Due to the interference of other components

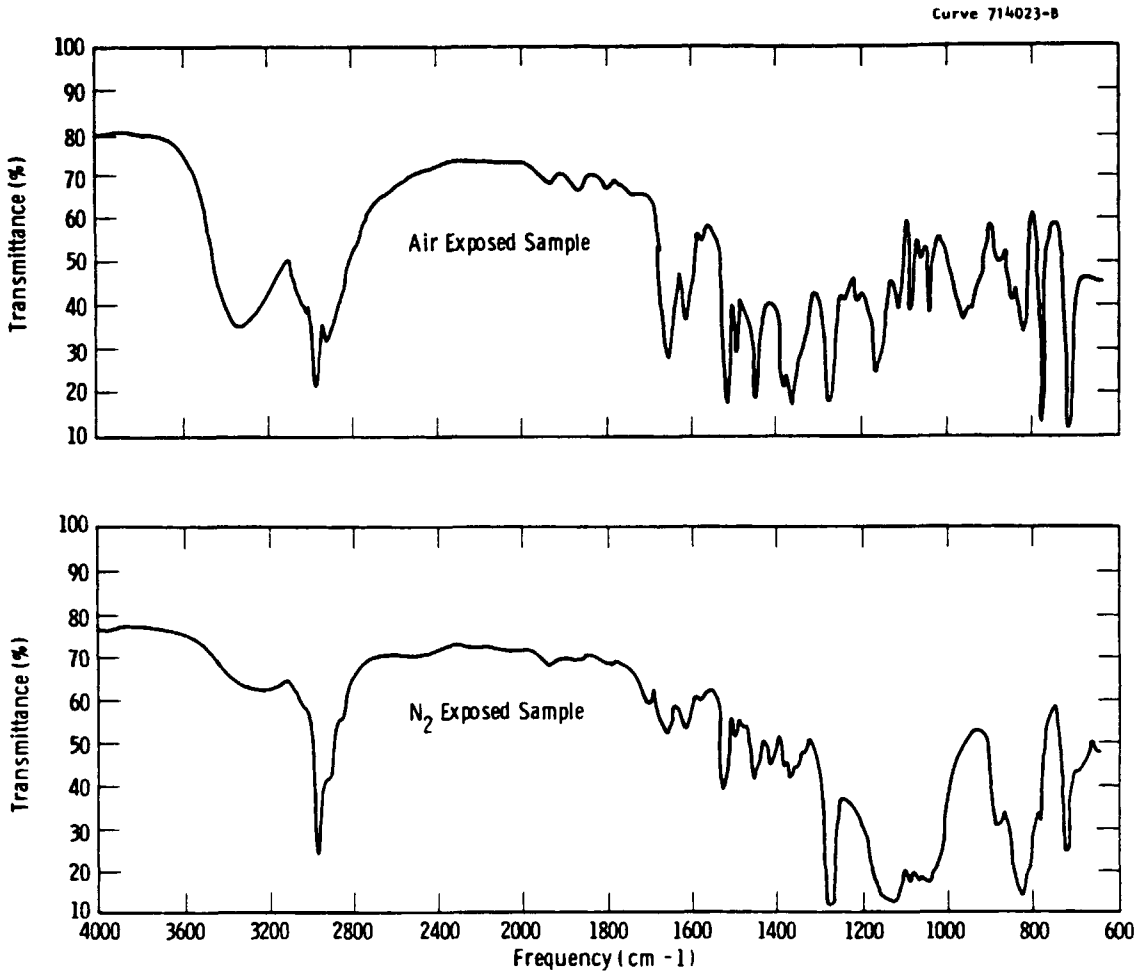

Figure 5 Infrared spectra of reaction products from Table IV (Run 2c) after 3 days: top—air sample; bottom—N_2 sample.

present, that is, N,N-DMpT and BS, the CHP absorption band at 1200 cm^{-1} was found unreliable and, therefore, was not used in evaluating CHP decomposition rates.

Aging Solutions in Ambient Air

In an attempt to investigate the interaction between components during storage, several solutions were prepared and stored over a period of time (Table II). Some substantial color changes occurred overnight with some of the samples. These color changes indicated the degree of CHP decomposition and the instability of the components during storage. It was assumed that color intensity was directly proportional to the CHP decomposition. Those solutions that were visibly colored were monitored at 610 nm using visible spectroscopy.

RESULTS

The visible spectrophotometer had been chosen as an additional instrumental technique for studying the kinetics of these anaerobic systems since it was hoped that these data would supplement those obtained via infrared spectroscopy. Visible spectroscopy was used to evaluate the reactivity of four formulations, prepared in Table II, in the storage stability studies (Fig. 3). These four formulations were different combinations of a six-component anaerobic resin (Table II). Resins *not* containing N,N-DMpT remained stable or gained stability after a short period of time as shown by the significant changes in absorption at 610 nm (Fig. 3, Runs 3a and 4a). By contrast, formulations containing N,N-DMpT never gained stability (Fig. 3, Runs 1a and 2a). The instability was greater when both CHP and N,N-DMpT were present than with N,N-DMpT alone.

