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Crystallization-induced reaction of aromatic copolyesters.

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CRYSTALLIZATION-INDUCED REACTION OF AROMATIC COPOLYESTERS

A Dissertation Presented

By

Alan N. Schuler

Submitted to the Graduate School of the University of Massachusetts in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY

July 1976

Major Subject Polymer Science & Engineering
CRYSTALLIZATION-INDUCED REACTION OF AROMATIC COPOLYESTERS

A Dissertation

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August 1976
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ABSTRACT

The effect of reaction parameters on the extent of reorganization of random poly(ethylene terephthalate-co-succinate) (PET/ES) copolyesters accomplished by crystallization-induced reaction was studied. Analysis of sequence length changes was performed using the NMR technique of Murano and Yamadera. To verify the accuracy of the NMR analysis an independent method of monomer analysis was developed. The copolyesters were saponified and monomer composition determined by gas chromatographic analysis of the trimethyl silyl derivatives of the saponification products. Comparison of results of these two analysis demonstrated that the NMR method was accurate to $\pm 1\%$ for the copolyesters employed.

The copolymers used in this investigation had a terephthalate content of 70-85% and melted in the temperature range 200-235°C. Crystallization-induced reactions were performed at temperatures from 0-35°C below the individual copolymers melting point. All of the copolymers treated showed increased melting points, degrees of crystallinity and terephthalate sequence lengths.

From the results, conclusions about the control of the CIR are drawn. These conclusions fall into two groups based on how close to the melting point of the copolymer
the CIR was performed. In a temperature zone greater than 15°C below $T_m$ those parameters which control the rate of the ester-interchange apparently control the extent of reaction. However, at temperatures closer to $T_m$ complicating effects appear and suggest that a more thorough study of the co-polymer's crystallinity are necessary to understand reaction control in this region.
Dedicated to
Karen and Michael
ACKNOWLEDGEMENT

The author wishes to acknowledge the many people who contributed to the success of this work. With sincere appreciation, thanks are extended to:

Dr. Robert Lenz for the knowledge he imparted, the guidance he rendered, and the friendship he extended.

The members of the Polymer Science and Engineering faculty, particularly Drs. MacKnight, Sanchez, and Vogl, for their advice and many helpful discussions.

The IBM corporation for its two years of financial assistance.

My father for his inspiration and advice.

My wife who's assistance in typing and proof reading this thesis was given with a smile.

My fellow students, particularly Bernie, Bob, John, and Tony, for their friendship and support.
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CHAPTER I

BACKGROUND AND OBJECTIVES

Introduction

In most cases a mixture of homopolymers is incompatible; thus copolymerization has often been utilized in an attempt to blend the properties of two homopolymers. The degree to which the copolymer retains the desirable properties of the homopolymers is affected by the comonomer ratio, but to an even greater degree by its chemical microstructure. Increased commercial utilization of copolymers has therefore made the control of their microstructure an important part of copolymer technology. For the most part, the approach taken has been the utilization of polymerization reactions which yield a controlled structure. However, for "reactive" copolymers, such as polyesters, the recently proposed crystallization-induced reaction may be used as a post-polymerization treatment which allows controlled microstructural modification.

Crystallization-Induced Reaction. The first postulation that polymer crystallinity could be employed as a driving force in copolymer reorganization was made in 1970. Lenz and coworkers noted an apparent anti-thermodynamic redistribution of acetal rings in several poly(ester acetals)
prepared from methyl azelaaldehyde glycerol acetal. They proposed the mechanism of crystallization-induced reaction to explain the observed results.

Figure 1 shows the four configurations in which the monomer may exist. As would be expected, polymerization of this monomer mixture gave several different copolymers depending upon the conditions employed. Polymerization at $250^\circ C$ gave a hard crystalline polymer which was rich in the five member ring (dioxolane) isomers, while that at $190^\circ C$ gave polymer which was apparently amorphous and had a lower content of dioxolane isomers. These results were in line with homogeneous equilibrium studies which indicated that the dioxolane form was the preferred structure at high temperature.

However upon standing at room temperature for several months the properties of the polymer prepared at $190^\circ C$ slowly changed. Examination of the monomer composition showed that the polymer had undergone a selective enrichment in dioxolane isomer content. The observed change was in apparent conflict with the equilibrium data.

To explain the anomalous behavior of this copolymer the authors postulated that the normally reversible equilibrium was altered by the presence of a crystalline phase in the polymer. In the homogeneous case, when the perturbing effect of the crystals is not present, the course of the reaction is governed by the equilibrium constant at the
Figure 1 — Isomers of Methyl Azeaaldehydate Glycerol Acetal

Cis. ISOMERS

Trans. ISOMERS

\[ R = (\text{CH}_2)_7 \text{ COCH}_3 \]
given temperature. However, in the solid-state when a non-crystallizable unit adjacent to a crystallite is replaced by a crystallizable unit, this new unit may be incorporated into the crystalline phase. Once crystallization occurs, the reverse reaction is much less likely due to the restrictions of the lattice. Thus, although the reaction in the amorphous phase tends toward the normal equilibrium, the crystallization of monomer units makes the overall reaction non-reversible and apparently anti-thermodynamic. A successive repetition of this sequence results in a selective enrichment of the copolymer in dioxolane content.

In a subsequent paper the theory of crystallization-induced reaction was outlined. For CIR to be successfully applied to a copolymer, the following four criteria must be satisfied: (1) the copolymer must be able to undergo a reversible reaction which will provide a means for reorganization to occur; (2) only one of the repeating units of the copolymer exist in a crystalline phase at the reaction temperature; (3) once a unit is incorporated into the crystalline phase it can no longer react; and (4) the reaction proceeds at a sufficiently rapid rate at a temperature below the melting point of the crystalline phase to allow reorganization to occur without degradation. If a copolymer which meets these criteria is subjected to conditions which will permit the reversible reaction in the
solid-state, the theory predicts that the reaction will appear to be anti-thermodynamic in direction and that block length of the crystallizable units will increase.

Depending upon the nature of the reversible reaction employed, the composition of the copolymer may also be effected. In the case of an isomerization reaction, the composition of the copolymer will drift toward increasing content of the crystallizable unit. The ester-acetal reorganization is an example of this type of CIR. On the other hand, an exchange or rearrangement reaction will cause no compositional change because the comonomers are simply redistributed. In either case, the sequence length of the crystalline unit increases and a multi-block structure is produced from initially random copolymers.

In addition to the original investigation of poly(ester acetals) which led to the development of the CIR theory, three additional experimental investigations of CIR have been reported. Lenz and Funt applied the concept of CIR to the photoisomerization of poly(1,4 - butadiene). The homogeneous photoisomerization leads to a 70-80% $\text{trans}$ content. In contrast, their investigation of the solid-state isomerization of a semi-crystalline copolymer rich in $\text{trans}$ content revealed an initial decrease, a minimum, and a rapid increase in $\text{trans}$ content as a function of time. The results were represented by an equation which predicts the $\text{trans}$ content on the basis of the opposing tendencies of the normal
reversible equilibrium and the CIR.

Subsequently, Lenz and Go$^{5,6}$ investigated the reorganization of two copolyesters when subjected to CIR. In one investigation copolymers of cis/trans 1,4-cyclohexylenedimethanol and terephthalic acid were utilized. Random copolymers were prepared by melt polycondensation, while block copolymers were synthesized by low temperature condensation of homopolymer blocks with terephthaloyl chloride.

When the random copolymers were subjected to CIR, the resulting polymers had melting points and solubilities which corresponded closely to those of the block copolymers. Redistribution of the comonomer units had thus proceeded in nonequilibrium manner as the theory predicts.

The second investigation was performed on random poly(ethylene terephthalate-co-methyl succinate), copolymers of varying composition. Employing nuclear magnetic resonance (NMR) spectroscopy to determine sequence lengths, the authors compared the copolymers structures before and after CIR. As a result of the solid-state treatment the sequence lengths of the copolymers increased 20 percent.

No additional investigations of solid-state polymerization reactions make direct reference to CIR; however, several reported results should be reinterpreted in light of the theory. Kibler, et.al.$^7$ reporting on the solid-state polymerization of cis/trans 1,4-cyclohexylenedimethanol
terephthalate oligomers found that the melting points of the solid-state polycondensation products were higher than those of similar copolymers prepared in the melt. Although they claimed the solid-state products were block copolymers, no explanation was offered.

Similar results were reported by Koretskaya, et.al. on the polycondensation of E-aminoeonanthic acid with PET oligomers. These authors found that the solid-state condensation yielded polymers melting @ 208°C as opposed to 138°C for melt polymerized material. Again the authors noted that the solid-state products were block copolymers but went no further. Finally, Schulken, et.al. have shown that the melting point of poly(cis/trans cyclohexylenedimethanol terephthalate) is irreversible increased when the copolymer is annealed close to its melting point in the presence of a catalyst. They also showed by turbidimetric titrations that the resulting copolymer had an enriched trans isomer content. In light of the results of Lenz and his coworkers, it seems probable that all of these findings may be interpreted as resulting from crystallization-induced reaction.

Objective and Scope of the Research

To date, investigations of CIR have been aimed toward demonstrating the validity of the theory. Several studies have indicated that reorganization does in fact
occur when appropriate copolymers are subjected to conditions which favor CIR. In the present study the CIR of copolyesters was investigated in order to determine to what extent the reorganization can ultimately be forced; and to determine the effect of the reorganization on some of the physical properties of the copolyesters. The maximum degree of reorganization which can be accomplished, and the effect of the reorganization on polymer properties will provide insight into the possible practical applications of CIR.

The research described in this thesis includes the investigation of techniques for determining the change in sequence distribution of copolyesters. The basic NMR technique of Murano was applied to determine both copolymer composition and sequence length distribution. To augment and verify the NMR results an independent method of monomer compositional analysis was also developed.

After demonstrating the veracity of the analytical method, random copolymers of poly(ethylene terephthalate-co-succinate) were subjected to CIR under various conditions. By selective variation of several reaction conditions and initial polymer properties, the effects of these parameters upon the extent of reorganization were ascertained. Finally, the tensile properties of a CIR product were compared to those of the starting copolyester to evaluate the effect of reorganization on the polyesters.
physical properties.

**Polyesterification**

The first detailed investigation of polyester formation was performed by Carothers and coworkers\(^{10}\) in the late twenties. Although they successfully prepared high molecular weight polymers by reacting aliphatic dibasic acids and diols, the inferior properties of these materials lead them to terminate their research of polyesterification. Not until the polymerization of poly(ethylene terephthalate) by Whinfield\(^ {11}\) in 1941 was interest in the polyesterification reaction rekindled.

Since that time an extensive literature has developed concerned with polyesters. Essentially all of the techniques useful in preparing low molecular weight esters have been utilized to prepare polyesters. In addition many different polymerization techniques, including solution, interfacial, melt, solid-state, and emulsion polycondensation have been reported. Reviews of these developments are presented in several recently published books.\(^{12-15}\)

Conceptually, the simplest method of preparing polyesters is the polycondensation of a diacid with a diol employed by Carothers. In practice this technique is rarely used due to the difficulty in obtaining high molecular weight polymers. The preparation of high molecular weight polyesters is governed by four criteria: (1) high monomer
purity; (2) an exact equivalence of functional groups; (3) the absence of side reactions; and (4) obtaining a high conversion. Many diacids are difficult to purify and undergo side reactions at high temperatures. Consequently, the most commonly used technique for preparing polyesters is ester-interchange.

**Polyesterification by Ester-Interchange.** The preparation of polyesters by ester-interchange involves the reaction of a diacid ester, usually the methyl ester, with a glycol. The polymerization is normally carried out in two stages with the in-situ generation of the "monomer" during the first stage and its subsequent polycondensation in the second. All of the reactions involved in this process are equilibrium reactions, therefore it is important to effectively remove the by-products of reaction to insure the formation of high molecular weight polymer.

In the first stage of the reaction the molar ratio of glycol to diester is customarily 2:1 to insure the formation of OH terminated materials. The reaction is carried out at a temperature well above the boiling point of methanol, yet below that of the glycol. An inert atmosphere is maintained by purging nitrogen through the system. Equation (1) illustrates the first stage process for the preparation of poly(ethylene succinate).
a CH$_3$OOCCH$_2$CH$_2$COOCH$_3$ + b HOCH$_2$CH$_2$OH $\xrightarrow{N_2,\Delta,\text{Cat.}}$

H(OCH$_2$CH$_2$OOCCH$_2$CH$_2$CO)$_n$OCH$_2$CH$_2$OH + 2a CH$_3$OH \hspace{1cm} (1)

b/a ≥ 2 \hspace{1cm} n = 1-5

The major product formed is the bis(2-hydroxyethyl) ester (n=1), the so called monomer. However a mixture of products up to the pentamer have been reported.\textsuperscript{16}

After the evolution of methanol ceases the reaction temperature is raised to a point above the melting point of the polyester to be formed. At this point the second or polycondensation stage begins by condensation of the products of reaction (1). The transesterification of a hydroxyl terminus with an ester linkage leads to the elimination of ethylene glycol. A vacuum is applied to the system to facilitate glycol removal thus driving the equilibrium toward formation of high molecular weight polymer (2).

a H(OCH$_2$CH$_2$OOCCH$_2$CH$_2$CO)$_n$OCH$_2$CH$_2$OH $\xrightarrow{\Delta,\text{Cat.}}$ Vac \hspace{1cm} (2)

an HOCH$_2$CH$_2$OH + H(OCH$_2$CH$_2$OOCCH$_2$CH$_2$CO)$_n$OCH$_2$CH$_2$OH

Although equation (2) serves to illustrate the overall result of the reaction, it is an overly simple view of
the polycondensation phase. The overall build-up of molecular weight occurs through a step-wise process which is the result of five types of ester-interchanges. The notation of Challa\textsuperscript{17} may be employed to illustrate these reactions.

In equations 3-7, \(U\) is the bis(2-hydroxyethyl) ester, \(G\) is ethylene glycol, and \(U_i\) is an i-mer of the polyester.

\[
\begin{align*}
U_1 + U_1 & \leftrightarrow U_2 + G \quad (3) \\
U_1 + U_i & \leftrightarrow U_{i+1} + G \quad i > 1 \quad (4) \\
U_i + U_j & \leftrightarrow U_{i+j} + G \quad i,j > 1 \quad (5) \\
U_{i+n} + U_j & \leftrightarrow U_i + U_{j+n} \quad (6) \\
U_{i+n} + U_{j+m} & \leftrightarrow U_{i+m} + U_{j+n} \quad (7)
\end{align*}
\]

Reactions (3-5) are those responsible for the build up of the number average molecular weight. In each case two small molecules condense to form one larger one. Equation (3) represents the condensation of two monomer units to form a dimer and ethylene glycol. Equation (4) illustrates the condensation of a monomer with the endgroup of an oligomer. While (5) represents the condensation of two oligomers through their endgroups.

Reaction (6) is the redistribution reaction which involves the condensation of an endgroup of one oligomer with
an ester linkage other than the terminal one of another oligomer. There is no change in the number of molecules as a result of this reaction thus the number average molecular weight is not effected. However, the molecular weight distribution is altered because the weight average molecular weight is controlled by the occurrence of reaction (6). In addition, the redistribution reaction is the reversible reaction of polyesters which may be utilized to study CIR. A further discussion of this process will be undertaken during the discussion of copolyesters.

Finally, equation (7) represents the proposed ester-ester exchange. The reaction involves the exchange between two internal ester linkages. As such it may also be viewed as a redistribution reaction. Although its occurrence between low molecular weight esters has been reported, other investigators discount its significance in polymers.

Along with the polymer-forming reactions, several side reactions occur during polycondensation. Chief among these are the formation of cyclic oligomers and diethylene glycol (DEG) units. Kirby, et.al have suggested that the formation of DEG occurs by the dehydration reaction between two alcoholic endgroups. However, Hovenkamp and Munting attribute the formation of DEG to the reaction shown in equation (8):
because of the kinetics of the reaction and the by-products they identified. These authors found that dioxane was produced during the reaction. The only way to rationalize its occurrence is to allow an intermolecular reaction of the type shown in equation (8) leading to dioxane and an acid (9).

\[
\text{RCOOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \rightarrow \text{RCOOH} + 0
\]

The formation of cyclic oligomers during the polymerization of polyesters and during the reheating of the polymer has received extensive study. Cooper and Semlyen, Goodman and Nesbitt, and Peebles, et al. have investigated the formation of cyclic oligomers in PET. It has been shown that 1-2 percent of the final polymer is in the form of cyclic oligomers, and that after removal of the oligomers subsequent heating to the melting point reestablishes their equilibrium content.

Goodman suggested that the cyclic oligomers resulted from an intramolecular ester-ester exchange. However, Peebles has demonstrated that their formation is dependent
upon the hydroxyl group content of the polyester. As a result he concludes that the oligomers arise from an intramolecular exchange between a terminal hydroxyl group and the appropriate ester linkage.

**Kinetics of Melt Polyesterification.** The kinetics of the preparation of PET by melt polycondensation have been studied by many investigators; however there is little agreement between the results of the different groups. A variety of equilibrium constants, kinetic orders, and rate constants have been reported. Considering the complexity of the reactions involved the lack of agreement is not surprising. Various assumptions concerning the ability to suppress or account for the reverse reaction and neglecting or accounting for the volume contraction of the melt have contributed to the divergence of the results.

Perhaps the two most detailed analysis of the kinetics of PET formation have been offered by Challa and Fontana. Both authors investigated the equilibrium and kinetics of the polycondensation. Challa used bis(2-hydroxyethyl) terephthalate, BHET, as his monomer and studied the polymerization in the absence of a catalyst. He measured monomer content, glycol content, and endgroup concentration.

The overall equilibrium constant $K$ was found to vary from 0.49 to 1.2, increasing with increasing degree of
polymerization but independent of temperature in the range 195-282°C. On the basis of these results, Challa challenged the applicability of the Flory principle of equal reactivity to the PET system.

To account for the changing value of $K$, Challa considered three equilibrium reactions (3-5). He concluded that the values of $K$ for these three reactions were in the ratio $1:1.8:(1.8)^2 (K_3:K_4:K_5)$. The activation energy for the polycondensation reaction was 23 K cal/mole, while that of the reverse reaction (glycolysis) was 24 K cal/mole. The $E_a$ for the monomer-monomer reaction was observed to be 22 K cal/mole. Notwithstanding the very similar values of activation energy, the rate constants for the three forward reactions (3-5) were found to obey the same relationship as the equilibrium constants.

The lower reactivity of the monomer was attributed to a greater loss in activation entropy when the monomer entered the transition state. The activation entropy for reaction between monomers was 41.4 cal/deg. mole.

Challa also reported on the kinetics of the redistribution reaction (6). The activation energy was found to be 31 K cal/mole, while the entropy was -23.4 cal/deg. mole. Further, the observed rate of redistribution at 254°C was $12 \times 10^{-2}$ l/mole hr. which was greater than the polycondensation rate of $8.2 \times 10^{-2}$ l/mole hr.

Fontana employed DMT and ethylene glycol as his
reactants and studied the effect of various catalysts on the equilibrium and kinetics. The reactions were carried out under conditions designed to minimize reverse reactions. Corrections for concentration changes due to the contraction of the melt volume were applied.

