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## Role of Amines in the Isomerization Reaction of Polycondensed Maleic Anhydride and Diethylene Glycol

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### ABSTRACT

Aniline and N-ethylaniline were used as model compounds to study the effect of aromatic primary and secondary amines on maleate-fumarate isomerization. Amines were added to the copolymerization reaction of maleic anhydride and diethylene glycol at different degrees of conversion (P). The effect of amines on the relative amount of isomerization was followed with proton NMR. The efficiency of fumarate production decreases in the order  $P = 0.62 > 0.76 > 0.35 > 0$ . Mechanisms to account for the effect of aniline and N-ethylaniline on the maleate-fumarate isomerization are outlined.

### INTRODUCTION

During the synthesis of polyester resin by thermally condensing maleic anhydride with glycol, with or without the modifying dicarboxylic acid (alkyl or aryl), isomerization to fumaric acid always occurs. Such cis-trans conversion is a highly desirable phenomenon since the fumarate form is more reactive than the maleate in the sub-

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sequent copolymerization with vinyl monomers such as styrene [1]. Prepolymers with a high fumarate content generally have shorter gelation and cure times. The higher the fumarate content in the final prepolymer, the better are the physicomechanical properties [2].

For the last two decades much effort has been expended to study the influence of temperature [3], glycols [4-6], acid-base catalysts, and other catalysts [7, 8] to achieve maximum cis-trans conversion. The catalytic action of ammonia was found to be effective in maleate-fumarate conversion [9]. Funke et al. [10] noted that aniline and piperidine at large concentrations can exert an isomerization effect. Some primary and secondary amines were recently identified as potential catalysts for maleate-fumarate isomerization [11, 12]. However, the reaction mechanisms were not reported and the intermediate products were not characterized.

Our aim is to find an effective catalyst which can (a) accelerate the cis-trans isomerization during the copolymerization reaction of maleic anhydride with glycol, (b) accelerate the subsequent copolymerization reaction of preoligoester resin with vinyl monomer without the addition of an external accelerator such as dimethyl aniline, and (c) produce a cross-linked polymer with improved physicomechanical properties.

The purpose of this paper is to report the influence of aniline and N-ethylaniline on the percent isomerization of maleate to fumarate in the copolymerization reaction of maleic anhydride with diethylene glycol using the proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ) technique. The differences that occur in cis-trans isomerization when amines are added at different degrees of conversion (P) in the oligomerization process are also reported.

## EXPERIMENTAL

### Oligoester Resin Preparation

Oligoester resins for this study were prepared in the laboratory under an inert atmosphere and controlled temperature. The apparatus for the resin synthesis consisted of a 500-mL, four-necked flask equipped with a stirrer, thermometer, nitrogen inlet, and a packed steam-jacketed condenser. Three sets of resins were prepared by the fusion method. The condensation reaction was stopped after 6 h in all sets of experiments.

### Diethylene Glycol-Maleate Oligoester

The diethylene glycol-maleate oligoester was prepared at  $190 \pm 1^\circ\text{C}$ . A 1.0/1.1 mol ratio of maleic anhydride to diethylene glycol was employed.

### Diethylene Glycol-Maleate-Amine Oligoester

In this set of resin preparations, aniline and N-ethylaniline were added in catalytic amounts (0.05 mol%). Diethylene glycol (1.05 mol, 111.4 g) plus the amine (0.5 mol, 4.65 g) were reacted with maleic anhydride (1.0 mol, 98.06 g) at  $190 \pm 1^\circ\text{C}$  to give a final resin. In the second series, the amines were added to the reaction mixture at the polymer degree of conversion (P) levels  $P = 0, 0.35, 0.62,$  and  $0.76$ .

### Synthesis of Maleanilic Acid: $\text{C}_6\text{H}_5\text{-NH-CO-CH=CH-COOH}$

Maleanilic acid was prepared by the Anschutz's method [13] from aniline and maleic anhydride in ether. When heated at  $190^\circ\text{C}$  for 30 min, the maleanilic acid was not converted to fumaranilic acid in other solvents such as alcohol, benzene, or toluene.

Melting point  $184\text{-}185^\circ\text{C}$  by capillary method. Elemental analysis for  $\text{C}_{10}\text{H}_9\text{NO}_3$  (191.2): Calculated: C, 62.82; H, 4.71; N, 7.33. Found: C, 62.60; H, 4.83; N, 7.64.