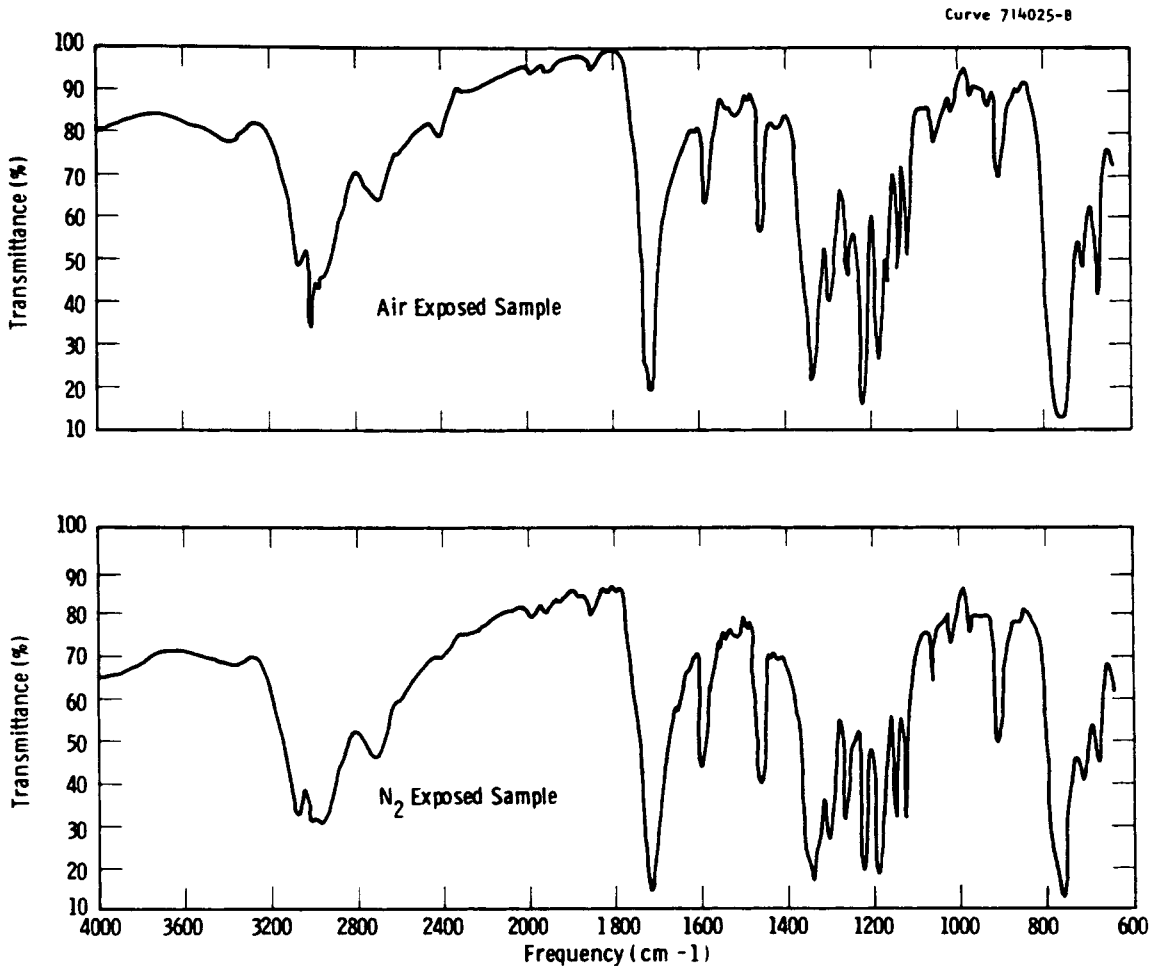

Figure 6 Infrared spectra of reaction products from Table IV (Run 2c) after 5 days: top—air sample; bottom—N_2 sample.

This prevailed even in the absence of the organosulfur coaccelerator BS.

The experiments 1c–4c (Table IV) were carried out to evaluate different reaction solvents. In these runs, the concentrations of components were constant while the durations of nitrogen sparging and air storage, and the type of inert solvent were varied. This evaluation was carried out mainly to obtain an inert solvent in which BS would be more soluble than in toluene. Preliminary experiments revealed that BS was more soluble in diacetone alcohol and methyl cellosolve acetate than in toluene. Diacetone alcohol also proved to be a better solvent for anaerobic curing resins on examination by visible and infrared spectrophotometry, since the rate of CHP decomposition was found to be greatly increased in this solvent. However, subsequent testing showed that there was an equal amount of decomposition and reactivity in the air sample. Diacetone alcohol absorptions obscure the 3450 cm^{-1} region of the infrared spectrum so the visible spectral technique described earlier was used for preparing a sample containing diacetone alcohol. The results indicated that the alcohol was probably reacting with the initiation system components through the -OH groups thereby interfering with the system reaction kinetics. This was evidenced by rapid color changes in the reaction solutions which were initially mistaken as being due to CHP decomposition. It was also established that the decomposition rate and reactivity of CHP in methyl cellosolve acetate was less than that of CHP in toluene. Based on infrared and visible spectrophotometry, no acceptable inert solvent has been found to replace toluene to date.

The HPLC data (Figs. 8–12) agreed with the results and interpretations reached during the course of infrared spectral studies. Because the BS concentration remained constant in the model resin system, it was used as a base reference for the other components in the air-stored versus nitrogen-stored