The equilibrium constant, $K$, was found to be 0.50 and was insensitive to temperature and degree of polymerization. This value was interpreted to mean that an hydroxyl group on a free glycol was twice as reactive as one on a BHET type oligomer. The 0.50 value of $K$ is in excellent agreement with that found by Challa at low DP, but it did not increase with DP as Challa reported. Fontana contends that the increasing value of $K$ is an experimental artifact. He suggests that since $K$ as calculated by Challa becomes very sensitive to the value $p_c$ (equilibrium extent of reaction) that measurement of endgroups and glycol content are not good determiners of $p_c$. It is pointed out that not all endgroups are hydroxyl groups and that the occurrence of acid endgroups could drastically alter the reported results. Since acid endgroups are known to develop with thermal treatment$^{31}$ and the divergence comes at high $p_c$ where thermal treatment has been longest, the measured conversion may well be too high. By recalculating Challa's results with these facts in mind he concludes that $K$ is invariant at 0.50. Thus PET follows a normal Flory-Schultz distribution.
In Fontana studies the order of reaction was observed to be third order overall. There was one order each for ester groups, glycol, and catalyst. The third order rate constants for catalysis by lead oxide, zinc acetate, and calcium salts were given by equations 10-12 respectively.

\[
\log k_{\text{III}} = -\frac{2740}{T} + 4.482
\]  \hspace{1cm} (10)

\[
\log k_{\text{III}} = -\frac{3290}{T} + 6.15
\]  \hspace{1cm} (11)

\[
\log k_{\text{III}} = -\frac{3170}{T} + 5.19
\]  \hspace{1cm} (12)

The activation energies were found to be 12.5 K cal/mole for lead oxide, 15 K cal/mole for zinc acetate, and 14 K cal/mole for calcium.

The results of the catalysis study were interpreted on the basis that the active catalyst was an alcoholate or polymer glycolate rather than the acid salt. On this basis the active catalyst was $M(OR)_x$. Fontana suggests that the accumulation of acid endgroups could be responsible for the deactivation of such a catalyst.

The role of antimony trioxide in the catalysis of PET polymerization was investigated and offered as support for the active alcoholate proposal. Antimony trioxide alone was shown to have negligible ester-interchange activity as well as negligible polycondensation activity. The great enhancement of the catalytic activity of other metallic
salts which $\text{Sb}_2\text{O}_3$ displays was attributed to its effectiveness in scavenging acid endgroups. By scavenging the endgroups it protects the metal alcoholate of the cocatalyst from deactivation and thus enhances the overall rate.

The effectiveness of many catalytic materials in polyesterification have been reported by Yoda,\textsuperscript{32} Stevenson and Nettleton,\textsuperscript{33} and Korshak and Vinogradova.\textsuperscript{13} Most of the materials studied were metal salts, however sulphonic acids, phosphoric acid, and metal surfaces were also reported to be catalytically active.

Copolymers

Copolymers are prepared by the simultaneous polymerization of two or more monomers. As was mentioned earlier, the properties of the resulting polymer are highly dependent upon its chemical microstructure. In general, linear copolymers may be divided into three broad classes based upon their microstructure:

1. Random copolymers - in which the monomer units are distributed in a statistically uniform manner;

2. Segmented or multi-block copolymers - in which the sequences are of intermediate and varied length;
3. Block copolymers - in which the monomer units occur in long uninterrupted sequences.

In discussing the results of the present research, these are used for convenience in discussing different copolymers with similar structural characteristics. Obviously more quantitative measures of randomness (blockiness) must be used to differentiate small changes in microstructural order. To facilitate a quantitative comparison of microstructures two parameters were chosen; the B number\textsuperscript{34} and the Theil Q value.\textsuperscript{35} A detailed discussion of the determination and significance of these values is presented in Chapter III.

For most copolymers, their microstructure is fixed at the time of polymerization and cannot be altered without destroying the copolymer. However, in the case of copolyesters each functional group remains reactive indefinitely. Thus their microstructure can be changed even during a post polymerization treatment. It was this "reactivity" of copolyesters which made them suitable materials for studying CIR.

The reactive nature of copolyesters arrises from the occurrence of the redistribution reaction (equation 6). Two polymer molecules undergo an ester-exchange or redistribution reaction when a terminal hydroxyl group of one attacks an internal ester linkage of another. In a homopolyester, the exchange is only effective in controlling
the molecular weight distribution; however in a copolyester such an exchange can result in a change of sequence distribution. If the hydroxyl group is attached to an A monomer and the ester linkage is composed of two B units, the exchange creates an A-B linkage while destroying a B-B linkage.

As a result of the redistribution reaction, random copolyesters can be prepared by two routes. Melt polycondensation of two diacids and a glycol or two glycols and a diacid will lead directly to a random copolymer. The stepwise nature of the polyesterification process and the equal reactivity of functional groups combine to insure this end.

At times, the different volatilities of the three components makes obtaining the desired copolymer by the above method impractical. To avoid the problem of volatility, the same random copolymer can be prepared by reacting the appropriate homopolymers. Again the reaction is carried out above the melting point of the polymer to be formed. In this case the desired copolymer results from the random occurrence of the redistribution reaction.

The initial reaction product is a block copolymer because ester-exchange occurs in very large segments. As the reaction continues, the large blocks are themselves attacked and the segment length continually decreases. The limiting segment length is reached when the comonomers
are distributed in a statistically uniform manner. At this point a dynamic equilibrium is established and the uniform distribution is maintained.\textsuperscript{21} Thus, in the molten state, a random copolyester represents an equilibrium condition toward which any copolyester will tend.

The importance of the ester-interchange reaction to the preparation of polyesters has been recognized since they were first polymerized. Several early investigations by Flory,\textsuperscript{36} Korshak and Vinogradova,\textsuperscript{37} Youngson and Mellville,\textsuperscript{38} and Izard\textsuperscript{39} among others, served to establish the nature and overall consequences of the redistribution-reaction.

Subsequently, Murano and Yamadera\textsuperscript{34} developed a technique for quantitatively measuring sequence distribution in copolyesters by NMR spectroscopy. This technique has been applied to study the ester-interchange reaction between PET and several aliphatic polyesters in the molten state.\textsuperscript{40,41} Murano and his coworkers reported that reaction followed second order kinetics and had a rate of 4.92 \textsuperscript{10}^{-2}/\text{min}. In three hours at 276°C a mixture of PET and poly(ethylene sebacate) had been completely converted to a random copolymer.

**Effect of Chemical Microstructure on the Properties of Copolyesters.** As is generally the case with copolymers, copolyesters of the same comonomer composition exhibit different properties depending upon the arrangement of
the monomer residues along the polymer backbone. Among the important properties of a copolymer which are effected by its microstructure are: (1) melting point; (2) glass transition temperature; (3) solubility; (4) modulus; (5) tensile strength; and (6) elasticity. In general, it is found that increased microstructural order (block character) leads to copolymers with superior properties.\textsuperscript{1}

Over a wide range of composition there is virtually no change in the melting point of block copolyesters; however comparable random copolymers show greatly depressed melting points. Coleman\textsuperscript{69} has reported that the incorporation of 30 wt.% poly(ethylene oxide) of molecular weight 2800, only depressed the melting point of PET by 4\textdegree C. Yet when 30\% of diethylene glycol (dimeric PEO) was used, the melting point was reduced by 80\textdegree C.

For copolymers of PET and poly(ethylene sebacate), Charch and Shivees\textsuperscript{70} found similar behavior. At a composition of 40/60 PET/PEO, the melting point of the random copolymer was 50\textdegree C lower than the corresponding block copolymer. Theil and Mandelkern\textsuperscript{71} have also studied the fusion of block copolymers of ethylene sebacate. They found that the melting point of the copolymers with ethylene adipate changed from 83.7\textdegree C with 80\% PEA to 80.5 with 205 PEA. Over a 60\% change in composition the melting point only changed 3\textdegree C. No correlation with random copolymers was given.
Although the relationship between the melting point and composition of a block copolymer is different than that for a random copolymer, the same is not true for the glass transition temperature. Iwakura et al.\(^{72}\) have shown that the experimentally determined \(T_g\) for block and random copolyesters follow the same curve.

A comparison of the mechanical properties of block versus random copolyesters have also been reported. It has been found that block copolyesters generally have better tensile and tear strengths than random copolymers.\(^{73}\) Further, block copolymers of PET/PES show improved stress decay as compared to their random counterparts. This improvement is accomplished without loss of modulus, tenacity, or elasticity.\(^{70}\)

A particularly interesting example of block copolyesters which have improved mechanical properties are copolymers typified by PES/poly(propylene adipate). Block copolymers of this type have extremely high impact strength because they phase separate.\(^1\) The phase separation, which accounts for the high impact strength, is possible only because the sequences of comonomer units are long enough. As a result, random copolymers have much lower impact strengths.

Kibler et al.\(^7\) have reported that random copolymers of cis/trans-cyclohexylenedimethanol and terephthalic acid are more soluble than block copolymers with the same
composition. Using this fact Go$^5$ developed a turbidimetric titration technique to follow changes in randomness of cis/trans PCHDT copolymers caused by CIR.

Solid-State Reactions of Polyesters

A true solid-state polymerization involves preparation of the polymer at temperatures below the melting point of the monomer. In recent years, the polymerization of many addition polymers by this technique have been reported.$^{42}$ However, among the condensation polymers only polyamides prepared from their nylon salts have been successfully polymerized by a true solid-state process.$^{43}$ Attempts to polymerize polyesters below the melting point of the monomers have generally failed. The polymerizations yield only low molecular weight oligomers (n=2-3).$^{44}$

Although high molecular weight polyesters cannot be prepared directly from the monomer, it has long been known that ester-interchange does occur in the solid-state.$^{45}$ As a consequence, polyesters can be prepared by solid-state polycondensation of oligomers (prepolymer). The polycondensation from oligomers is a two step process. The prepolymer is first prepared by a molten state condensation; then it is further condensed to high molecular weight in the solid-state.

The early investigation of the solid-state preparation of PET was described by Coover et.al.$^{46}$ A prepolymer is
prepared by the conventional melt polycondensation method \( (\eta = 0.2-0.4) \) then is solidified and ground to pass a 20 mesh sieve. The powder is then placed in the reaction vessel and heated to a temperature 35-90°C below its melting point. The powder is stirred and a \( \text{N}_2 \) atmosphere is purged through the system at 100-1000 ml/minute to facilitate removal of ethylene glycol. As reaction occurs, the temperature is increased in such a way that the powder remains fluid until the final temperature is 20°C below the \( T_m \) of PET.

Since this initial disclosure, numerous modifications and improvements to the basic solid-state polycondensation procedure have appeared in the patent literature. Among the important improvements have been those of Barkey,\textsuperscript{47} Heighton and Most,\textsuperscript{48} and Russin, et.al.\textsuperscript{7}

Barkey claimed a dramatic improvement in the rate of solid-state polycondensation by employing a PET prepolymer with an amorphous phase which did not undergo crystallization at the reaction temperature. The stable amorphous phase was prepared by crystallizing the prepolymer in thin sheets under carefully controlled conditions.

Heighton and Most reported the preparation of PET using a fluidized-bed column. The processes are basically the same as that of Coover, et.al.; however the prepolymer powder is polycondensed in a column fluidized by nitrogen. The inert gas stream (which is scrubbed and recycled)
provides better contact with the powder, leading to better removal of the glycol and an improved rate.

Russin, et.al. have investigated the preparation of PET from scrap polymer by solid-state polycondensation. They found that the scrap polymer must be reacted with ethylene glycol in the melt to generate an active prepolymer before solid-phase molecular weight build up was possible. These results suggest that hydroxy terminated oligomers are necessary to polymerize at a reasonable rate.

An investigation of the solid-state polymerization of BHET and PET prepolymer oligomers has been published by Bamford and Wayne. They found that the solid-state polycondensation of BHET proceeded at extremely slow rates and that the only identifiable product was the dimer.

When they used oligomeric PET as the starting material, high molecular weight products were produced. The activation energy for the polymerization of a prepolymer, where \( \mathcal{N} = .297 \) and particle size was 14-25 BSS mesh, was calculated to be 20.4 K cals/mole. A comparable value of 21.8 K cals/mole has recently been reported by Simonova, et.al. for particles of ~1mm.

Bamford and Wayne also investigated the effect of particle size and initial percent crystallinity of the prepolymer on the reaction rate. Although they found that crystallinity did not effect the rate, they suggest that
recrystallization to the same degree during heating up to the reaction temperature may explain this observation. On the other hand, a marked increase in reaction rate was observed with decreasing particle size. This suggests that the reaction which leads to molecular weight build-up occurs near the surface of the particle. The hindered diffusion of the glycol is presumable responsible for this observation. The farther from the surface the glycol is liberated the more likely the occurrence of the reverse reaction is before the glycol escapes the particle. In fact, Pell and Davis\textsuperscript{50} report that even in the melt, in static films, diffusion of the glycol is the rate limiting step at depths greater than 0.28 mm.

A mathematical model for the solid-state polymerization of PET has been devised by Chang.\textsuperscript{51} The model is based upon diffusion control and it is in good agreement with the reported data. It was shown that the diffusion of the glycol was the rate controlling step for temperatures $> 210^\circ\text{C}$ and particle size $< 100$ mesh. Thus increases in temperature and decreases in percent crystallinity accelerated the reaction.

Mifune\textsuperscript{52} has also investigated the solid-state polycondensation of PET oligomers. As was the case in the other investigations cited, he concluded that the diffusion of ethylene glycol was the rate limiting step of the reaction. The observation which makes this study worth noting
however, is that the molecular weight distribution of the solid-state product is broader than obtained by melt polycondensation. No explanation of the difference was offered.

Subsequently, a number of investigations of related solid-state polycondensations have confirmed this report. Cha\textsuperscript{53} and Wunderlich\textsuperscript{54} reported the same result in their investigation of PET, while Zimmerman\textsuperscript{55} reported that a similar broadening of molecular weight distribution occurred in polyamides prepared by solid-state polymerization. The same explanation of the abnormal distribution was offered by both Wunderlich and Zimmerman. They suggested that the polymer endgroups which are necessary for reaction occur entirely in the amorphous regions. Thus the reaction takes place in the amorphous region of the polymer. The crystalline segments are not accessible to reaction due to lattice restrictions. As the reaction proceeds, successive polymerization and crystallization occur, and because the crystalline regions are not susceptible to further reaction (ie. redistribution) longer chain length than normally obtained in melt polymerization result. It is interesting to note that with minor modifications to account for including a comonomer, this mechanism is the same as that proposed for CIR.

Wunderlich and Lee\textsuperscript{56} have suggested that under the above conditions extended chain crystals are likely to
occur. That is, when the amorphous phase is the only locus of reaction in a semi-crystalline polymer and subsequent crystallization occurs, the product should exhibit an extended chain crystalline morphology. This expectation has been confirmed by Kawai and Komoto. They found that solid-state polymerization of L and D,L, alinine N-carboxyanhydrides resulted in extended chain crystals.

The fact that extended chain crystals can be formed during solid-state polymerization suggests that care by employed in interpreting the results of thermal analysis of these materials. The formation of extended chain crystals usually leads to higher values of $T_m$ and may be misleading; especially if the melting point (first cycle only) of a copolymer is being used as a structural or compositional indicator.

Thermal Stability of Polyesters

Crystallization-induced reaction is a solid-state reorganization which must be carried out at temperatures approaching the melting point of the copolymers. Since polyesters may undergo degradation at such elevated temperatures it is important to consider their thermal stability.

Degradation of a polyester occurs when they are heated to temperatures above their melting points. The rate of degradation is effected by the temperature, the duration
of treatment, and the presence of oxygen or a catalyst. Prolonged heating leads to a deterioration of molecular weight, color formation, and under some conditions to gel formation (crosslinking).

In the absence of oxygen, Yoda, et al.\textsuperscript{31} report that PET is relatively stable. Heating the polymer at $300^\circ$C under a nitrogen purge only caused a 3.8\% weight loss and no insoluble gel was formed in four hours. The authors offer no further analytical data on the heated PET sample so the reason for the weight loss cannot be assessed. It is possible that production of vinyl esters and subsequent loss of acetaldehyde were responsible; however, under the conditions employed (800 ml/min N\textsubscript{2}) further polymerization with loss of ethylene glycol is also a possibility. In either case the polymer may be assumed to be relatively uneffected by this treatment.

Heating of the polymer for longer periods does lead to degradation. Pohl\textsuperscript{58} has investigated the initial degradation of PET and concluded that the cleavage of the chain occurs in a random fashion primarily at the methylene group $\beta$ to the ester linkage. The products of the chain scission are a vinyl ester and carboxylic acid. If 2-hydroxyethyl endgroups are present in sufficient concentrations, these initial reaction products are consumed with reformation of the chains. Reaction of the 2-hydroxyethyl groups to maintain the chains explains why the
degradation of molecular weight in polyesters increases as their molecular weight increases. The stabilizing effect of the hydroxy endgroups are shown in equations (13), (14), and (15).

\[
\begin{align*}
\text{C}_6\text{H}_4\text{COOCCH}_2\text{CH}_2 & + \text{HOCH}_2\text{CH}_2\text{OOCC}_6\text{H}_4 \\
\text{CH}_3\text{CHO} & + \text{C}_6\text{H}_4\text{COOCCH}_2\text{CH}_2\text{OOCC}_6\text{H}_4
\end{align*}
\] (13)

\[
\begin{align*}
\text{C}_6\text{H}_4\text{COOH} & + \text{HOCH}_2\text{CH}_2\text{OOCC}_6\text{H}_4 \\
\text{H}_2\text{O} & + \text{C}_6\text{H}_4\text{COOCCH}_2\text{CH}_2\text{OOCC}_6\text{H}_4
\end{align*}
\] (14)

\[
\begin{align*}
\text{C}_6\text{H}_4\text{COOCOC}_6\text{H}_4 & + \text{HOCH}_2\text{CH}_2\text{OOCC}_6\text{H}_4 \\
\text{C}_6\text{H}_4\text{COOH} & + \text{Polymer}
\end{align*}
\] (15)

When the endgroup (hydroxyl) gets too low, chain scissions become permanent and the molecular weight drops rapidly.

The increased concentration of vinyl ester and acid leads to the formation of vinyl polymer, polyanhydrides, and acetaldehyde. In addition, gaseous products are evolved. The major constituent of the gases produced is always acetaldehyde. The other gases detected are CO, CO\textsubscript{2}, H\textsubscript{2}O, C\textsubscript{2}H\textsubscript{4}, CH\textsubscript{4}, and C\textsubscript{6}H\textsubscript{6}. Ratios of these latter products vary with the temperature and the conditions of degradation.

The activation energy for the pyrolysis of PET was found to be in the range of 32-40 K cals/mole. On
theoretical grounds, the activation energy for a heterolytic ester pyrolysis should be $\sim 60$ K cals, thus the lower experimental value suggested a radical mechanism. However, the degradation of PET is not inhibited by radical scavengers so a radical mechanism has been rejected. Buxbaum$^{59}$ and Pohl$^{58}$ suggest heterolytic cleavage of the ester bond via a cyclic intermediate (16).

\[ P \text{C}_6\text{H}_4\text{COOCH}_2\text{CH}_2\text{OOC-C}_6\text{H}_4 \rightarrow [\text{C}_6\text{H}_4\text{C}=\text{CH-OOCC}_6\text{H}_4] \quad (16) \]

\[ P \text{C}_6\text{H}_4\text{COOH} + \text{CH}_2=\text{CH}-\text{OOCC}_6\text{H}_4 \rightarrow P \]

Studies with model compounds such as ethyl dibenzoate which yields vinyl benzoate and benzoic acid when heated to 250-300°C support the validity of this proposal.$^{61}$

Further reaction of the vinyl esters gives rise to the products listed before. A mechanism which accounts for the known products has been advanced by Zimmerman, et.al.$^{62}$ and Yoda, et.al.$^{31}$ An outline of this mechanism appears in Figure 2.

