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**EFFECT OF ESTER IMPURITIES IN PMR-POLYIMIDE RESIN**

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# EFFECT OF ESTER IMPURITIES IN PMR-POLYIMIDE RESIN

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## ABSTRACT

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Spectral and chromatographic studies were conducted which established the presence of tri- and tetraester impurities in aged monomer solutions employed in fabrication of PMR-polyimide resin composites. The equilibrium constant and apparent rate of the esterification were determined. It was demonstrated, using differential scanning calorimetry, that the ortho-ester moiety of these impurities does not completely react at typical cure conditions. It is concluded that voids formed in composites fabricated with aged monomer solution are due to gaseous decomposition products evolved by ester impurities and/or unreacted amine during elevated temperature post-cure treatment.

## INTRODUCTION

The purpose of this investigation was to identify the factors responsible for void formation in PMR-polyimide resin composites fabricated with aged monomer solutions. The high temperature resistant, addition-type, polyimide resin system (designated PMR) developed at Lewis Research Center (Ref. 1) was found to exhibit excellent fabrication characteristics for making low void, high performance composite materials. However, problems appeared during a program (Ref. 2) to develop fabrication technology for a composite fan blade employing the PMR resin. Non-reproducible properties (mechanical strength and thermal stability) due to void formation were observed after elevated temperature post-cure treatment (up to 16 hours at 344<sup>o</sup> C) of the composites.

The in situ PMR approach for synthesis of thermally stable polyimides employs three monomeric reactants (Fig. 1): monomethylester

of 5-norbornene-2,3-dicarboxylic acid (NE), 4,4'-methylenedianiline (MDA), and dimethylester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE). The reaction is postulated to follow the path indicated in Fig. 1. Initially, short chain polyamide-acids are formed on the reinforcing fibers; subsequently, water is eliminated to form the desired polyimide structure. Final curing occurs by addition polymerization of the norbornenyl endcaps to form the crosslinked structure. The ideal time/temperature/pressure sequence for curing the resin is predicated on completion of the condensation reactions to form the imide prior to the final addition crosslinking. This permits the evolution of condensation products (methanol and water) before the viscosity of the resin greatly increases due to formation of the crosslinked network.

The PMR resin is employed as a high-solids content methanol solution of the monomers. Because both MDA and NE can be commercially obtained as well characterized solids, they can be introduced into the resin reproducibly. In earlier studies (Refs. 1, 3) employing the resin, the BTDE was isolated as a solid. However, the difficulties with isolating the isomer mixture in large quantities led to the direct use of methanol solutions of the monomer for preparation of the resin. The preparation or purchase of bulk quantities of BTDE/methanol solution led in turn to more extended periods of storage prior to use. It was ultimately observed (Ref. 2) that the presence of voids in post-cured composite samples could be correlated with the use of aged BTDE solutions, and this prompted the more detailed study of the PMR resin system described in this report.

## EXPERIMENTAL

Reagents. - The monomethylester of 5-norbornene-2,3-dicarboxylic acid (NE), melting point 97 to 100<sup>o</sup> C, the 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), melting point 215 to 217<sup>o</sup> C, and the 4,4'-methylenedianiline (MDA), melting point 90 to 91<sup>o</sup> C, were commercially available materials used without further purification. Anhydrous, electronic grade methanol was employed. The tetramethylester

of 3, 3', 4, 4'-benzophenonetetracarboxylic acid (BTTE), melting point 93 to 94<sup>o</sup> C, was prepared by refluxing BTDA in methanol for two hours, then bubbling dry HCl through the solution for one hour to force the reaction to completion. The methanol was removed at reduced pressure and the product recrystallized in heptane/ethyl acetate (2:1).

Monomer solutions. - The solutions employed in this study were selected from bulk working solutions prepared for use in composite fabrication. These solutions were, with one exception, prepared by refluxing BTDA in methanol for approximately two hours. The solutions were formulated to give 50 weight percent BTDE at the end of the reaction. Samples were stored at ambient conditions in closed plastic containers (loss of methanol during extended periods of storage appeared minimal). The unique sample was commercially prepared and was 85 weight percent BTDE in methanol.

