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Substituted aromatic polyesters: Degradation studies

Scott Lee

SUBSTITUTED AROMATIC POLYESTERS:

DEGRADATION STUDIES

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<u>Studies</u>

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Abstract

Two liquid crystalline aromatic polyesters were studied by isothermal degradation techniques. Both polymers contain a common phenyl side chain group. However, one contains a styryl side chain and the other contains an α-methylstyryl side chain. Isothermal degradations under nitrogen and air were carried on both polymers. From the GC/MS analysis of the cold traps, it showed that both polymers gave off benzene or oxygenated benzene related products. Homopolymers containing only phenyl or α-methylstyryl side chain were prepared by solution polymerization techniques. Then isothermal degradation under air were also carried out on both homopolymers. The GC/MS analysis showed that the α-methylstyryl side chain was responsible for the formation of the oxygenated benzene products.

The activation energies determined for the polyesters did not show the relative stability of the polyesters as expected. Solution polymerized polyester 6 was studied initially under both air and nitrogen atmospheres using the Perkin-Elmer TGS-2 TGA. For polyester 6 under nitrogen, the activation energy (E_a) was determined to be 43 kcal/mole. Polyester 6 under air, the E_a determined were 31 kcal/mole for the initial rate and 28 kcal/mole for the final rate.

Then using the Seiko thermal instrumentation, all of the polyesters were studied under flowing air. The E_a for polyester 6 was determined to be 22 kcal/mole for the initial rate and 12 kcal/mole for the final rate. Solution polymerized polyester **7** had calculated E_a of 36 kcal/mole. Melt polymerized polyester **7** had calculated E_a of 14 kcal/mole for the initial rate and 11 kcal/mole for the final rate. Solution polymerized polyester **8** had calculated E_a of 16 kcal/mole for the initial rate and 12 kcal/mole for the final rate. Solution polymerized polyester **9** had calculated E_a of 20 kcal/mole for the initial rate and 16 kcal/mole for the final rate.

INTRODUCTION

The behavior of liquid crystalline materials have been known since 1888 when Reinitzer[1] observed that cholesteryl benzoate melted to form a turbid melt that eventually cleared at high temperatures. The term liquid crystal was coined by Lehmann[2] to describe this type of material.

Liquid crystal[3] is a term used to describe materials that exhibit partially ordered fluid phases that are intermediate between the three dimensionally ordered crystalline state and the disordered or isotropic liquid state. They are considered neither pure liquid nor true solids so they have been referred to as a fourth state of matter. Pure liquids are isotropic molecules, meaning that the molecules lack order and solid or crystalline materials are anisotropic, meaning that the molecules are ordered. Liquid crystals occur when molecules become aligned in a crystalline array while still in the liquid state and their appearance are often turbid or opalescent.

The liquid crystalline state is recognized by long or short range orientationally ordered molecules. There are three types of molecular orientations, nematic, smectic, and cholesteric. The nematic phase permits for translational mobility of the molecule while in the smectic phase the translational mobility is minimized. Molecular orientation of the two phases are shown in Figure 1 below:
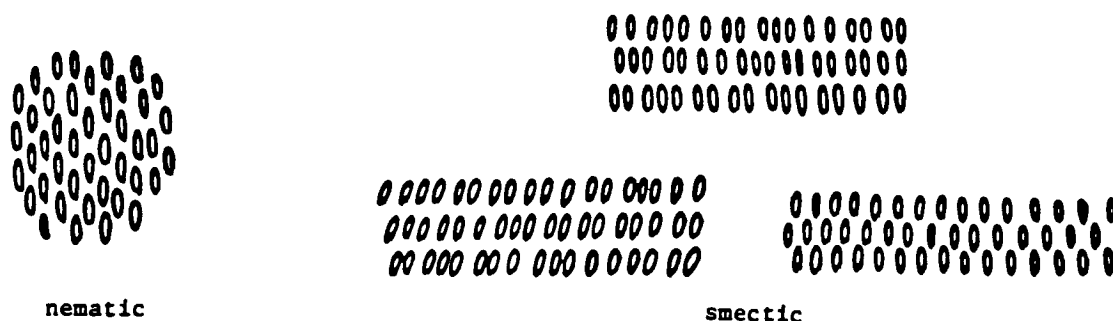
nematic

smectic

Figure 1. Molecular orientation of smectic and nematic mesogenic phases.

The most highly ordered phase is the smectic phase. The smectic phase has a two dimensional order. The nematic phase mesogens are aligned with adjacent mesogens (rigid backbone groups). The cholesteric phase is a special type of twist nematic phase. The constituent molecules are chiral thus giving rise to an asymmetrical helical orientation of "sheets" because the spontaneous twist resulting form the chirality of the molecule. the cholesteric mesophase is viewed as layers of nematics with each consecutive layer being rotated by a specific angle. A schematic of cholesteric molecular orientation is shown in Figure 2.
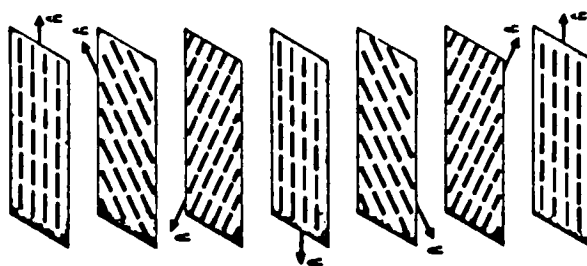
Figure 2. Molecular orientation of cholesteric mesogenic phase

Classification of Liquid Crystals:

Two classifications of liquid crystals are lyotropic and thermotropic. Lyotropic liquid crystals are formed under critical concentration in solution while thermotropic liquid crystals form under melting. Liquid crystalline phases are not observed for lyotropic liquid crystal polymers, primarily because the melting points of these materials are generally so high that they will degrade before melting.[4]

The first thermotropic liquid crystal polymers were reported in the mid 1970's by Sirigu[5] et. al. and Kuhfuss.[6] et. al.. Sirigu et. al., prepared new polyalkanoates from p,p'-dihydroxy-α,α'-dimethylbenzalazine and appropriate acyl chlorides to give the polymeric structure **1** shown on page 3.

$$\left[O\text{—}\langle\!\!\!\bigcirc\!\!\!\rangle\text{—C=N-N=C}\text{—}\langle\!\!\!\bigcirc\!\!\!\rangle\text{—O-C-(CH}_2)_n\text{-C} \right]_m$$

with CH$_3$ substituent on the central carbon, and the two carbonyl oxygens as drawn.
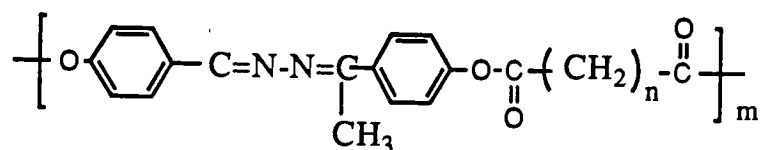
n = 6, 8, 10

1

All of the above polymers examined, melted to give fluid anistropic phases whose properties appear to be similar to those observed with conventional liquid crystals.

Thermotropic liquid crystals usually have the following structure features: 1) high length : breadth (axial) ratio, 2) rigid units such as 1,4-phenylene, 1,4-cyclohexyl, etc., 3) rigid central linkages such as -COO-, -CH=CH-, -N=N-, and etc. between the rings. Included in the thermotropic polymers are side chain and main chain polymers. The name implies the location of the mesogenic (liquid crystalline) group. In side chain polymers, the pendant liquid crystalline unit is connected to the polymer main chain by a flexible spacer group such as methylene units. This flexible connection maintains the delicate interactions between the pendant liquid crystalline units by dampening the main chain motion from that of the pendant group. An example of a side chain polymer is shown in structure **2** below:

$$\left[\text{— CH}_2\text{—} \underset{\underset{\displaystyle COO(CH_2)_n\text{- O-}\langle\!\!\!\bigcirc\!\!\!\rangle\text{-COO-}\langle\!\!\!\bigcirc\!\!\!\rangle}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}} \right]$$
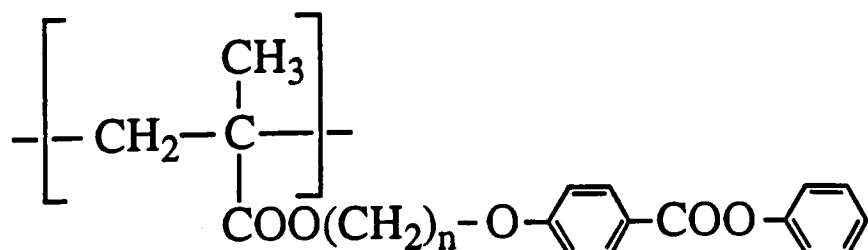
2

Alternatively, main chain polymers have the mesogenic units

3

directly connected into the main polymer chain. An example of a main chain polymer is the copolyester **3** with the structure shown on page 4:[7]

$$\cdot\left[-OC\text{-}\bigcirc\text{-}COOCH_2CH_2-\right]\cdot\left[OC\text{-}\bigcirc\text{-}O-\right]-$$
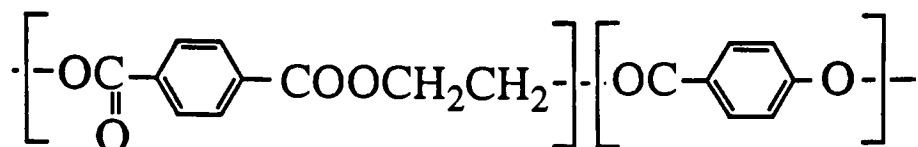
3

With their unique hybrid characteristic, liquid crystals exhibit properties that are not found in liquid or crystalline states alone. Their morphology may be altered by external magnetic or electric fields, they sometimes change color with temperature, and some exhibit very high optical rotation.

Liquid Crystal Polymers (LCPs):

Liquid crystals have been used in widespread commercial applications because of their unique properties. Low molecular weight liquid crystals are often used as video display screen for calculators and televisions. Whereas high molecular weight liquid crystals are used as engineering plastics or high strength fibers. Liquid crystalline polymers are thermally stable, flame resistant and have excellent mechanical properties. A common example of high molecular weight, aromatic lyotropic liquid crystalline polymer is Du Pont's Kevlar ™,

$$\cdot\left[-\overset{O}{\overset{\|}{C}}\text{-}\bigcirc\text{-}\overset{O}{\overset{\|}{C}}-NH\text{-}\bigcirc\text{-}NH-\right]-$$
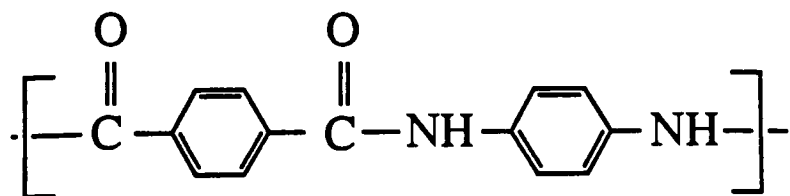
4

A sulfuric acid solution of the polymer shows the liquid crystalline phase. Extrusion of Kevlar into a fiber results in the alignment of the molecules. This uniform alignment gives Kevlar the tensile strength which is much greater than that of steel but with a much lower density.[8] Kevlar's common uses are in bullet-proof vests, automobile exterior panels, brake linings, and many other high strength applications. An example of a thermotropic liquid crystal polyester is the Celanese Vectra® resins with the structure shown below:
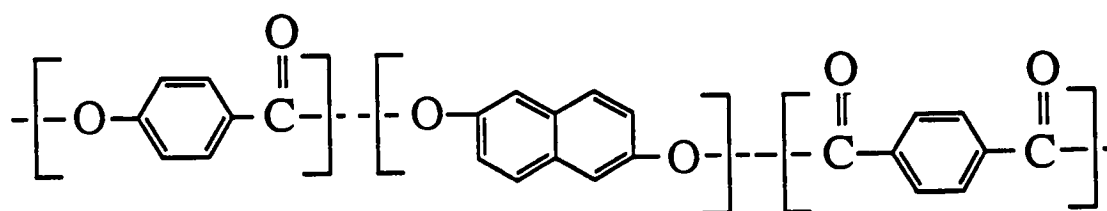
5

This polyester is a thermoplastic which can be formed into molded parts with application of heat and pressure.

<u>Stability of LCPs:</u>

Major concerns of rigid liquid crystalline aromatic polymers are that they have high melting points and are difficult to dissolve in common organic solvents. Since they have a very high melting points (Tm), their corresponding glass transition (Tg) temperatures and decomposition temperatures will also be high.

Stability of polymers is of critical interest to both the manufacturer and the researcher. The degree of stability of the polymer depends on the application and the environment at which the polymer perform its task. Stability is a measure of the polymer's ability to withstand thermal and thermo-oxidative forces that make polymers decompose. The main reason why synthetic polymers have yet to replace its metal and ceramic counterparts is the inability of most polymers to maintain their

physical properties at high temperatures.[9]

There are three principal methods of polymer degradation; chemical, thermal, and radiative. The chemical method is limited to only reactions involving the breakdown of the polymer's backbone by chemical reactions. The thermal method is based on the reactions involving only the pendant groups and does not usually break the polymer's backbone if the degradation is a non-chain scission type of reaction. This type of degradation normally occurs in aromatic polymers where the backbone is stable and rigid. Thermal degradation normally involves pyrolysis or heat induced breakdown of the polymer and its mechanism normally takes place through a free radical mechanism.[10] Radiative polymer degradation on the other hand can occur by both main-chain and pendant group scission. The procedure takes place by allowing exposure of polymer samples under UV light for long periods of time and then study the rate of breakdown of the polymer as a function of time. The breakdown normally occurs autocatalytically at the weak points of the polymer where radical attacks are more susceptible.

Thermal and Thermooxidative Stabilities of LCPs:

Ordinarily, when organic compounds are heated to high temperatures they have a tendency to form aromatic compounds. Therefore, aromatic polymers should be resistant to high temperatures. Thermal stability is primarily dependent on the nature of the chemical bond. When temperature rises to the point where the vibrational energy causes bond rupture, the polymer degrades.