Identification of the products which cause the coloration of the polymer as it degrades has proved to be very
Figure 2 - Mechanism for the Thermal Degradation of Poly(ethylene terephthalate)
difficult. It is generally conceded that at least part of the chromophoric species is attached to the polymer; however, the nature of the products are debated. Gooding\textsuperscript{63} asserts that the chromophor arrises from the acetaldehyde in the form of polyenaldehydes. Yet Zimmerman\textsuperscript{62} has shown that polyvinylesters lead to color formation. Since both products are known to occur during degradation, it is likely that both contribute to the discoloration.

The thermoxidative stability of PET has also been investigated. Marshall and Todd\textsuperscript{64} found that the rate of degradation increased linearly with the oxygen concentration. There are several mechanisms which account for the oxygen dependence. It is generally agreed that free radicals are produced by the action of oxygen on a methylene group (17).

\[
P\overset{\sim}{\overset{C_{6}H_{4}COOCH_{2}CH_{2}OC_{6}H_{4}}{}}\overset{0_{2}}{\overset{P}{\rightarrow}}P\overset{\sim}{\overset{C_{6}H_{4}COOCHCH_{2}OC_{6}H_{4}}{}}\overset{P}{\sim}\]

\[
OOH + P\overset{C_{6}H_{4}COOCHCH_{2}OC_{6}H_{4}}{\sim} P
\]

Yoda, et.al.\textsuperscript{31} suggest that crosslinking occurs by reaction of the vinyl esters produced by thermal degradation with these radicals (18).
However Nealy and Adams\textsuperscript{65} and Spanninger\textsuperscript{66} suggest that crosslinking occurs due to the action of the phenyl radical via arylation of terephthalate rings. The production of phenyl radicals results from cleavage of the radical produced by reaction (19) as shown.

By metholyzation of the gel formed compounds I-IV were isolated and offer support for the arylation mechanism.
The thermal stability of poly(ethylene succinate) has been investigated by Carothers and coworkers. They found that in the absence of oxygen, the polymer degrades to the cyclic dimer of ethylene succinate. Treatment of PES at 270°C gave 80% distillation with no gel formation in 4 hours. Ninety five percent of the distillate was the cyclic dimer and no monomer or monomeric cyclic ethylene succinate were found. Effective ester interchange catalysts were found to increase the rate of depolymerization.
Poly(ethylene terephthalate) is also subject to degradation to cyclic esters; however, the extent of reaction is far less, presumable due to the lower volatility of its cyclic oligomers. Goodman and Nesbitt have reported that after extracting the cyclic oligomers formed during the polymerization of PET, that heating the sample above its melting point leads to the formation of more cyclic oligomers. These oligomers amount to only about 1.5 wt.%. Although cyclic oligomers are formed above Tm, these authors report that no cyclic materials were found after heating for 160 hours just below the melting point.
CHAPTER II

EXPERIMENTAL

Reagents

**Dimethyl Terephthalate (DMT).** Practical grade DMT obtained from Eastman Chemical Co. was purified by double recrystallization. Thus, 50 grams of DMT was dissolved with heating in 1000 ml of absolute ethanol, filtered, heated to redissolve the DMT, and allowed to stand at room temperature for 24 hours. Crystals so obtained were collected by suction filtration and washed with two 100 ml portions of cold (0°C) ethanol. The DMT from the first recrystallization was subjected to a repetition of the above process and the crystals were dried 18 hours at 40°C in a vacuum oven. Yield 38 grams: mp 143°C.

**Dimethyl Succinate (DMS).** Dimethyl succinate obtained from Eastman Chemical was mixed with 10 grams of predried anhydrous magnesium sulfate per 100 grams and allowed to stand overnight. The mixture was transferred to a distillation flask and the DMS was vacuum distilled. The fraction amounting to the middle 70% was collected at a constant boiling point of 37-38°C @ 1mm Hg.
Bis(hydroxyethyl) Terephthalate (BHET). The model compound BHET was prepared by reacting an excess of ethylene glycol with DMT. Thus 20 grams of DMT, 31 grams of ethylene glycol, and 0.3% Ca(Ac)$_2$ were placed in a single neck round bottom flask fitted with a distillation head. The flask was heated at 205°C until the temperature of the distillate reached 185°C and then the contents were poured into one liter of ice water. The crude BHET was recovered by filtration, recrystallized twice from distilled water, and then dried at room temperature in a vacuum oven. The recrystallized material melted at 109.5-110°C.

Ethylene Glycol. Under a dry nitrogen atmosphere, 10 grams of freshly cleaned sodium was dissolved in one liter of ethylene glycol. After refluxing the mixture for 2 hours under nitrogen, it was cooled and vacuum distilled: the first 15 and last 25 percent were discarded. The boiling point of the middle fraction was 51°C @ 0.8 mm Hg.

Trifluoroacetic Acid (TFA). For use as a reprecipitation solvent, TFA obtained from Aldrich in 99.5% purity was used without additional purification. For the NMR measurements, one 500 g bottle of 99.5% TFA had 2% (w/v) hexamethyl disiloxane added as reference and was used for all NMR spectra recorded for this thesis research. Periodic NMR spectra were run on this material to insure against contamination.
N,0,- Bis(trimethyl silyl) acetamide (BSA). BSA was obtained from Pierce Chemical Co. in 1 ml ampules. The ampules were stored in the refrigerator and any unused portion from an open ampule was discarded.

Bis-(methoxy)-ethyl Ether. Bis-(methoxy)-ethyl ether was dried by refluxing 200 ml over 10 grams of freshly cleaned sodium for 4 hours and subsequent distillation into a dried bottle sealed with a septum. Boiling point of the middle fraction (80%) was 162-163°C.

Triethyl Amine. Triethyl amine was purified by refluxing over barium oxide for 3 hours and distilled into a dry sealed bottle. Boiling point was 88-89°C.

Acetonitrile. The acetonitrile used was a silination grade acetonitrile provided by Pierce Chemical in a septum bottle.

Other. All other reagents used were ACS certified grades. Solvents employed were obtained from the stock room and used without purification.

Preparation of Copolymers

Copolyesters for this research were all prepared by melt polycondensation to insure a random distribution of monomer residues. All of the polymerizations were performed in an analogous manner, thus only the preparation of the 74% terephthalate poly(ethylene terephthalate-co-succinate)
will be detailed here. Feed ratios, reaction times and temperatures for the other copolymerizations are collected in Table 1.

The polymerization reactor was a 100 ml, 1 neck, round bottom flask fitted with a special polymerization head as illustrated in Figure 3. The head was fitted with a N2 inlet, stirring adapter, condensor, and vacuum outlet. A seal was effected between the stirring shaft and the ball joint (SJ) adapter by wiring a piece of vacuum tubing to the adapter, the shaft, and the stirring motor. The adapter and shaft were allowed to turn with the motor. A well greased ball joint served as a seal between the adapter and polymerization head.

After charging 25 grams of DMT (0.129 moles), 8 grams of DMS (0.055 moles), 25.1 grams of ethylene glycol (0.368 moles), and 0.050 grams of calcium acetate dihydrate to the flask, the system was purged with nitrogen for 15 minutes before being lowered into a constant temperature bath maintained at 160°C. In 3 hours time, methanol evolu-
tion had ceased and the bath temperature was raised to 265°C over 45 minutes; upon reaching this temperature .011 gram of Antimony trioxide was added and vacuum was applied slowly (30 minutes) until a pressure of less than 0.1 mm Hg was reached. These conditions were maintained for 7 hours, then the flask was removed from the bath and allowed to
### TABLE I

**REACTION CONDITIONS FOR PET/ES COPOLYMERIZATIONS**

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>DMT  g (moles)</th>
<th>DMS</th>
<th>ETHYLENE GLYCOL</th>
<th>FIRST STAGE*</th>
<th>SECONDSTAGE**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>hrs</td>
<td>oC</td>
</tr>
<tr>
<td>B</td>
<td>13.3(0.068)</td>
<td>2.5</td>
<td>12.0(0.215)</td>
<td>3</td>
<td>160</td>
</tr>
<tr>
<td>D</td>
<td>19.6(0.100)</td>
<td>4.86</td>
<td>17.3(0.279)</td>
<td>3</td>
<td>160</td>
</tr>
<tr>
<td>G</td>
<td>19.6(0.100)</td>
<td>4.23</td>
<td>16.9(0.273)</td>
<td>4</td>
<td>160</td>
</tr>
<tr>
<td>I</td>
<td>25.0(0.129)</td>
<td>8.0</td>
<td>25.1(0.368)</td>
<td>3</td>
<td>160</td>
</tr>
</tbody>
</table>

* CATALYST: 0.16% Ca(Ac)$_2$·2H$_2$O (based on total weight of esters).

** CATALYST: 0.03% Sb$_2$O$_3$ (based on total weight of esters).
Figure 3 - Polymerization Reactor
cool under a nitrogen atmosphere. The polymerization catalyst was removed by dissolving the copolymer in trifluoroacetic acid and precipitating into a ten fold excess of methanol. The polymer was recovered by suction filtration, dried in a vacuum oven for 24 hours, ground in a Wiley mill to pass a 20 mesh sieve, and annealed 5 hours over refluxing bis-(methoxy)-ethyl ether (b.p. 162°C).

Crystallization-Induced Reorganization

Copolymers from which the polymerization catalyst had been removed by reprecipitation were impregnated with catalyst by slurring them in a solution of the desired catalyst, and slowly evaporating the solvent with dry filtered nitrogen. The tetraethyl orthotitinate and the tetrabutyl orthotitinate were applied from predried bis-(methoxy)-ethyl ether in a closed flask purged with dry nitrogen. Calcium acetate was applied from a 95/5 (V/V) methanol/water solution, while the antimony trioxide was applied from 3% methanolic HCL solution.

The copolymers were slurred for 2 hours and then the solvent was slowly stripped off with a dry nitrogen stream. After initial drying the copolymers were ground to insure uniformity and dried for 24 hours in a vacuum oven to remove the last traces of solvent.
To protect the orthotitinates from deactivation by moisture, the vacuum oven was evacuated with $P_2O_5$ inside. It was allowed to stand for 2 hours, thenpurged with dry nitrogen before the copolymers were finally dried.

Except that the orthotitinate samples were transferred to their reaction flasks in a dry bag to prevent deactivation, all samples were treated in an analogous manner from this point on. One half gram of copolyester was transferred to a 25 ml erlenmeyer flask which was sealed with a wired on septum. Each flask was purged with nitrogen for at least 15 minutes and left under slight positive pressure. The flasks were then placed in a constant temperature bath maintained at the desired temperature. Reorganization times of 1 to 36 hours were employed. Upon removal from the bath the flasks were labeled and the polymers were reprecipitated and annealed (at 162°C) before characterization.

Copolymer Characterization

Inherent Viscosity. The inherent viscosity, $\eta_{inh}$, of all polymer samples were measured on 1g/dl solution in $o$-chlorophenol. An Ubbelohde #100 dilution type viscometer which had a solvent flow time, $t$, of 159 sec. was employed to measure the viscosities. All measurements were made at $25^{\pm}.02^\circ C$. 
Determination of exact values of molecular weights were not attempted because no "K" and "a" values are known for these copolyesters. Since these parameters will change with molecular weight distribution and composition - both of which change during CIR - no attempt was made to determine their values. However, relative values of molecular weight may be gauged by comparison with those determined by G.P.C. Several copolymer samples were run by Dr. Overton of Tennessee Eastman on their G.P.C. in m-cresol @ 125°C. The values determined by G.P.C., the corresponding inherent viscosities, and the inherent viscosities of the copolyesters employed for the CIR are collected in Table 2.

Ellery\textsuperscript{74} has reported that the melting point of aliphatic copolymers of PET reach the invariant plateau in the M.W. vs $T_m$ curve at molecular weights between 2000-3000. The results shown in Table 2 indicate that all of the copolymers employed in this research are above these values. Thus it may be concluded that melting point increases which occur as a result of CIR are not a result of molecular weight increase.

**Thermal Characterization.** A Perkin-Elmer DSC-2 Differential Scanning Calorimeter was used to measure the melting points, recrystallization temperatures, heats of fusion, and percent crystallinity of the copolymers. Samples of 7-10 mg of 20 mesh powder were sealed in aluminum sample pans and run at 10°C per minute. Melting points
TABLE 2

Molecular Weight Vs. Inherent Viscosity

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>( \eta_{\text{inh}}^* )</th>
<th>( \bar{M}_w^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.245</td>
<td>9779</td>
</tr>
<tr>
<td>2</td>
<td>.239</td>
<td>8381</td>
</tr>
<tr>
<td>3</td>
<td>.201</td>
<td>5287</td>
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<tr>
<td>B</td>
<td>.190</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>.272</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>.346</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>.781</td>
<td></td>
</tr>
</tbody>
</table>

a. \( \bar{M}_w \) determined by G.P.C. in terephthalate equivalent molecular weight.

* 0.25% solutions in o-chlorophenol.
and recrystallization temperatures were determined by comparison to a calibration curve (Figure 4) constructed by measuring the melting points of lead, tin, indium, benzoic acid and naphthalene. For the purpose of this research the melting point was defined as the point at which the DSC trace returned to the baseline; the recrystallization temperature was defined as the point at which the DSC curve departed from the baseline on the cooling cycle. The heat of fusion of the copolyesters were determined by cutting out the area under the endothermic peak and comparing it to the area of a standard indium endotherm. Using equation (20), the copolyesters' heats of fusion were calculated:

\[
Hp = \frac{Ap \cdot Rpol \cdot Si \cdot Wi \cdot Hf}{Ai \cdot Rind \cdot Sp \cdot Wp}
\]  

(20)

where,

- \( Hf \) = heat of fusion of indium 6.80 cal/gram.
- \( Ap \) = area of copolymer endotherm.
- \( Ai \) = area of indium endotherm.
- \( Wp \) = weight in mg of copolymer sample.
- \( Wi \) = weight in mg of indium sample.
- \( Rp \) = range setting used for copolymer thermogram.
- \( Ri \) = range setting used for indium thermogram.
- \( Sp \) = chart speed used for copolymer thermogram.
- \( Si \) = chart speed used for indium thermogram.
Figure 4 — DSC Calibration Curve
Employing the results obtained from equation (20), the DSC percent crystallinity of the copolymers was calculated by employing equation (21).

\[
\% X_c = \frac{Hp (T \cdot M_1) + (S \cdot M_2) \cdot 100}{H_o (T \cdot M_1)}
\] (21)

where,

- \( T \) = mole percent terephthalate in the copolymer.
- \( M_1 \) = molecular weight of ethylene terephthalate repeat unit (192).
- \( S \) = mole percent succinate in the copolymer.
- \( M_2 \) = molecular weight of the ethylene succinate repeat unit (144).
- \( H_o \) = heat of fusion per gram of repeat unit of poly(ethylene terephthalate) 32.2 cal/g.

**Monomer Analysis of Copolyesters.** To determine the absolute monomer composition of the copolyesters a saponification-gas chromatography analysis was employed. A silylation procedure similar to one reported for nylons was developed. Samples of 0.2 gram of the copolyesters were placed in a 25 ml erlenmeyer flask and saponified at 85°C with 5 ml of 1N NaOH for 36 hours. Although the polymers "dissolve" to form a clear solution in \( \sim \)1 hour, the long reaction time is necessary, because up to 30
hours a terephthalate derivative identifiable as bis (hydroxyethyl) terephthalate is still present in the reaction media.

One milliliter of the saponificate was transferred to a conical vial and slowly evaporated. After drying, the sample was carefully neutralized with 3N HCl taking care not to allow the exothermic acid-base reaction to cause the contents of the vial to boil over. The sample is then dried in an air oven maintained @ 40°C. If the oven temperature is higher than 40°C, the succinic acid apparently co-distills with the water/HCl because all samples dried above this temperature were extremely low in succinate content.

Upon completion of this step, the sample was washed with distilled water to remove residual HCl, redried in the air oven, azeotropically dried with methylene chloride in the air oven, and dried over P₂O₅ for 12 hours in a vacuum oven. The reaction vials were then sealed with rubber septa and 60 ul of triethyl amine and 300 ul of acetonitrile were added through a needle. The contents of the vials were then stirred for 20 minutes under a slow dry deoxygenated nitrogen purge before 400 ul of BSA were added by syringe. The BSA was allowed to react 10 hours at 65°C and then the sample was chromatographed.
A Varian Areograph 1520 gas chromatograph fitted with 5' x 1/8" 10% SE-30 on Chromasorb W columns was employed for the analysis. Operating conditions were:

1. Injection temperature = 250°C
2. Detector temperature = 250°C
3. Column temperature programmed:
   - Initial temperature 120°C hold 3 minutes;
   - Program 4°C/minute 3 minutes;
   - Program 12°C/minute 3 minutes; hold
4. Carrier gas = helium 25 ml/minute
5. Thermal conductivity detector (150 mamp)

The monomer composition of the copolymers was determined by comparison with a calibration curve. The calibration curve was constructed by chromatographing known samples of terephthalic and succinic acid carried through the whole procedure described above in parallel with the saponifications.

Measurement of Sequence Length Distributions. The measurement of sequence length distribution was accomplished by nuclear magnetic resonance (NMR) spectroscopy. The spectra of the copolyesters were recorded using a Perkin-Elmer R32 (90 MHz) NMR operating at 70°C.

Samples for analysis were prepared by dissolving 0.1 gram of the copolyester in 1 ml of TFA. Hexamethyl disiloxane (2%) was employed as an internal standard.
The areas of the various resonance peaks were determined by integration of the 100 Hz expanded scale spectra of the appropriate regions. The average value of five integrations was considered to be the area. From these areas the sequence lengths and compositions were calculated from the equations presented in Chapter III.

Determination of Tensile Properties. The changes in physical properties which occurred as a result of crystallization-induced reaction were determined by comparing the tensile strength, elongation at break, and modulus of a copolyester before and after reorganization. A Tensilon UTM - 11 was employed to record the stress-strain curves of the samples.

Test specimen were in the form of cylindrical, dumbbell-like tensile bars. The tensile bars were prepared by melting the polymer at 250°C and extruding it into a stainless steel mold maintained at 220°C. After filling, the mold and test bar were slowly cooled to room temperature.
CHAPTER III

CRYSTALLIZATION INDUCED REACTION OF PET/ES COPOLYESTERS: EXPERIMENTAL RESULTS AND DISCUSSION

Introduction. Ester-interchange is a reversible reaction which is known to occur at a reasonable rate in the solid state.\textsuperscript{44,51} As such, it may be utilized to study the CIR process. Copolyesters which are subjected to ester-interchange in a semi-crystalline state should reorganize to yield products with increased block character. Lenz and Go\textsuperscript{5,6} have reported the successful reorganization of copolyesters by this process. The results of their work have thus confirmed the validity of the theory. The present investigation was undertaken to determine the parameters which control the extent of reorganization. A quantitative understanding of the maximum extent of reorganization which may be accomplished by CIR will help to elucidate the practical significance of the reaction. If significant alterations of copolymer properties can be attained without degradation, the CIR process may be useful to prepare new materials.