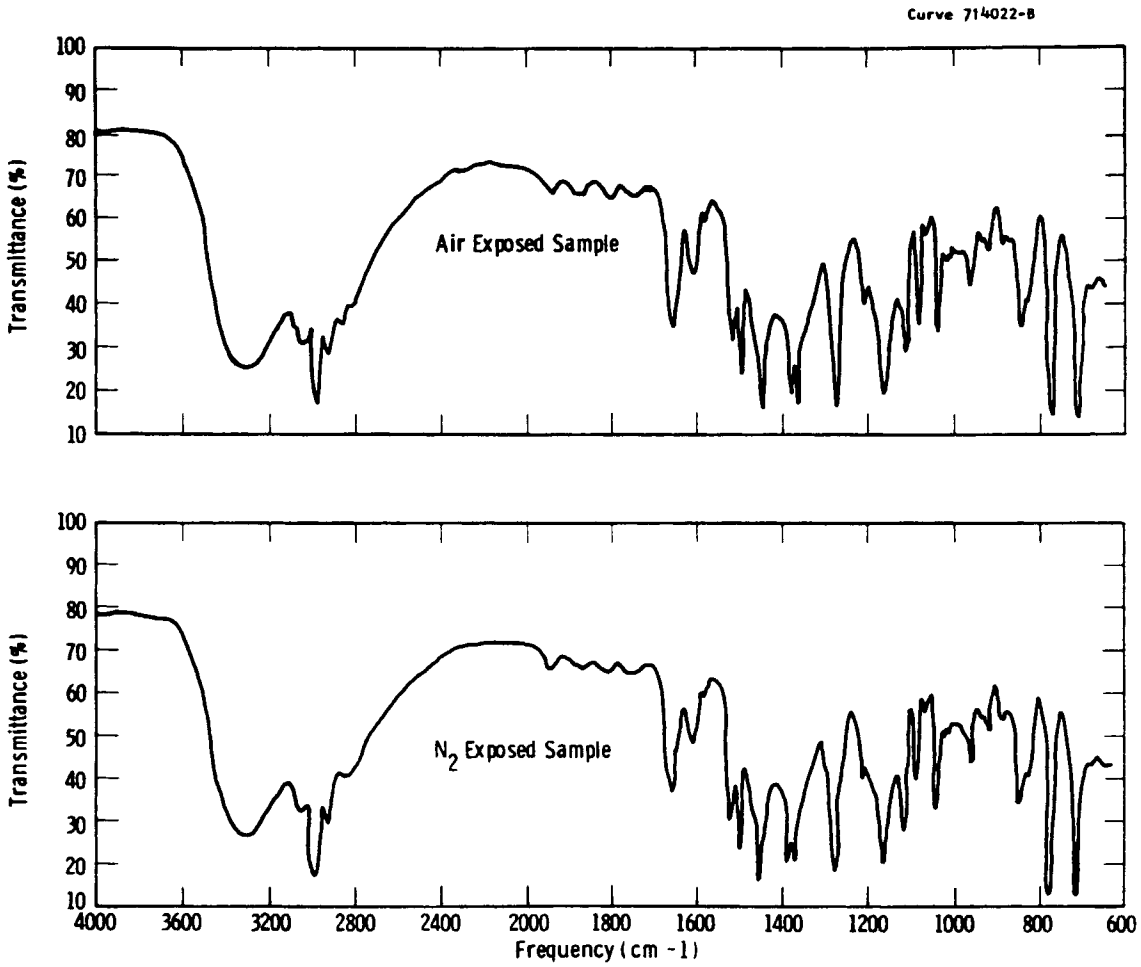

Figure 7 Infrared spectra of reaction products from Table IV (Run 3c) after 5 days: top—air sample; bottom—N_2 sample.

samples (Table V). It was found that in the case of Run 1c (Table IV), there was 30% less CHP in the nitrogen sample than in the air-exposed one. In the same run, no residual N,N-DMpT could be found in the nitrogen sample. The formation of several new products as well as an intensification of color were also detected in the nitrogen-exposed sample. In the air sample, the color intensified at a much slower rate. Also, there were no new reaction products found in the air-stored sample.

Because of the total depletion of N,N-DMpT found in Run 1c (Table IV), a second model system was prepared (Run 5c) with a ten-fold increase in the amount of N,N-DMpT. This was done to determine the limiting reactive component in the system. It was found that there was a 51% decrease in the amount of N,N-DMpT in this system over five days under N_2 (Figs. 10–12). It is reasonable to predict a greater decrease would have occurred had the sample been stored for nine days as the previous samples were (Figs. 8 and 9). These HPLC data suggest that the N,N-DMpT is the limiting reactive component and is consumed during the initiation step of anaerobic cure.

DISCUSSION

Careful examination of the IR spectral data (Figs. 4–7 and 13–18) reveal that in many cases, the reactive species produced, for a given "model" system, in a N_2-sparged environment are very different to those produced in air. This is particularly apparent in Figures 5, 16, and 17. In these instances, very noticeable differences are observed between the N_2 and air samples. The IR spectra in Figures 4, 6, 7, and 18 show less distinctive differences but even with these latter spectra, minor absorption band variations can be detected between the anaerobic and aerobic samples.

The spectral variations described above probably indicate not only differences in the initiation mechanisms in these systems, but also differences in the

Table V Retention Distance and Peak Heights for Figures 11 and 12 (High Performance Liquid Chromatographic Data)

Retention Distance (cm)	Air Peak Ht. (cm)	N_2 Peak Ht. (cm)	Identification
0.5	0.29	—	CHP (impure)
1.1	off scale	off scale	Toluene
1.55	1.87	—	N,N-DmpT
1.85	1.23	1.16	
2.00	0.29	—	
2.18	0.48	0.83	
2.44	0.89	0.87	
2.98	1.51	1.00	CHP
5.60	1.00	1.00	BS
6.60	0.06	0.09	
10.45	0.71	—	
11.20	—	1.02	

termination processes occurring with the various reactive intermediate species. This is particularly likely in the presence of air since O_2 is a well-known terminator for certain types of reactive species.

In some of the experiments, for example, the IR spectra in Figure 5, there is some evidence that sol-

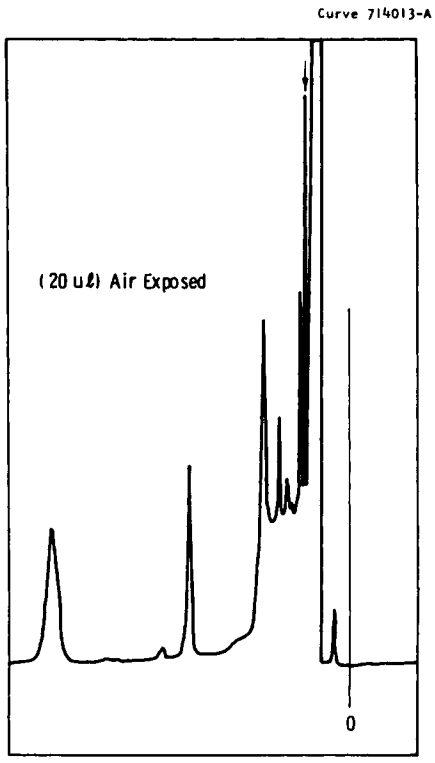

Figure 8 High performance liquid chromatograph of reaction products from Table IV (Run 1c) after 9 days (air sample).