The atmosphere to which the polymer is exposed during degradation affects the polymer's decomposition temperature as well as the degradation products that are produced. A polymer decomposed under an inert atmosphere such as nitrogen will have a higher stability than under air or oxygen. Oxidation of the polymer is the most important type of thermal analysis because it has a direct bearing on the polymer's durability and thus its

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stability. The presence of air or oxygen has little effect on the initial decomposition temperature, so bond rupture is dependent on thermal rather than oxidative process.

Thermogravimetry Study of Polymers:

Thermogravimetry (TG) is a thermal analysis technique that measures the change in weight of a substance as a function of temperature and/or time. It's widely used for obtaining information on the thermal stability of a polymer system. TG can be used to determine sample purity, identification, solvent retention, reaction rate, and activation energy.

Two types of TG analysis can be performed to study the stability of the polymer, dynamic and isothermal techniques. The isothermal technique follows weight change as a function of time. This technique monitors at a specified temperature where bond scission reaction is taking place. Thus, bond scission reaction rate parameters can be obtained directly. This method is time consuming because a fresh sample is needed for each temperature. However, the activation energy values obtained are more accurate than the dynamic technique.

The dynamic method studies the weight change as a function of temperature. Fewer weight loss curve obtained from a set of different heating rate are used to provide information equivalent to a family of isothermal weight loss curves. This time saving approach covers a wide range of temperatures continuously. However, the precision is dependent on the equation in use which are derived by mathematical treatments and simplified assumptions.[11] The validity of the dynamic or non-isothermal method has been much criticized.[12,13] The data obtained from the thermograms are analyzed through the entire temperature range. If simultaneous reactions occur within that temperature range, the activation energy obtained would be inaccurate.

Factors that effect the weight loss TG curve of a sample are furnace heating rates, furnace atmosphere, amount of sample, sample packing, and the thermobalance used. Weight loss in TG

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is a diffusion controlled process. The furnace heating rate affects the TG curve by shifting the decomposition temperature to a higher temperature if a faster heating rate is used. The shifting is due to the slow equilibration of the sample with the furnace temperature, thus, causing a lag behind the furnace temperature. The decomposition curve is more accurate at a low rate of heating than at a faster rate for identical samples.[14] This is due to the better equilibration of the sample with the furnace temperature.

The reaction type, the decomposition products, and the type of atmosphere used will have a profound effect on the shape of the TG curve. An inert atmosphere such as nitrogen or argon is used when gaseous decomposition products need to be removed. Nitrogen is also used to prevent the sample from reacting with oxygen or other reactive atmospheres.[15] The sample amount used is of the most important factors that can cause a TG curve change. When a large sample is used, the sample may not equilibrate with the furnace temperature fast enough to give a true decomposition profile. When too much sample is used, the volatile decomposition products can not diffuse through the sample matrix readily. This will result in an inaccurate percent conversion at a specific time or temperature. The design and placement of the thermobalance used will also affect the TG curve results. There are two types of thermobalances commercially available, hang-down and horizontal beam. The hang-down balance has the sample bucket suspended by a platinum wire from the balance beam. Balances of this type are noted for their sensitivity . Their main disadvantage is that they are sensitive to gaseous turbulence and the inconvenience of the placement of the temperature sensor in contact with the sample. The temperature thermocouple is located just below the sample pan but not in touch with the pan. A schematic of this type of balance is shown in Figure 3 on page 9.[16]
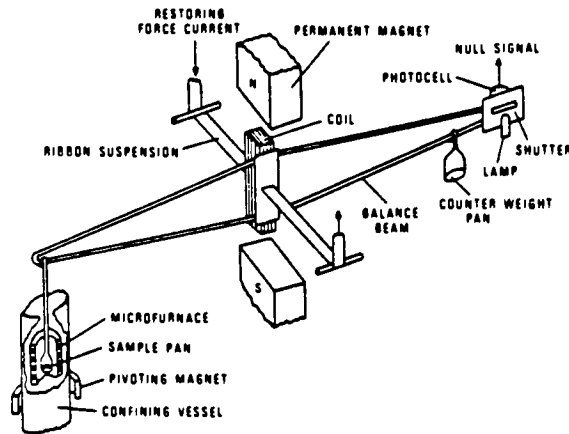
Figure 3. Hang-Down Balance (Perkin-Elmer TGS-2 TGA)

The horizontal beam balance on the other hand does have the floating thermocouple in contact with the sample. This type of balance is designed for high temperature ceramic applications and can be used with larger samples.
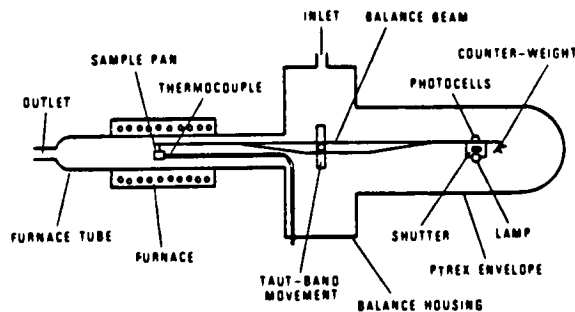
Figure 4. Horizontal Beam Balance (Seiko TG/DTA 220)

One of the leading source of errors in thermogravimetry is temperature measurement. If the sample temperature is taken as the temperature measured by the thermocouple located either just above or just below the sample container, the true sample temperature will either lead or lag behind the furnace temperature.

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Thermogravimetric Analysis Kinetics:

Activation energies of Poly(ethylene terephthalate) or PET, a commonly used polyester, have been calculated by means of the Arrhenius equation on the basis of rate constants using both dynamic heating rates[17,18] and isothermal methods.[19,20] Other methods have been used to determine the activation energies of PET such as intrinsic viscosity, carboxylic end point titration, and hydronium end point.[21]

Hay and Kemmish[22] also studied poly(aryl ether ketone)s or PEEK, and poly(aryl ether ketone)s or PEK by isothermal conditions to determine their decomposition kinetics. In their experiment, the volatile products evolved from the tube furnace were condensed in liquid nitrogen traps and were analyzed by mass spectroscopy.

The isothermal weight loss method was used for this degradation kinetics study. Separate tests were conducted at a number of temperatures in order to determine activation energies. The advantage of this method is that a virgin polymer sample is tested at each temperature. Samples of the dynamic heating of the Flynn-Wall[23,24] or Ozawa[25] method present at high temperatures may have been modified by reactions at lower temperatures. The maximum rate loss which occurs at a specific isothermal temperature is taken as the rate constant for that temperature.

The weight loss recorded in TG thermograms under isothermal conditions can be strictly described by the equation[19,20]

$$\ln (m - m_f / m_o - m_f) = -kt \qquad (1)$$

or
$$\ln (1-W) = -kt \qquad (2)$$

where $\quad m \;$ = weight of the sample
$\qquad m_o$ = initial weight

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m_f = final weight

k   = velocity constant

t   = time

$w = (m_o-m)/(m_o-m_f)$

For the case of first order kinetics, the rate of the reation is

$$r = dw/dt = k(1-w) \qquad (3)$$

where the rate constant, k, depends on the absolute temperature of the system.

$$k = k^o \exp(\Delta H/RT) \qquad (4)$$

Combining equations 3 and 4, the resulting equation is

$$\ln [(dw/dt)/(1-w)] = \ln [(dm/dt)/(m-m_f)] \qquad (5)$$

or $\qquad\qquad \ln k^o - (\Delta H/RT) \qquad (6)$

where k^o is the pre-exponential factor and R is the universal gas constant.

By plotting the left side of equation 2 versus time, a straight line with a slope of k is obtained. Then using the rate constants, k, the activation energy can be determined from the following Arrhenius equation:

$$k = A [\exp(E_a/RT)]. \qquad (7)$$

Taking natural log of both sides gives equation 4,

$$\ln k = \ln A + E_a /RT \qquad (8)$$

plotting the left hand side of equation 8 versus the reciprocal of the absolute temperature, the activation energy can be determined from the slope of the curve.

Objective

The objective of this project is to determine the reaction activation energy and kinetics for the thermal decomposition of two aromatic thermotropic liquid crystalline polyesters shown in structures **6** and **7** below:

6

7
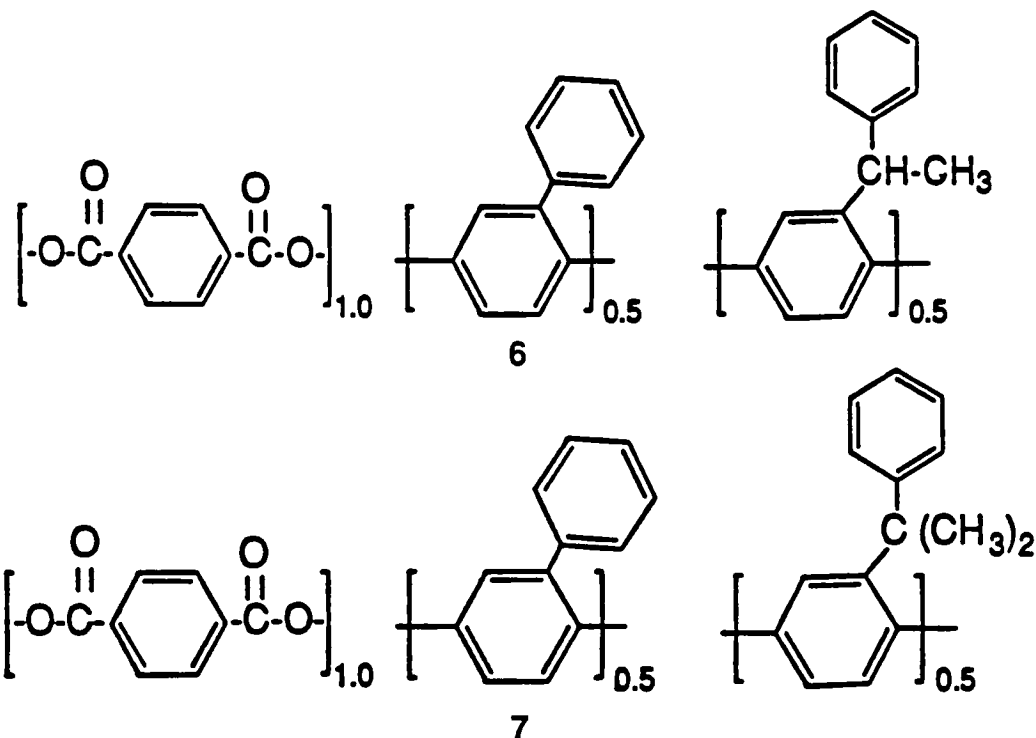
Energies of Activation and Reaction Kinetics:

By assuming the main chain of the polymer does not break and also the fact that side chain scission process follows first order kinetics. The activation energy of the broken bond will be determined from isothermal TG method. The corresponding side chain causing the formation of the decomposition products can also be determined. The thermal decomposition products of the two polymers will be studied after isothermal heating under both air and nitrogen atmosphere using the HP 5995 GC/MS.

One of the most commonly used methods for determining the stability of a polymer is to find its activation energy for the corresponding bond scission that occurs in degradation. The

activation energy of the decomposition reaction of the polymer's side chain is considered to be a measure of the stability of the polymer.[26]

Polyesters **8** and **9** will also be synthesized using either interfacial polymerization or solution polymerization. Their isothermal decomposition products and activation energies will also be determined.
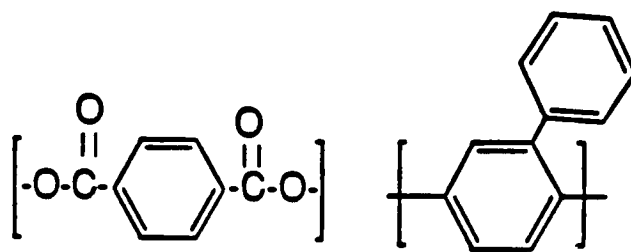
8
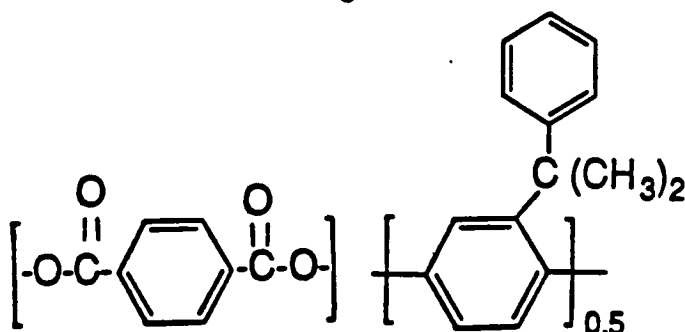
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The results obtained for these two polymers will explain if the benzene and oxygenated benzene decomposition products obtained from polyester **6** and **7** comes from the phenyl, styryl or α-methylstyryl side chain. The corresponding activation energy for bond scission will also support the findings.

Results and Discussion

The thermal degradation reaction is a homolytic or free radical reaction caused by the rupture of chemical bonds with the formation of radicals. The specific radicals formed are dependant upon their thermodynamic stability. A less stable bond will be easier to break than a more stable one. Aliphatic bonds found in the styryl side chain for example are weaker than the aromatic bonds found in the phenyl side chain.
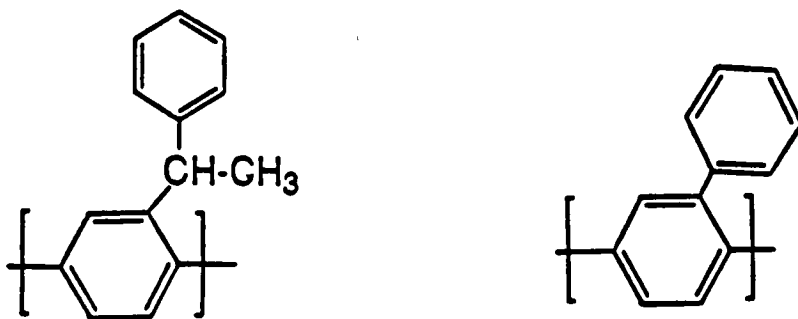
Figure 5.   Styryl and aryl side chain

Table I lists the respective bond dissociation energies of various chemical bonds.