In the reorganization of a polyester by CIR, the only ester-interchange reactions which can effect the microstructure are those which occur adjacent to a crystallite.
Thus the extent of reorganization is dependent upon the incorporation of the crystallizable units into the existing lattice as well as the rate of the reversible reaction. Therefore, the extent of the reorganization should be controlled by the following parameters:

1. Time of Reaction
2. Temperature of Reaction
3. Catalyst and Catalyst Concentration
4. Molecular weight, i.e. end group concentration
5. Degree of Crystallinity

Copolyesters of PET/ES of different compositions were synthesized by melt polycondensation to insure a random distribution of monomer units and then subjected to CIR. By selective variation of the above parameters, their affect on the reorganization of the copolyesters was studied. The results of these experiments are reported in subsequent sections of this thesis.

Poly(ethylene terephthalate-co-succinate) (PET/ES) was chosen for this investigation because changes in its microstructure could be analyzed by the NMR technique of Murano and Yamadera. These authors found that the protons of the ethylene glycol residues of copolyesters exhibited different resonances depending upon their placement along the backbone of the polymer. In PET/ES, there are three possible internal placements which the glycol residue
may assume (22, 23, 24).

\begin{equation}
\text{O-C-} \begin{array}{c}
\text{O} \\
\text{C-O-C-CH}_2\text{CH}_2\text{O-C-} \\
\text{C-O}
\end{array}
\begin{array}{c}
\text{O} \\
\text{C-O-C-CH}_2\text{CH}_2\text{O-C-CH}_2\text{CH}_2\text{C-O}
\end{array}
\tag{22}
\end{equation}

\begin{equation}
\text{T - G - T}
\end{equation}

\begin{equation}
\text{O-C-} \begin{array}{c}
\text{O} \\
\text{C-O-C-CH}_2\text{CH}_2\text{O-C-CH}_2\text{CH}_2\text{C-O}
\end{array}
\begin{array}{c}
\text{O} \\
\text{C-O-C-CH}_2\text{CH}_2\text{O-C-CH}_2\text{CH}_2\text{C-O}
\end{array}
\tag{23}
\end{equation}

\begin{equation}
\text{T - G - S}
\end{equation}

\begin{equation}
\begin{array}{c}
\text{O-C-CH}_2\text{CH}_2\text{C-O-C-CH}_2\text{CH}_2\text{O-C-CH}_2\text{CH}_2\text{C-O}
\end{array}
\tag{24}
\end{equation}

\begin{equation}
\text{S - G - S}
\end{equation}

Each of these placements gives rise to a different chemical shift for the protons of the glycol residue. Since the area of an NMR peak is a quantitative measure of the number of protons of a given type in the sample, these differences in chemical shift permit the determination of both homo-unit and hetero-unit dyad content of the polyester. From this information the microstructure of the copolymer can be defined.

The number average sequence length, $L_n$, is one measure of the degree of randomness of a copolymer. As $L_n$ increases the units occur in longer blocks, and therefore
the polymer becomes less random. $L_n$ is readily calculated from the NMR data using equation (25) and (26):  

$$L_nT = \frac{2(T)}{T-G-S}$$  \hspace{1cm} (25)  

$$L_nS = \frac{2(S)}{T-G-S}$$  \hspace{1cm} (26)  

where (T) and (S) are the mole fraction of terephthalic and succinic acids, and T-G-S is the mole fraction of hetero-unit dyads. The hetero-unit dyad concentration is calculated by dividing the area of the T-G-S peak by the total area of all glycol residue peaks. The value of $L_nT$ however, is not independent of compositional changes, so care must be exercised in applying it as a measure of randomness.

Two measures of microstructure which are independent of the composition of the copolymer are the B index of Murano and the Theil Q. Murano has defined B as:

$$B = P_{TS} + P_{ST}$$  \hspace{1cm} (27)  

where $P_{TS}$ is the probability of a terephthalate unit being followed by a succinate unit and $P_{ST}$ is the probability of a succinate unit followed by a terephthalate. The probabilities may be calculated from the mole fraction of hetero-unit dyad T-G-S, and the mole fractions of terephthalic (T)
and succinic acids (S) measured by the NMR, according to equations (28) and (29).

\[ P_{TS} = \frac{T-G-S}{2T} \] (28)

\[ P_{ST} = \frac{T-G-S}{2S} \] (29)

In a random copolymer \( B = 1 \); in a mixture of homopolymers \( B = 0 \); and in an alternating copolymer \( B = 2 \). Thus as \( B \) decreases from one to zero the polymer becomes increasingly blocky.

The Q number is defined as:

\[ Q = \frac{(P_{TT})(P_{SS})}{(P_{TS})(P_{ST})} \] (30)

where

\[ P_{TT} = 1 - P_{TS} \] (31)

and

\[ P_{SS} = 1 - P_{ST} \] (32)

Because a given terephthalate unit in a random copolyester has an equal probability of being followed by a succinate or a terephthalate, \( P_{TT} = P_{TS} \) and \( P_{SS} = P_{ST} \); thus \( Q = 1 \). For a block copolymer \( P_{TT} > P_{TS} \) and \( P_{SS} > P_{ST} \), thus \( Q \) increases without limit. Values of \( Q > 1 \) imply that the comonomer units are connected in blocks.
As was discussed previously, the thermal characteristics of a copolymer are dependent upon its microstructure. Because CIR causes a change in microstructure of a copolymer, the thermal properties of that copolyester should also change. In particular, their melting points and degrees of crystallinity should increase. Qualitative substantiation of the extent of reorganization can be obtained by measuring these quantities after the effects of annealing are accounted for; therefore, the melting point and percent crystallinity as measured by DSC, are reported for all samples.

For the purpose of this research, the melting point of a sample was defined as the point at which the DSC trace returned to the baseline. Figure 5 illustrates how the melting point of a sample was defined. This definition was applied because of the wide melting ranges of the samples. The desire was to determine the maximum possible temperature at which crystallinity persisted, thus allowing the CIR to be carried out at the highest possible temperature. The method of calculating percent crystallinity is described in Chapter II.

Results and Discussion

The NMR Spectra of PET/ES Copolymers. For the purpose of this research six copolymers of varying terephthalate content were prepared. To insure an adequate rate of
"MELTING POINT"
ester-interchange at the reaction temperatures possible with these copolymers, low molecular weight materials were used. The copolyesters employed had inherent viscosities of 0.19 - 0.76. The utilization of such low molecular weight materials caused initial difficulty in interpreting the NMR spectra of the copolymers.

Figures 6-8 show the 90 MHz NMR spectra of poly(ethylene terephthalate), poly(ethylene succinate), and PET/ES (copolymer B). Of particular interest is the glycol region of the copolymer's spectrum. Instead of the three peaks which should occur, five are observed. By comparison to the homopolymer, spectra peaks A, C, D, (Figure 8), which occur at 4.49, 4.29, and 4.09 ppm $\delta$, may be identified as arising from T-G-T, T-G-S, and S-G-S placement respectively. The occurrence of resonances B and E were unexpected.

Because the copolymerizations were carried out such that low molecular weight, hydroxy-terminated polymers would be formed, two placements of glycol residues neglected by Murano might be detectable. These two structures occur when glycol residues are at chain ends (33) and (34).
Figure 6 – 90 MHz NMR Spectrum of Poly (ethylene terephthalate)
Figure 8 — 90 MHz NMR Spectra of Poly (ethylene terephthalate/ethylene succinate) Copolymer
In high molecular weight copolyesters, such as those used by Murano, the infrequent occurrence of chain ends would make their detection impossible; however in the present case one might detect these units. To test this hypothesis attempts to prepare model compounds were undertaken.

Bis(2-hydroxyethyl terephthalate) (35) was chosen as a model for TOH endgroups. BHET was synthesized and characterized by a technique described in the literature. Figure 9 shows the NMR spectra of BHET. The glycol resonance of BHET occurs at 4.42 $\delta$, which is exactly where resonance B occurs. On this basis, B was assigned to a TOH resonance.

Attempts to prepare BHES were unsuccessful. No description of this compound was found in the literature, thus no physical property data were available to aid in its isolation.
Figure 9 - 90 MHz NMR Spectrum of Bis (hydroxy ethyl terephthalate)
Reaction of DMS with a 3-4 mole excess of ethylene glycol yielded a yellowish liquid. Attempts to isolate BHES from this product by fractional distillation, crystallization and preparative gas chromatography were unsuccessful. The NMR spectrum of the crude product was too complicated by the resonances of higher oligomers, ethylene glycol and DMS to provide an accurate assignment of peaks. Thus, resonance E was assigned to a SOH resonance by analogy to the BHET results. The full assignment of chemical shifts for the polyesters are collected in Table 3.

To further substantiate this assignment of chemical shifts, an analysis of the internal consistency of the NMR spectra of PET/ES copolymers was performed. There are seven sharp singlet resonances in the spectrum of a copolyester; the five assigned to the glycol residues, one at \( 7.78 \) \( \delta \) from the terephthalate residues, and one at \( 2.46 \) \( \delta \) from the succinate residues. Proper analysis of the intensity of these resonances allows one to calculate the monomer composition in two different ways. If the assignment of the 4.42 and 4.02 ppm peaks is correct, these two values should agree.

The calculation of composition from the acid residues is accomplished by simply dividing the intensity of each resonance by the sum of their intensities because they
<table>
<thead>
<tr>
<th>Compound</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Terephthalate Residue</td>
<td>7.78</td>
</tr>
<tr>
<td>Glycol Residues</td>
<td></td>
</tr>
<tr>
<td>TT</td>
<td>4.49</td>
</tr>
<tr>
<td>TOH</td>
<td>4.42</td>
</tr>
<tr>
<td>TS</td>
<td>4.29</td>
</tr>
<tr>
<td>SS</td>
<td>4.09</td>
</tr>
<tr>
<td>SOH</td>
<td>4.04</td>
</tr>
<tr>
<td>Succinate Residue</td>
<td>2.46</td>
</tr>
</tbody>
</table>
both result from four proton residues. On the basis of the above assignment of the glycol resonances the composition may be calculated from equations (36) and (37):

\[
\%T = TT + TH + \frac{1}{2}(TS) \tag{36}
\]
\[
\%S = SS + SH + \frac{1}{2}(TS) \tag{37}
\]

where TT, TH, TS, SS, SH are the molar percentages of T-G-T, T-OH, T-G-S, S-G-S, and S-OH linkages determined by dividing the individual intensities by the total intensity of the glycol residues.

Table 4 contains data for several copolyesters which compare the values of composition obtained by both methods. The results in Table 4 are in excellent agreement, indicating that the assignment of peaks in the glycol region is the correct one.

Monomer Compositional Analysis

The internal consistency of the NMR results alone was not enough to assure the accuracy of the quantitative determination of microstructural changes. The previous investigation of copolyesters subjected to CIR showed only slight changes in the sequence lengths of the copolymers. It also showed a 3-5% change in the terephthalate content of the treated copolymers. Although the results were reported on the basis of the Theil Q factor which is independent of monomer composition, it was felt that an
**TABLE 4**

**COMPARISON OF COMPOSITION BASED ON ACID AND GLYCOL RESONANCES**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area T</th>
<th>Area S</th>
<th>%T (A)</th>
<th>TGT</th>
<th>TOH</th>
<th>TGS</th>
<th>GS</th>
<th>SOH</th>
<th>%T (G)</th>
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<td>1</td>
<td>96.3</td>
<td>20.7</td>
<td>82.3</td>
<td>51.2</td>
<td>6.4</td>
<td>29.3</td>
<td>2.1</td>
<td>1.0</td>
<td>82.2</td>
</tr>
<tr>
<td>2</td>
<td>75.8</td>
<td>17.2</td>
<td>81.5</td>
<td>59.4</td>
<td>6.6</td>
<td>29.0</td>
<td>3.3</td>
<td>1.7</td>
<td>80.5</td>
</tr>
<tr>
<td>3</td>
<td>86.9</td>
<td>16.1</td>
<td>84.4</td>
<td>67.2</td>
<td>5.6</td>
<td>24.4</td>
<td>1.6</td>
<td>1.1</td>
<td>85.0</td>
</tr>
<tr>
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<td>124.1</td>
<td>28.1</td>
<td>81.5</td>
<td>58.9</td>
<td>5.3</td>
<td>30.8</td>
<td>2.9</td>
<td>2.1</td>
<td>79.7</td>
</tr>
<tr>
<td>5</td>
<td>130.0</td>
<td>30.2</td>
<td>81.1</td>
<td>59.6</td>
<td>5.2</td>
<td>30.4</td>
<td>2.8</td>
<td>2.1</td>
<td>80.0</td>
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<td>6</td>
<td>121.1</td>
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<td>7</td>
<td>140.1</td>
<td>27.9</td>
<td>83.4</td>
<td>61.5</td>
<td>6.6</td>
<td>29.7</td>
<td>1.4</td>
<td>0.9</td>
<td>83.0</td>
</tr>
</tbody>
</table>
independent technique for determining composition was desirable to insure the accuracy of the NMR analysis.

Many techniques have been reported for the analysis of copolyesters. Mitchell and Chiu\textsuperscript{76} and Nissen et.al.\textsuperscript{77} have compiled extensive reviews on this subject. Techniques such as infrared spectroscopy, gravity and saponification-gas chromatography have been reported. Due to various characteristics of the present system; among them, the insolubility of terephthalic acid, the incompatability of DMT and DMS in solvents, and the complex nature of the IR spectra of the copolyesters, none of these methods was directly applicable. However a modification of the trimethylsilylation technique for analyzing nylons\textsuperscript{78} was found suitable for determining the composition of PET/ES polyesters.

A detailed discussion of the procedure developed has already been presented in the experimental section; thus only a brief description will be given here. The copolyester is saponified by heating in NaOH and then the resulting acid salts are neutralized with HCl. Following careful drying, the sample is derivatized with N,0-bis (trimethylsilyl)acetamide and then gas chromatographed. The monomer composition is determined by analysis of the G. C. traces and comparison to a calibration curve. Figure 10 shows a chromatograph of the trimethylsilyl derivatives
Figure 10 — Gas Chromatogram of the TMS Derivatives from the Saponification of a PET/ES Copolymer
of the saponification products from a PET/ES copolymer. The retention times of the various trimethylsilyl derivatives are listed in Table 5.

A quantitative determination of monomer composition is accomplished by measuring and comparing the peak areas. It must be noted that the peak areas represent the bis (trimethylsilyl) (TMS) derivatives and not that of the acids. Conversion of the measured peak ratios to monomer ratios may be accomplished using equation (38);

$$A = D \times \frac{(MW_A)}{(MW_D)}$$

where

- $D$ = measured peak area
- $MW_A$ = molecular weight of the monomer
- $MW_D$ = molecular weight of the TMS derivative
- $A$ = calculated area for monomer

The monomer composition (% by weight) is then calculated by dividing the individual acid peak areas by their sum.

The calibration curve for this analysis was constructed by subjecting samples of known terephthalate/succinate composition to the full procedure utilized to saponify the copolymers. Table 6 lists the experimentally found terephthalate compositions and the actual values for the standard samples. In Figure 11 these results are plotted and fitted to a least squares line. The slope
### TABLE 5

<table>
<thead>
<tr>
<th>Component</th>
<th>Retention Time (mins.)</th>
<th>Reference&lt;sup&gt;a&lt;/sup&gt; Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>0.9</td>
<td>1</td>
</tr>
<tr>
<td>Triethyl Amine</td>
<td>1.0</td>
<td>2</td>
</tr>
<tr>
<td>N,O - BSA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.3</td>
<td>3</td>
</tr>
<tr>
<td>Ethylene Glycol (TMS)</td>
<td>2.0</td>
<td>4</td>
</tr>
<tr>
<td>Succinic acid (TMS)</td>
<td>3.9</td>
<td>5</td>
</tr>
<tr>
<td>Terephthalic acid (TMS)</td>
<td>14.1</td>
<td>6</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reference number to Figure 10.

<sup>b</sup> N,O, - bis(trimethylsilyl)acetamide.
TABLE 6

CALIBRATION STANDARDS FOR G.C. ANALYSIS

<table>
<thead>
<tr>
<th>Sample</th>
<th>%T actual&lt;sup&gt;a&lt;/sup&gt;</th>
<th>%T found&lt;sup&gt;b&lt;/sup&gt;</th>
<th>%T&lt;sub&gt;a&lt;/sub&gt;/%T&lt;sub&gt;f&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>76.0</td>
<td>75.3</td>
<td>.990</td>
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<tr>
<td>2</td>
<td>80.1</td>
<td>79.8</td>
<td>1.003</td>
</tr>
<tr>
<td>3</td>
<td>84.3</td>
<td>84.9</td>
<td>.993</td>
</tr>
<tr>
<td>4</td>
<td>89.9</td>
<td>90.3</td>
<td>.995</td>
</tr>
</tbody>
</table>

<sup>a</sup> determined by weighing

<sup>b</sup> determined from G.C. traces
Figure 11 – Least Squares Calibration for G.C. Monomer Analysis
of this line was used as a correction factor for detector response.

The G.C. analysis of seven copolyesters was performed to determine the accuracy of the NMR technique. In order to compare the compositional values it was necessary to convert the mole percent data of the NMR to weight percent. In Table 7 the results of the chromatographic analysis are recorded and compared to those obtained from the NMR spectra. The quantities recorded in Table 7 are: the measured peak areas of the trimethylsilyl derivatives (TMS-T and TMS-S); the calculated areas for the monomers (T and S); the weight % terephthalate from the G.C. analysis; and the weight % terephthalate as determined by the acid residues in the NMR spectra.

The composition of the copolymers as determined by NMR and G.C. analysis are in good agreement. Since the deviation between results show no suggestion of being systematic, it is probable that both values are accurate and that the average deviation is a good representation of the reliability of either result. On this basis, one may conclude that the composition measured by NMR is accurate to \( \pm 1.5\% \). Furthermore, the values of B, Q, and \( \overline{L}_n T \) calculated from the intensities of the glycol resonances must be of comparable accuracy because of the previously demonstrated internal constancy of the NMR
<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Area of a TMS-T</th>
<th>Area of TMS-S</th>
<th>Area of T</th>
<th>Area of S</th>
<th>Wt. %T</th>
<th>Wt. %T by NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-2</td>
<td>880</td>
<td>208</td>
<td>470.8</td>
<td>94.0</td>
<td>83.0</td>
<td>82.4</td>
</tr>
<tr>
<td>D-2</td>
<td>871</td>
<td>170</td>
<td>465.0</td>
<td>76.5</td>
<td>85.4</td>
<td>84.8</td>
</tr>
<tr>
<td>I-2</td>
<td>900</td>
<td>341</td>
<td>481.5</td>
<td>153.4</td>
<td>75.5</td>
<td>76.4</td>
</tr>
<tr>
<td>ISb/2-1</td>
<td>726</td>
<td>218</td>
<td>388.4</td>
<td>98.1</td>
<td>79.4</td>
<td>80.6</td>
</tr>
<tr>
<td>BSb-5</td>
<td>657</td>
<td>109</td>
<td>351.5</td>
<td>49.1</td>
<td>87.3</td>
<td>85.6</td>
</tr>
<tr>
<td>DSb-3</td>
<td>1066</td>
<td>120</td>
<td>570.6</td>
<td>54.0</td>
<td>90.8</td>
<td>91.5</td>
</tr>
<tr>
<td>B-2b</td>
<td>546</td>
<td>118</td>
<td>292.1</td>
<td>48.5</td>
<td>84.2</td>
<td>82.4</td>
</tr>
</tbody>
</table>

a. in arbitrary units as determined by a plenimeter.
b. second determination of Copolymer B-2.
results. Thus the accuracy of the NMR measurement of sequence distribution may be placed at $\pm 1.5\%$.