Instrumental measurements. - Nuclear magnetic resonance spectra were obtained on a commercial, 60 MHz, continuous wave instrument. Data were referenced to internal tetramethylsilane. Sample solutions were diluted approximately four fold with deuterio-chloroform for the measurements. Due to the high methanol concentration, the spectra exhibited some inconsistencies in chemical shift. All data was electronically integrated. Solutions of thermally reacted binary mixtures of monomers were prepared in perdeuterodimethylsulfoxide (DMSO).

High pressure liquid chromatography was performed on a micro-particulate reverse phase column (column: 2.2 mm x 25 cm; packing: bonded hydrocarbon on 10 micron silica). Constant volume syringe pumps were employed at 150 ml/hr. Spectrophotometric detection was employed at 254 nm wavelength with a sensitivity of 0.5 absorbance units full scale. Sample solutions were diluted approximately forty fold with methanol and injections of about 1 microliter were made using the stop/flow technique. Composition of the solvent was varied continuously from 100 percent water to 100 percent methanol. The gradient program was: 100 percent water for one minute; addition of methanol at 5 percent per minute for two minutes; and addition of methanol at 10 percent per minute for nine minutes.

Differential scanning calorimetry (DSC) was performed on a

commercial thermal analysis unit employing a high pressure DSC attachment. Sample size was approximately 5 mg. Aluminum sample pans were employed; the pans were covered, but not crimped closed. A heating rate of  $10^{\circ}$  C per minute was used for all runs. A static pressure of approximately  $3.8 \times 10^5$  N/m<sup>2</sup> (55 psi) of dry nitrogen was maintained over the sample.

Infrared spectral measurements were made on a commercial, double-beam spectrometer. PMR resin was cast as a film on a NaCl salt plate for spectral monitoring. The plate was placed in an air circulating oven at  $204^{\circ}$  C and removed intermittently for spectral measurements.

## RESULTS AND DISCUSSION

### Analysis of Ester Impurities

Solutions of the monomer BTDE are formed by reacting the dianhydride, BTDA, in methanol as shown in the first step of Fig. 2. It was generally assumed that only the first step of the reaction sequence shown in Fig. 2 was of significance because the rate of additional esterification is slow. While this assumption may be reasonable for short times, the presence of the higher ester impurities (tri- and tetraester) in a BTDE solution (85 weight percent) aged for 19 months is demonstrated by the liquid chromatogram shown in Fig. 3. The reverse phase separation adequately resolved the three major chemical constituents in the solution. The principal component, the diester, elutes very quickly; two partially resolved peaks due to the isomers of the triester elute after approximately 6 minutes; and, the tetraester elutes last. The elution times for the di- and tetraesters were verified by direct comparison with chromatograms of the pure components. The triester was not isolated, but the assignment is based on: (1) elution time - this component should be bracketed by the di- and tetraesters because of the relative number of polar groups in this series; and (2) relative intensity of the elution peak - assuming similar extinction coefficients for the tri- and tetraesters, there should be (statistically) twice as much tri- as tetraester. Because the

triester was not isolated, its extinction coefficient was not determined and the liquid chromatography data was not analyzed quantitatively. At the experimental conditions employed for these measurements, no higher ester impurity was observed in BTDE solutions which had been aged for one month.

The nuclear magnetic resonance spectra provided a more convenient basis for documenting quantitatively the formation of the higher esters with time. The general features of the spectra were: (1) a complex multiplet due to the phenyl protons of the substituted benzophenone compounds centered near 8 ppm; (2) a broad singlet exhibiting variable chemical shift (5 to 7 ppm) due to the labile protons (ROH, H<sub>2</sub>O); (3) a sharp multiplet at 4 ppm due to the methylester protons; and (4) a sharp singlet at 3.3 ppm due to the methyl protons of methanol. The aged solutions did show additional peaks in both the phenyl and the methylester multiplets although, qualitatively, the spectra did not change dramatically because of peak overlap.