	E_a(kcal/mol)
1. C_6H_5-H $\longrightarrow$ $C_6H_5\cdot$ + $\cdot$H	104
2. C_6H_5-C_6H_5 $\longrightarrow$ $C_6H_5\cdot$ + $\cdot C_6H_5$	100.5
3. C_6H_5-CH_3 $\longrightarrow$ $C_6H_5\cdot$ + $\cdot CH_3$	94
4. C_6H_5-CH_2-CH_3 $\longrightarrow$ C_6H_5-$\overset{.}{C}H$-CH_3 + $\cdot$H	81.6
5. C_6H_5-CH-$(CH_3)_2$ $\longrightarrow$ C_6H_5-$\overset{.}{C}H$-CH_3 + $\cdot CH_3$	68.7

Table I. Bond dissociation energies for various chemical bonds.

Polyester **6** is an aromatic polyester which is prepared from the solution polymerization·of terephthaloyl chloride with equal amounts of 2-phenyldroquinone and 2-styrylhydroquinone. The primary products observed from the isothermal oxidative

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degradation studies under air were identified as benzene, styrene, benzaldehyde, phenol, and acetophenone. Most of the products were collected in the first trap with the spill-over products collected in traps 2 and 3. GC/MS was used to analyze the contents of the traps. The observed products can be attributed to the lability of the carbon bonds found in the phenyl or the styryl side chain substitutents in polyester **6**.
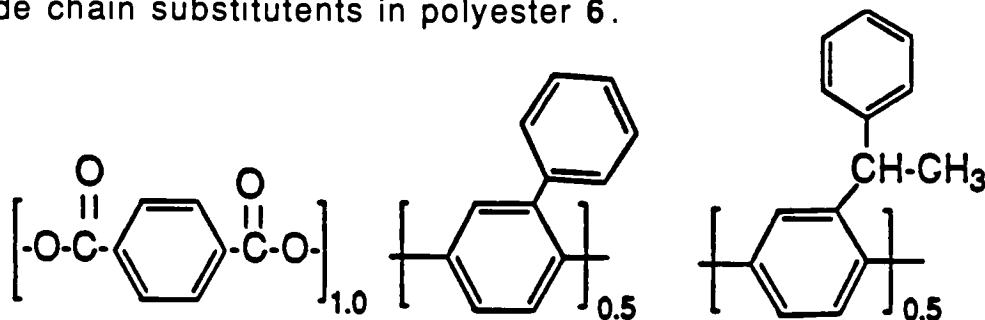
The results of the GC/MS analysis of cold trap #1 is shown in Table II.

Temperature (°C)	φH	Products Styrene	φCHO	φOH	φCOCH₃
260			*t*	••	*t*
270	*t*	*t*	•	•••	•
290	*t*	*t*	•	•••	•
310	*t*	*t*	•	•••	*t*
330	*t*	•	•	•••	*t*
350	*t*	•	•	•••	•

• Relative abundances based upon ion peak heights   t = trace

Table II. GC/MS analysis summary of trap #1 for polyster 6 under air atmosphere.

From Table II it seems that at the lower temperature of 260°C, the primary products were benzaldehyde, phenol, and acetophenone. The critical temperature for the thermal stability

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of polyester **6** seems to be between 260 - 270°C. At 270°C, the polymer decomposes to give benzene and styrene along with benzaldehyde, phenol, and acetophenone in larger amounts. The identity of the products were confirmed by matching their retention times and mass fragmentation patterns with known compounds. Possible reaction pathway for the decomposition product formation is shown in Figure 6.
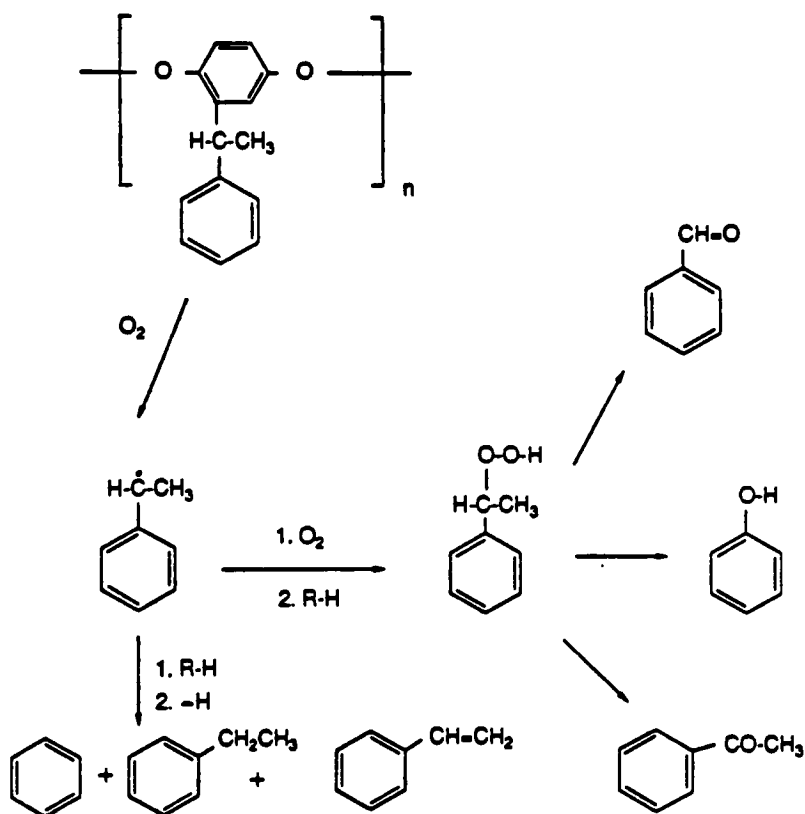
Figure 6. Proposed reaction pathway for formation of degradation products for polyester **6** under air.

By comparison of the two side chain substitutents, the styryl pendant group should give a more stable radical than the phenyl radical. Therefore, all the degradation products should be derivative of the styryl side chain.

From the pathway, the degradation products can be derived from a 1-phenylethyl radical. Elimination of a hydrogen atom

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results in a styrene molecule. Homolysis of 1-phenylethyl radical to a phenyl radical proceeded by a hydrogen abstraction yields benzene. The decomposition of the hydroperoxide of 1-phenylethane, formed by the reaction of 1-phenylethyl radical with oxygen accounts for the oxygen containing product of benzaldehyde, phenol and acetophenone. It also should be noted that all low boiling gases such as methane, ethane, carbon dioxide, and carbon monoxide are expected products but are not monitored.

Polyester **6**, studied isothermally under nitrogen atmosphere resulted in non-oxygenated aromatic products. The primary products observed were benzene, toluene, ethylbenzene, styrene, and xylenes. The mechanism for the formation of the degradation products is show in Figure 7.

$$C_6H_5\cdot \ + \ R\text{-}H \ \longrightarrow \ C_6H_5\text{-}H \ + \ R\cdot$$

$$C_6H_5\cdot \ + \ CH_3\cdot \ \longrightarrow \ C_6H_5\text{-}CH_3$$

$$CH_3\text{-}C_6H_4\cdot \ + \ CH_3\cdot \ \longrightarrow \ C_6H_4\text{-}(CH_3)_2$$

$$C_6H_5\text{-}\overset{\bullet}{C}H\text{-}CH_3 \quad \overset{R\text{-}H}{\underset{\text{-}H\cdot}{\nearrow\searrow}} \quad \begin{array}{l} C_6H_5\text{-}CH_2\text{-}CH_3 \\ \\ C_6H_5\text{-}CH\text{=}CH_2 \end{array}$$
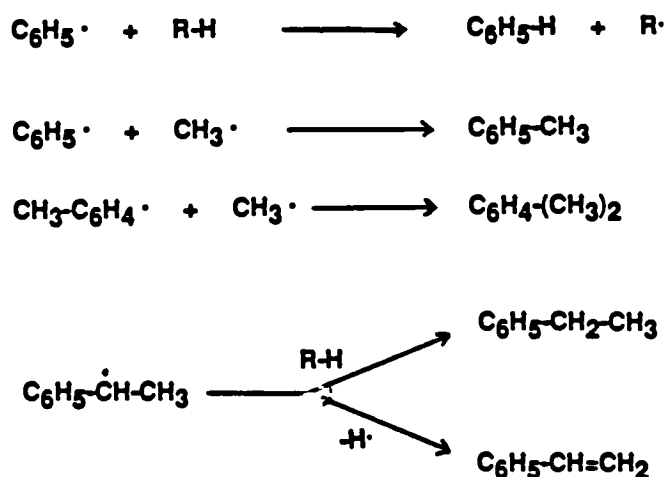
Figure 7. Proposed reaction pathway for the formation of decomposition product for polyester **6** under nitrogen.

The predominant products were ethylbenzene and styrene and they are derived from a 1-phenylethyl radical. A hydrogen abstraction yields ethylbenzene, while a hydrogen elimination gives styrene. Homolysis of the 1-phenylethyl radical gives the phenyl radical. Abstracting a hydrogen gives benzene, while toluene is a combination product of a phenyl and methyl radical. Xylene is the result of a combination reaction of a tolyl radical

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with a methyl radical. The GC/MS product analysis of trap #1 is summarized in Table III.

Temperature (°C)	Products				
	Benzene	Toluene	Ethylbenzene	Styrene	Xylenes
270	t				
290	t				
300	t				
310	t				
320	t				
330	t				
340	t	t	t	t	
350	t	t	•	t	
360	t	t	t	•	
370	•	••	•••	••	t

• Abundance based upon ion peak heights   t = trace

Table III. GC/MS analysis summary of trap #1 for polyster 6 under nitrogen atmosphere.
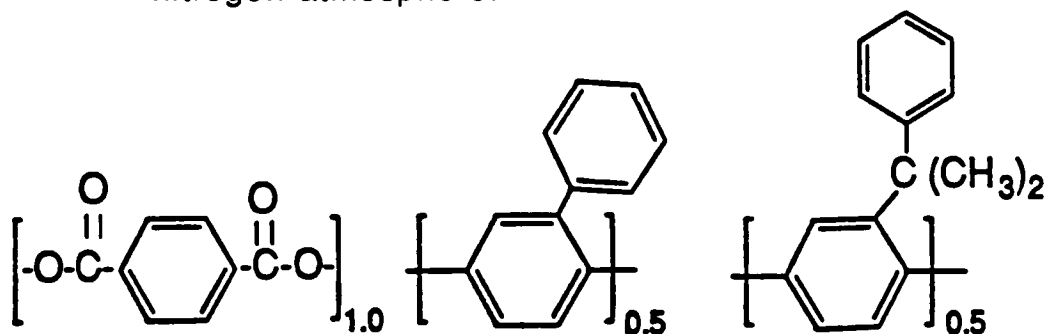
Polyester **7**, like polyester 6 has the phenyl side chain but instead of a styryl side chain, it has an α-methylstyryl side chain. The α-methylstyryl groups are labile and is most likely to undergo thermal or thermo-oxidative decomposition. The aliphatic bonds present in the α-methylstyryl side chain are also weaker than the phenyl side chain and are susceptible to homolysis or oxygen attack. Polyester **7** was provided by Granmont Inc. and was prepared by a melt polymerization of terephthalic acid with equal amounts of the diacetate esters of 2-phenylhydroquinone and 2-methylstyrylhydroquinone. The degradation products for polyester **7** collected in trap #1 under

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air are listed in Table IV.

Temp. (°C)	Products							
	HAc	φH	φCH₃	φEt	Sty	Cumene	φCHO	α-MeSty
220	•	-	-	-	-	-	-	t
240	•	-	-	-	-	-	t	t
260	••	-	-	-	-	-	t	•
280	••	-	-	-	-	-	•	•
300	••	-	-	-	-	-	t	•
320	••	-	-	-	-	-	t	••
340	•••	-	t	-	-	•	t	••
360	•••	-	•	-	t	••	t	•••
380	•••	•	•	•	t	••	t	••
400	•••	••	••	•	t	•	t	••

• Relative abundances based upon ion peak heights   t = trace

Table IV. GC/MS analysis summary of trap #1 for polyester **7** under air atmosphere.