**Effect of Reaction Parameters on the Extent of Reorganization by CIR**

**Catalyst.** In the previous investigation of the reorganization of copolyesters by CIR,$^5,^6$ the polymerization catalyst was used to promote the ester-interchange reaction during the solid state treatment. To facilitate a more thorough investigation of the effect of catalysts on the reorganization, the polycondensation catalyst, antimony trioxide, was removed from the copolyesters employed in this research. The catalyst was removed by reprecipitation from triflouroacetic acid into excess methanol. Bamford and Wayne$^{44}$ have shown by X-ray fluorescence analysis, that this is an effective method of removing the antimony trioxide. Starting with a copolymer free of catalyst, the effect of various catalysts and catalyst concentrations were measured.

Table 8 contains the results of the reorganization of copolymer D-2 as a function of the catalyst employed. The catalysts tested were antimony trioxide (DSb 3 and 4), calcium acetate (DCa 1 and 2), tetrabutyl orthotitinate (DTB 1 and 2), and tetraethyl orthotitinate (DTE 1 and 2). Catalyst concentration was 3\% by weight in each case. All reorganizations were carried out at 215$^\circ$C in a closed
TABLE 8

EFFECT OF VARIOUS CATALYSTS ON CIR OF PET/ES AT 215°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (hrs)</th>
<th>Tm °C</th>
<th>( \eta ) inh(^a)</th>
<th>B</th>
<th>Q</th>
<th>%T</th>
<th>( \overline{L} ) ( n ) T</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET/ES D-2</td>
<td>--</td>
<td>236</td>
<td>0.256</td>
<td>0.92</td>
<td>1.60</td>
<td>80.5</td>
<td>5.44</td>
</tr>
<tr>
<td>DSB-3</td>
<td>13</td>
<td>248</td>
<td>0.270</td>
<td>0.84</td>
<td>2.83</td>
<td>86.3</td>
<td>8.57</td>
</tr>
<tr>
<td>DCA-1</td>
<td>12</td>
<td>240</td>
<td>0.275</td>
<td>0.92</td>
<td>1.59</td>
<td>81.0</td>
<td>5.50</td>
</tr>
<tr>
<td>DTB-1</td>
<td>12</td>
<td>241</td>
<td>0.259</td>
<td>0.93</td>
<td>1.56</td>
<td>83.5</td>
<td>6.47</td>
</tr>
<tr>
<td>DTE-1</td>
<td>12</td>
<td>239</td>
<td>0.251</td>
<td>0.92</td>
<td>1.61</td>
<td>83.5</td>
<td>6.36</td>
</tr>
<tr>
<td>DSB-4</td>
<td>23</td>
<td>249</td>
<td>0.311</td>
<td>0.78</td>
<td>4.27</td>
<td>87.5</td>
<td>10.31</td>
</tr>
<tr>
<td>DCA-2</td>
<td>24</td>
<td>239</td>
<td>0.273</td>
<td>0.90</td>
<td>1.90</td>
<td>81.3</td>
<td>6.40</td>
</tr>
<tr>
<td>DTB-2</td>
<td>18</td>
<td>240</td>
<td>-----</td>
<td>0.93</td>
<td>1.57</td>
<td>83.5</td>
<td>6.45</td>
</tr>
<tr>
<td>DTE-2</td>
<td>18</td>
<td>241</td>
<td>-----</td>
<td>0.94</td>
<td>1.48</td>
<td>83.3</td>
<td>5.09</td>
</tr>
</tbody>
</table>

a. \( \eta \) inh in 1% o-chlorophenol
system under a nitrogen atmosphere. Details of the sample preparation appear in Chapter II.

The results shown in Table 8 indicate that antimony trioxide (Sb$_2$O$_3$) is the most effective catalyst tested. In 13 hours of treatment, the value of B for sample DSb-3 changed 7.6% from 0.92 to 0.85. For the same time period, the copolymers treated with the other catalysts showed only insignificant changes in B. After 23 hours, differences in the degree of reorganization are even more significant. For sample DSb-4, B decreased 15.4% from 0.92 to 0.78, where as that for DCa-2 decreased only 2.1%, and DTB-2 and DTE-2 evidenced little change. In fact, the values of B measured for these samples show an apparent increase; implying that randomization occured. This apparent randomization was investigated further and will be discussed later in this section.

The greater increase in block character of samples treated with Sb$_2$O$_3$ was also confirmed by the measured values of Q and $\bar{L}_n T$. For sample DSb-4, Q increased from 1.60 to 4.27 and $\bar{L}_n T$ increased from 5.44 to 10.31. Sample DCa-2, which showed the second largest degree of reorganization showed changes of 1.60 to 1.90 and 5.44 to 6.40 for Q and $\bar{L}_n T$. Again samples DTB-2 and DTE-2 showed only minor changes.

The change in melting points recorded in Table 8 show the same trend as the sequence distribution results.
After 13 hours of heating at 215°C, the melting point of DSb-3 increased from 236 to 248°C, an increase of 12°C. Results for the other three catalysts show a maximum increase of 5°C in a similar time.

It should be noted that these melting points were determined on reprecipitated samples which had been annealed under constant conditions. The increase in melting point is therefore not a result of improved crystal structure. Proof of this statement is provided by the fact that the first cycle melting points of these samples were reproduced by the second cycle melting points in all cases. Several investigations of polymers whose melting point increases upon heating due to improved crystal perfection alone have demonstrated that the second cycle melting point decreased to the same value recorded before annealing. 9,79

Furthermore the molecular weight of the starting copolymer was sufficiently high such that increases in molecular weight do not effect the melting point. The molecular weight of PET/ES D-2 was ~5000, well above the value of 2-3000 at which Ellery 74 reported that the melting point of PET copolymers became invariant. Therefore, this increase in melting point indicates increased block character.

On the basis of these results the following scale of effectiveness may be constructed:
$\text{Sb}_2\text{O}_3 \gg \text{Ca(Ac)}_2 \gg \text{Ti(OEt)}_4 \gg \text{Ti(0Bu)}_4$  (39)

The greater activity of $\text{Sb}_2\text{O}_3$ as compared to $\text{Ca(Ac)}_2$ is understandable on the basis of results reported in the literature. Several investigators$^{30,80}$ have shown that $\text{Ca(Ac)}_2$ functions effectively only in the first stage, transesterification, of the polyesterification of dimethyl terephthalate with ethylene glycol. On the other hand, $\text{Sb}_2\text{O}_3$ was shown to exert its major effect on the ester-interchange reaction. Since ester-interchange is responsible for reorganization during CIR, $\text{Sb}_2\text{O}_3$ should be the more effective catalyst.

The apparent inactivity of the orthotitintates is surprising however, because they are reported to be excellent polycondensation catalysts.$^{44,81}$ Their lack of activity in this case may be due to the circumstances of the reaction. Although every effort was made to exclude moisture from these samples, the surface coating of catalyst that was employed makes them extremely susceptible to deactivation by water. Deactivation by moisture may account for their inactivity.

A further study was undertaken to explore the effect of catalyst concentration on CIR. Reorganizations were performed with 0, 1.5, and 3% concentrations of $\text{Sb}_2\text{O}_3$. The data from these experiments are collected in Tables 9A and 9B.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Time hrs.</th>
<th>Catalyst</th>
<th>Tm°C</th>
<th>η inh</th>
<th>B</th>
<th>Q</th>
<th>%T</th>
<th>$\bar{L}_nT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-2</td>
<td></td>
<td>Starting Material</td>
<td>208</td>
<td>.782</td>
<td>0.94</td>
<td>1.34</td>
<td>73.9</td>
<td>4.09</td>
</tr>
<tr>
<td>ISb/2-1</td>
<td>12</td>
<td>3%</td>
<td>235</td>
<td>.807</td>
<td>0.88</td>
<td>1.84</td>
<td>75.6</td>
<td>4.71</td>
</tr>
<tr>
<td>ISb/2-2</td>
<td>20</td>
<td>3%</td>
<td>235</td>
<td>.819</td>
<td>0.85</td>
<td>2.21</td>
<td>78.2</td>
<td>5.39</td>
</tr>
<tr>
<td>ISb/2-3</td>
<td>36</td>
<td>3%</td>
<td>243</td>
<td>.831</td>
<td>0.83</td>
<td>2.50</td>
<td>79.4</td>
<td>5.83</td>
</tr>
<tr>
<td>ISb-A</td>
<td>12</td>
<td>1.5%</td>
<td>234</td>
<td>.796</td>
<td>0.90</td>
<td>1.53</td>
<td>74.7</td>
<td>4.21</td>
</tr>
<tr>
<td>ISb-B</td>
<td>20</td>
<td>1.5%</td>
<td>236</td>
<td>.835</td>
<td>0.85</td>
<td>2.19</td>
<td>77.7</td>
<td>5.26</td>
</tr>
</tbody>
</table>

TABLE 9A

EFFECT OF CATALYST CONCENTRATION ON THE REORGANIZATION OF COPOLYESTER I-2 at 201°C
TABLE 9B

EFFECT OF CATALYST CONCENTRATION ON THE REORGANIZATION OF COPOLYESTER D-2 @215°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time hrs.</th>
<th>Catalyst</th>
<th>Tm°C</th>
<th>η/inh</th>
<th>B</th>
<th>Q</th>
<th>%T</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-2</td>
<td>--</td>
<td>--</td>
<td>236</td>
<td>0.256</td>
<td>0.92</td>
<td>1.60</td>
<td>80.5</td>
</tr>
<tr>
<td>DCa-0</td>
<td>12</td>
<td>0%</td>
<td>226</td>
<td>0.256</td>
<td>1.04</td>
<td>--</td>
<td>83.5</td>
</tr>
<tr>
<td>DNC</td>
<td>28</td>
<td>0%</td>
<td>---</td>
<td>---</td>
<td>0.94</td>
<td>--</td>
<td>83.5</td>
</tr>
<tr>
<td>DSb-0</td>
<td>36.5</td>
<td>0%</td>
<td>233</td>
<td>0.311</td>
<td>0.94</td>
<td>1.43</td>
<td>84.3</td>
</tr>
<tr>
<td>DSb-6</td>
<td>36.5</td>
<td>1.5%</td>
<td>236</td>
<td>0.401</td>
<td>0.79</td>
<td>3.69</td>
<td>88.2</td>
</tr>
<tr>
<td>DSb-5</td>
<td>36.5</td>
<td>3%</td>
<td>244</td>
<td>0.377</td>
<td>0.73</td>
<td>5.34</td>
<td>88.7</td>
</tr>
</tbody>
</table>
Table 9A shows that for copolymer I-2, which had a molecular weight of \( \sim 20,000 \) and a terephthalate content of 73.9%, the change in catalyst concentration from 1.5% to 3% had no effect on the extent of reaction. During twenty hours of reaction, sample ISb/2-2 had undergone the following changes; B decreased by 0.09 while Q increased 0.87. In the same time interval, sample ISb-B which was reacted with only 1.5% Sb\(_2\)O\(_3\) showed changes of 0.09 and 0.85 for the same parameters.

When a lower molecular weight material was utilized, the data in Table 9B shows that changing the catalyst concentration did effect the extent of reorganization. Sample DSb-0 which had no added catalyst showed a small increase in B from 0.92 to 0.94. Sample DSb-6, which had 1.5% catalyst, evidenced a decrease of 0.13, and in the same time DSb-5 showed a decrease of 0.19 when treated with 3% catalysts.

Thus in one case, the catalyst concentration had no apparent effect on the reorganization, while in a second, substantial differences were noted. Similar results were reported by Go\(^{82}\) for poly(ethylene terephthalate-co-methyl succinate) (PET/MS) copolymers. Table 10 reproduces results recorded in Tables 20 and 21 of Go's thesis. In the case of the 72.0 and 72.3% terephthalate copolyesters, 1% catalyst caused a decrease in B of 0.04 whereas 3%
### TABLE 10

**EFFECT OF CATALYST CONCENTRATION ON CIR OF PET/MS COPOLYESTERS**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Catalyst conc&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Time hrs</th>
<th>Temp&lt;sup&gt;°C&lt;/sup&gt;</th>
<th>Tm&lt;sup&gt;°C&lt;/sup&gt;</th>
<th>B</th>
<th>Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start 72 %</td>
<td>1%</td>
<td>0</td>
<td>208</td>
<td>0.898</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>72 %</td>
<td>1%</td>
<td>10</td>
<td>205</td>
<td>---</td>
<td>0.858</td>
<td>1.93</td>
</tr>
<tr>
<td>72 %</td>
<td>1%</td>
<td>20</td>
<td>205</td>
<td>---</td>
<td>0.858</td>
<td>1.93</td>
</tr>
<tr>
<td>Start 72.3%</td>
<td>3%</td>
<td>0</td>
<td>217</td>
<td>0.898</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td>72.3%</td>
<td>3%</td>
<td>10</td>
<td>205</td>
<td>---</td>
<td>0.832</td>
<td>2.19</td>
</tr>
<tr>
<td>72.3%</td>
<td>3%</td>
<td>20</td>
<td>205</td>
<td>---</td>
<td>0.822</td>
<td>2.32</td>
</tr>
<tr>
<td>Start 78.5%</td>
<td>1%</td>
<td>0</td>
<td>228</td>
<td>0.883</td>
<td>1.89</td>
<td></td>
</tr>
<tr>
<td>78.5%</td>
<td>1%</td>
<td>10</td>
<td>220</td>
<td>---</td>
<td>0.859</td>
<td>2.12</td>
</tr>
<tr>
<td>78.5%</td>
<td>1%</td>
<td>20</td>
<td>220</td>
<td>---</td>
<td>0.843</td>
<td>2.45</td>
</tr>
<tr>
<td>Start 75.1%</td>
<td>3%</td>
<td>0</td>
<td>224</td>
<td>0.887</td>
<td>1.77</td>
<td></td>
</tr>
<tr>
<td>75.1%</td>
<td>3%</td>
<td>10</td>
<td>220</td>
<td>---</td>
<td>0.858</td>
<td>2.13</td>
</tr>
<tr>
<td>75.1%</td>
<td>3%</td>
<td>20</td>
<td>220</td>
<td>---</td>
<td>0.847</td>
<td>2.30</td>
</tr>
</tbody>
</table>

<sup>a</sup> catalyst was titanium tetrabutoxide.

<sup>b</sup> heated with a continuous purge of N<sub>2</sub>. 
caused a change of 0.08. For the 78.5 and 75.1% terephthalate PET/MS, changes in B were 0.04 regardless of catalyst concentration. No data on molecular weight is furnished.

It is interesting to note that for both sets of data, catalyst concentration had no effect upon the reorganization when CIR was performed 3-12°C below the melting point of the starting material. On the other hand, when it was carried out 15-21°C below the melting point, the catalyst concentration had a marked effect.

The above results were obtained from two different experiments in which different copolyesters, catalysts, methods of catalyst application, and conditions for performing the CIR were utilized. The differences between the two experiments make explanations which rely on any of these reaction conditions untenable. Therefore, the results strongly suggest that a change of rate controlling steps occurred. For reorganizations run more than 15°C below the melting point of the starting material, the rate of ester-interchange controlled the reaction and the catalyst concentration altered the extent of reorganization. However, in those cases where CIR was performed closer to the melting point, some other property is controlling the extent of reaction. A further discussion of these results will be undertaken at a later point when further
examples of the change in control have been presented.

During the investigation of the effect of catalyst on the extent of reorganization, two anomalous features of the CIR of PET/ES copolyesters were discovered. The first unusual result was that several of the copolyesters apparently randomized during the reorganization reactions. The results in Table 9B, which contains the data for reorganization of copolymer D2 in the absence of catalysts, illustrate this point. Sample DCa-0 which was heated for 12 hours showed an increase of B number from 0.92 to 1.02. Subsequent heating of 24 hours lowered the B value to 0.94, however even this polyester was more random than D-2. Further evidence of the randomization of copolyesters subjected to CIR comes from the data on samples DTB-1 and 2 and DTE-2 shown in Table 8. Although in most cases the increase in randomness was slight, the increase of 0.10 recorded for DCa-0 was certainly not within the experimental error of the NMR analysis. Thus it was concluded that under some conditions the copolymers randomized.

The second feature of the reorganization which was noted was the increased terephthalate content of the treated copolyesters. The results recorded in Tables 8, 9A and 9B show that the terephthalate content of all samples increased from 3 to 8% during CIR. In seeking an
explanation for the increased terephthalate content of the reorganized copolyesters, the randomization of the copolyesters mentioned above was also explained.

One method of rationalizing the increase in terephthalate content was fractionation during reprecipitation. If a low molecular weight fraction rich in ethylene succinate was formed during CIR, it might be lost during reprecipitation because of its higher solubility relative to the PET rich fractions. To test this explanation two samples which had been reorganized were divided in half; one half was reprecipitated, annealed, and then analyzed by NMR, while the other half was analyzed without reprecipitation. In both cases the results of the NMR analysis for composition and randomness as reflected by the B and Q numbers were in very close agreement. Table 11 shows these results. The close agreement found during this test eliminated fractionation as a viable explanation for the compositional change; however it also served to indicate that all of the reorganization detected happened during the CIR and no alterations of the copolymers occurred during subsequent treatments.

The depletion of the succinate content in treated copolyesters was finally shown to be the result of selective degradation. Careful examination of the reaction flasks indicated that a semisolid sublimate was condensed
TABLE 11

EFFECT OF REPRECIPITATION ON THE ANALYSIS OF COPOLYESTERS

<table>
<thead>
<tr>
<th>Sample</th>
<th>%T</th>
<th>B</th>
<th>Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>DNC-2A</td>
<td>83.3</td>
<td>1.004</td>
<td>.969</td>
</tr>
<tr>
<td>DNC-2B*</td>
<td>83.5</td>
<td>1.008</td>
<td>.961</td>
</tr>
<tr>
<td>DCa-3A</td>
<td>84.1</td>
<td>.901</td>
<td>1.90</td>
</tr>
<tr>
<td>DCa-3B*</td>
<td>83.8</td>
<td>.897</td>
<td>1.86</td>
</tr>
</tbody>
</table>

* denotes the half of the sample which was reprecipitated and annealed.
at the top of the flask. The quantity of material deposited was never in excess of 5 mg; because it was a mixture, conventional chemical analysis was impossible. However, by carefully collecting the sublimate from the flasks an NMR spectrum of several different sublimates was obtained. Figure 12 shows the spectrum of one of these samples.

In the figure, peaks A and B result from ethylene glycol which was presumable eliminated during polycondensation. Resonance C at 2.46 $\delta$ is the result of succinate residues while resonance D at 7.78 $\delta$ is from terephthalate residues. Intergration of the intensities of peaks C and D indicated that the sublimate contained a succinate: terephthalate ratio of 9:2. The evolution of succinate residues at a rate 4.5 times faster than terephthalate residues is the reason why the polymers show enriched terephthalate content after CIR.

For the purpose of explaining the compositional drift of the treated copolymers it was not necessary to determine what form the succinate or terephthalate residues were in. However by making such a determination the randomization of the copolyesters during some of the crystallization induced reorganizations was clarified. The two remaining peaks in Figure 12, E and F, occur in the glycol region of the NMR. Identification of resonance F as resulting from T-G-S linkages is accomplished by comparison to the chemical shift data in Table 3.
Figure 12 - 90 MHz NMR Spectrum of CIR Sublimate
The origin of peak E is somewhat more difficult to determine due to the proximity of the S-G-S and SOH resonances, but careful evaluation of 100 Hz expanded scale scans of the region between 4.5 and 3.5 ppm proved the resonance E resulted from S-G-S linkages. Small quantities of PES homopolymer were added to the sublimate sample and its NMR spectrum was again recorded. If resonance E were the result of SOH placements, two peaks would have resulted in the 4.0 to 4.1 ppm region. Since the only effect of the addition of PES was to increase the intensity of E, S-G-S linkages must be responsible for its occurrence.