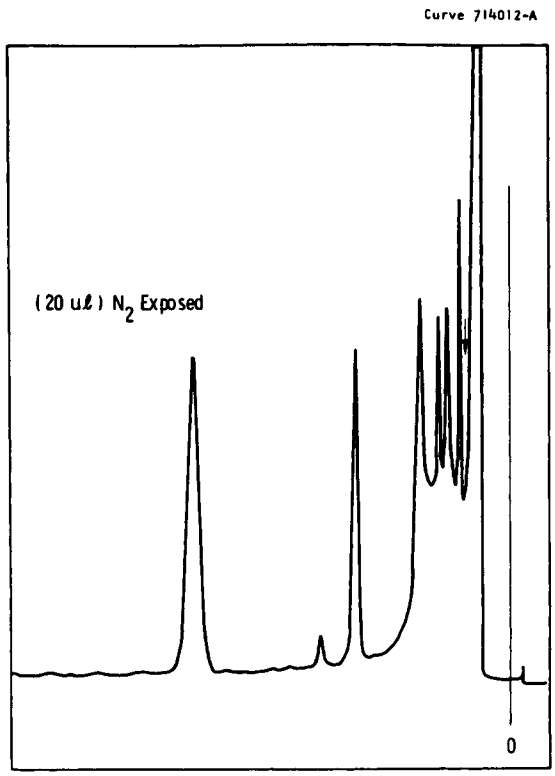

Figure 9 High performance liquid chromatograph of reaction products from Table IV (Run 1c) after 9 days (N_2 sample).

vent participation in the reaction kinetics is definitely occurring as shown by the enhanced absorption at 3400 cm^{-1} and 1000 cm^{-1} for the air exposed sample. This is presumably from hydroxy (OH) absorption bands in the reaction products, suggesting that the solvent (diacetone alcohol) is reacting with the initiation species and thereby being incorporated into the final reaction products.

The extreme complexity of the spectral patterns for the IR curves make detailed interpretation for each experiment very difficult. However, the IR spectral patterns in Figures 4–7 and Figures 13–18 contain a wealth of kinetic information and detailed interpretation is presently being attempted. So far, the IR spectral data indicate, in almost every experiment, that very different reactive species are produced in the aerobic and anaerobic samples.

The visible spectra shown in Figures 13–15 are also of great interest. These spectra were obtained in Runs 7c and 8c (Table IV) in which acetic acid was added to the toluene solvent to increase the acidity of the reaction solution. The main absorption bands for the air and N_2 samples, for both these runs, show very interesting differences. In Figure 13, the air-exposed sample exhibits (N_2) sample,

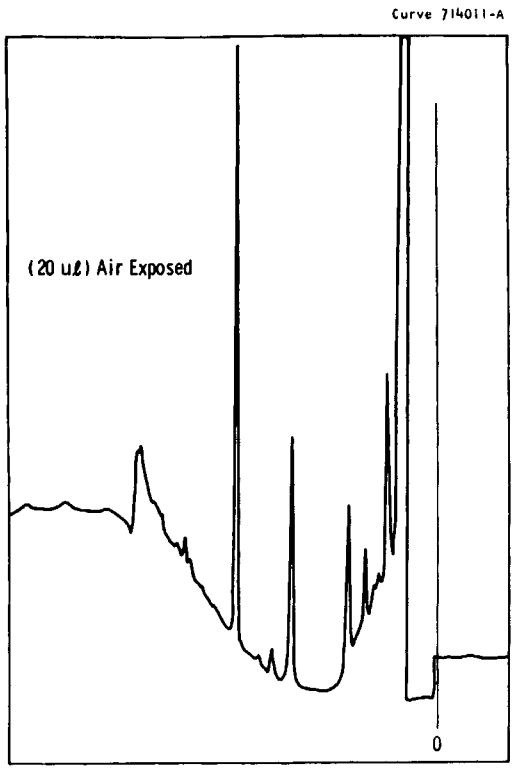

Figure 10 High performance liquid chromatograph of reaction products from Table IV (Run 5c) after 5 days (air sample).

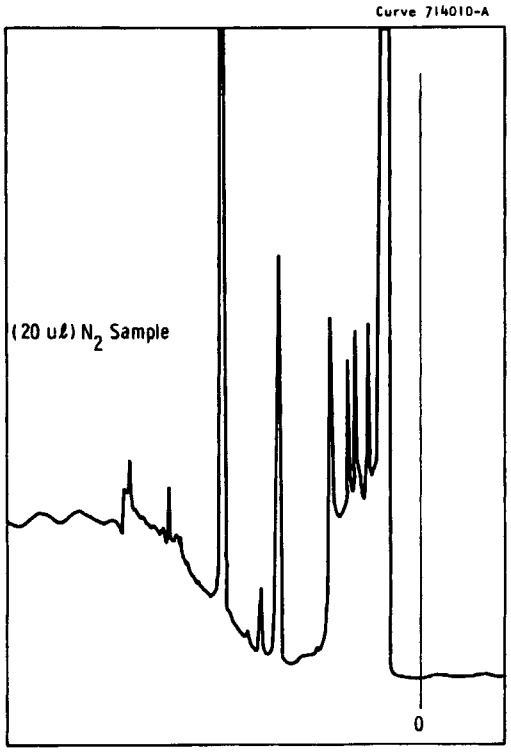

Figure 11 High performance liquid chromatograph of reaction products from Table IV (Run 5c) after 5 days (N_2 sample).