The major products were benzaldehyde, acetic acid and α-methylstyrene. The products were first observed forming at the low temperature of 220°C. The acetic acid may have been produced by a chain extension reaction involving acetate ester and carboxylic acid end groups shown below,

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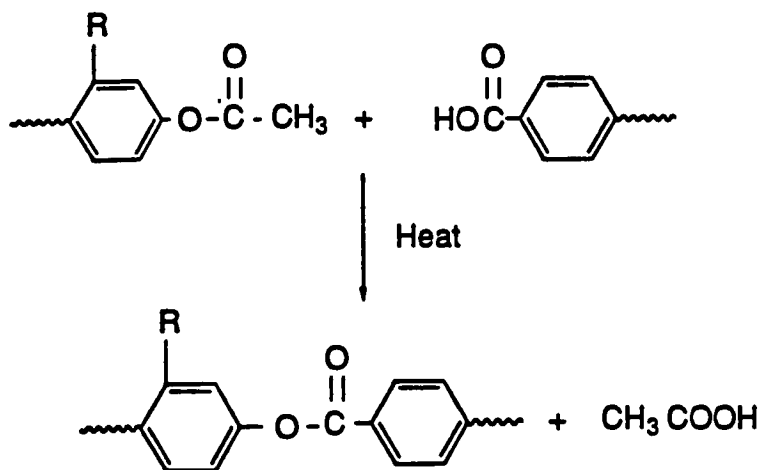
At the critical temperatures ranging from 360-380°C, products such as benzene, toluene, ethylbenzene, styrene and cumene were observed. The only oxygenated product observed was benzaldehyde. Unlike polyester 6, phenol was not observed as a degradation product. The probable pathway for the formation of the decomposition products is illustrated in Figure 8.
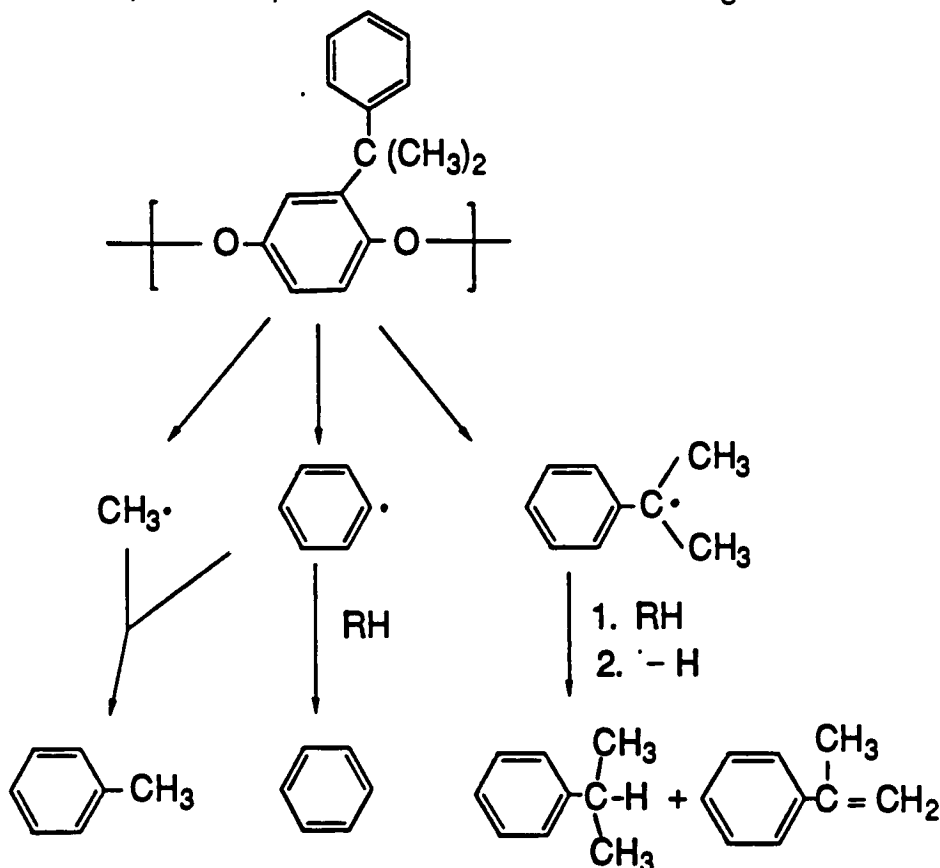
Figure 8. Proposed reaction pathway for the formation of degradation products for polyester **7** under air.

The decomposition products are derived from the α-methylstyryl side chain. Homolysis of the side chain yields phenyl, methyl, and 1-methyl-1-phenylethyl radicals. Phenyl radical abstraction of a hydrogen atom yields benzene. Combination of methyl and phenyl radicals to give toluene and xylene. The 1-methyl-1-phenylethyl radical can either abstract or eliminate a hydrogen atom to yield cumene and α-methylstyrene respectively. Benzaldehyde formation is a probable result of a secondary reaction by the decomposition of a hydroperoxide.

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When polyester **7** was studied under flowing nitrogen, the primary products observed were all non-oxygenated benzene products. The degradation products are listed in Table V.

Temp (°C)	Products				
	HAc	∅H	∅CH₃	Cumene	α-MeSty
270	••	•	•	t	•
310	••	t	t	t	•
330	••	t	t	•	••
350	••	t	t	•	••
370	•••	•	•	•	••
390	•••	••	••	•	••
410	•••	••	••	•	•

• Relative abundances based upon ion peak heights   t = trace

Table V. GC/MS analysis summary of trap #1 for polyester **7** under nitrogen atmosphere.

The primary products were acetic acid, cumene, and α-methylstyrene. Benzene and toluene were observed at the critical temperatures ranging from 350 to 370°C. The reaction pathway are identical to the one shown in Figure 7.
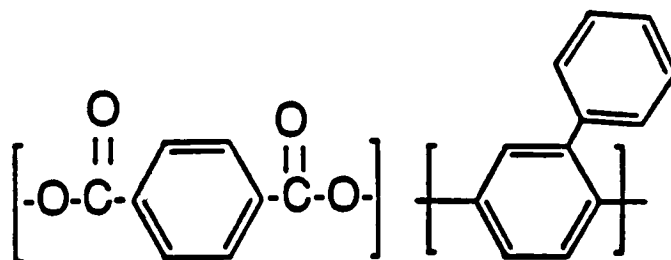
Polyester **8** was prepared from the reaction of equal parts of terephthaloyl chloride and 2-phenylhydroquinone using solution polymerization techniques. It was decomposed isothermally under flowing air from 260 to 340°C in 20°C increments. A study of the decomposition products by GC/MS showed the absence of benzene and oxygenated benzene products. This suggests that the

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formation of benzene and oxygenated benzene products observed in the decomposition of polyesters 6 and 7 are formed by the decomposition of the styryl and α-methylstyryl pendant groups which are present in these polymers.
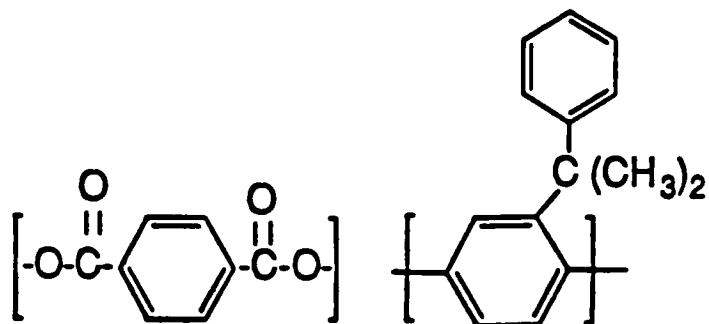
Polyester 9 was made from reaction of equal parts of terephthaloyl chloride and α-methylstyrylhydroquinone. It was also decomposed under air at the same temperature range. The decomposition products are listed in Table VI.

Temp. (°C)	Products						
	∅H	∅CH₃	∅CHO	α-MeSty	∅CH₂OH	Cumene	∅COOH
260	t	t	t	t	t	t	t
280	t	t	•	•	•	•	•
300	t	•	•	•	•	•	•
320	t	•	••	••	••	•	•
340	t	••	•••	••	••	••	••

*Relative Abundance based upon ion peak heights   t = trace

Table VI. GC/MS analysis summary of trap #1 for polyester 9 under air atmosphere.

The degradation products of polyester 9 are identical to the degradation products observed for polyester 7 with the exception that benzoic acid and benzyl alcohol were also observed. These two products may be the result of secondary oxidation reactions.

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The activation energies of the polyesters were calculated by finding the rate constants k for specific times during the two hour isothermal study period. The rate constant, k, is determined by using equation 2 found on page 11. The slope of the curve of ln (1-w) versus time gives the rate constant k. The variable w can be determined from the isothermograms of the variuos polymers. w is the difference between the initial sample weight, M_o, and sample weight, M, at a specific time divided by the difference between initial weight, M_o, and final weight, M_f.

$$W = (M_o - M) \; / \; (M_o - M_f) \qquad (9)$$

The variable m_f (an assumed theoretical value) was taken as the weight of the polymer repeating unit after elimination of the pendant side chains.

$$M_f = M_o - [M_o \times (\text{side chain percent composition})] \qquad (10)$$

The side chain percent weight composition for polyesters **6, 7, 8,** and **9** are 37, 38, 24, and 33% respectively.

Isothermogram of trial #1 for polyesters **6, 7, 8, 9,** and solution polymerized polyester **7** are shown in Figures 9 - 13 respectively. From The Arrhenius plot of ln k versus the reciprocal of the absolute temperature, 1/T, gives the curve whose slope is E_a/R where R is the universal gas constant.

Polyester **6** was initially studied using the Perkin-Elmer TGS-2 TGA under flowing air and nitrogen at temperatures ranging from 320 to 400°C at increments of 10 degrees. A total of sixteen runs were carried out for polyester **6** under nitrogen, two trials for each temperature increment. A total of twenty-four runs were carried out for polyester **6** under air, three trials for each temperature increment.

Polyesters **6, 7, 8,** and **9** were then studied using the Seiko TG/DTA 220 under flowing air at temperatures ranging from 260
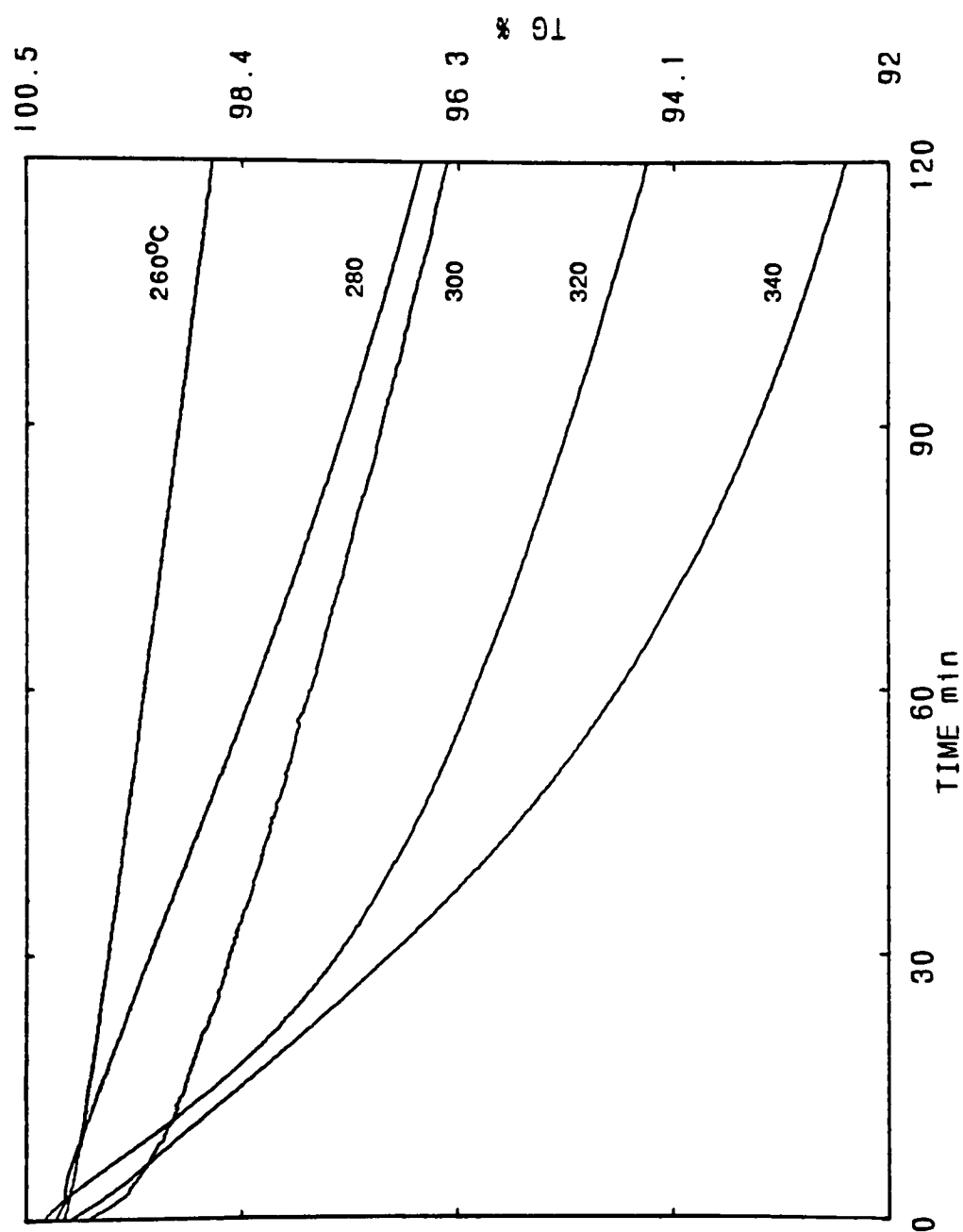
23