The lack of endgroup peaks in the spectrum of the sublimate leads to the conclusion that either the S-G-S and T-G-S linkages occur in high molecular weight polymers or in cyclic structures. Since the solid was soluble in acetone and ethanol and neither PET/ES nor PES are, the former possibility was rejected. Thus resonances E and F must result from cyclic structures. These compounds are most probable the cyclic dimer of ethylene succinate (40) and the mixed cyclic dimer of ethylene succinate and ethylene terephthalate (41).
The occurrence of such cyclic structures are well known in the literature. 10,20,22,83-85 Of particular interest to the present question are the reports of Carothers, 83 Goodman and Nesbitt, 20 and Peebles et.al. 22 Carothers found that PES degrade totally to compound (40) upon heating in the presences of an ester-interchange catalyst. While Peebles, et.al. have demonstrated the occurrence of mixed cyclic dimers of ethylene terephthalate and diethylene terephthalate in the degradation of PET. Thus the presence of compounds (40) and (41) results from known degradation reactions. The apparent absence of the cyclic dimer of PET may be rationalized by the
results of Goodman and Nesbitt. These authors found that no cyclic oligomers were formed in PET which was heated for 160 hours just below its melting point. Since CIR are performed in the solid state no PET dimers should be formed.

The randomization of certain of the polyesters subjected to CIR may be explained by the relative concentrations of the cyclic dimers. From the intensities of the acid residues and the proposed structures of the cyclic dimers the ratio of (40) to (41) may be 7:1. The more rapid loss of the succinate dimer, which translates into the loss of succinate homo-unit dyads, causes an increase in the hetero-unit dyad concentration. This increase in hetero-unit dyad concentration occurs because the number of T-G-S linkages decreases less rapidly than the total number of dyads. In the absence of other reactions, the increasing concentration of T-G-S dyads will cause the copolyesters to randomize. However, if the CIR occurs at a sufficiently rapid rate to overcome volatilization, the copolyester will become more ordered. Thus for reorganizations in the absence of catalyst or with ineffective catalysts (the orthotitinates) randomization occurred, while with an effective catalyst ($\text{Sb}_2\text{O}_3$) the CIR overcame the rate of volatilization and multi-block copolymers resulted.
Effect of Reaction Time. Information on the extent of reorganization of PET/ES copolymers B-2 and I-2 as a function of CIR time is presented in Tables 12 and 13. The tables contain the melting point, percent crystallinity, inherent viscosity, and various measures of the sequence distribution of the copolymers before and after treatment. All reorganizations were carried out in the presence of 3% antimony trioxide. The crystallization-induced reactions of I-2 and B-2 were performed in closed systems under a nitrogen atmosphere. Although the two copolyesters had approximately the same composition, their molecular weights were different. Copolymer B-2 had an inherent viscosity of 0.190 whereas the value for I-2 was 0.783.

Figure 13 shows a plot of the B values recorded in Tables 12 and 13 versus reaction time. The values of B were plotted because they are independent of copolymer composition (B=1 for any random copolymer) thus they reflect the true extent of reorganization regardless of the fact that the terephthalate content of all samples increased during the CIR. The three curves in Figure 13 show the results for: the ISb/1 series, (13A); the ISb/2 series, (13B); and the BSb series, (13C).

Figure 13 shows that copolymer B-2 underwent randomization, as indicated by an increase in the B factor, after 1 hour of heating. Following this initial randomization,
### TABLE 12

**EXTENT OF REORGANIZATION VERSUS TIME OF TREATMENT FOR PET/ES B-2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction Conditions</th>
<th>Thermal Properties</th>
<th>Sequence Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (hrs)</td>
<td>Temp°C</td>
<td>Tm°C</td>
</tr>
<tr>
<td>B-2</td>
<td>0</td>
<td>---</td>
<td>212</td>
</tr>
<tr>
<td>BSb-1</td>
<td>1</td>
<td>201</td>
<td>217</td>
</tr>
<tr>
<td>BSb-2</td>
<td>4</td>
<td>201</td>
<td>219</td>
</tr>
<tr>
<td>BSb-3</td>
<td>12</td>
<td>201</td>
<td>232</td>
</tr>
<tr>
<td>BSb-4</td>
<td>20</td>
<td>201</td>
<td>232</td>
</tr>
<tr>
<td>BSb-5</td>
<td>36</td>
<td>201</td>
<td>234</td>
</tr>
</tbody>
</table>
## TABLE 13

EXTENT OF REORGANIZATION VERSUS TIME OF TREATMENT FOR PET/ES I-2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction Conditions</th>
<th>Thermal Properties</th>
<th>Sequence Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (hrs)</td>
<td>Temp°C</td>
<td>Tm°C</td>
</tr>
<tr>
<td>I-2</td>
<td>0</td>
<td>---</td>
<td>208</td>
</tr>
<tr>
<td>ISb/1-1</td>
<td>4</td>
<td>195</td>
<td>---</td>
</tr>
<tr>
<td>ISb/1-2</td>
<td>12</td>
<td>195</td>
<td>232</td>
</tr>
<tr>
<td>ISb/1-3</td>
<td>20</td>
<td>195</td>
<td>232</td>
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<tr>
<td>ISb/1-4</td>
<td>36</td>
<td>195</td>
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</tr>
<tr>
<td>ISb/2-1</td>
<td>12</td>
<td>201</td>
<td>232</td>
</tr>
<tr>
<td>ISb/2-2</td>
<td>20</td>
<td>201</td>
<td>232</td>
</tr>
<tr>
<td>ISb/2-3</td>
<td>36</td>
<td>201</td>
<td>233</td>
</tr>
</tbody>
</table>
Figure 13 — B Number versus Reaction Time
the subsequent reorganization of the copolymer resulted in a decrease in randomness during the next 35 hours. The initial increase of randomness shown by B-2 sample BSb-1 may be attributed to loss of the cyclic dimers detailed in the previous section. Peebles, et.al.²² have shown that the formation of such dimers occurs through an intramolecular ester-interchange between hydroxyl endgroups and internal ester linkages. Because PET/ES B-2 was a low molecular weight polymer (\( \sim 5200 \)), and thus had a high concentration of hydroxyl endgroups, the rate of dimer formation would be rapid initially. The rapid formation and volatilization of dimer (40) would cause a decrease in succinate homo-unit dyads, and an increase in randomness. However, as the formation of the dimer proceeded, the number of succinate-succinate linkages (-S-G-S-OH) which occurred at chain ends would decrease. If essentially all of the succinate dyads at chain ends were volatilized off, the formation of cyclic dimer would stop. As a consequence, the CIR would take over, and the copolymer would increase in blockiness. The reorganization of the polymer would undoubtedly lead to the formation of additional succinate dyads, but because their formation occurs on the average only once in every four interchanges (TGS, TGT, and SGT linkages are also formed), the rate of volatilization can never exceed the rate of CIR again.
Therefore, after the initial loss of S-G-S linkages, the polymer would continue to increase in blockiness with only minor changes in composition.

The results recorded in Table 12 support the above description of the competition between CIR and dimer formation in the reorganization of copolymer B-2. In the first hour of the reorganization the terephthalate composition of the product changed 2.0%, while in the following 3 hours it changed only 0.1%. Essentially all of the succinate dyads must have been removed in the first hour. Additionally, in the last 35 hours of the reorganization, the change in composition was only 1.4%. Thus 60% of the compositional change occurred in the first 3% of the reaction, during which time randomization occurs. Once the crystallization-induced-reaction became evident the change in composition was very slow and the blockiness of the product increased as was predicted above. In the case of the high molecular weight copolymer the concentration of endgroups was evidently so low that the CIR rate was always greater than that for dimer formation and no randomization was observed.

Except for the initial randomization of copolymer B-2, the kinetic behavior of both polyesters is very similar. Although there are differences in the rate of reorganization, due to molecular weight and reaction temperature
which will be discussed in subsequent sections, the overall shape of curves (13A), (13B), and (13C) are the same. In the first one-third of the reaction time, the value of B decreases very rapidly. As a percentage of the total change in B, the decrease in the first 12 hours amount to 67% for series ISb/1; 54% for ISb/2; and 73% for BSb copolymers. During the next 24 hours of thermal treatment the decrease of the B factor is gradual, and is apparently approaching a limit. These results suggest that under the reaction conditions employed, the copolyesters reach a limiting blockiness.

There are three reasons why the copolyesters might show such behavior. First, as the CIR proceeds, the mobility of the endgroups is reduced by the increasing crystallinity of the sample; leading to a reduced rate of ester-interchange. Go provides a review of the literature concerned with solid state polycondensation which support this conclusion and has attributed the limiting blockiness he observed in the CIR of PET/MS copolymers to reduced endgroup mobility.

The second reason why the reorganization might attain a limiting value is due to the poisoning of the antimony trioxide catalyst. The poisoning of the catalyst would reduce the ester-interchange rate and thus reduce the extent of reorganization. Stevenson has demonstrated
that a volatile component of the reaction mixture in the polymerization of PET reacts reversibly with antimony trioxide rendering it inactive. In the present case the CIR was carried out in a closed system, so such a deactivation must be considered.

Finally, there is a limiting blockiness beyond which the copolymer cannot be reorganized due to the mechanism of CIR. Effective reorganization occurs only when a succinate unit next to a crystal of terephthalate blocks is replaced by a terephthalate unit. As the number of T-G-S linkages is reduced by block formation, the number of reaction sites available for crystallization-induced reaction is also reduced, thus the rate of reorganization must decrease. Ultimately, the rate will be very slow because there are so few T-G-S linkages left.

Results of two experiments which help determine what caused the limitations of reorganization shown by Figure 13 are recorded in Tables 14 and 15. Table 14 contains the results of CIR performed on PET/ES copolyester D-2 at 215°C with 3% antimony trioxide. For the samples of this series (DSb series), the reaction flasks were sealed under nitrogen, but they were vented after being heated to 215°C and remained open during the remainder of the reaction.
## TABLE 14

**EXTENT OF REORGANIZATION VERSUS TIME OF TREATMENT FOR PET/ES D-2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction Conditions</th>
<th>Thermal Properties</th>
<th>Sequence</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time (hrs)</td>
<td>Temp°C</td>
<td>Tm°C</td>
<td>Crystallinity %</td>
</tr>
<tr>
<td>D-2</td>
<td>0</td>
<td>---</td>
<td>233</td>
<td>37</td>
</tr>
<tr>
<td>DSb-1</td>
<td>1</td>
<td>215</td>
<td>240</td>
<td>--</td>
</tr>
<tr>
<td>DSb-2</td>
<td>4</td>
<td>215</td>
<td>240</td>
<td>31</td>
</tr>
<tr>
<td>DSb-3</td>
<td>13.5</td>
<td>215</td>
<td>248</td>
<td>37</td>
</tr>
<tr>
<td>DSb-4</td>
<td>22.5</td>
<td>215</td>
<td>249</td>
<td>43</td>
</tr>
<tr>
<td>DSb-5</td>
<td>36.5</td>
<td>215</td>
<td>249</td>
<td>45</td>
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</table>
**TABLE 15**

**EXTENT OF REORGANIZATION VERSUS TIME OF TREATMENT FOR PET/ES I-2**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction Conditions</th>
<th>Thermal Properties</th>
<th>Sequence Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Time <em>(hrs)</em></td>
<td>Temp °C</td>
<td>Tm °C</td>
</tr>
<tr>
<td>I-2</td>
<td>0</td>
<td>---</td>
<td>208</td>
</tr>
<tr>
<td>ISb/3-1</td>
<td>12</td>
<td>195</td>
<td>236</td>
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<tr>
<td>ISb/3-2</td>
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<tr>
<td>ISb/3-3</td>
<td>36</td>
<td>195</td>
<td>235</td>
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</table>

*Total time at 195°C.
Table 15 contains the results for a series of reorganizations performed on PET/ES I-2 at 195°C. Two grams of I-2 which contained 3% antimony trioxide was heated for 12 hours in a closed system. The polymer was then removed from the reaction flask, reprecipitated, annealed and analyzed (sample ISb/3-1). To the portion of sample ISb/3-1 which remained after analysis, 3% Sb\textsubscript{2}O\textsubscript{3} was added (reprecipitation had removed the initial catalyst); and the polymer was then heated in a closed system for an additional 8 (ISb/3-2) and 24 hours (ISb/3-3). Figure 14 shows a plot of B factor versus reaction time for the ISb/3 series (14A) and the DSb series (14B). By way of comparison, the results of the ISb/1 series (13A) are also included.

The reaction conditions used to prepare the ISb/3 series of copolyesters were identical to those employed for the ISb/1 series except for the introduction of fresh antimony trioxide after the first 12 hours of reorganization. Figure 14 shows that the decrease in randomness, as reflected by the B factor, during the first 12 hours was identical for both series. This behavior was to be expected because reaction conditions were the same up until this point. However, after the new catalyst was added, (14A) shows a much greater decrease in B value over the remainder of the reaction time than (13A) does.
Figure 14 - B Number versus Reaction Time
The total time of thermal treatment for both ISb/3-3 and ISb/1-3 was 36 hours; yet, the values of B were 0.79 and 0.85 respectively. Thus copolymer ISb/3-3 had a significantly greater block character. Because both series of copolyesters had the same degree of randomness after 12 hours, and therefore, the same concentration of hetero-unit dyads, the continued decrease in randomness of the ISb/3 series indicates that the limiting reorganization shown by (13A) is not due to the decreasing concentration of T-G-S reaction sites.

Separating the effects of catalyst deactivation and reduced mobility of endgroups is not possible from these data alone. The reprecipitation of sample ISb/3-1 effectively erased the excess crystallinity developed by the thermal treatment to that point. In addition, a new aliquot of Sb$_2$O$_3$ was added at this time. Therefore, the continued decrease of randomness may have resulted from the addition of active catalyst and/or the increased mobility of endgroups caused by the reduced crystallinity.

Preventing the accumulation of the volatile by-products of the CIR would avoid the deactivation of the catalyst. Such a procedure would also have the advantage that the whole reaction could be run without interrupting it to add fresh catalyst. Consequently, the crystallinity developed by the thermal treatment would not be disrupted and the effect of the deactivation of catalyst could be
accurately gauged. The DSb series of copolyesters were prepared in such a manner. Running the CIR in an open system prevented or at least greatly reduced the accumulation of volatile by-products in the reaction flasks.

Figure 14, (14B), shows the change of B factor with reaction time for this series. The initial increase in B value, 0.92 to 0.96, is not surprising in light of the results of the BSb series of reorganizations because copolymer D-2 was also a low molecular weight polymer. The significant feature of (14B) is the rapid decrease in B which occurs up to 24 hours. In contrast, the results in Figure 13 have shown that a limiting value of B was approached in about 12 hours. The differences which existed in both reaction temperature and molecular weight had no apparent effect on these results, other than to raise or lower the value of the limit.

In drawing conclusions from these results it is important to note that, as in the case of the ISb/1, ISb/2, and BSb series of reorganizations, the crystallinity developed during the CIR of the DSb series was not disrupted. On this basis, if the reduction of endgroup mobility by crystallization was responsible for the limiting of block character development, it should have the same effect on the DSb copolymers. Because it did not, and because the decrease in randomness continued in the ISb/3 series after
the addition of antimony trioxide, the limiting value of randomness obtained in a closed system must be attributed to deactivation of the catalyst in this case.

**Effect of Molecular Weight.** The mechanism by which copolyesters reorganize during crystallization-induced reaction involves a series of ester-interchanges between the hydroxyl endgroups and internal ester linkages of the polymer. Because the concentration of endgroups of a polymer is directly related to its molecular weight, a change in molecular weight should alter the rate of crystallization-induced reaction. To determine quantitatively the degree to which molecular weight effected the extent of reorganization of PET/ES copolymers, two sets of copolyesters were prepared. Each pair had approximately the same composition, but differed in molecular weight. The data in Table 16 indicate the effect of CIR on copolymers D-2 and G-2, while that in Table 17 shows the effect of reorganization of I-2 and B-2.

The results recorded in Table 16 are from copolyesters subjected to crystallization-induced reaction at 215°C in an open system. The temperature was approximately the same number of degrees below the melting point of both D-2 and G-2. The data shows that after 36 hours of thermal treatment, the B value of DSb-5 had decreased to 0.753 from 0.940. The average sequence length \( L_T \) increased from 5.44 to 11.74 for the same polyester. For the higher
TABLE 16

EFFECT OF MOLECULAR WEIGHT ON THE EXTENT OF CRYSTALLIZATION INDUCED REACTION OF PET/ES COPOLYMERS AT 215°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (hrs)</th>
<th>Temp°C</th>
<th>Crystallinity %</th>
<th>Sequence Distributiona</th>
<th>B</th>
<th>Q</th>
<th>%T</th>
<th>η inh</th>
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<tbody>
<tr>
<td>G-2</td>
<td>0</td>
<td>---</td>
<td>36</td>
<td>0.953</td>
<td>1.33</td>
<td>82</td>
<td>0.346</td>
<td></td>
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<tr>
<td>GSb-1</td>
<td>1</td>
<td>215</td>
<td>--</td>
<td>0.937</td>
<td>1.43</td>
<td>84.3</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>GSb-2</td>
<td>13</td>
<td>215</td>
<td>--</td>
<td>0.939</td>
<td>1.41</td>
<td>88.4</td>
<td>0.345</td>
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<tr>
<td>GSb-3</td>
<td>23.5</td>
<td>215</td>
<td>39</td>
<td>0.902</td>
<td>1.67</td>
<td>88.9</td>
<td>0.411</td>
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<td>36</td>
<td>215</td>
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<td>1.99</td>
<td>91.0</td>
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<tr>
<td>D-2</td>
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<td>0.918</td>
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<td>80.5</td>
<td>0.256</td>
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</tr>
<tr>
<td>DSb-1</td>
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<td>215</td>
<td>--</td>
<td>0.960</td>
<td>--</td>
<td>82.4</td>
<td>--</td>
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</tr>
<tr>
<td>DSb-3</td>
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<td>86.2</td>
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<td>4.27</td>
<td>87.6</td>
<td>0.311</td>
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<tr>
<td>DSb-5</td>
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<td>45</td>
<td>0.753</td>
<td>5.34</td>
<td>88.4</td>
<td>0.377</td>
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a. determined from reprecipitated polymers
<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction Conditions</th>
<th>Sequence Distribution</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>Time (hrs)</td>
<td>Temp°C</td>
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<tr>
<td>B-2</td>
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<tr>
<td>BSb-3</td>
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<td>201</td>
</tr>
<tr>
<td>BSb-4</td>
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<td>BSb-5</td>
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<td>I-2</td>
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</tr>
<tr>
<td>ISb/2-1</td>
<td>12</td>
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</tr>
<tr>
<td>ISb/2-2</td>
<td>20</td>
<td>201</td>
</tr>
<tr>
<td>ISb/2-3</td>
<td>36</td>
<td>201</td>
</tr>
</tbody>
</table>
molecular weight sample, GSb-5, the B factor decreased from 0.958 to 0.867 while $\bar{L}_nT$ increased from 4.97 to 8.23.