### Synthesis of N-Phenylacetimide

This model compound was prepared by Sudborough's [14] general method from acetic anhydride and aniline.

Melting point  $37\text{-}38^\circ\text{C}$  capillary method. Elemental analysis for  $\text{C}_{10}\text{H}_{11}\text{NO}_2$  (177.2): Calculated: C, 67.82; H, 6.21; N, 7.91. Found: C, 68.01; H, 6.17; N, 7.97. IR (solution film):  $1701\text{ cm}^{-1}$  (strong  $\nu\text{C=O}$ ).

### $^1\text{H-NMR}$ Analysis

Samples were withdrawn from the reaction flask during the resin preparation and their proton NMR spectra were recorded on a Varian-EM 360 spectrometer at 60 MHz. The samples were dissolved in deuterated acetone so that the total concentration of the sample for analysis was 10-20%. The signal of the solvent was used as an internal standard at  $\delta = 2.05$ . The spectra were recorded at room temperature. The signals observed were the olefinic proton of the fumarate group at  $\delta = 6.98$  and the olefinic proton of the maleate group at  $\delta = 6.55$ .

### FT-IR Analysis of the Sample

N-Phenylacetimide was ground and pressed with KBr into a pellet. Oligoesters taken at specific time intervals were formed into thin films between KBr disks. Absorbance spectra were recorded at  $2\text{ cm}^{-1}$  resolution between  $3600$  and  $600\text{ cm}^{-1}$  wavenumbers on a Digilab FTS-20E

FT-IR spectrometer. 200 scans of sample and reference were co-added to obtain a high signal-to-noise ratio. A nitrogen-cooled MCT detector insured maximum signal stability.

## RESULTS AND DISCUSSION

$^1\text{H-NMR}$  is a quite useful technique for studying the cis-trans isomerization since the area under the absorption peak is proportional to the number of protons causing that absorption. In the NMR spectrum of oligoester resin the maleic proton resonance peak is located at a different chemical shift ( $\delta$ ) than the fumaric. Determination of the area under the maleate and fumarate absorption peaks allows calculation of relative amounts of cis-trans double bonds. The first sample for  $^1\text{H-NMR}$  spectroscopy is withdrawn from the reaction flask after the upheating cycle is complete. Figure 1 is the  $^1\text{H-NMR}$  spectrum of the product of the condensation reaction of maleic anhydride with diethylene glycol in the presence of aniline after 3 h of the condensation process. The signals were assigned as follows: The signal at 0.028 ppm is the signal of the internal standard (TMS), in the region of 2.1 ppm the signal is of solvent (acetone-d); in the region of 3.6-3.8 ppm the signal is of the multiplet of methylene protons of  $\text{CH}_2\text{-O-CH}_2$ ; in the region of 4.2-4.5 ppm are triplet proton signals of  $\text{CH}_2\text{OCO}$  units; the signal of olefinic protons of maleate units appear at 6.4 ppm and those of fumarate units at 6.8 ppm; and the aromatic proton signal of the benzene ring appears at 7.05 ppm. In order to study the kinetics of isomerization and the influence of amines at different degrees of conversion, the condensation time in all sets of experiments is fixed at 6 h. The samples are withdrawn from the reaction mixture at 0.5, 1, 2, 3, 5, and 6 h. In order to study the isomerization kinetics, the NMR spectrum was integrated to obtain the area under the absorption peaks for fumarate and maleate. The value of  $i$ , the degree of isomerization, was calculated. The  $i\%$  was calculated by the equation  $i\% = a/(a + b) \cdot 100$  (where  $a$  = signal area corresponding to the fumarate and  $b$  = signal area corresponding to the maleate). The percent fumarate content is plotted against the isomerization time for systems with aniline at different degrees of conversion ( $P$ ) and without it. This is shown in Fig. 2. For each oligoester resin, four runs for NMR analysis and for ( $P$ ) were made. The average relative error is found to be  $\pm 2\%$ . The degree of conversion ( $P$ ) is calculated by

$$P = 1 - \frac{\text{the acid number of the resin at a given reaction time (C)}}{\text{the initial acid number (C}_0\text{)}}$$

A similar plot was drawn for the N-ethylaniline catalyzed system and the plot is shown in Fig. 3. The final and number percent acid remain-