Figure 9. Isothermogram of trial #1 for polyester 6 (Seiko).
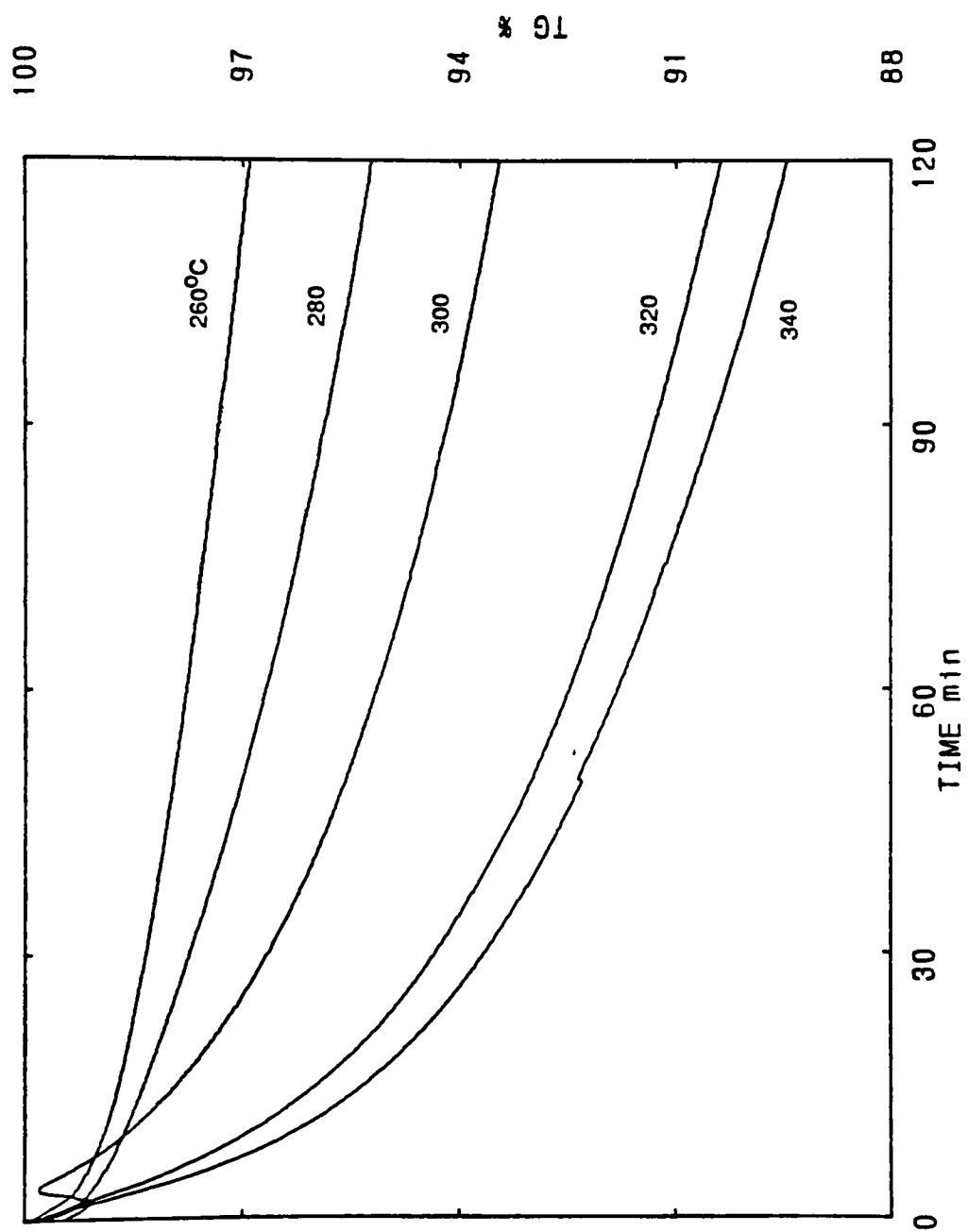
24

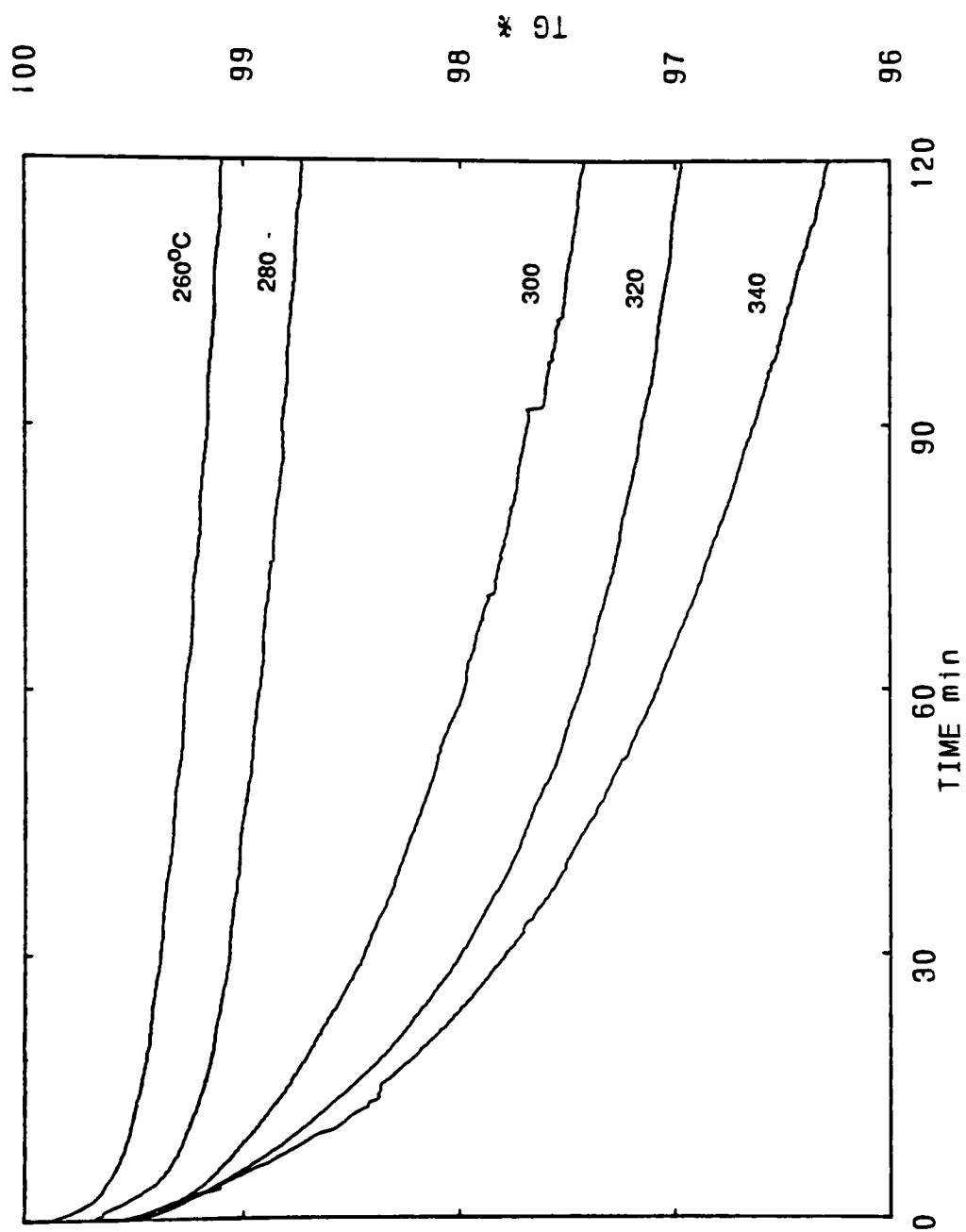Figure 10. Isothermogram of trial #1 for polyester **7** (Seiko).

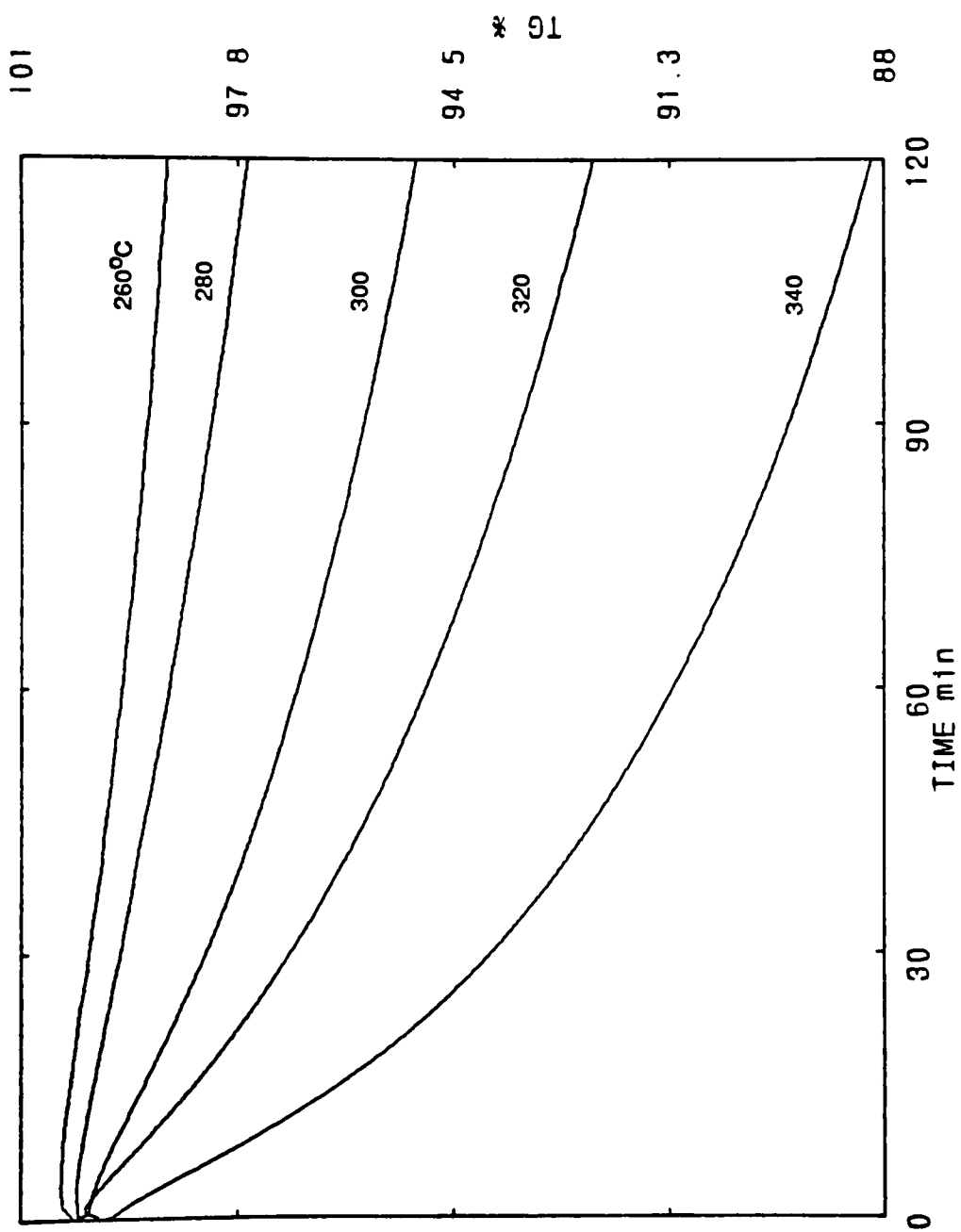Figure 11. Isothermogram of trial #1 for polyester 8 (Seiko).

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Figure 12. Isothermogram of trial #1 for polyester 9 (Seiko).

27
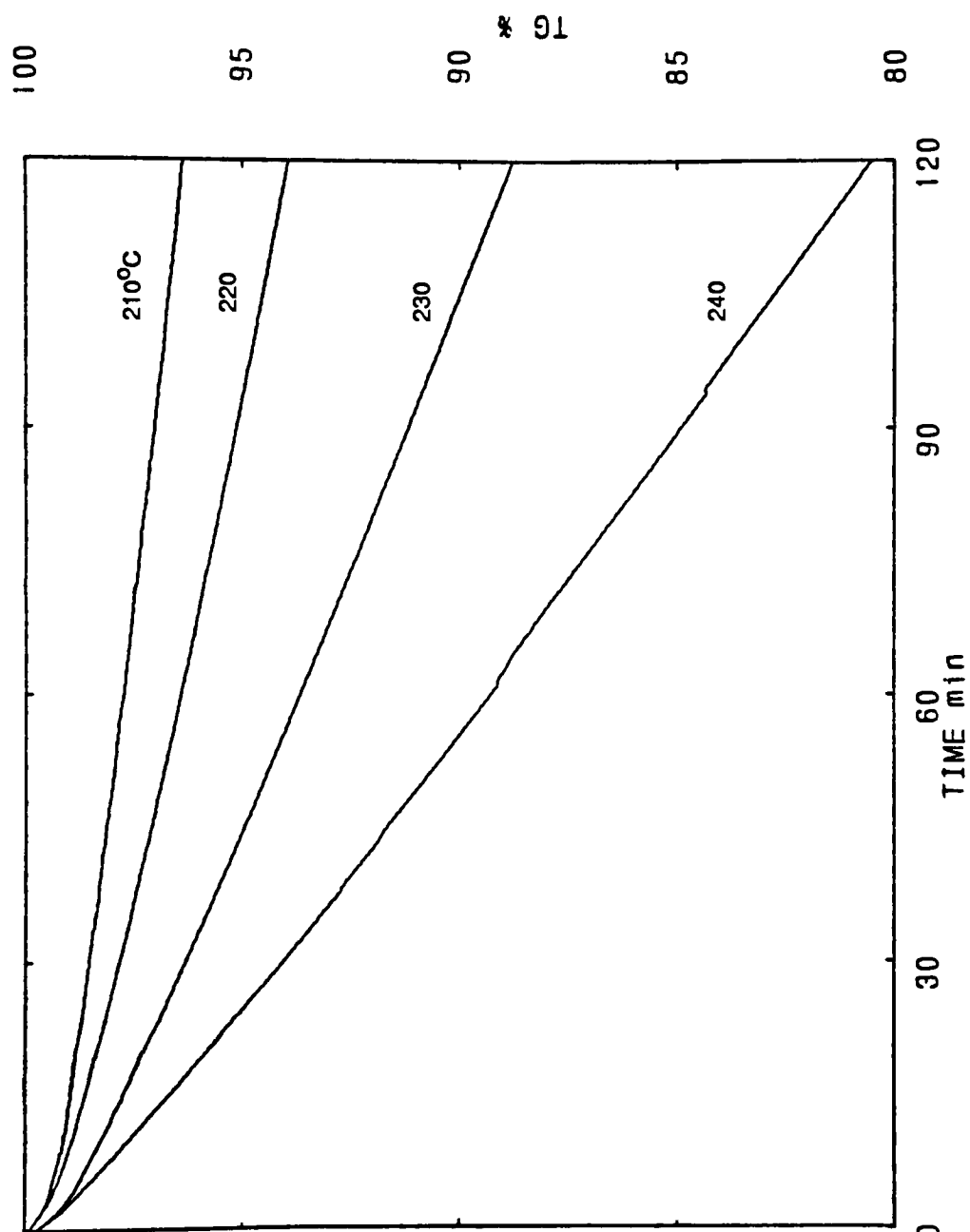
Figure 13. Isothermogram of trial #1 for solution polymerized polyester 7.

to 340°C at increments of 20 degrees. A total of twenty-five runs were carried out for each polyester under air, five trials for each temperature increment. Solution polymerized polyester **7** was studied under flowing air from 210 to 240°C at increments of 10 degrees. A total of 20 runs were carried out for solution polymerized polyester **7** under air, five trials for each temperature increment. All of the polymers studied were prepared by solution polymerizations with the exception of polyester **7**, which is prepared by a melt polymerization.