Shown in Fig. 4 is a comparison of the spectra for the pure diester (Fig. 4(a)) and an aged BTDE solution (Fig. 4(b)). Neither the phenyl multiplet nor the methylester multiplet was completely resolved at the experimental conditions employed. This did not prevent quantitative analysis of the data, however, because the total integrated peak areas for each multiplet provided sufficient information to determine the equilibrium constant and apparent rate of the esterification. The expected trend in total peak area for the multiplets can be seen in the integral curves shown in Fig. 4. When the areas are normalized to 6 for the phenyl multiplet (six protons on each substituted benzophenone), we see (Fig. 4(a)) that the peak area of the methylester multiplet for the pure diester is 6 (as expected for six protons on the two ester groups). For the pure tetraester, the area would be 12 (expected for four methylester groups). Necessarily, the triester or mixtures of di-, tri-, and tetraesters present in an aged BTDE solution would show normalized peak areas between 6 and 12 (Fig. 4(b)). The normalized peak area indicates the average number of methylester protons per molecule in the sample, or three times the average number of methylester groups. The normalized peak areas and average number of methylester groups per molecule are given in Table I

for five solutions of varying age. The trend in these data can be better seen graphically in Fig. 5. Again we see that, at these experimental conditions, higher esters were not detected until one month of storage time had elapsed. The point at 21 months was calculated from the equilibrium constant discussed below and the time was assigned by extrapolation of the short time data points. Based on this calculated end-point for esterification in a 50 weight percent solution of BTDE, the apparent half-time for the reaction is estimated to be in excess of eleven months.

The actual rate of the reaction will be sensitive to the pH of the solution, and this must change significantly during the course of the reaction as acid is consumed and water is generated. The contribution of this factor was not examined.

The magnetic resonance integral data were also used to calculate actual concentrations of the additional ester formed. For the oldest solution tested (the 85 weight percent solution, stored for 19 months), it was assumed that equilibrium had been established and the concentration data were used to calculate the equilibrium constant for the net reaction:



The equilibrium constant,  $K$ , is defined in terms of known concentrations as:

$$K = \frac{([E] + [HE])([H_2O])}{([A] - [HE])([CH_3OH] - [HE])}, \quad (2)$$

where

[A] = initial concentration of available acid groups  
 =  $2 \times [\text{BTDE}]$

[E] = initial concentration of ester groups  
 =  $2 \times [\text{BTDE}]$

[CH<sub>3</sub>OH] = initial concentration of methanol



$[\text{HE}]$  = concentration of higher ester groups formed

= concentration of acid groups consumed

= concentration of methanol consumed

$[\text{H}_2\text{O}]$  = concentration of water formed

=  $[\text{HE}]$

For the 85 weight percent solution, the initial molar concentrations were.  $[\text{BTDE}] = 0.22 \text{ M}$  and  $[\text{CH}_3\text{OH}] = 0.47 \text{ M}$ . The integral data from the nuclear magnetic resonance spectrum of the solution indicated 2.7 methylester groups per molecule which means that, on the average, 0.7 of the two available acid groups has reacted. Thus, the fraction of available acid groups reacted,  $0.7/2$ , times the known concentration of available acid groups,  $2 \times [\text{BTDE}] = 0.44 \text{ M}$ , gives the desired concentration value:  $[\text{HE}] = 0.154 \text{ M}$ . Substituting these concentration values in Eq. (2) gives approximately  $K = 1.0$  for the equilibrium constant.

Employing this equilibrium constant and the appropriate initial concentrations for the 50 weight percent solution:  $[\text{BTDE}] = 0.13 \text{ M}$  and  $[\text{CH}_3\text{OH}] = 1.56 \text{ M}$ , the equilibrium concentration of additional higher ester can be calculated:  $[\text{HE}] = 0.195 \text{ M}$ . This result was verified by measurement of the nuclear magnetic resonance data for a 50 weight percent solution of BTDE which was accelerated toward equilibrium by acidification with  $\text{H}_2\text{SO}_4$ . The normalized integral for the methylester showed 3.5 ester groups per molecule or approximately:  $[\text{HE}] = 0.20 \text{ M}$ , which agrees with the calculated value of 0.195 M.