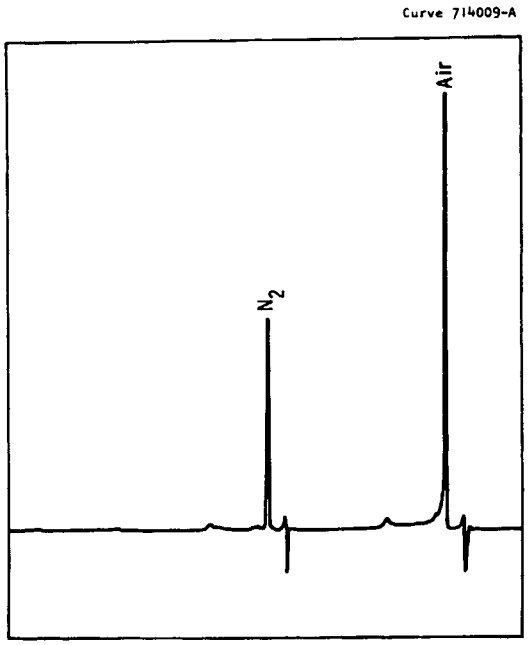

Figure 12 High performance liquid chromatograph of N,N-DmpT (air + N_2) from Table IV (Run 5c).

initially, shows a noticeable band at 475–525 nm. This is also shown in Figure 14 for Run 8c where the samples were spectrally analyzed after storing for 8 h at room temperature. However, as shown in Figure 15, after 24 hours, the visible spectrum for the anaerobic sample has changed appreciably with the absorption band at 475–525 nm being barely detectable. By contract, the aerobic (air) sample exhibits almost the same spectral trace after 24 h as it did after 8 h. At the end of 32 h, the spectrum for the anaerobic sample is changed even further, as shown in Figure 15, with a new (weak) absorption band appearing at 525 nm to 550 nm and an even stronger absorption occurring beyond 575 nm.

The changes in the visible spectrum shown in Figures 13–15 give conclusive evidence that the initiation mechanisms (or CHP decomposition kinetics) are significantly different in aerobic (air) and anaerobic (N_2) environments. Further, the intermediate species produced under anaerobic conditions are more reactive than those occurring in air, as demonstrated by the rapid changes for the visible spectra shown in Figures 14 and 15 over a 32-h period.

Visual observations indicated that these solutions (both the aerobic and anaerobic) underwent a series of interesting color changes. The initial solution color was yellow, but within a few hours, both solutions had changed to a purple color. The nitrogen sparged solution remained purple until it was ex-

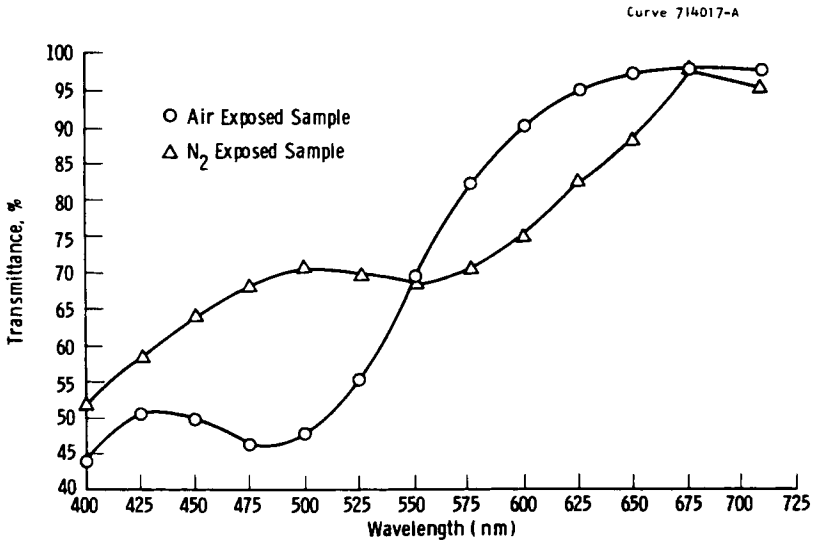

Figure 13 Visible spectra of reaction products from Table IV (Run 7c) after 24 h.

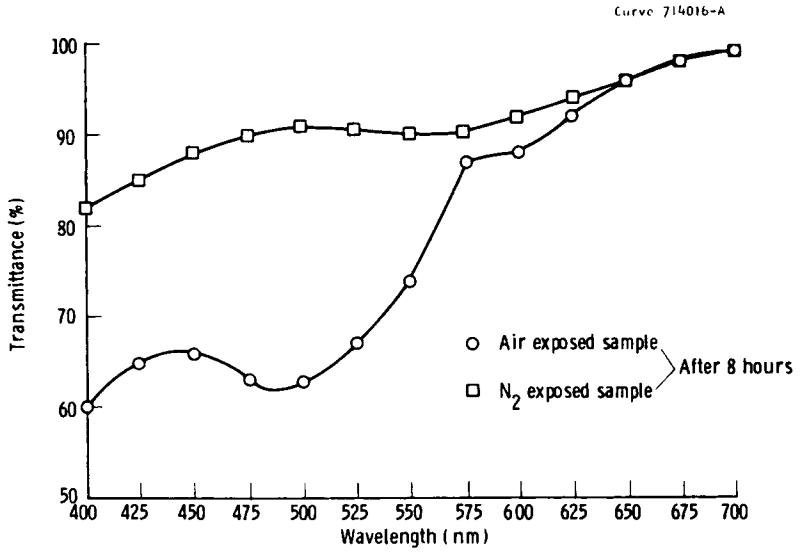

Figure 14 Visible spectra of reaction products from Table IV (Run 8c) after 8 h.

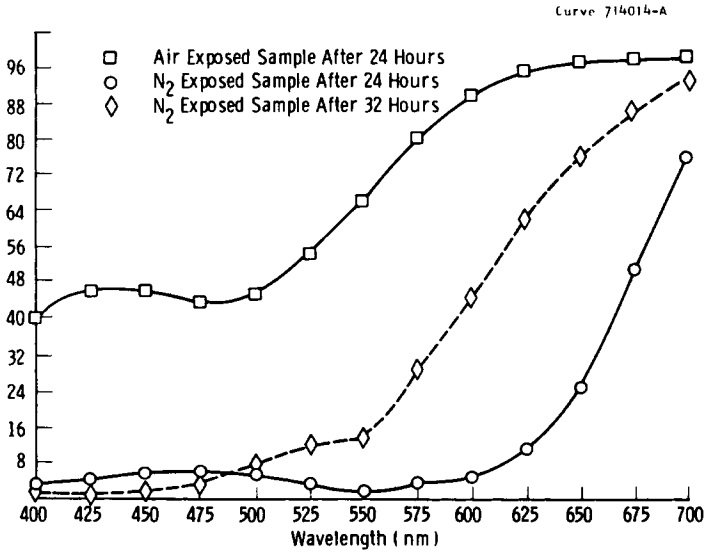

Figure 15 Visible spectra of reaction products from Table IV (Run 8c) after 24 h.