The activation energies of polyesters **6, 7, 8, 9**, and solution polymerized polyester **7** calculated from both the Perkin-Elmer and Seiko instrumentations are listed in Table VII.

Polymer	Ea (kcal/mole)	Instrumentation
Polyester 6 in N2	43	PE
Polyester 6 in air	31(init.), 28(final)	PE
Polyester 6 in air	22(init.), 12(final)	Seiko
Soln. Poly. 7 in air	36	Seiko
Polyester 7 in air	14(init.), 11(final)	Seiko
Polyester 8 in air	16(init.), 12(final)	Seiko
Polyester 9 in air	20(init.), 16(final)	Seiko

Table VII. Summary of calculated activation energies.

Polyester **6** was initially studied using the Perkin - Elmer TGS-2 TGA under flowing air and nitrogen at temperatures ranging from 320 to 400°C at increments of 10 degrees. A total of sixteen runs were carried out for polyester **6** under nitrogen, two trials for each temperature increment. A total of twenty-four runs were carried out for polyester **6** under air, three trials

for each temperature increment.

The activation energies obtained for polyester **6** using the Perkin-Elmer TGS-2 TGA under both air and nitrogen were not compared to the data obtained from the Seiko instrumentation. The two thermobalance configurations found in these instruments are completely different and do not allow a valid comparison of kinetic data. Under nitrogen, the activation energy for polyester **6** was determined to be 43 kcal/mole. The linear Arrhenius plot showed that no simultaneous decomposition reactions were taking place. The Arrhenius plot is shown in Figure 14 on page 31.

The Arrhenius plot for polyester **6** under air was non-linear and showed two distinct linear regions evident of two reactions taking place. The activation energies for polyester **6** under air were found to be 31 kcal/mole for the initial reaction and 28 kcal/mole for the final reaction. The Arrhenius plot for polyester **6** under air is shown in Figure 15 on page 32. The Perkin-Elmer results showed that polyester **6** is more thermally stable in nitrogen than in air as would normally be expected.

The rate constant data plots of ln (1-w) versus time for all of the polyesters with the exception of solution polymerized polyester **7** showed two distinct linear regions. it was apparent that two decomposition reactions were taking place and the activation energies obtained from using this unseparated data would not be valid. An example of a rate constant plot showing the two linear regions for polyester **6** is shown in Figure 16 on page 33. In order to obatin valid data, the rate constant curves were divided into two regions, corresponding to the initial and final decomposition rate. New rate constant plots were constructed for the initial and final rates and they were used to determine activation energies for the polyesters. The newly constructed rate constant plots for polyesters **6, 7, 8, 9,** and solution polymerized polyester **7** are shown in Figures 17 - 21 respectively.

The activation energy for polyester **6** (containing phenyl and styryl side chain groups) was determined to be 22 kcal/mole and

y = 28.530 - 2.1699e-2x   R^2 = 0.985
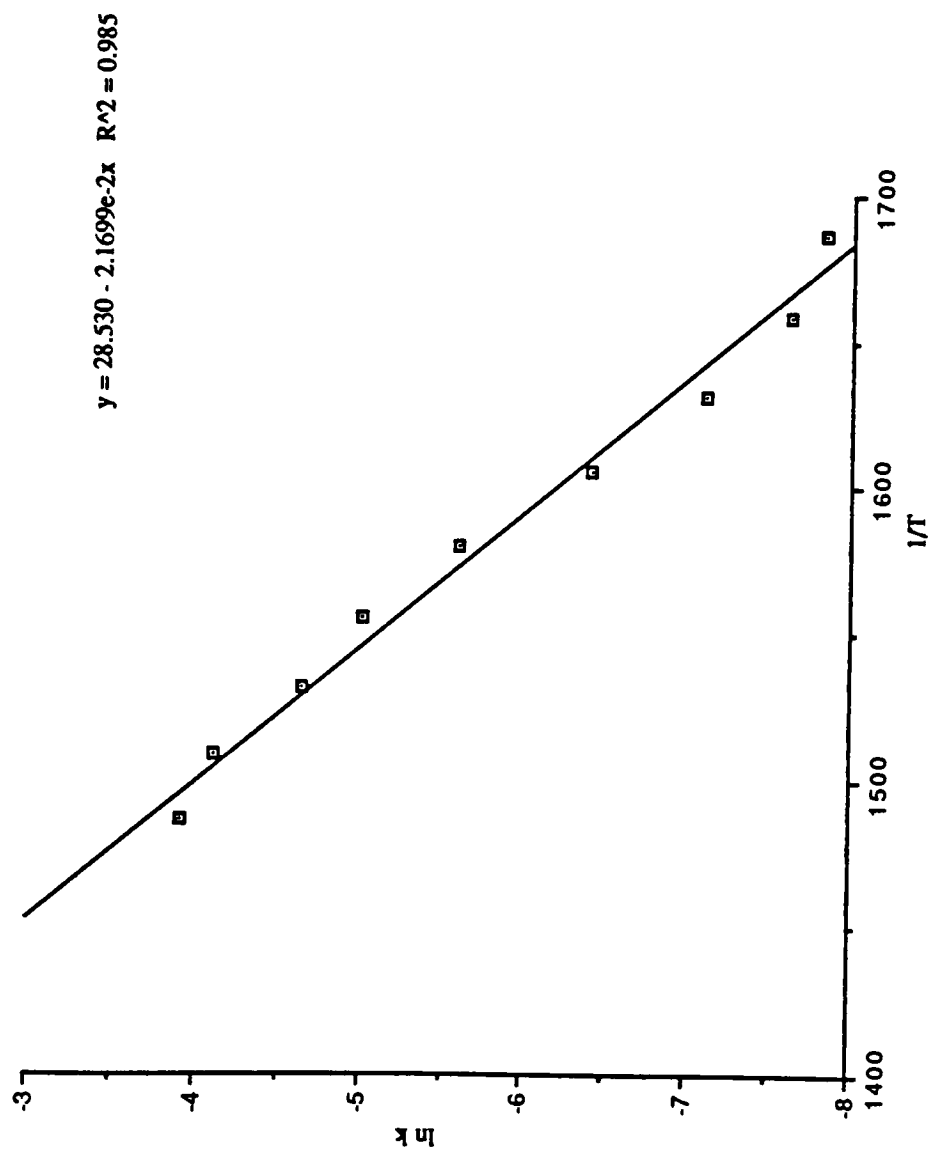
Figure 14.   Arrhenius plot for polyester 6 under nitrogen (Perkin- Elmer).

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ki = 18.917 - 1.5375e-2x   R^2 = 0.967

kf = 16.287 - 1.4261e-2x   R^2 = 0.959

□ Initial rate (0-60 min.)

♦ Final rate (60-120min.)
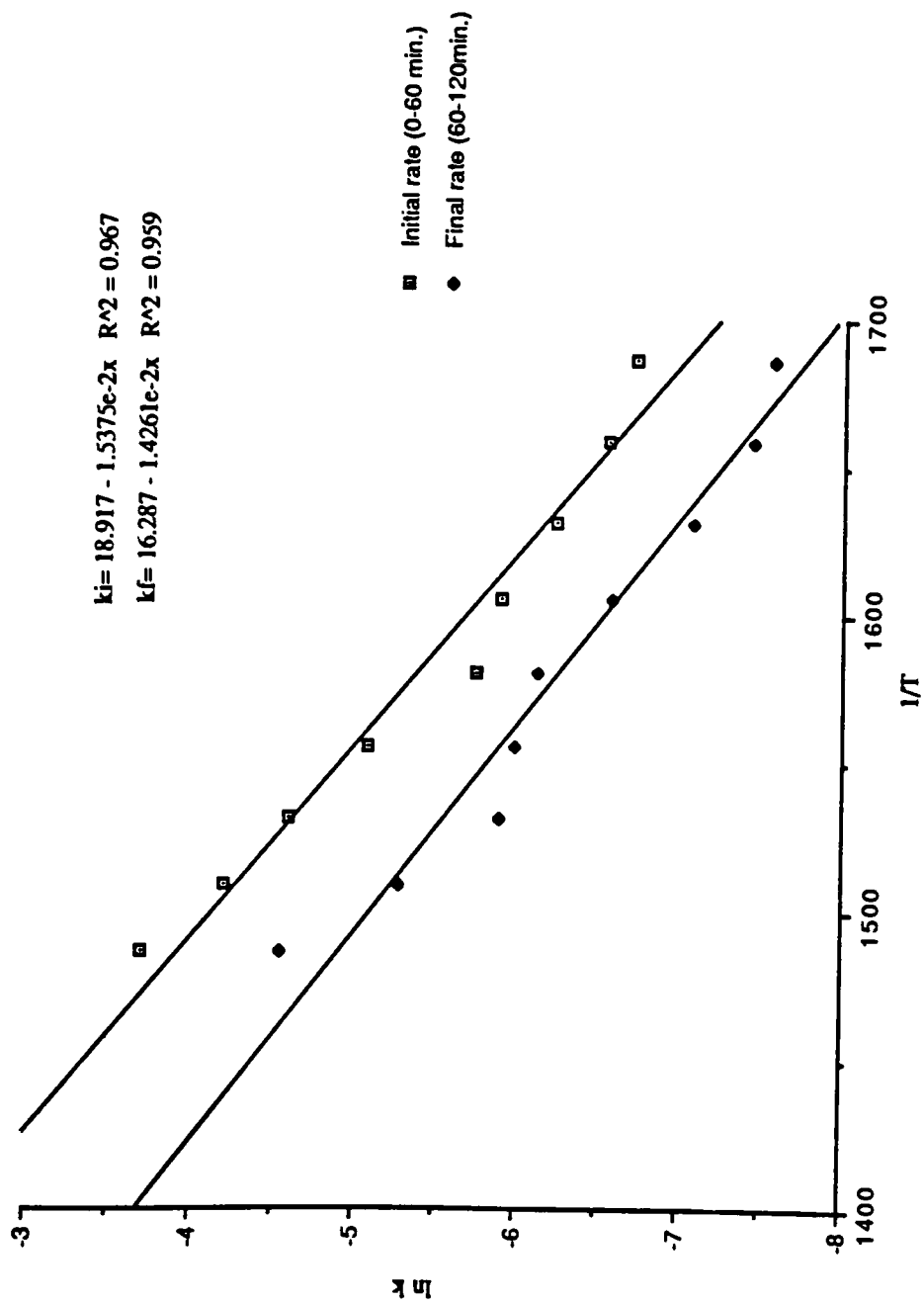
Figure 15.   Arrhenius plot for polyester 6 under air (Perkin- Elmer).

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Figure 16. Rate constant plot for polyester 6 under air (unseparated, Seiko).

260C
280C
300C
320C
340C

Time (min)