The effect of concentration is evident from these results. At 85 weight percent (where  $[\text{CH}_3\text{OH}]/[\text{available acid}] \approx 1$ ), the reaction proceeds until 68 percent of all the carboxyl groups are esterified (an average of 2.7 methylester groups per molecule). However, for the 50 weight percent solution (where  $[\text{CH}_3\text{OH}]/[\text{available acid}] \approx 6$ ), the reaction proceeds until 88 percent of the carboxyl groups are esterified (3.5 methylesters per molecule). Thus, the six fold increase in methanol concentration provides significant impetus for additional ester formation. It should be recalled, however, that we have not attempted to account for the kinetic effects of

changing pH and it might be that, at short times, the 85 weight percent solution would exceed the 50 weight percent solution in concentration of higher esters due to the greater concentration of acid in the 85 weight percent solution.

### Relative Reactivity of Ester Impurities

We postulate that the relationship of the observed impurities to the void formation lies in several possible reactions of the ortho-ester groups to form undesirable intermediates. These fail to form the desired imide structure or react more slowly than the amide-acids of BTDE or NE. Figure 6 illustrates three such intermediates in which the resultant chemical structures have one common feature: These structures are less stable than the imide ring at elevated temperatures and will decompose or rearrange evolving volatile materials. The evolution of volatiles late in the cure cycle or during post-cure treatment is the apparent cause of void formation.

A previous study (Ref. 4) has shown that ortho-amide and ortho-ester substituted polyamide intermediates require higher temperatures for imidization than the polyamide-acid. Thus, if the impurities react to form amide intermediates (such as those shown in Fig. 6), then these intermediates would imidize more slowly than the bulk of the resin and evolve condensation products late in the cure cycle. Evolution of volatiles by the "no reaction" path cannot be discounted because the steric barrier imposed by the ortho-ester would be expected to hinder reaction at the carboxyl groups. Hence, volatiles could be produced by decomposition of unreacted amine or ester, or by slow evolution of condensation as some reaction occurs at higher temperatures.

The relative reactivity toward MDA of the ortho-ester moiety (in the tetraester) is qualitatively compared to the acid-esters of BTDE and NE in Fig. 7. The principal features of the differential thermograms for the indicated binary mixtures are: (a) sharp endotherms below 100<sup>o</sup> C; (b) a large endotherm between 125 and 200<sup>o</sup> C for the NE/MDA and BTDE/MDA mixtures; and (c) a relatively small broad endotherm between 175 and

300° C for the tetraester/MDA mixture. The features below 100° C are due to the melt of the monomers. No chemical reaction is apparent at this temperature. The nuclear magnetic resonance spectra of the mixtures of monomers showed no changes after the mixtures were heated to 100° C. The large endotherms, (b), are due to the loss of methanol and water as amide and imide are formed. Infrared spectral monitoring of imide formation showed that the reaction is nearly complete (for condensation of the amide-acids) after 15 minutes at 204° C. The large apparent noise level in region (b) of the thermograms is typical of agitation of the sample due to evolution of volatiles. It is significant that the tetraester/MDA mixture shows little or no reaction in the temperature range in which the other monomer mixtures imidize. While the reaction that does occur (feature (c)) was not characterized completely, it was observed that even after raising the sample temperature to 250° C at 10° C per minute, the magnetic resonance spectrum of the mixture still showed some unreacted methylester.

Thus, while these data do not define a single reaction path, they do confirm that the ortho-ester moiety reacts significantly slower than the amide-acids and that those reactions which do occur are not complete at a temperature of 250° C. In a typical cure cycle, the resin is held at 204° C for about one hour for imidization. It is doubtful that the ester impurities would react completely (if at all) during this staging.

#### SUMMARY OF RESULTS AND CONCLUSIONS

Spectral, chromatographic and thermal studies were conducted to identify the factors responsible for void formation in PMR-polyimide resin composites fabricated with aged monomer solutions. It was demonstrated that:

(1) Detectable quantities of tri- and tetraester impurities form in 50 weight percent solutions of the diester of 3, 3', 4, 4'-benzophenonetetracarboxylic acid (BTDE) after approximately one month of storage at ambient conditions.