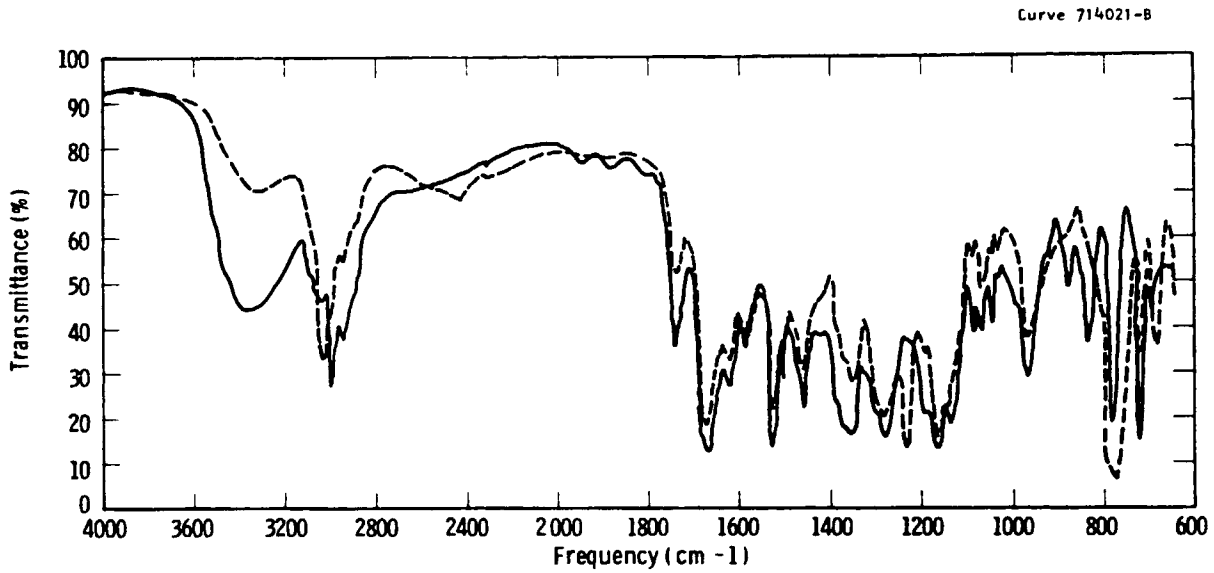

Figure 16 Infrared spectra of reaction products from Table IV (Run 6c) overnight: —— air sample; --- N_2 sample.

posed to air, at which point it changed to a reddish-orange color; the air sample had become this color a few hours after its first color change.

The various rapid color changes produced in this group of experiments, suggest the formation of radical-ionic species rather than the normally expected free-radical intermediate produced from CHP decomposition. It is a well-known phenomenon in polymerization kinetics that radical ionic species (e.g., radical-cations and radical-anions) will produce brightly colored intermediate species in solution.[17] The Szwarc living polymers are examples of this.[18,19] Free radicals are not normally known to produce colored species absorbing in the visible part of the spectrum.

The HPLC experimental data described previously indicated that N,N-DMpT was depleted during initiation while BS was not. This leads one to the conclusion that the colored radical-ionic species must be derived from N,N-DMpT. (These species are unlikely to be formed from CHP or its decomposition fragments). Attempts are now being made to identify the radical-ionic species derived from N,N-DMpt.

The presence of air (or O_2) would probably prevent the formation of or destroy these radical-ionic

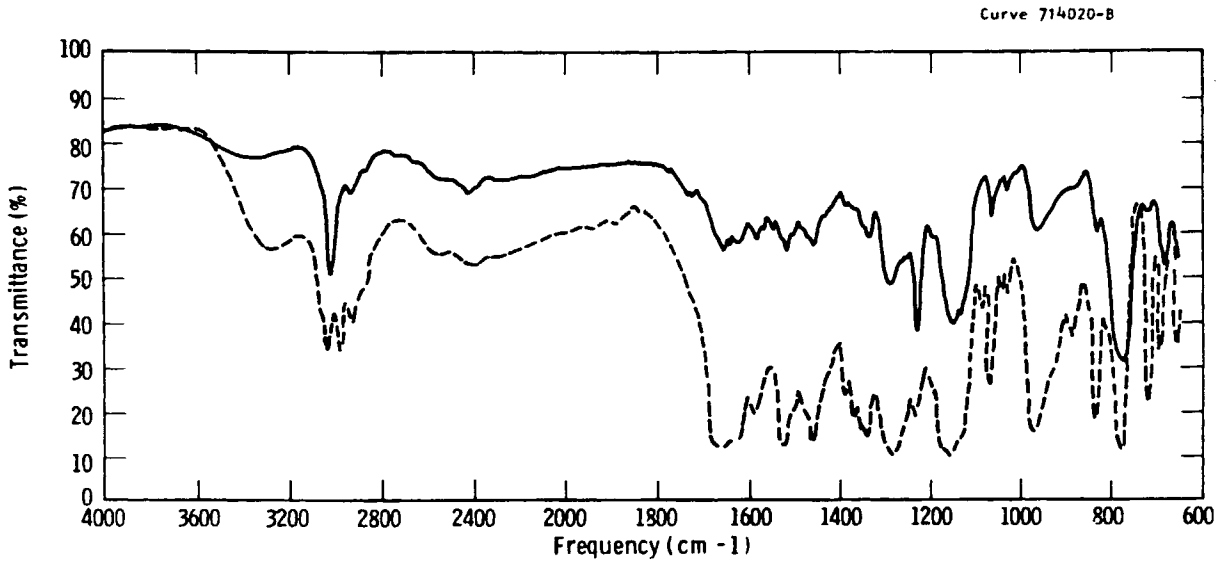

Figure 17 Infrared spectra of reaction products from Table IV (Run 7c): —— air sample; --- N_2 sample.