ln (1-W)
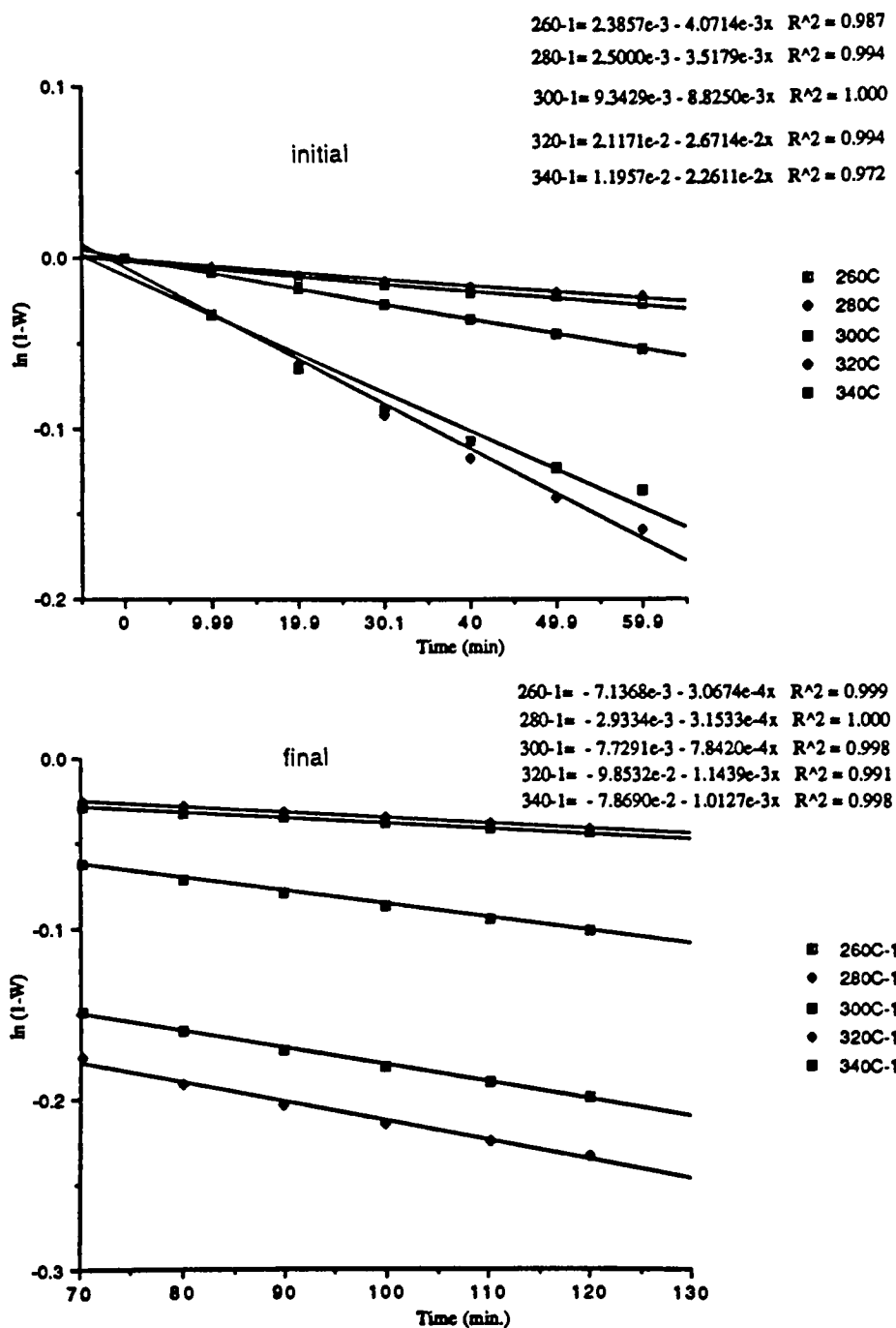
Figure 17. Rate constant plot for polyester 6 under air (Seiko)
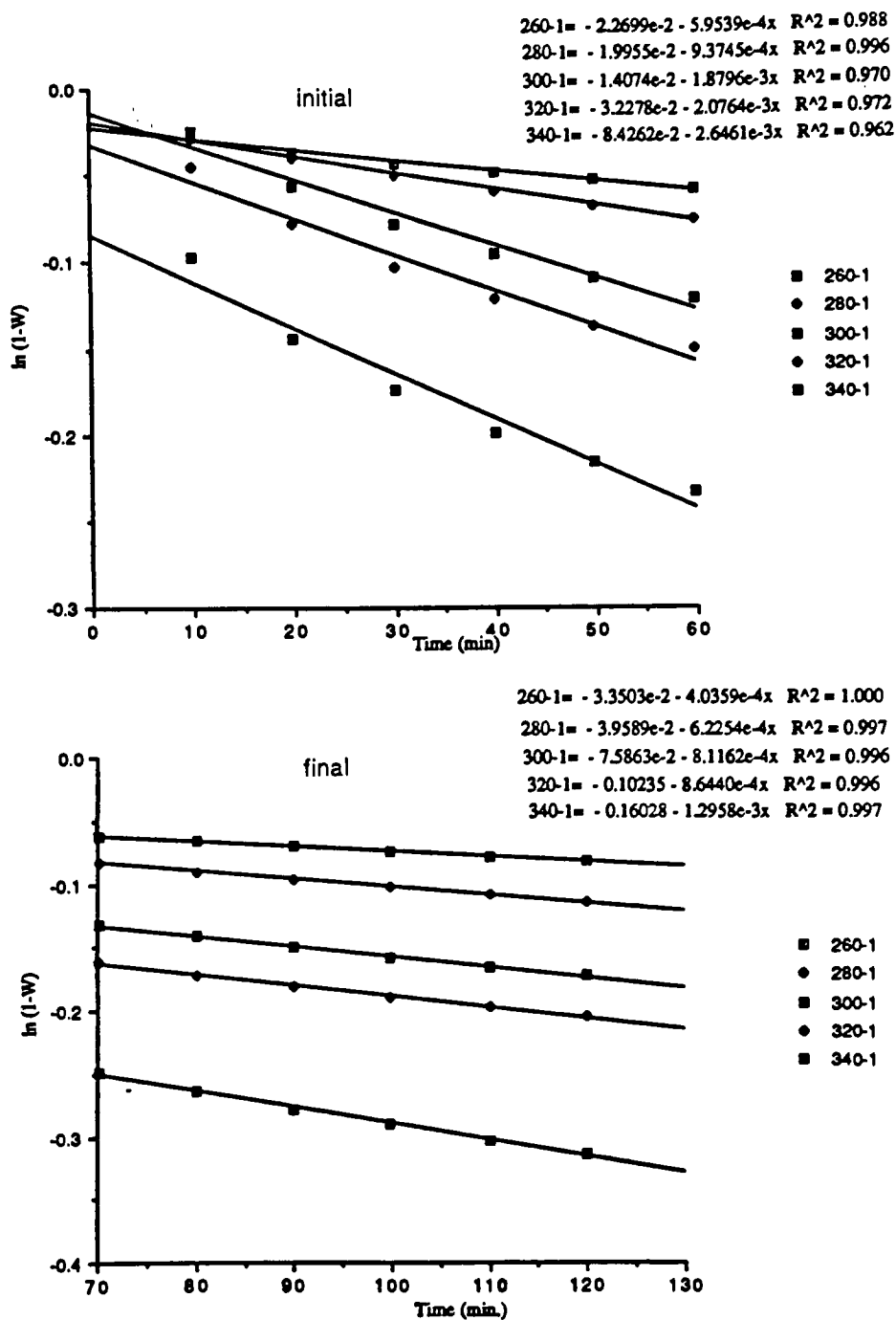
Figure 18. Rate constant plot for polyester 7 under air (Seiko).

$260\text{-}1 = -1.2425e\text{-}2 - 2.6252e\text{-}4x$ $R^{\wedge}2 = 0.958$
$280\text{-}1 = -1.4095e\text{-}2 - 2.0276e\text{-}4x$ $R^{\wedge}2 = 0.965$
$300\text{-}1 = -1.8092e\text{-}2 - 8.1855e\text{-}4x$ $R^{\wedge}2 = 0.982$
$320\text{-}1 = -2.6118e\text{-}2 - 1.1132e\text{-}3x$ $R^{\wedge}2 = 0.961$
$340\text{-}1 = -3.2367e\text{-}2 - 1.3242e\text{-}3x$ $R^{\wedge}2 = 0.978$

initial

■ 260-1
● 280-1
■ 300-1
● 320-1
■ 340-1

$260\text{-}1 = -1.9970e\text{-}2 - 1.3017e\text{-}4x$ $R^{\wedge}2 = 0.997$
$280\text{-}1 = -1.9395e\text{-}2 - 1.1439e\text{-}4x$ $R^{\wedge}2 = 0.990$
$300\text{-}1 = -4.1643e\text{-}2 - 4.1269e\text{-}4x$ $R^{\wedge}2 = 0.990$
$320\text{-}1 = -7.1299e\text{-}2 - 3.2707e\text{-}4x$ $R^{\wedge}2 = 0.990$
$340\text{-}1 = -7.4985e\text{-}2 - 5.9007e\text{-}4x$ $R^{\wedge}2 = 0.996$

final

■ 260-1
● 280-1
■ 300-1
● 320-1
■ 340-1

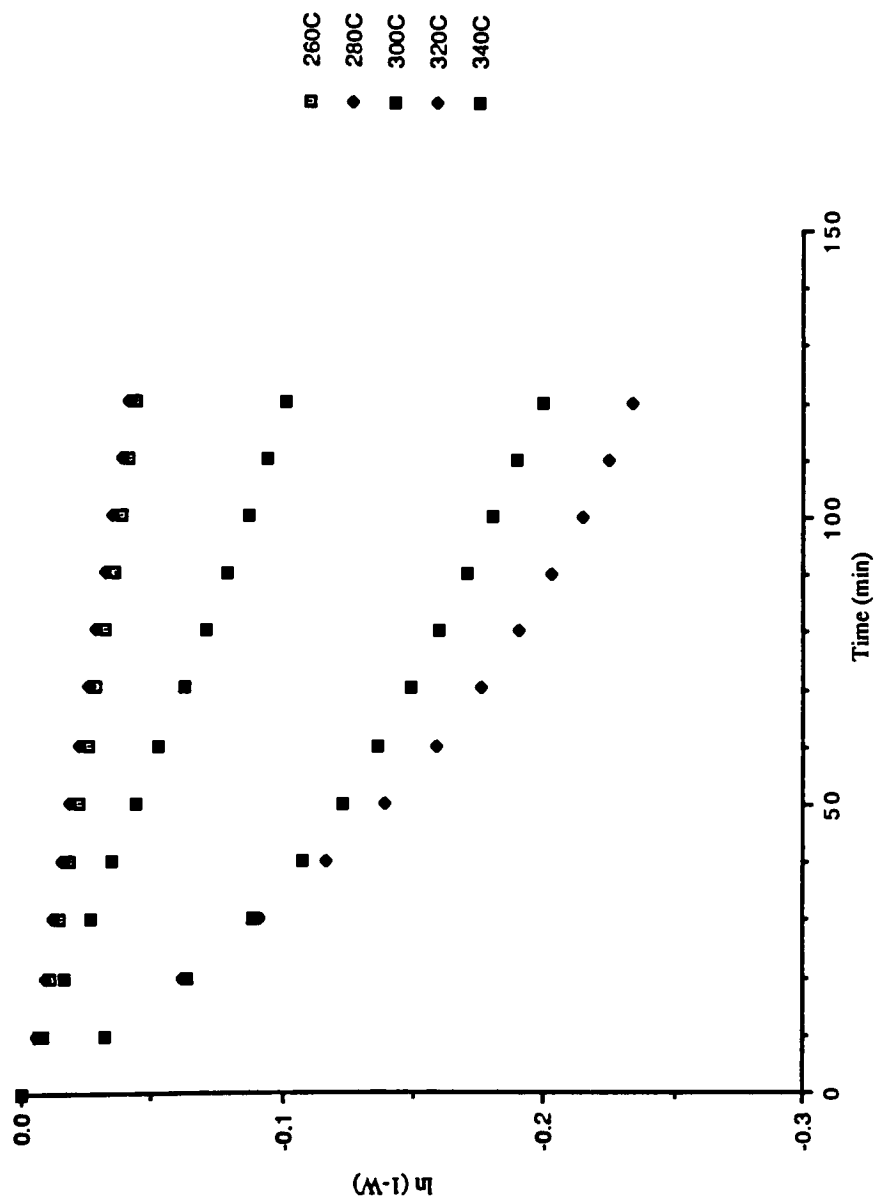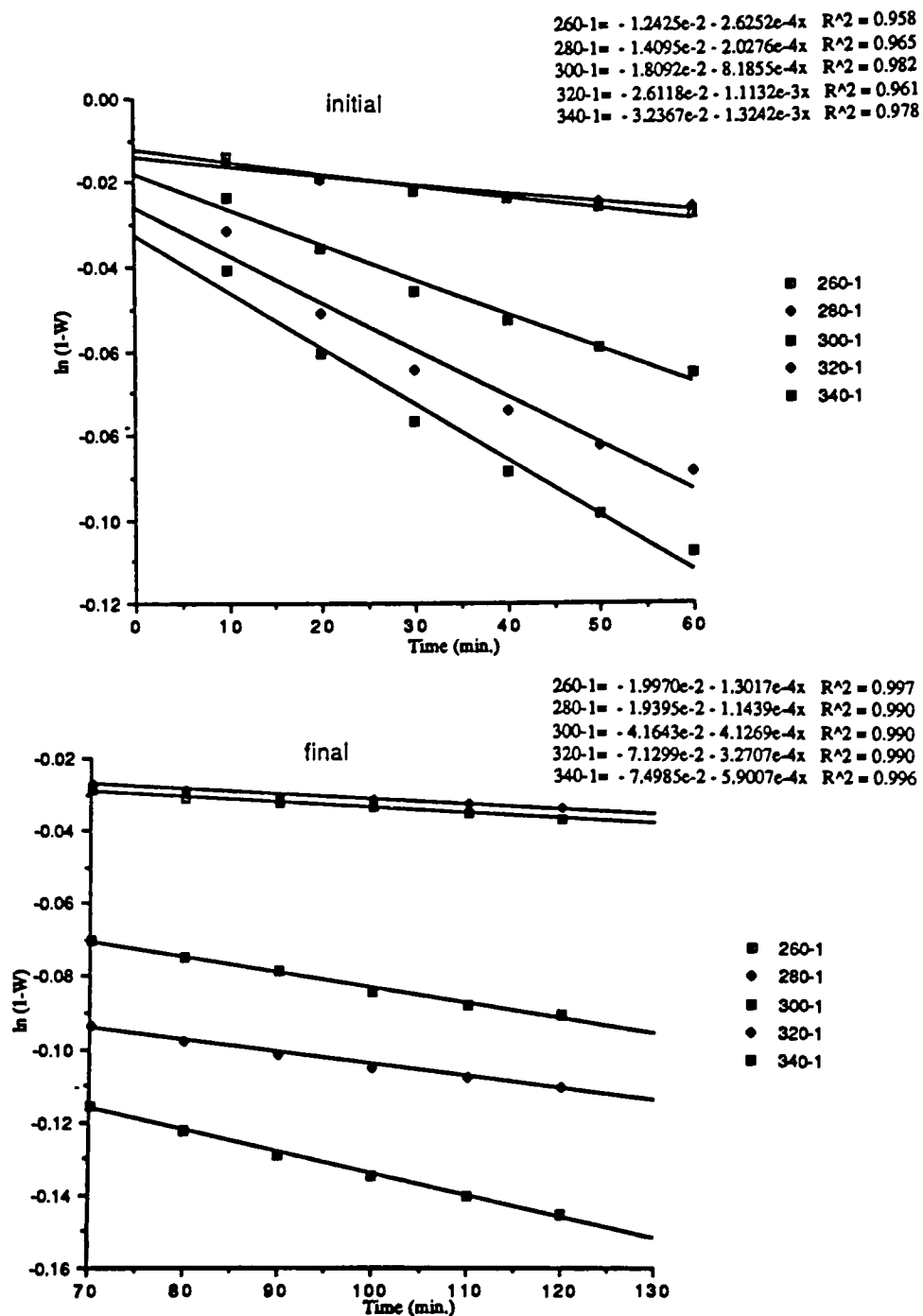Figure 19. Rate constant plot for polyester 8 under air (Seiko)