(2) The rate of formation of the ester impurities is slow (apparent half time in excess of eleven months), however, their formation is favored in the equilibrated solution.

(3) The ester impurities react with aromatic amines more slowly than the BTDE.

From these results we conclude:

(1) It is undesirable to store methanol solutions of the monomer BTDE for periods greater than one month at ambient conditions.

(2) Voids are formed in PMR-polyimide resin composites by gaseous products evolved by ester impurities and/or unreacted amine which react slowly or decompose during elevated temperature post cure treatment.

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2. Cavano, Paul J.: Resin/Graphite Fiber Composites. (TRW-ER-7581F, TRW Equipment Labs.; NAS3-15829), NASA CR-121275, 1974.
3. Delvigs, Peter; Serafini, Tito T.; and Lightsey, George R.: Addition-Type Polyimides from Solutions of Monomeric Reactants. NASA TN D-6877, 1972.
4. Scrafini, Tito T.: High-Temperature Resin-Matrix Composites. Aerospace Structural Materials. NASA SP-227, 1967, pp. 207-215.

**TABLE I. - NORMALIZED NMR PEAK AREAS  
AND CALCULATED NUMBER OF ESTER GROUPS  
FOR AGED BTDE SOLUTIONS**

Storage time (months)	Normalized peak area		Average number of methylester groups per molecule
	H(phenyl)	H(methyl-ester)	
0	6	6	2.0
1	6	~6	2.0
2	6	6.3	2.1
3.5	6	6.6	2.2
6	6	7.2	2.4

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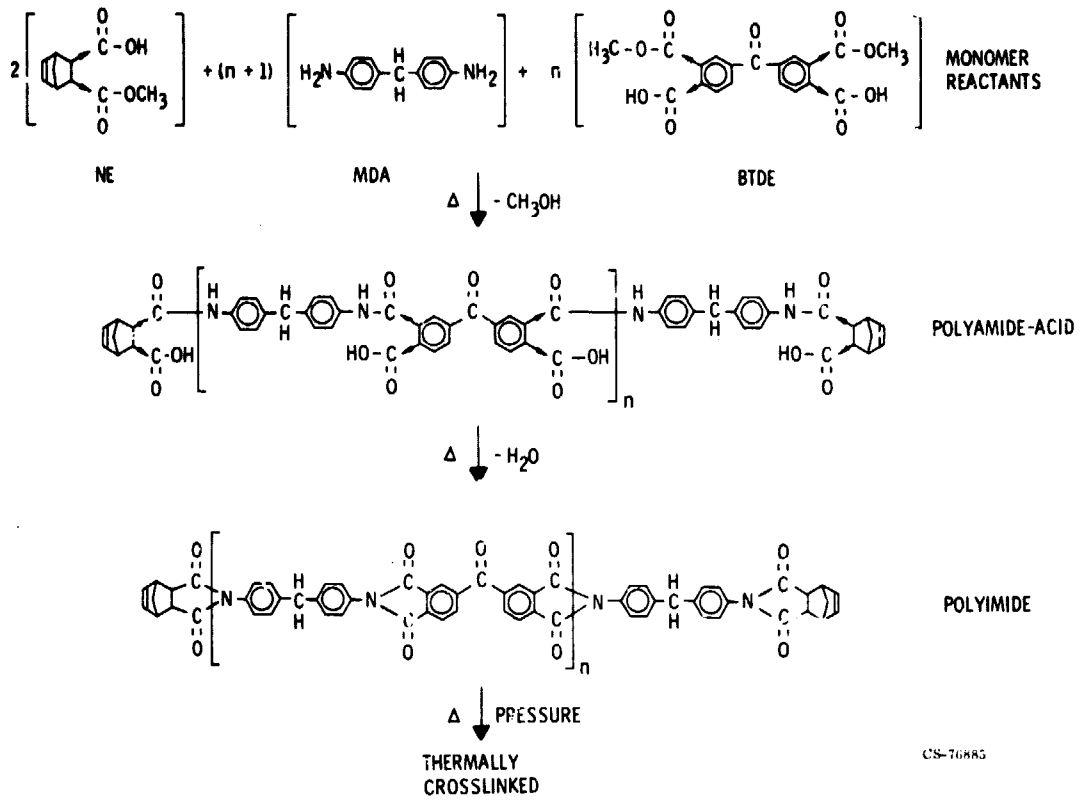


Figure 1. - Reaction sequence for PMR-polyimide resin.