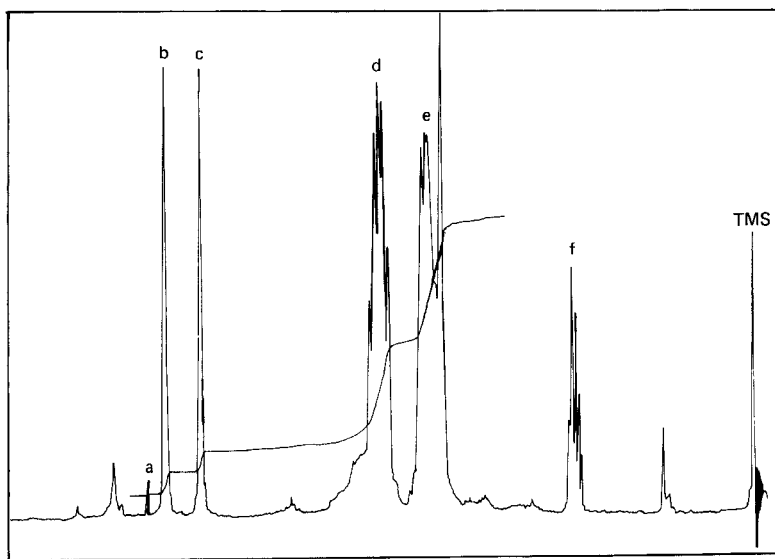


FIG. 1.  $^1\text{H}$ -NMR spectrum of maleate-fumarate proton absorption for oligoester resin prepared in the presence of aniline. Sample taken after 3 h of upheated cycle: (a) aromatic protons, (b) fumarate, (c)

maleate, (d)  $\text{CH}_2\text{-O-C}(=\text{O})$ , (e)  $\text{CH}_2\text{-O-CH}_2$ , (f) acetone-d.

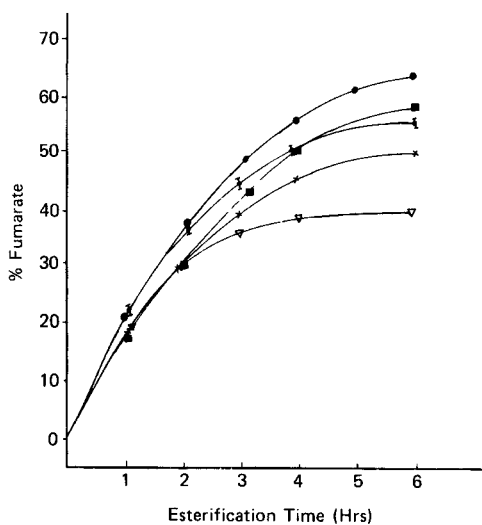


FIG. 2. Fumarate percent during synthesis of diethylene glycol maleate oligoester with and without aniline. Without aniline ( $\nabla$ ). With aniline for the system  $P = 0$  ( $\times$ ),  $P = 0.35$  ( $\bullet$ ),  $P = 0.76$  ( $\square$ ),  $P = 0.62$  ( $\bullet$ ).

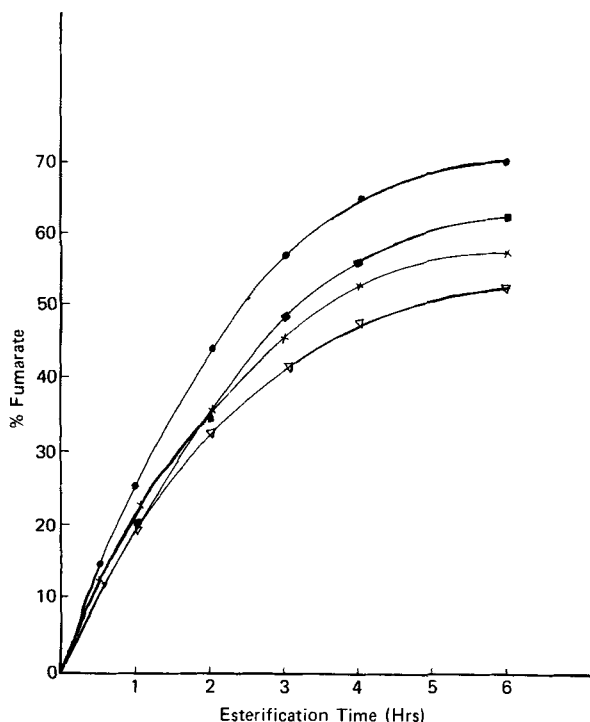


FIG. 3. Fumarate percent during the synthesis of diethylene glycol maleate oligoester in the presence of N-ethylaniline. In the presence of N-ethylaniline for the system  $P = 0$  ( $\nabla$ ),  $P = 0.35$  ( $\times$ ),  $P = 0.76$  ( $\square$ ),  $P = 0.62$  ( $\bullet$ ).