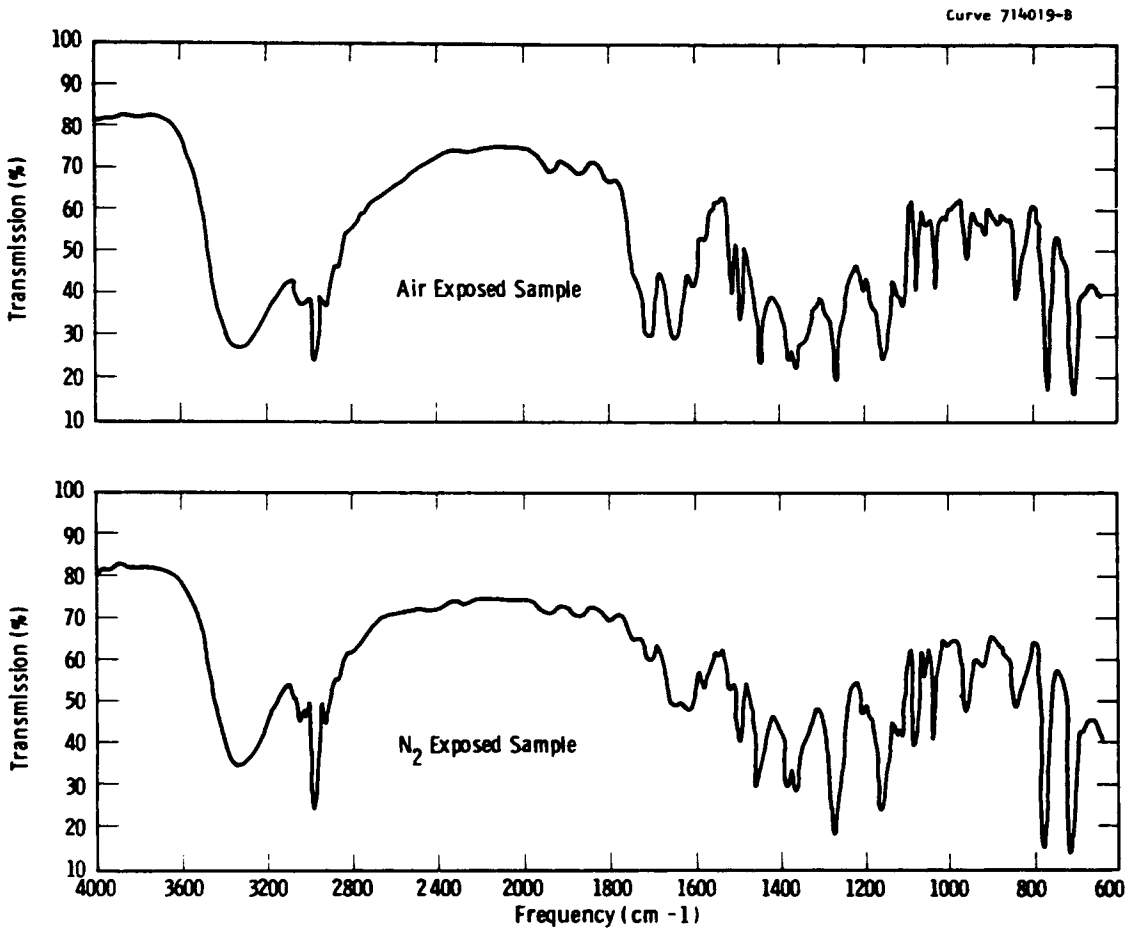

Figure 18 Infrared spectra of reaction products from Table IV (Run 8c) overnight: top—air sample; bottom—N_2 sample.

species, thereby preventing initiation of polymerization under aerobic conditions.

INITIATION MECHANISM

Although it is somewhat premature to postulate exact mechanisms for the initiation reaction involved in these anaerobic systems, there is already some indication as to the nature of the more important molecular interactions involved.

The initiation reaction obviously involves the decomposition of the cumene hydroperoxide, under anaerobic conditions, to form reactive free radical species which are able to initiate polymerization of monomer. This decomposition reaction can be simply stated as follows:

$$R^{\cdot} + H^{\cdot} + O_2 \underset{O_2}{\overset{N_2}{\rightleftharpoons}} ROOH \underset{O_2}{\overset{N_2}{\rightleftharpoons}} RO^{\cdot} + {}^{\cdot}OH$$

$$N_2 \Big\| O_2$$

$$ROO^{\cdot} + {}^{\cdot}H$$

The role of the nitrogen (either flow or pressure) would appear to be one of removing oxygen and moving the equilibrium towards the free radical formation side.