Table 17 contains the results for CIR of PET/ES I-2 and B-2 at 201°C. In this case the reaction was performed in a sealed flask under nitrogen pressure. Copolymer BSb-5 evidenced an increase in Q factor from 1.40 to 2.85 in 36 hours of reaction, and an increase of $\bar{L}_nT$ from 1.40 to 2.85. During the same period, ISb/2-3, the higher molecular weight sample, showed a smaller change in both parameters. The $\bar{L}_nT$ for this sample was 5.85 as compared to 4.94 for the starting material, while Q increased from 1.34 to 2.50.

In both cases, the copolymer with the lower molecular weight evidenced a greater increase in microstructural order than the higher molecular weight material of equal composition. This observation is in accord with the mechanistic prediction and therefore substantiates the crystallization-induced reaction theory. However, the magnitude of the changes in blockiness are not in accord with the molecular weight differences. The difference in molecular weight between the starting materials for producing BSb-5 and ISb/2-3 is substantially greater than that for GSb-5 and DSb-5. It would be expected therefore, that the former pair of copolymers would show a greater difference in rates of reorganization. Yet, from the NMR data
it may be shown that the increase in blockiness for GSb-5 was 49% of that for DSb-5, while the increase for ISb/2-3 represents 58% of the BSb-5 reorganization. The disparity between the expected and observed differences in reorganization rate indicate that a reevaluation of the assumptions made in predicting this behavior is warranted.

Although it was not explicitly stated, it was assumed that the extent of the reorganization accomplished by crystallization-induced reaction was controlled by the overall rate of ester-interchange in the amorphous phase. The rate of interchange in the amorphous phase, however, is not necessarily equal to the "effective" rate of interchange. Due to the mechanism of crystallization-induced reaction, only those interchanges which replace a non-crystallizable unit at the edge of a lattice with a crystallizable one are effective in altering the microstructure. Thus the degree and type of crystallinity will alter rate of crystallization-induced reaction, but will show no effect on the amorphous phase reaction. In the present case, Table 16 shows that both samples had an equivalent degree of crystallinity at the start of the reaction. As a result, each contained approximately the same number of effective interchange sites and the differences in the rate of reorganization were unaffected by crystallinity. Table 17 shows that the crystallinity of B-2 was only 19%
as compared to 25% for I-2. This difference in crystallinity apparently caused a rather large difference between the rates of effective ester-interchange in the samples. Instead of reflecting the difference in reaction rate due to endgroup concentration, these results probably represent a mixed effect of endgroup concentration and crystallinity (ie. effective reaction site concentration).

From the data two important conclusions may be drawn. First, the molecular weight of a copolyester directly effects the rate at which it undergoes crystallization-induced reaction. This result was expected from theoretical considerations and the previous investigations of copolyester reorganization; however, confirmation of the fact that even a copolymer of a molecular weight of \(~20,000\) can be reorganized to a substantial degree (86% increase in \(Q\)) is important in determining the practicality of crystallization-induced reaction. Secondly, the apparent effect of crystallinity on the extent of reorganization has been indicated and deserves careful consideration. A discussion of ways to investigate the effect of crystallinity and crystallization is presented in a later section of this chapter.

**Effect of Reaction Temperature.** PET/ES copolymer I-2 was subjected to crystallization-induced reaction at different temperatures. Various measures of the extent of
reorganization of the products are presented in Tables 18-21. Three sets of data were collected from isothermal treatments; ISb/1 at 195°C; ISb/2 at 201°C; and ISb/4 at 210°C. The fourth set of copolymers, ISb/5, was prepared using a programmed increase in temperature during the reaction. An explanation of the thermal treatment for this series appears with Table 21. Again the catalyst was 3% wt/wt antimony trioxide.

Table 18 shows results obtained from the ISb/4 series of copolyesters. These materials were prepared by thermal treatments at 210°C, which is 2°C above the melting point of the starting material I-2. Under these reaction conditions the polymer remains molten throughout the thermal treatment. The purpose behind running this experiment was to determine if the para-crystalline order reported to persist in PET slightly above the melting point could serve as sites for crystallization-induced reaction. The data indicate that no reorganization occurred in any of the ISb/4 samples. After 20 hours of reaction, the Q factor for ISb/4-2 was 1.36 as compared to 1.34 for the starting material.

Table 21 indicates the effect of thermal treatments of I-2 which involved a programmed increase in reaction temperature from 201°C to 231°C. Sample ISb/5-2, which was heated at 201°C for six hours, 211°C for six hours,
<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (hrs)</th>
<th>Temp°C</th>
<th>Tm°C</th>
<th>B</th>
<th>Q</th>
<th>$\bar{L}_n$ T</th>
<th>%T</th>
</tr>
</thead>
<tbody>
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<td>I-2</td>
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<td>208</td>
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<td>1.34</td>
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<td>74.1</td>
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<tr>
<td>ISb4/1</td>
<td>12</td>
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<td>235</td>
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<td>4.44</td>
<td>75.3</td>
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<td>ISb4/2</td>
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<td>4.67</td>
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<td>ISb4/3</td>
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<td>210</td>
<td>234</td>
<td>.90</td>
<td>1.72</td>
<td>5.19</td>
<td>78.6</td>
</tr>
<tr>
<td>Sample</td>
<td>Time (hrs)</td>
<td>Temp°C</td>
<td>$T_m$ °C</td>
<td>B</td>
<td>Q</td>
<td>$L_0T$</td>
<td>%T</td>
</tr>
<tr>
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</tr>
<tr>
<td>I-2</td>
<td>0</td>
<td>---</td>
<td>208</td>
<td>0.94</td>
<td>1.34</td>
<td>4.09</td>
<td>74.1</td>
</tr>
<tr>
<td>ISb/1-1</td>
<td>4</td>
<td>195</td>
<td>---</td>
<td>0.92</td>
<td>1.51</td>
<td>4.31</td>
<td>74.9</td>
</tr>
<tr>
<td>ISb/1-2</td>
<td>12</td>
<td>195</td>
<td>232</td>
<td>0.90</td>
<td>1.67</td>
<td>4.57</td>
<td>75.7</td>
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<tr>
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<td>232</td>
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<td>5.04</td>
<td>76.9</td>
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<td>ISb/1-4</td>
<td>36</td>
<td>195</td>
<td>233</td>
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<td>2.44</td>
<td>5.55</td>
<td>78.1</td>
</tr>
<tr>
<td>Sample</td>
<td>Time(hrs)</td>
<td>Temp°C</td>
<td>$T_m$°C</td>
<td>B</td>
<td>Q</td>
<td>$\bar{L}_n$T</td>
<td>%T</td>
</tr>
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<td>-----</td>
</tr>
<tr>
<td>I-2</td>
<td>--</td>
<td>---</td>
<td>208</td>
<td>0.94</td>
<td>1.34</td>
<td>4.09</td>
<td>74.1</td>
</tr>
<tr>
<td>ISb/2-1</td>
<td>12</td>
<td>201</td>
<td>232</td>
<td>0.88</td>
<td>1.84</td>
<td>4.71</td>
<td>75.9</td>
</tr>
<tr>
<td>ISb/2-2</td>
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<td>201</td>
<td>232</td>
<td>0.85</td>
<td>2.21</td>
<td>5.39</td>
<td>78.2</td>
</tr>
<tr>
<td>ISb/2-3</td>
<td>36</td>
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<td>233</td>
<td>0.83</td>
<td>2.50</td>
<td>5.83</td>
<td>79.4</td>
</tr>
</tbody>
</table>
TABLE 21

TEMPERATURE PROGRAMMED REORGANIZATION OF PET/ES COPOLYMER I-2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time /Temp(^\circ)C (hrs)</th>
<th>(T_m)(^\circ)C</th>
<th>B</th>
<th>Q</th>
<th>(\bar{L}_nT)</th>
<th>%T</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-2</td>
<td>0</td>
<td>208</td>
<td>0.94</td>
<td>1.34</td>
<td>4.09</td>
<td>74.1</td>
</tr>
<tr>
<td>ISb/5-1</td>
<td>6/201(^\circ) + 6/211(^\circ)</td>
<td>233</td>
<td>0.87</td>
<td>1.99</td>
<td>--</td>
<td>77.0</td>
</tr>
<tr>
<td>ISb/5-2</td>
<td>6/201(^\circ) + 6/211(^\circ) + 8/221(^\circ)</td>
<td>231</td>
<td>0.85</td>
<td>2.26</td>
<td>--</td>
<td>79.1</td>
</tr>
<tr>
<td>ISb/5-3</td>
<td>6/201(^\circ) + 6/211(^\circ) + 8/221(^\circ) + 16/231(^\circ)*</td>
<td>226</td>
<td>0.918</td>
<td>1.58</td>
<td>--</td>
<td>78.9</td>
</tr>
</tbody>
</table>

* Sample melted at 231\(^\circ\)C.
and then 221°C for eight hours, evidenced an increase in Q of 68% from 1.34 to 2.26. For the last 14 hours of treatment of this sample the temperature was above the melting point of the starting material. Thus CIR may be performed at temperatures above the melting point of the starting material if the initial treatment is below this point. However, care must be utilized to insure against melting the reorganized copolymer because randomization will occur on melting. When sample ISb/5-3 had reached 20 hours of reaction, it had been treated in the same manner as ISb/5-2 but the last 16 hours of heating were performed at 231°C and the sample was observed to fuse. Although, it undoubtedly had the same block character as ISb/5-2 after 20 hours, it randomized after fusion. The Q value of this sample was 1.58, a decrease of 0.68 from that of ISb/5-2.

The data in Tables 19 and 20 show the effect of changes in reaction temperature on the extent of reorganization by crystallization-induced reaction under isothermal conditions. Sample ISb/1-3 shows an increase in Q value from 1.34 to 2.08, and an increase in $\bar{L}_n T$ of 0.95 from 4.09 to 5.04 in 20 hours of reaction at 195°C. Increasing the reaction temperature to 201°C caused a change in Q from 1.34 to 2.21 and in $\bar{L}_n T$ from 4.09 to 5.39 for sample ISb/2-2 over the same reaction time.
The results obtained from the ISb/4 series of copolymers clearly establishes the fact that the melting point of the copolyester sets a definite upper limit to the initial temperature at which crystallization-induced reactions can be successfully performed. The para-crystalline or local order reportedly present in the melt of PET, if it is present in the copolymer, is not sufficiently constrained to act as a sink for crystallizable units. As a result the copolymer behaves exactly as would be expected of a molten polyester.

On the other hand, initial thermal treatment below the melting point allows one to perform successful crystallization-induced reactions well above the limit imposed by the starting materials' melting point. Presumably the reorganization which occurs because of the initial heating increases the melting point, of at least some fraction of the material, enough so that higher treatment temperatures can be employed.

Comparing the change in Q factor obtained from the isothermal crystallization-induced reactions demonstrates that the extent of reorganization accomplished in a given period increases as higher reaction temperatures are employed. The changes in the Q number of the copolyester amounted to 18.6\% at 185^\circ\text{C}, 55.2\% at 195^\circ\text{C}, and 64.9\% at 201^\circ\text{C}. However, it should be noted that the extent of
reorganization is apparently less dependent on reaction temperature as the melting point of the polymer is approached. In fact, sample ISb/5-2, which was ultimately reacted at 221°C showed the same 64.9% increase in Q noted for the copolymer treated at 201°C. It appears that the initial treatment of this sample at 201°C for six hours set the pattern for the reorganization even though the reaction temperature was raised 20°C.

It is apparent that some mechanism other than the rate of the ester-interchange is responsible for the decreasing effect of temperature on the extent of reorganization as the melting point of the copolyester is approached and for the fact that the temperature programmed sample attained the same degree of reorganization as one treated at 201°C. It should be noted that all of the other results which cannot be explained on the basis of ester-interchange rate changes, occurred at temperatures near the melting point of the starting material. Thus the effectiveness of changes in catalyst concentration differed as one approached the melting point and the anomalous behavior of the different molecular weight samples were also observed at temperatures close to Tm. This persistent occurrence of results which cannot be readily explained makes a careful examination of the crystallization-induced reaction mechanism imperative.
Any model constructed to explain the mechanism of crystallization-induced reaction must include a provision for ester-exchange near the lattice surface. Depending upon the degree of perfection of the crystallites, the geometric requirements for approach and attack near their surface will be more or less stringent. Therefore, the rate of a chemical transformation in this zone would be influenced by these restrictions. If a pair of copolyester samples contained different types and/or degrees of crystallinity, the "effective" rate of reorganization could well be altered even though the samples were from the same copolyester.

Because of defining the melting point of the copolymers as the point of return to the DSC baseline, one has defined the point at which the biggest or most perfect crystallites of the sample melt. As a result, for temperatures close to the defined melting point, the thermal treatment effectively fractionates the sample on the basis of crystallite perfection. The smaller (and less perfect) crystallites are melted out by heating the sample in this range (Figure 15). Thus samples treated at different temperatures are not the same material even though they are from the same copolymer.

These differences could manifest themselves in several ways. First, as the melting point is approached more of the crystalline material is melted out. At the temperature
Figure 15 — Fraction of Original Crystalline Material which remains at various Reaction Temperatures
of reaction the melted crystalline material, which of necessity is highly ordered, will be subject to randomization because it is not constrained in a lattice. In addition fewer crystalline surfaces are available for reaction. The randomization of the lower melting PET blocks, and the reduced number of reactive sites change the "effective rate" of reorganization. Secondly, the fractionation provides a more perfect crystalline phase to nucleate the reaction as the melting point is approached. The more stringent geometric requirements for reaction at the surface can also serve to alter the rate of reorganization.

It has been demonstrated that at the melting point the "effective rate" of transformation is zero (ISb-series); yet it is well known that the chemical reaction rate is very high at this temperature. The zero rate is a result of the lack of crystallites necessary to shift the equilibrium. At temperatures near the melting point the effect of the crystalline properties on the extent of reorganization will also be pronounced. Because of the smaller number of crystallites and the increasingly stringent geometric requirements for attack at such surfaces, the "effective rate" of interchange will eventually be governed by the surface characteristics rather than the overall rate of ester exchange. Changes in reaction conditions which increase the rate of the chemical transformation, i.e. catalyst concentration, molecular weight and temperature, will
become ineffective in changing the extent of reorganization. Thus, close to the melting point a change in rate control will be encountered. The results not explainable by changes in ester-interchange rate may be rationalized on the basis of altered crystalline properties.

Furthermore, the fact that the temperature programmed treatment was no more effective than a similar treatment at 201°C may also be explained. In both cases the initial treatment was at 201°C, the crystallites which remained unmelted were the same for both samples. As a result both reorganizations were nucleated by the same type of crystallites. If the crystal growth mechanism was one leading to extended chain crystals, the exposed surface of these crystals would not change in perfection during the reaction,²⁸ and therefore the extent of reorganization would be dependent upon the nucleating crystals. As a consequence, both samples would show the same degree of reorganization.

The formation of extended chain crystals during solid state polymerization reactions is well documented in the literature. Wunderlich⁸⁸ found that polymerization of PET oligomers in the solid state lead to extended chain crystals. Kawai⁵⁷ also found extended chain crystals in the heterogeneous polymerization of synthetic polypeptides. Additionally, for the few samples of reorganized polyesters
which were melted without reprecipitation, the melting point decreased some 10-15°C on a second melting cycle indicating a non-equilibrium crystallite was produced. Thus the extended chain postulate is a reasonable one.

The above suggestion cannot be verified on the basis of the results obtained from the analytical methods employed. To fully interpret the effect of crystallinity on crystallization-induced reaction near the melting point, it would be necessary to have information on the actual degree and perfection of crystallinity at the start of the reaction, and their growth mechanism during the reaction. Such results cannot be obtained from DSC measurements because the crystalline properties of PET and its copolymers change during the heating cycle. Furthermore, the samples were reprecipitated to deactivate the catalyst and do not represent the properties of the as-reacted materials. Because the crystalline properties of the copolymers could well be the cause for the unexpected results they should be investigated in future attempts to define the extent of crystallization-induced reaction.

**Thermal Properties.** Analysis of the NMR data presented above indicates that subjecting the PET/ES copolymers to CIR caused an increase in block character in all cases. To determine what effect these changes in microstructure had on the thermal properties of the copolyester,
the melting point \( (T_m) \), crystallization temperature \( (T_c) \), and percent crystallinity \( (\%X) \) were determined for each reorganization product. A differential scanning calorimeter, DSC 2, was employed to measure these quantities.

All of the quantities measured were obtained after the copolymer had been reprecipitated from trifluoroacetic acid to deactivate the reorganization catalyst, and to erase the copolymer's thermal history. The reprecipitated copolymers were ground (to pass a 20 mesh sieve), and then annealed for five hours at 162°C before being encapsulated in aluminium pans and melted in the DSC. Tables 22 and 23 show the variation of the copolymers thermal properties as a function of reaction conditions.

Table 22 shows that the melting point of copolymer B-2 increased from 212°C to 232°C after being heated for 12 hours at 201°C with 3% Sb\(_2\)O\(_3\) as catalyst. During a subsequent 24 hours of heating, the melting point remained essentially unchanged in spite of the fact that the block length as measured by the Q factor continued to increase.

For reorganized copolymers of the I-2 series, which had an approximately equal composition (74.1 vs 77.2% terephthalate), Table 23 indicates the following changes in T\(_m\) resulted during the initial 12 hours of reaction: ISb/1-2 increased from 208 to 232°C; ISb/2-1 increased from 208 to 232°C; and ISb/3-1 increased from 208 to 231°C.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (hrs)</th>
<th>Temp $^\circ$C</th>
<th>$T_m$ $^\circ$C</th>
<th>%X</th>
<th>$T_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-2</td>
<td>0</td>
<td>---</td>
<td>212</td>
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<td>broad</td>
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<tr>
<td>BSb-3</td>
<td>12</td>
<td>201</td>
<td>232</td>
<td>40.9</td>
<td>189</td>
</tr>
<tr>
<td>BSb-4</td>
<td>20</td>
<td>201</td>
<td>235</td>
<td>42.2</td>
<td>191</td>
</tr>
<tr>
<td>BSb-5</td>
<td>36</td>
<td>201</td>
<td>234</td>
<td>45.3</td>
<td>193</td>
</tr>
</tbody>
</table>

TABLE 22

THERMAL PROPERTIES OF REORGANIZED PET/ES COPOLYMER B-2
<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (hrs)</th>
<th>Temp °C</th>
<th>T_m °C</th>
<th>%X</th>
<th>T_c</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-2</td>
<td>0</td>
<td>---</td>
<td>208</td>
<td>25</td>
<td>137</td>
</tr>
<tr>
<td>ISb/1-2</td>
<td>12</td>
<td>195</td>
<td>232</td>
<td>32</td>
<td>188</td>
</tr>
<tr>
<td>ISb/1-3</td>
<td>20</td>
<td>195</td>
<td>232</td>
<td>34</td>
<td>192</td>
</tr>
<tr>
<td>ISb/1-4</td>
<td>36</td>
<td>195</td>
<td>233</td>
<td>37</td>
<td>192</td>
</tr>
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<td>ISb/2-1</td>
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<td>232</td>
<td>34</td>
<td>184</td>
</tr>
<tr>
<td>ISb/2-2</td>
<td>20</td>
<td>201</td>
<td>232</td>
<td>35</td>
<td>190</td>
</tr>
<tr>
<td>ISb/2-3</td>
<td>36</td>
<td>201</td>
<td>233</td>
<td>42</td>
<td>191</td>
</tr>
<tr>
<td>ISb/3-1</td>
<td>12</td>
<td>195</td>
<td>231</td>
<td>--</td>
<td>173</td>
</tr>
<tr>
<td>ISb/3-2</td>
<td>20</td>
<td>195</td>
<td>234</td>
<td>41</td>
<td>192</td>
</tr>
<tr>
<td>ISb/3-3</td>
<td>36</td>
<td>195</td>
<td>235</td>
<td>43</td>
<td>194</td>
</tr>
</tbody>
</table>
As in the previous case the initial large increase in $T_m$ was followed by a negligible change during the next 24 hours of reaction.