ing and percent fumarate are listed in Table 1. The isomerization rate constants,  $k_i$ , were evaluated graphically by plotting  $1/(1 - i)$  versus the oligomerization time. A straight line is observed. Such a plot for diethylene glycol maleate oligoester prepared in the presence of aniline is shown in Fig. 4. The straight line indicates a second-order rate constant and the values are summarized in Table 2.

In our studies it was observed that the fumarate content in all systems (with and without amines) is about the same in the first two hours of synthesis. After the second hour of condensation the highest fumarate percent was found in the system  $P = 0.62$ , moderate in the system  $P = 0$ , and the least in the absence of amines. The effect of various factors on the isomerization kinetics of unsaturated polyester based on propylene oxide and maleic anhydride in the presence of secondary amines was studied by Klyuchnikov et al. [15]. They observed that the initial sections of kinetic curves were described by a first-order reaction for the polyester and the catalyst. The deviation from first-order kinetics after

TABLE 1. Influence of Primary and Secondary Amines on the cis-trans Isomerization. Addition at Different Degrees of Conversion in the Condensation Reaction of Maleic Anhydride (1.0 mol) with Diethylene Glycol<sup>a</sup> (1.05 mol)

Amine (0.05 mol)	Degree of conversion <sup>b</sup> (P)	Final solids acid number	Acid remaining (%)	Fumarate (%)
None	0	37	21	37
Aniline	0	35	14	50
Aniline	0.35	36	16	55
Aniline	0.62	32	14	64
Aniline	0.76	36	16	58
N-Ethylaniline	0	42	19	53
N-Ethylaniline	0.35	43	19	58
N-Ethylaniline	0.62	41	18	70
N-Ethylaniline	0.76	43	19	62

<sup>a</sup>The initial concentration of diethylene glycol in the absence of amines is 1.1 mol.

<sup>b</sup>The degree of conversion (P) at which the amine is added.

60 min of reaction is explained by secondary reactions during which the catalyst is used up. Probable methods of using up the catalyst involve a reaction with the free maleic anhydride impurity contained in polyester and with carboxyl endgroups of polyester. On the basis of our percent isomerization calculations using proton NMR for the system in the absence of amine, the fumarate content of the resin is 37%. Vancso-Szmercsanyi et al. [16] studied the maleate-fumarate conversion in the copolymerization reaction of maleic anhydride with various glycols. From polarographic analysis they found 31% fumaric acid in samples polymerized with diethylene glycol. The percent fumarate content (Table 1) indicates that the introduction of aromatic primary and secondary amines into the reaction system enhances the cis-trans isomerization. However, the efficiency of the reaction decreases depending on the addition of aniline and N-ethylaniline at different degrees of conversion (P) during the synthesis, in the following order:  $P = 0.62 > P = 0.76 > P = 0.35 > P = 0$ . The effect of amine addition to the half-ester is significantly different from the addition at the initial stage of the esterification process.

To explain the lesser isomerization in the case of system  $P = 0$ , where all the initial reagents are charged at once, aniline ( $pK_a = 4.63$ )