In the presence of a tertiary amine such as N,N-DMpT, and an organosulfur compound like benzoic sulfimide (BS), the mechanism could very probably proceed as follows:

$$P + A \rightarrow [P^{-}A^{+}] \xrightarrow{N_2} [P^{-}A^{+}] + S \rightarrow R^{\cdot}_{+} \text{ or } R^{\cdot}_{-} \rightarrow \text{Polymer Formation}$$

charge-transfer complex formation

initiating free radicals or radical-ions

P = organic peroxide or hydroperoxide (CHP)

A = tertiary amine (N, N-DMpT)

S = organo-sulfur compound (BS)

Complex formation between a tertiary amine and a hydroperoxide, such as CHP, is a likely possibility.[20,21] This charge-transfer complex, for the most part, would be stable under ambient conditions, al-

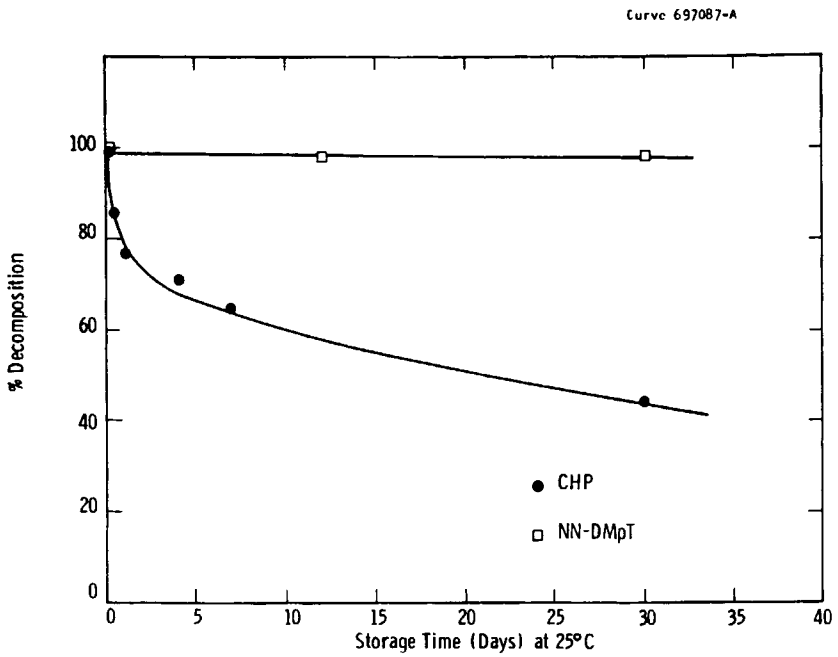

Figure 19 Decomposition rates of 1 : 1 CHP/N,N-DMpT solutions in toluene (from IR data).

though the experimental data obtained on *aged* samples (Fig. 19) suggest that a *slow* decomposition of hydroperoxide might be occurring at room temperature.

However, in freshly prepared samples, the amine–hydroperoxide complex is stable enough to play a major role in the initiation mechanism. Interaction between this amine–hydroperoxide complex and an organosulfur compound, like benzoic sulfimide, leads to dissociation of the complex and rapid decomposition of the hydroperoxide to reactivate radical species. This latter reaction step essentially occurs only under anaerobic conditions, thereby suggesting that the function of oxygen (or air) would be that

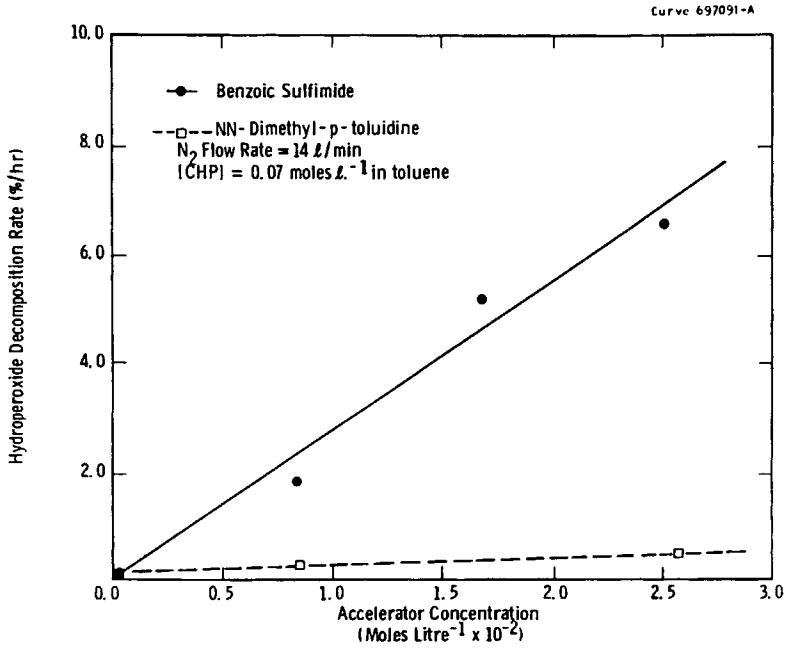

Figure 20 Effect of accelerator concentrations on cumene hydroperoxide decomposition rates.

of stabilizing the amine–hydroperoxide complex or perhaps of inhibiting the interaction of the organosulfur compound with this complex.

The rate determining step in the initiation reaction is probably the rate at which the organosulfur compound brings about dissociation of the cumene hydroperoxide–amine complex. This effect is very strongly suggested by the experimental data shown in Figure 20. If this effect is genuine, then obviously the gel times of anaerobic curable resins could be appreciably improved by using organosulfur compounds more reactive than benzoic sulfimide. Such interactions between hydroperoxides and organosulfur compounds have been described in the scientific literature.[22-25]

It is intriguing to postulate the exact role of the tertiary amine, N,N-DMpT, in these anaerobic resin systems. In doing this, it is important to distinguish between freshly prepared samples of resin and aged ones. In the freshly prepared materials, the N,N-DMpT appears to be necessary to give acceptable gelation times under anaerobic cure conditions. This has been shown by conducting experiments without N,N-DMpT, where extremely slow gel times are found. However, as mentioned previously, the N,N-DMpT appears to be responsible for causing a slow decomposition of hydroperoxide during storage, thereby effecting a loss in gelation reactivity in anaerobic formulations.

Humphreys[26] has identified peroxyamines and aryl-substituted secondary amides as being among some of the major products resulting from the reaction between N,N-DMpT and CHP, although it should be pointed out that the reactions were carried out at a considerably higher temperature (100°C) than for the work reported here.

Finally, it should be mentioned that possible transfer reactions with monomer and the monomer radical have not been considered with this present model initiation system. Work is now under way, using anaerobic initiation systems with various acrylic monomers, to evaluate the propagation and termination stages of these polymerization processes. The results of this particular study will be reported in the near future.

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