The DSC curves from which the melting point data in Tables 22 and 23 were obtained are reproduced in Figures 16-19. Figure 20 shows all of the curves on one scale. From Figure 20 it can be seen that regardless of the starting copolyester (B-2 or I-2), and the conditions of the reorganization, the reorganized copolymers all have melting points in the five degree range 230 to 235°C. Although only the first cycle melting points are shown, the second cycle melting point was within $\pm 1^\circ$C in all cases.

It should be noted that all of these copolymers were reprecipitated and annealed under constant conditions before they were analyzed. Therefore, their thermal properties do not represent those of the material "as reacted" but rather some sort of equilibrium crystallized material.

To determine if the "as reacted" material was significantly different than the reprecipitated copolymers, two reorganization products were analyzed without reprecipitation. The remaining portion of copolymer I-2 was divided into two samples and subjected to CIR under the same conditions as ISb/2-1. Both of the samples had first cycle melting points which were 10-12°C higher than ISb/2-1.
Figure 16 – DSC Thermograms of the BSb Series
Figure 17 — DSC Thermograms of the ISb/1 Series
Figure 18 — DSC Thermogram of the ISb/2 Series
Figure 19 — DSC Thermograms of the ISb/3 Series
Figure 20 — Composite of DSC Curves of all PET/ES Copolyesters
However, their second cycle melting points were again found in the range 230-235°C. The decrease in $T_m$ which occurred on the second cycle melt suggests that the "as reacted" material contained non-equilibrium crystals which revert to an equilibrium form upon melting.$^9$,$^90$

Together with the results obtained for the reprecipitated copolymers, these results suggest that some type of limiting crystalline form is reached by all of the copolyesters after a certain block length is reached. A tentative explanation of this limiting form will be offered in subsequent paragraphs. First it is important to establish that the melting point increases observed are a result of increases in sequence length.

There are four reasons why the melting point of a copolymer might increase after a prolonged, high temperature, thermal treatment. In the case where no chemical reaction occurred, an increased crystal perfection could result in higher melting products. When reaction occurs, an increase in molecular weight, a change in the relative comonomer composition, or an alteration of the chemical microstructure could all lead to an increased melting point.

Three of these suggestions may be eliminated from consideration, by carefully reviewing the experimental results. First, the melting point increase cannot be
attributed to an improved crystal structure because each copolymer had the same thermal history. Although the copolymers were treated for a variety of different times at temperatures near their melting points, they were each dissolved, reprecipitated, and annealed under identical conditions. Thus their thermal histories at the time of measurement were the same.

Further, several investigations\(^9,7^9\) have shown that polymers whose melting point increases upon annealing due to altered crystal perfection alone, exhibit second cycle melting points at the same temperature as prior to the thermal treatment. As a means of determining if the melting point increase was a result of differences in crystalline form, the second cycle melting point of the samples were determined. In all cases, both melting points were the same within \(+1^\circ\text{C}\). Thus crystal perfection is not responsible for the changes in melting points observed.

Second, the higher melting points of the reorganization products cannot be attributed to an increase in molecular weight. Edgar and Ellery\(^7^4\) have reported that the melting point of PET copolymers with aliphatic polyesters becomes invariant with molecular weight above a number average molecular weight of 2-3,000. Copolymers B-2 and I-2, the starting materials for these reorganizations, had weight average molecular weights of \(~5,200\) and \(~20,000\) respectively.
Finally, the change in composition noted after reorganization cannot account for more than a tiny fraction of the observed change. If it is assumed that the copolymers remained random throughout the heating period, the melting point/composition relationship of Flory\textsuperscript{21} (Equation 42) may be employed to determine the increase in melting point which could have resulted from the slight increase in terephthalate content of the reorganized copolymers.

\[ \frac{1}{T_m} - \frac{1}{T_{m_0}} = (R / \Delta H_u) \ln P_{AA} \]  \hspace{1cm} (42)

Employing values of $T_{m_0} = 265^\circ C$, $\Delta H_u = 32.2$ cal/gr, $R = 1.987$ cal/gr$^\circ C$, and the values of $P_{AA}$ determined by NMR, values of $T_m$ were calculated. In the case of ISb/2-3, where the largest change in composition was noted, the increase amounts to only $2^\circ$ or about 9% of the observed $24^\circ$ increase.

Thus, the large increase in melting point which occurred when PET/ES copolymers were subjected to CIR must be attributed to changes in their chemical microstructure demonstrated by the NMR results. What remains to be explained is why the initial large increase in $T_m$ was followed by a period where the microstructure continued to increase in blockiness, yet the melting point was unaffected.
This phenomena was also observed by Go\textsuperscript{36} but was reported without comment. Table 24 reproduces the pertinent results of Go's investigation.

Before attempting to explain the results, a discussion of the definition of a polymer's melting point employed in this research is warranted. The melting point of a polymer was defined as the temperature at which the DSC trace returned to the baseline after the endothermic melt peak. By defining $T_m$ in this way, the temperature at which all crystallinity disappears is recorded.

For the purpose of these experiments such a definition is justified. The desire was to define the temperature above which CIR could not be performed and to react the copolymers as close as possible to that point. The results of the ISb/4 series demonstrate that these goals were accomplished. Crystallization-induced reactions could be performed effectively up to a maximum temperature which coincides well with the defined melting point. If the more standard definitions of $T_m$ had been utilized, the embarrassing situation of performing a crystallization-induced reaction above the "melting point" of the copolymer would have developed.

Since the definition of $T_m$ employed measures the temperature where all crystallinity vanishes, it approximates the melting point of the most perfect crystals. Therefore, the invariance of melting point suggests that
TABLE 24

EFFECT OF CRYSTALLIZATION-INDUCED REACTION ON THE PHYSICAL PROPERTIES OF PET/MS COPOLYESTERS

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th>Temp °C</th>
<th>Time (hrs)</th>
<th>Percent PET</th>
<th>Melting Point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>205</td>
<td>0**</td>
<td></td>
<td>72.3</td>
<td>217</td>
</tr>
<tr>
<td>205</td>
<td>10</td>
<td></td>
<td>71.6</td>
<td>222</td>
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<td>205</td>
<td>20</td>
<td></td>
<td>72.6</td>
<td>225</td>
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<td>225</td>
</tr>
<tr>
<td>220</td>
<td>0*</td>
<td></td>
<td>78.5</td>
<td>228</td>
</tr>
<tr>
<td>220</td>
<td>10</td>
<td></td>
<td>78.2</td>
<td>237</td>
</tr>
<tr>
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<td>220</td>
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<td>220</td>
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<td>232</td>
</tr>
<tr>
<td>220</td>
<td>20</td>
<td></td>
<td>79.3</td>
<td>232</td>
</tr>
</tbody>
</table>

* 1% Titanium tetrabutoxide as catalyst.
** 3% Titanium tetrabutoxide as catalyst.
somewhere between the initial random copolymer and the 10 hour reorganization sample a type limiting crystal perfection develops. After it is reached, further increases in sequence length do not effect the melting point of the crystals.

The apparent limiting perfection of the copolyester crystals is not totally understood at this time. Further studies which include X-ray diffraction and selective degradation techniques capable of following changes in crystalline properties will be necessary to render an unequivocal explanation. However, a tentative explanation consistent with the available data is offered here.

Overton and Haynes\textsuperscript{79} have clearly demonstrated that the melting point of PET is dependent upon the fold period in which it crystallizes. Several additional studies\textsuperscript{9,90,91} demonstrated similar behavior for other polyesters. Although copolyesters present a somewhat different situation, the occurrence of chain folding should still be of importance. Once the terephthalate sequence length in the copolymer reaches a certain value, call it $X$ units, the units in this sequence are sufficiently separated from the co-monomer units to be unaware of their presence. At this point they are free to behave as units in the homopolymer and seek the preferred crystalline habit. For PET segments this will be a chain folded structure.
The original copolyesters which are totally random contain a sufficient amount of the comonomer to preclude the formation of long enough sequences of terephthalate units to chain fold. When they are subjected to crystallization-induced reaction this situation is altered. The existing crystalline regions act as "sinks" for terephthalate units causing the sequence length to increase.

At some point the critical value of sequence length, X, is reached and chain folding can occur. After this value is reached, and sequences x+1, x+2, x+3, etc. units long would be incorporated into the lattice as X units because of chain folding. Thus as \( \overline{L}_n T \) continued to increase the most perfect crystals would be chain folded ones and the melting point would be unaltered.

As a consequence of this mechanism one should also observe that the melting range narrows, with the peak moving to the high temperature end. This would result from the fact that the smallest sequences are disappearing while the upper end is fixed; ie. sequences of greater than X units in length melt at the same temperature as X length units. Examining Figures 16-19 shows that both of these trends can be observed.

Although the melting point of the copolyesters tended toward a constant value with time, the two additional thermal properties measured behaved in the expected manner.
The crystallization temperature, $T_c$, showed a continual increase with increasing block length. Tables 22 and 23 contain the results of the $T_c$ measurements. Figure 21 shows a typical set of DSC curves as a function of reaction time.

The measurement of $T_c$ was accomplished by heating the copolymers to a constant temperature above the melting point ($535^\circ$K) and using a programmed auto cool cycle of $10^\circ$C/minutes. The point at which the curves deviate from the base line was considered to be $T_c$.

The results show that $T_c$ increased as the extent of reorganization increased. This is the expected behavior because longer sequences of crystallizable monomer should increase the probability of forming a critical size nuclei to start crystallization. The probability being increased at any given temperature means that the onset of crystallization occurs at higher temperatures.

The fact that $T_c$ continued to increase while the $T_m$ remains constant is not contradictory. The formation of a critical size nuclei is not dependent upon the mode of final crystallization. 35

Accompanying the increase in $T_c$ was a continual increase in the percent crystallinity. Again Tables 22 and 23 contain the results. For the BSb series the crystallinity increased from 18.1 to 45% in 36 hours of reaction.
Figure 21 – First Cycle Recrystallization behavior of the ISb/1 Series
A similar trend was observed for the reorganization of PET/ES Copolymer I-2. After reaction at 195°C, ISb/1-4 was 37% crystalline while ISb/3-3 was 43% crystalline. Sample ISb/2-3, reacted at 201°C, had a final crystallinity of 42%. Each sample showed a substantial increase over the starting materials' 25% crystallinity.

The increased crystallinity of the reorganized samples is to be expected on the basis of the sequence distribution changes demonstrated by the NMR analysis. The decrease in randomness means more uninterrupted terephthalate sequences are available to crystallize.

Effect of CIR on the Physical Properties of PET/ES

The effect of CIR on the physical properties of the PET/ES copolymers was investigated by measuring the tensile properties of a copolymer before and after reorganization. The results of these measurements are recorded in Table 25. Copolyester I-2 is the starting material, i.e. the random copolymer; ISb/2-2 is a sample of I-2 which was subjected to CIR at 201°C for 20 hours.

Table 25 shows that the tensile strength and modulus of the CIR product are slightly higher than those of the starting material whereas the elongation at break is somewhat lower. Although there is no substantial change in any of the quantities measured, the significant point is
<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Strength (dynes/cm²)</th>
<th>Elongation at Break %</th>
<th>Modulus (dynes/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-2</td>
<td>1.23 x 10¹⁰</td>
<td>1.09</td>
<td>1.37 x 10⁸</td>
</tr>
<tr>
<td></td>
<td>1.40 x 10¹⁰</td>
<td>1.09</td>
<td>1.47 x 10⁸</td>
</tr>
<tr>
<td></td>
<td>1.51 x 10¹⁰</td>
<td>1.17</td>
<td>1.18 x 10⁸</td>
</tr>
<tr>
<td>average</td>
<td>1.38 x 10¹⁰</td>
<td>1.12</td>
<td>1.34</td>
</tr>
<tr>
<td>ISb/2-2</td>
<td>1.86 x 10¹⁰</td>
<td>0.80</td>
<td>1.81 x 10⁸</td>
</tr>
<tr>
<td></td>
<td>2.16 x 10¹⁰</td>
<td>0.72</td>
<td>1.68 x 10⁸</td>
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<tr>
<td>average</td>
<td>2.01 x 10¹⁰</td>
<td>0.76</td>
<td>1.74</td>
</tr>
</tbody>
</table>
that there was no deterioration of properties as a result of the extended high temperature reaction. The slight increase in strength noted can be readily understood on the basis of the microstructural changes which occurred.

The starting material, copolyester I-2, was a random copolymer which had a crystallinity of 25% as measured by DSC. On the other hand, ISb/2-2 was found to be only 85% random. As a result of this increased structural order it had a substantially larger percent crystallinity. Not only did the crystallinity measured from the melt endotherm increase (ethylene terephthalate sequences), but as was the case with all the reorganized copolyesters, crystallinity developed in the ethylene succinate phase. Due to the diffuse nature of the succinate transition, its contribution to the crystallinity was not measurable with any degree of accuracy. Nevertheless, the value of 37% crystalline obtained for ISb/2-2 must be viewed as a lower limit. For at room temperature where the tensile tests were run, the succinate units are some 60°C below their melting point and will contribute to the stiffness of the copolyester.

Thus ISb/2-2 is a stiffer polymer than I-2 and its tensile properties would be expected to reflect this difference. The changes in properties noted in Table 25 are in line with these observations. The increased stiffness
of ISb/2-2 lead to greater resistance to deformation and therefore a reduced elongation at break and a higher modulus and tensile strength.
CHAPTER IV

SUMMARY

Before attempting to apply the Murano technique for sequence distribution analysis of copolyesters to determining microstructural changes caused by CIR, the method was investigated to determine its accuracy. To facilitate this investigation, copolyesters of PET/ES were chosen because their NMR spectra should consist of five sharp singlets: three from the glycol-acid dyads, and one each from the diacid residues. By appropriate data reduction methods it would be possible to calculate two monomer composition ratios from different resonances; thus ensuring internal consistency of the analysis. It was important to be able to perform such a check because the glycol-acid dyad resonances were expected to overlap to some degree, therefore, an internal check would ensure that the proper separation of resonances had been performed.

When the actual copolyesters used in this project were prepared it became apparent that the low molecular weight of the products complicated their NMR spectra. Two additional resonances were observed in the glycol region. The preparation of the model compound BHET identified one of the resonances as ethylene terephthalate
endgroups, and suggested that the other resulted from ethylene succinate endgroups. However, the BHES compound could not be isolated so no firm assignment of the remaining resonance could be made on the basis of NMR alone.

In addition, the accuracy of measuring succinate-succinate dyads in copolyesters with low ethylene succinate content had to be established because of the desire to use copolymers in the 80-95% ethylene terephthalate composition range. To solve these problems an independent method of comonomer analysis was needed.

A method for determining the monomer composition of a copolyester by a combination saponification-gas chromatography technique was developed because existing techniques were not readily applicable to PET/ES copolymers. Although the method was developed specifically for PET/ES copolymers, it should be applicable to copolyesters in general and thus represents a useful addition to analytical techniques presently available.

For the purpose of this research the analysis was utilized to verify the NMR determination of sequence distribution, and the assignment of the fifth glycol resonance. Further, the use of this technique demonstrated that the NMR analysis could be used to analyse changes in sequence distribution on PET/ES copolymers with succinate contents as low as 10%. The overall accuracy being ± 1.5%.
The results of this research have again confirmed the occurrence of CIR. All of the copolyesters studied evidenced an increase in average sequence length, melting point and degree of crystallinity as predicted by the theory.

Efforts to determine the parameters which exert the controlling influence on the extent of reorganization by CIR demonstrated that the chemical reaction rate is not the sole control. The results obtained can be divided into two groups based upon the temperature at which the CIR occurred; i.e. the proximity of the reaction temperature to the melting point of the starting material.

At temperatures greater than 15°C below the copolyester’s melting point those parameters which exert their primary effect on the chemical reaction rate control the extent of reorganization. Thus, in this temperature region the proper choice of catalyst, the catalyst concentration, molecular weight, time and temperature of reaction all exert major effects on the extent of reaction.

The most important variable was found to be the appropriate choice of catalyst. Antimony trioxide was found to be far superior to calcium acetate, tetraethyl orthotitanate, and tetrabutyl orthotitinate in promoting reorganization. Increasing the catalyst concentration also increased the rate of change in the range 1-3% catalyst concentration.
After choice of catalyst, changes in the molecular weight of the sample (endgroup concentration) gave the most pronounced differences in rate. For two copolymers of 81% terephthalate content, both reacted at 215°C, a change in $\eta_{\text{inh}}$ from .256 to .346 caused the latter copolymer to reorganize only 8% whereas the former showed a 21% change.

At temperatures closer to the starting materials' melting point chemical reaction rate does not appear to be a controlling factor. Samples of widely differing molecular weights with different catalyst concentrations, and with or without temperature programmed treatments exhibit comparable extents of reorganization. These results suggest that as the melting point is approached, a change in rate controlling step is encountered.

A similar type of occurrence is reported by Chang concerning the controlling step in the polymerization of PET in the solid-state. Below 210°C the rate of polymerization is subject to changes in the chemical reaction rate. Above 210°C diffusion through the solid polymer is the controlling step and parameters which effect the chemical reaction rate become ineffective as controls.
CHAPTER V

Suggestions For Further Investigations

As the name implies, crystallization-induced reactions are caused by the crystallinity of the copolymer. In the past too little attention has been paid to the crystallinity of the copolymers studied. When one carries out a CIR near the melting point, the nature of the crystalline phase becomes important to understanding the mechanism of the reaction. At different temperatures in the melting zone, a different number and type of crystallite is present to nucleate the reaction.

The effect of crystalline properties on the reaction can only be studied by isolating and measuring them at the same time as the average sequence information was obtained by NMR analysis. One method of accomplishing this would be as follows: after the samples have been prepared, selective degradation of the amorphous material and X-ray diffraction could be employed to characterize the size and perfection of the crystallites. By heating the sample to the reaction temperature close to $T_m$ for a short time and quickly quenching it, followed by X-ray and degradation studies, the changes caused by melting of crystalline material could be determined. These experiments combined
with NMR data would define the starting material.

The CIR would then be run in three simultaneous determinations. One would be a blank (no catalyst), one would be a crystallization rate experiment run in a dilatometer (with catalyst) and one would be a normal CIR. Both the blank and CIR samples are removed together and quenched. X-ray analysis of both would yield average crystallite size and perfection data. NMR results would provide sequence distributions. The dilatometer experiment would provide crystallization rate data. By combining these results a much clearer picture of crystallization-induced reaction in the region of Tm would be gained.

A second experiment worth considering is the nucleating of CIR in an otherwise amorphous (at the reaction temperature) PET copolymer by well defined oligomeric crystals obtained by degradation. In this system the effect of reaction rate variables could be separated from crystal properties because the crystallites responsible for the reaction, and the copolymer would be constant factors.
BIBLIOGRAPHY


78. Rhodes, James. Private Communication.