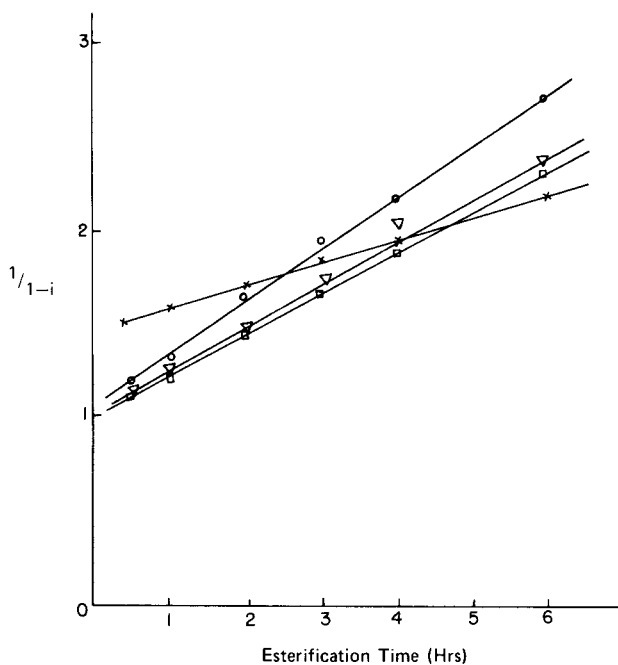


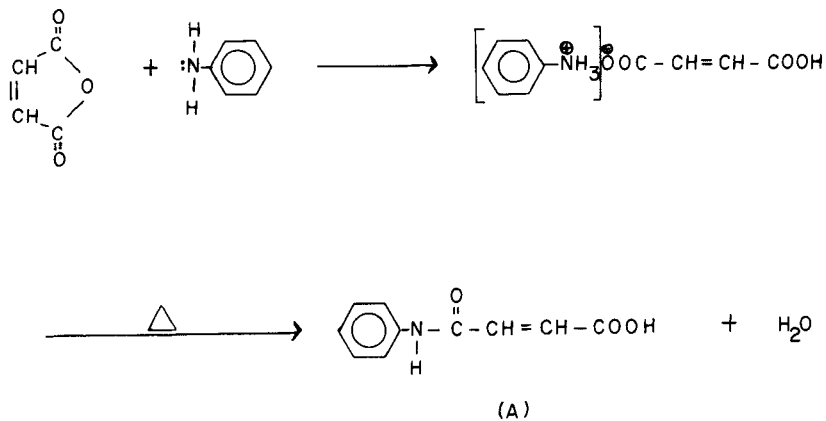
FIG. 4.  $1/(1-i)$  versus oligomerization time plot for diethylene glycol maleate oligoester prepared in the presence of aniline. In the presence of aniline for the system  $P = 0.35$  ( $\times$ ),  $P = 0.62$  ( $\square$ ),  $P = 0.76$  ( $\nabla$ ),  $P = 0.62$  ( $\circ$ ).

TABLE 2. Rate Constants ( $k_1$ ) of cis-trans Isomerization in Diethylene Glycol Maleate Oligoester Synthesized in the Presence of Aniline (0.05 mol) or N-Ethylaniline (0.05 mol)

Amine (0.05 mol)	Degree of conversion <sup>a</sup> (P)	Molecular weight	Rate constant $k_1 \times 10^{-2}$ $\text{mol}^{-1} \cdot \text{s}^{-1}$
Aniline	0	1603	3.62
Aniline	0.35	1558	2.36
Aniline	0.62	1753	4.86
Aniline	0.76	1558	3.77
N-Ethylaniline	0	1336	3.83
N-Ethylaniline	0.35	1305	3.06
N-Ethylaniline	0.62	1368	6.72
N-Ethylaniline	0.76	1305	4.65

<sup>a</sup>The degree of conversion (P) at which the amine is added.





SCHEME 1.