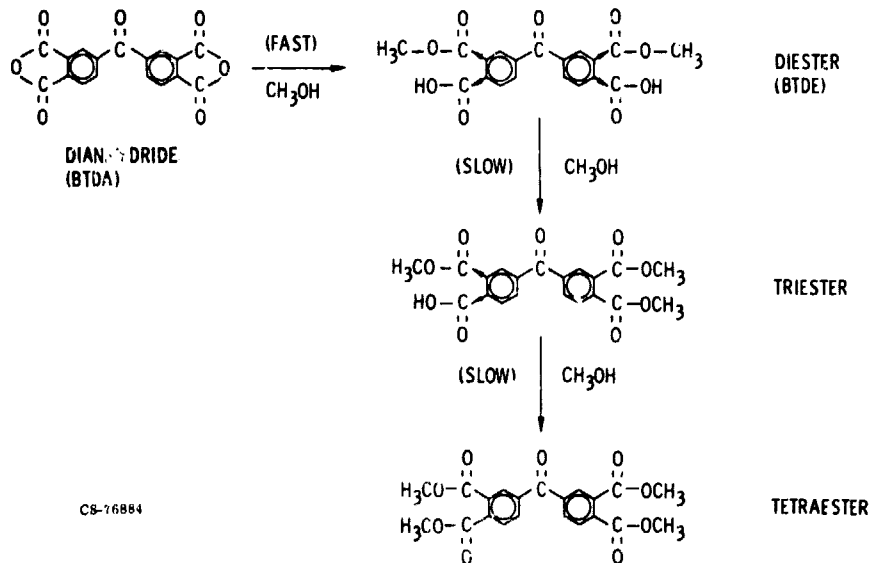


Figure 2. - Reaction sequence for esterification of 3,3',4,4'-benzophenonetetracarboxylic dianhydride.

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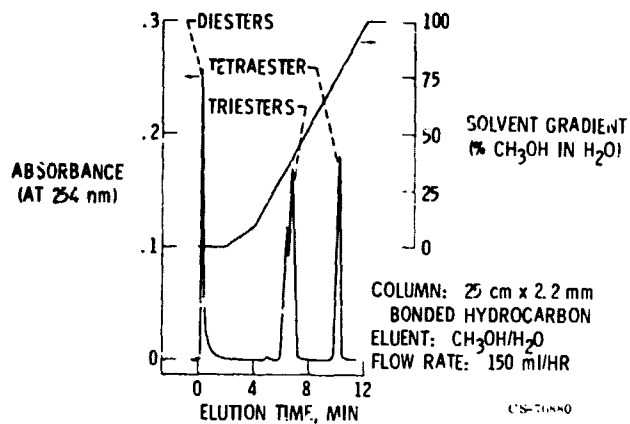
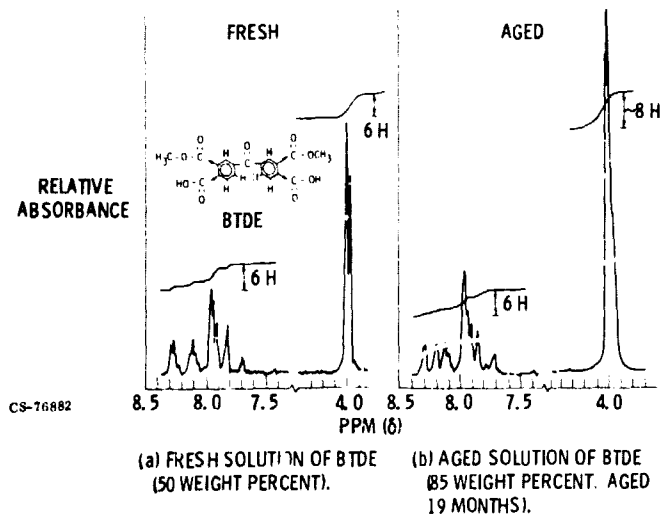


Figure 3. - Liquid chromatogram and elution gradient for an aged BTDE solution (85 weight percent; aged 19 months).