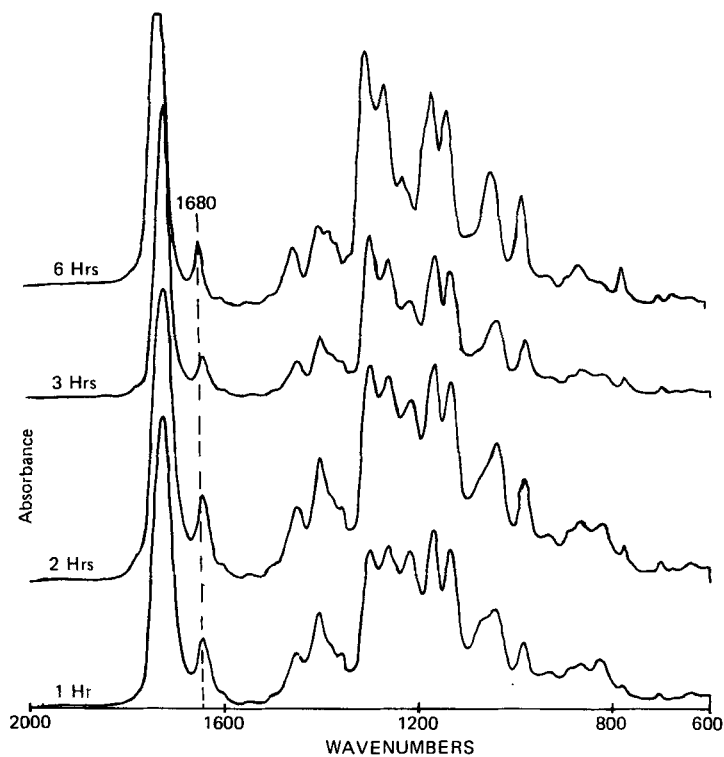
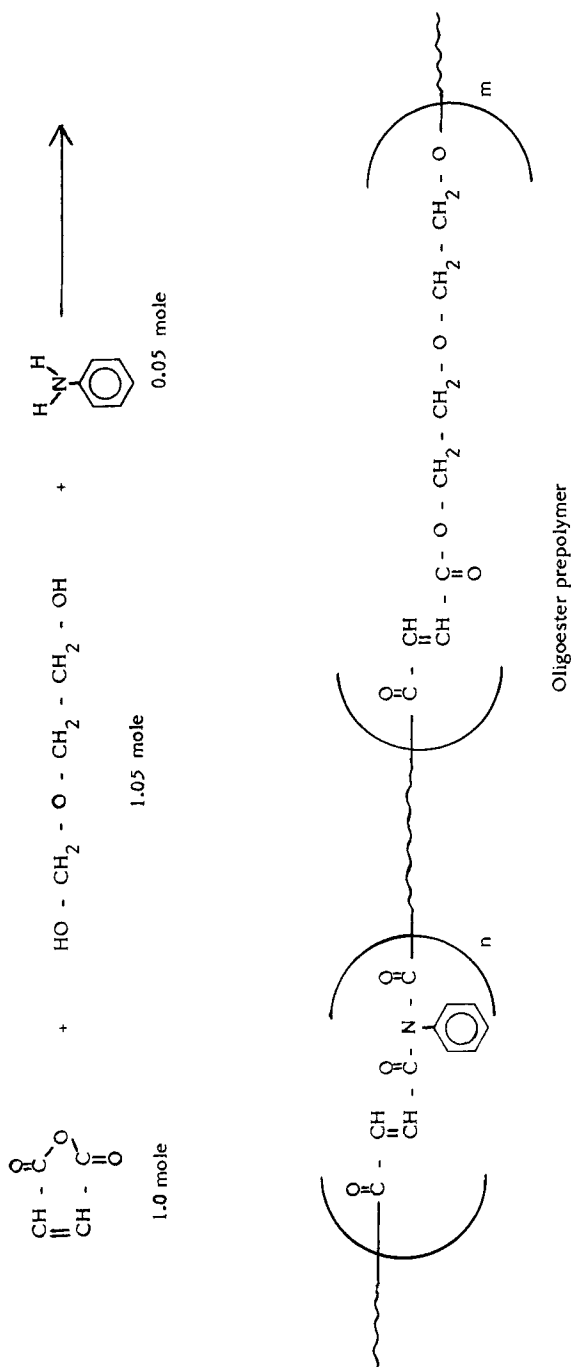


FIG. 5. FT-IR absorption spectra of oligoester resin samples withdrawn from the reaction mixture at 1, 2, 3, and 6 h of duration. The resin was prepared in the presence of aniline.





SCHEME 3.

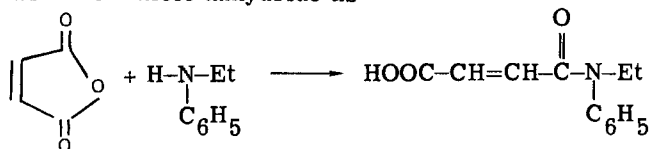
carbon-carbon double bonds of the half-ester and a possible free rotation about the single bond as shown in Scheme 4. At  $P = 0.62$  a certain amount of linear chain oligoester formation is expected. By the addition of aniline at this stage of condensation, the amine may preferably add to the maleic double bonds of the growing oligoester chain. By the nucleophilic attack of aniline to the double bonds, a transition state enol ion (I) may be formed. However, due to the bulkiness of adjacent ester groups, there is a strong ester repulsion at I. Therefore, this keto form may undergo a rapid free rotation due to the single bond character between the two carbon atoms to give the geometrically and sterically more favorable (trans) enol form (II). Depending on the relative magnitudes of  $k_1$ ,  $k_2$ , and  $k_3$  stability of the addition complex, the Intermediate II can either tautomerize to Complex III, regenerate the primary amine and trans-form (IV), or return to maleate. Clemo et al. [9] found that organic bases are only effective as catalysts when they contain amino or imino hydrogen. They suggest that the mechanism of ethenoid inversion involves catalyst addition to the double bonds, allowing free rotation with the formation of the trans-form.