(a) FRESH SOLUTION OF BTDE (50 WEIGHT PERCENT).

(b) AGED SOLUTION OF BTDE (85 WEIGHT PERCENT, AGED 19 MONTHS).

Figure 4. - Nuclear magnetic resonance spectra of phenyl protons (near 8 ppm) and methylester protons (near 4 ppm) with peak integrals.

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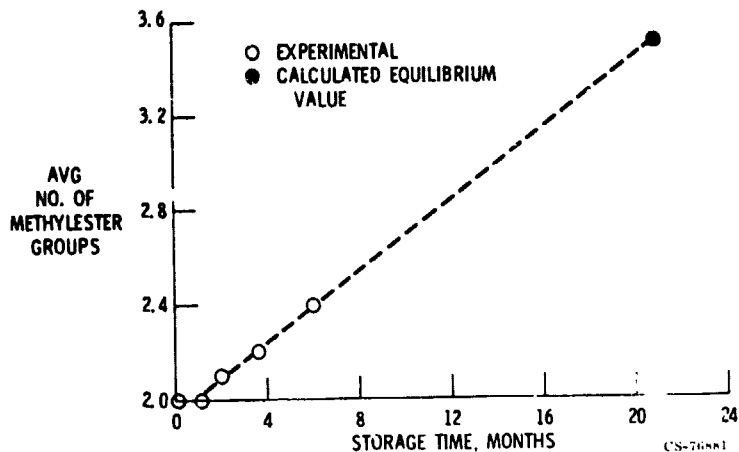


Figure 5. - Increase in number of methylester groups per molecule during storage of 50 weight percent solutions of BTDE.

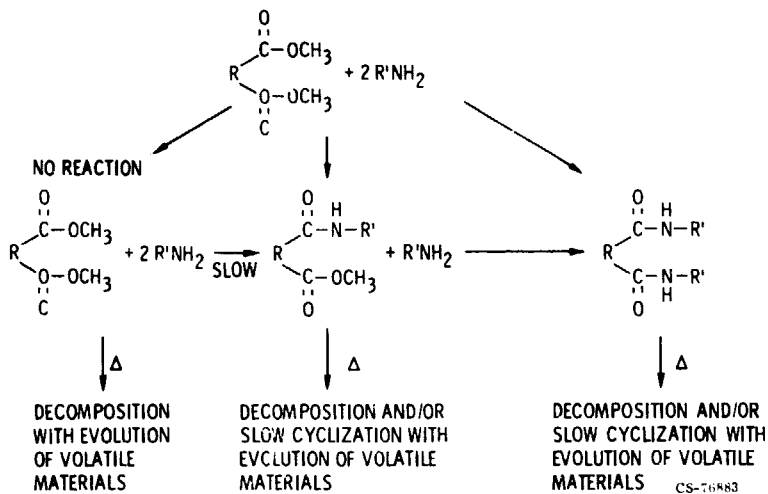


Figure 6. - Possible reactions of ortho-ester groups with amines.

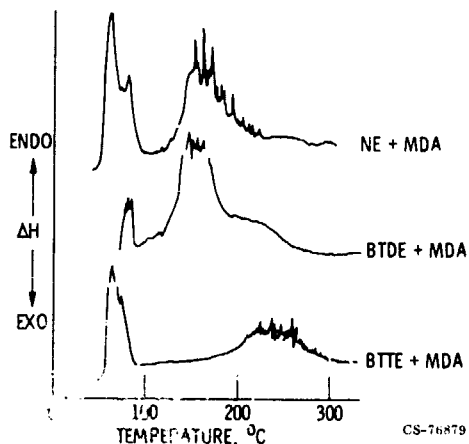


Figure 7. - Differential calorimeter scans of binary mixtures of monomers.