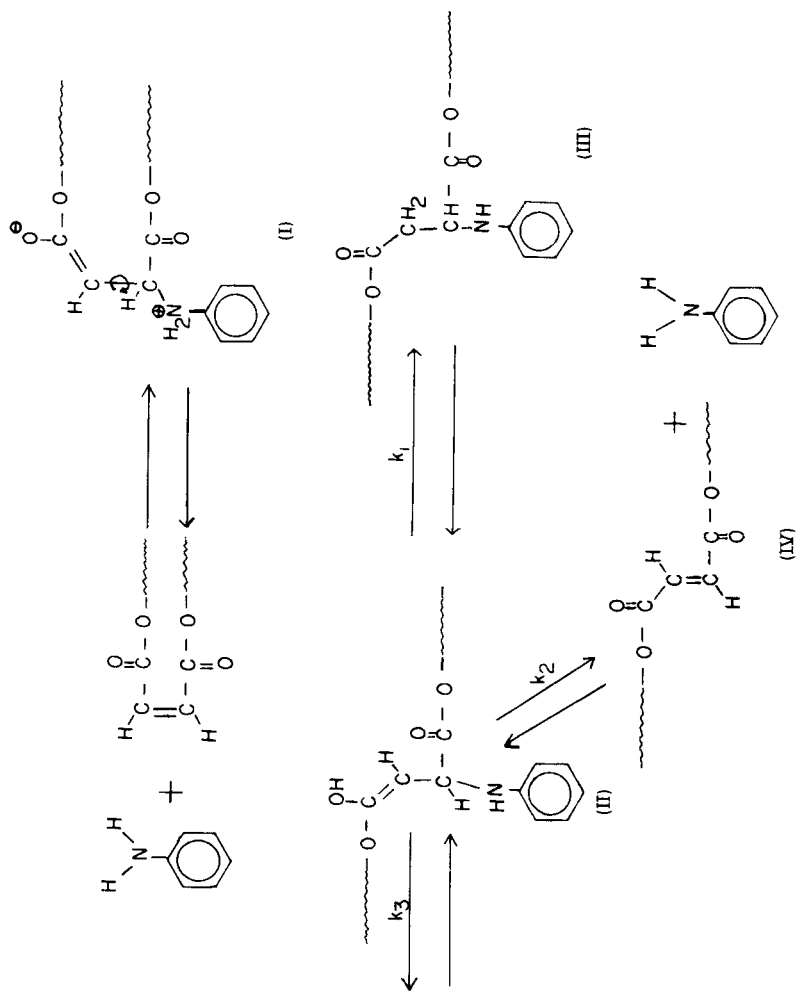
A large number of patents and publications have appeared in the literature on the catalytic effect of secondary amines in cis-trans isomerization. For instance, a trace of piperidine transforms methyl maleate in a few seconds into a crystalline mass of the fumarate [9]. Dimethylamine, diethylamine, piperazine, and N-ethylaniline also effect the change, although some of them do not bring about a complete transformation. Otsu et al. [11] showed that 100% conversion of diethyl fumarate is achieved by using propyl, dipropyl amines, morpholine, and piperidine.

We observed that an N-ethylaniline catalyzed system for  $P = 0.62$  shows an increased efficiency in the cis-trans conversion over the other systems (see Fig. 3). This is analogous with the aniline catalyzed system. Slightly higher percent isomerization in secondary amine and  $P = 0.62$  systems can be explained as follows.

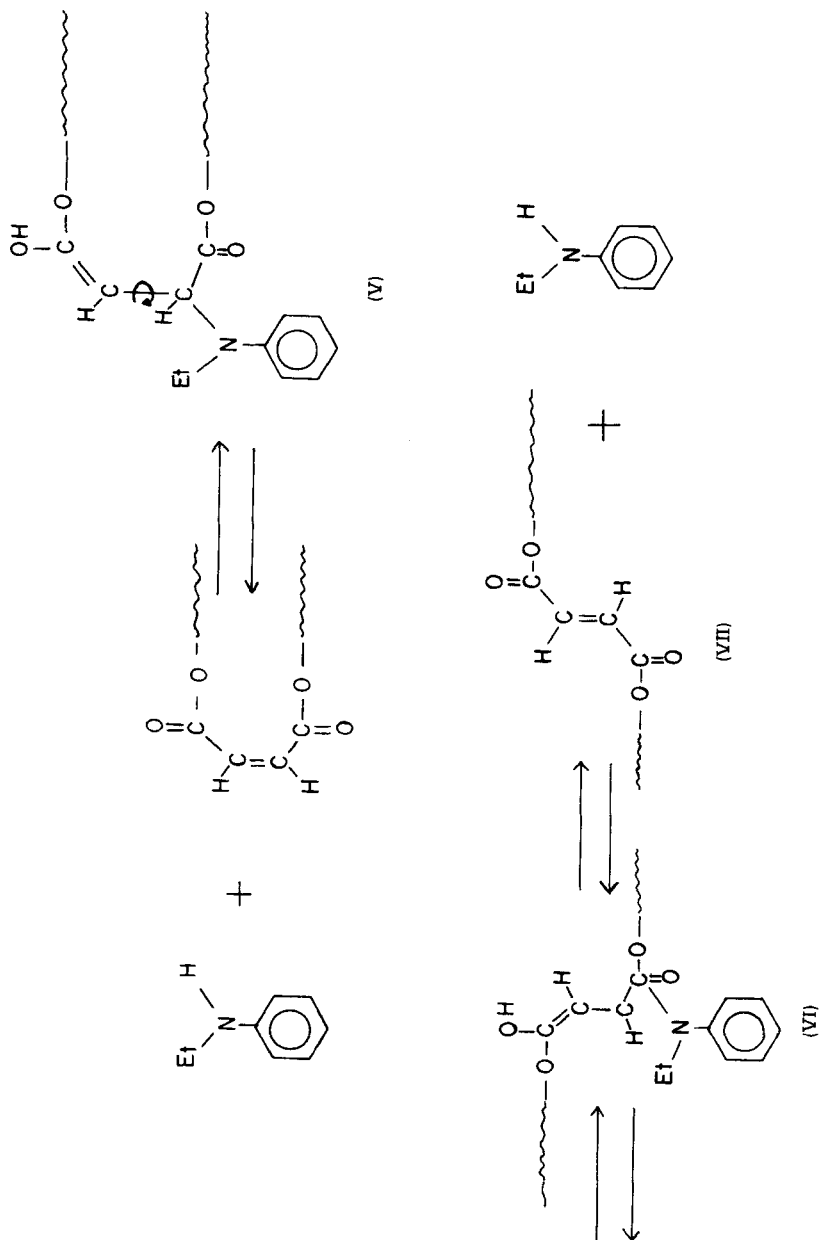
The nucleophilic addition of N-ethylaniline to  $\alpha,\beta$ -unsaturated double bonds in the oligoester chain is expected to give enol of Type V (Scheme 5) as described in Scheme 4. This allows the addition complex to freely rotate with the formation of the sterically favorable trans-form (VI). The Intermediate VI will then regenerate the secondary amine and the stable trans-form (VII). Thus the added amine can catalyze further cis-trans conversions. Such a reversible 1,4 addition of the secondary amine to the  $\alpha,\beta$ -unsaturated double bond for the cis-trans isomerization has been suggested [24].

Lesser degrees of conversion in the system  $P = 0$  could be explained by the inference that all or part of the added N-ethylaniline ( $pK_a = 5.12$ ) reacts with the maleic anhydride as





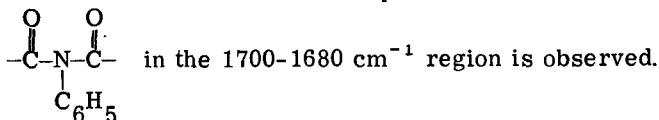
SCHEME 4.



SCHEME 5.



The IR spectra of polyester resins prepared in the presence of N-ethylaniline and for the systems  $P = 0$ ,  $P = 0.35$ ,  $P = 0.62$ , and  $P = 0.76$  were recorded. No absorption band for  $\nu$  C=O of



The kinetics of copolymerization and the mechanism of cross-linking of these amine-modified oligoester resins with styrene and some of the physicomechanical properties of such cured resins are under study.

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