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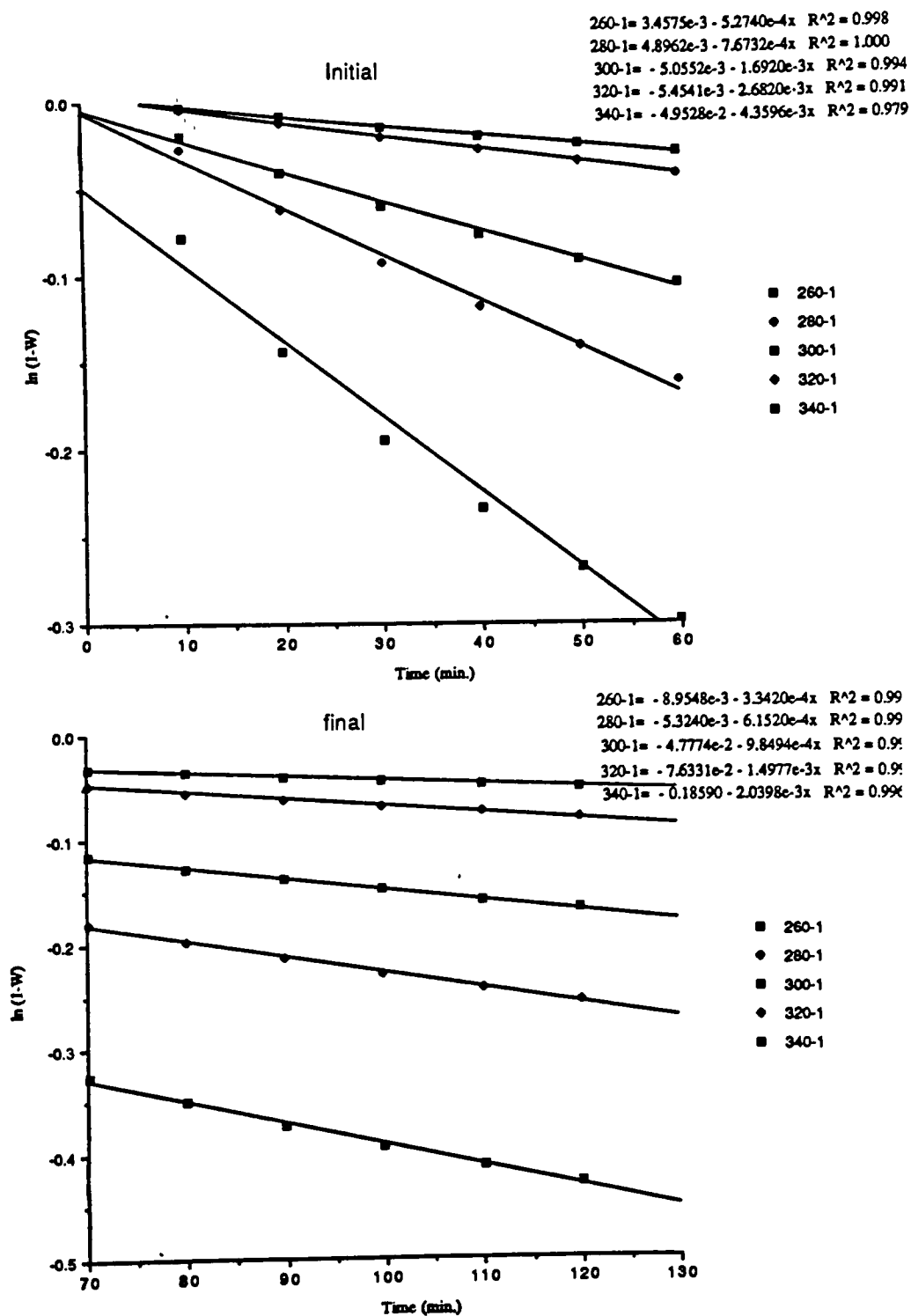
Figure 20. Rate constant plot for polyester 9 under air (Seiko).

210-1= - 1.6045e-2 - 6.8920e-4x   R^2 = 0.998
220-1= - 1.7253e-2 - 1.2806e-3x   R^2 = 0.999
230-1= - 1.3530e-2 - 2.6843e-3x   R^2 = 1.000
240-1= 1.3589e-2 - 5.6984e-3x   R^2 = 0.996

210-1
220-1
230-1
240-1

Time (min.)

ln (1-W)

Figure 21.   Rate constant plot for solution polymerized
polyester **7** under air (Seiko).

12 kcal/mole for the initial and final decomposition reactions respectively.

Polyester **7** was obtained from Granmont Inc., was prepared by a melt polymerization technique and as such contained carboxylic acid and acetate end groups as well as pendant phenyl and α-methylstyryl side chains. The major product observed in the GC/MS decomposition product study was acetic acid, formed by a chain extension reaction. The activation energies determined for melt polymeriz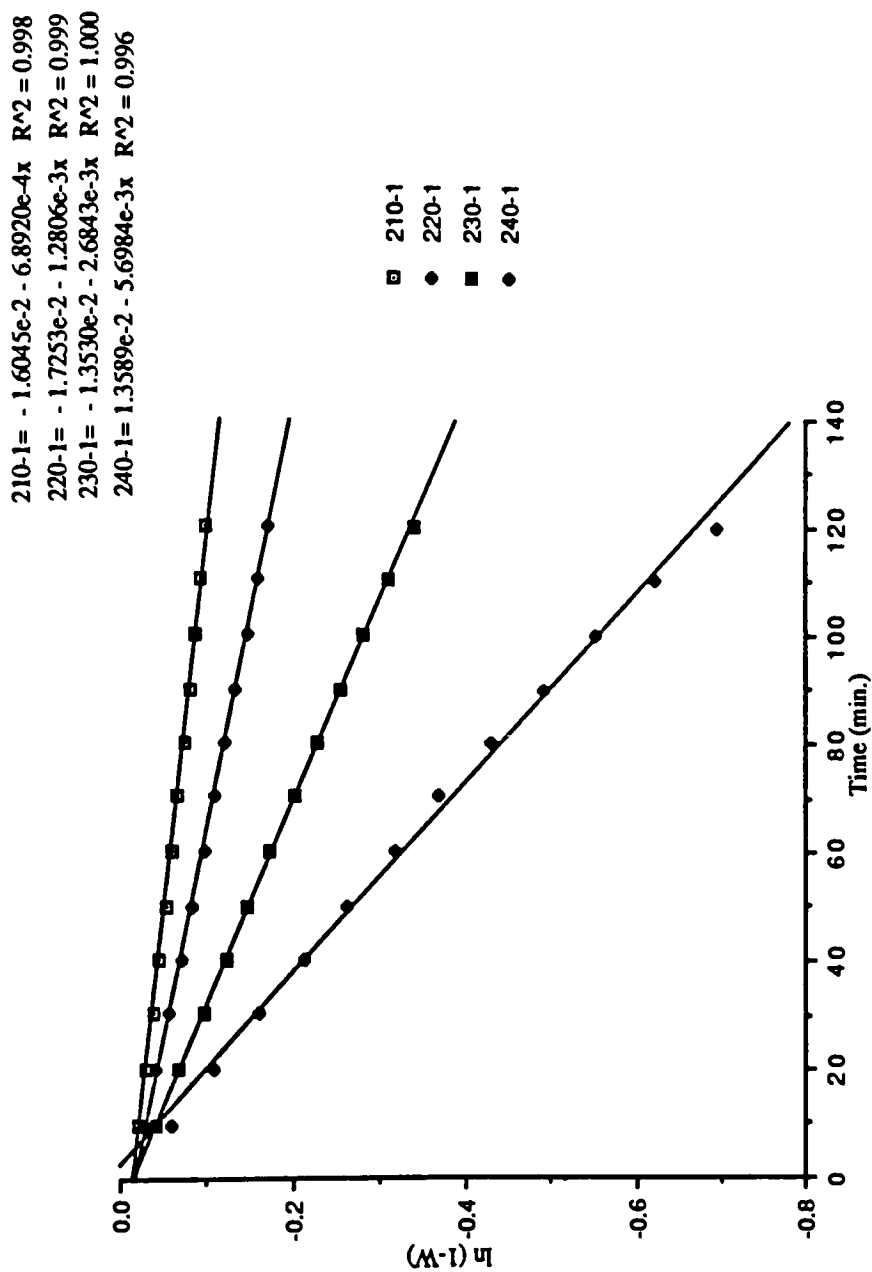ed polyester **7** were 14 kcal/mole for the initial reaction and 11 kcal/mole for the final reaction. We believe that these low results are due to chain extension liberation of acetic acid and not the decomposition of the pendant side chain.

In order to make a valid comparison between the polymer structures in polyesters **6** and **7**, polyester **7** was prepared by a solutiuon polymerization technique. Polyester structures **6**, and **7** would then have the same carboxylic and phenolic end groups, but differing only in their side chain groupings. The activation energy for solution polymerized polyester **7** was determined to be 36 kcal/mole. We expected this value to be lower than the value for polyester **6** because the α-methylstyryl side group is more labile than the styryl. We have no ready explanation for this anomalous result. The inherent viscosity for this material was determined to be 0.7 dL/g, which is evidence for a high molecular weight polymer.

However, polyester **6** had lower activation energy when compared to solution polymerized polyester **7** (containing phenyl and α-methylstyryl side chain groups) with 36 kcal/mole. Solution polymerized polyester **7** was expected to have a lower activation energy than solution polymerized polyester **6** but the results obtained were not consistent. The Arrhenius plots of polyester **6, 7**, and solution polymerized polyester **7** are shown in Figures 22 - 24 respectively.

The inconsistency can be explained by comparing the dynamic TG thermograms of the polymers. The dynamic TG

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ki= 14.256 - 1.0858e-2x   R^2 = 0.937

kf= 3.0510 - 6.1023e-3x   R^2 = 0.969

■ Initial rate (0-60 min.)

♦ Final rate (60-120 min.)
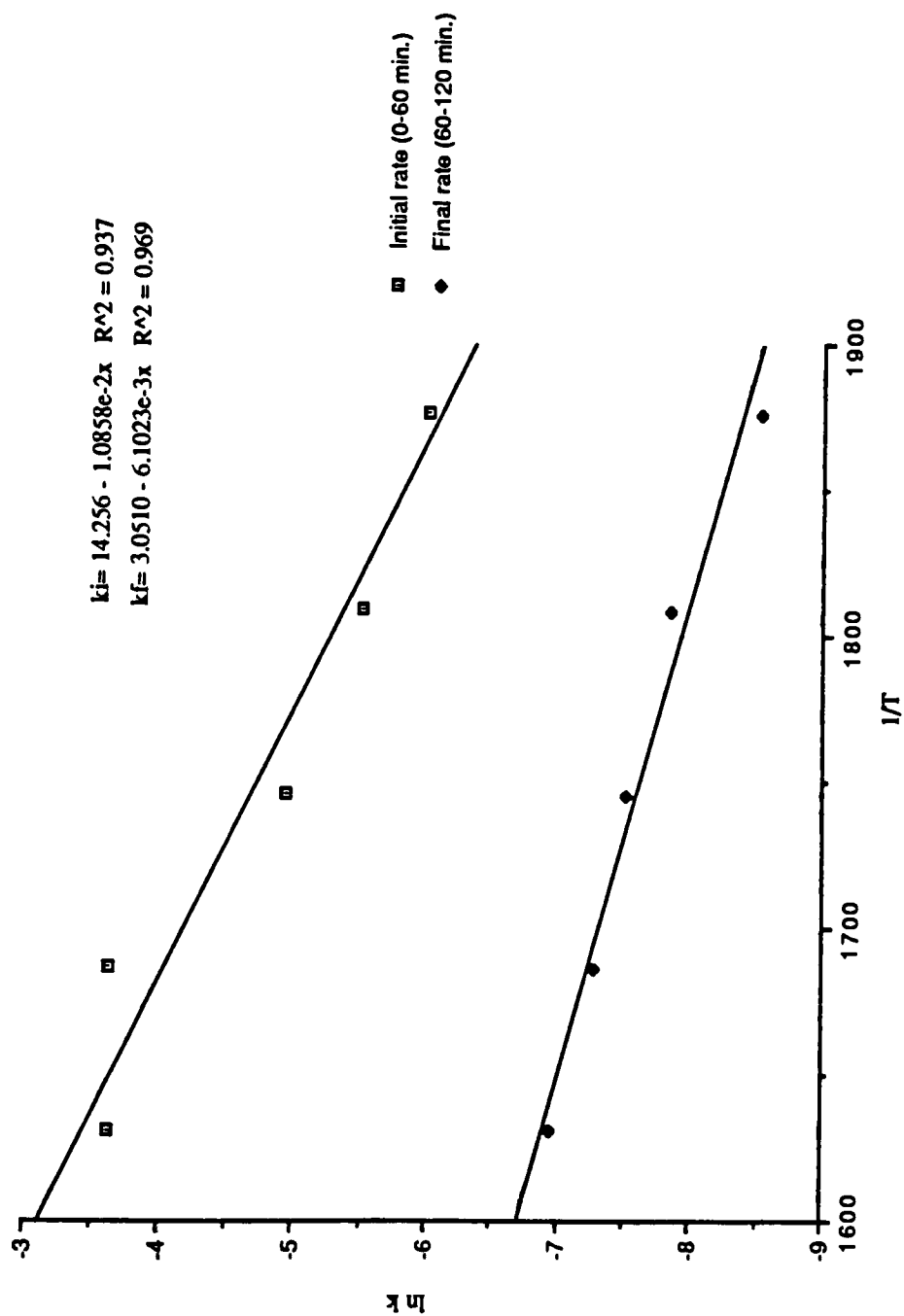
Figure 22.   Arrhenius plot for polyester 6 under air (Seiko).

ki= 5.3143 - 6.7771e-3x   R^2 = 0.967

kf= 2.8747 - 5.7360e-3x   R^2 = 0.842

□ Initial rate (0-60 min.)

◆ Final rate (60-120 min.)

1/T

ln k

-5

-6

-7

-8

-9

1600   1700   1800   1900
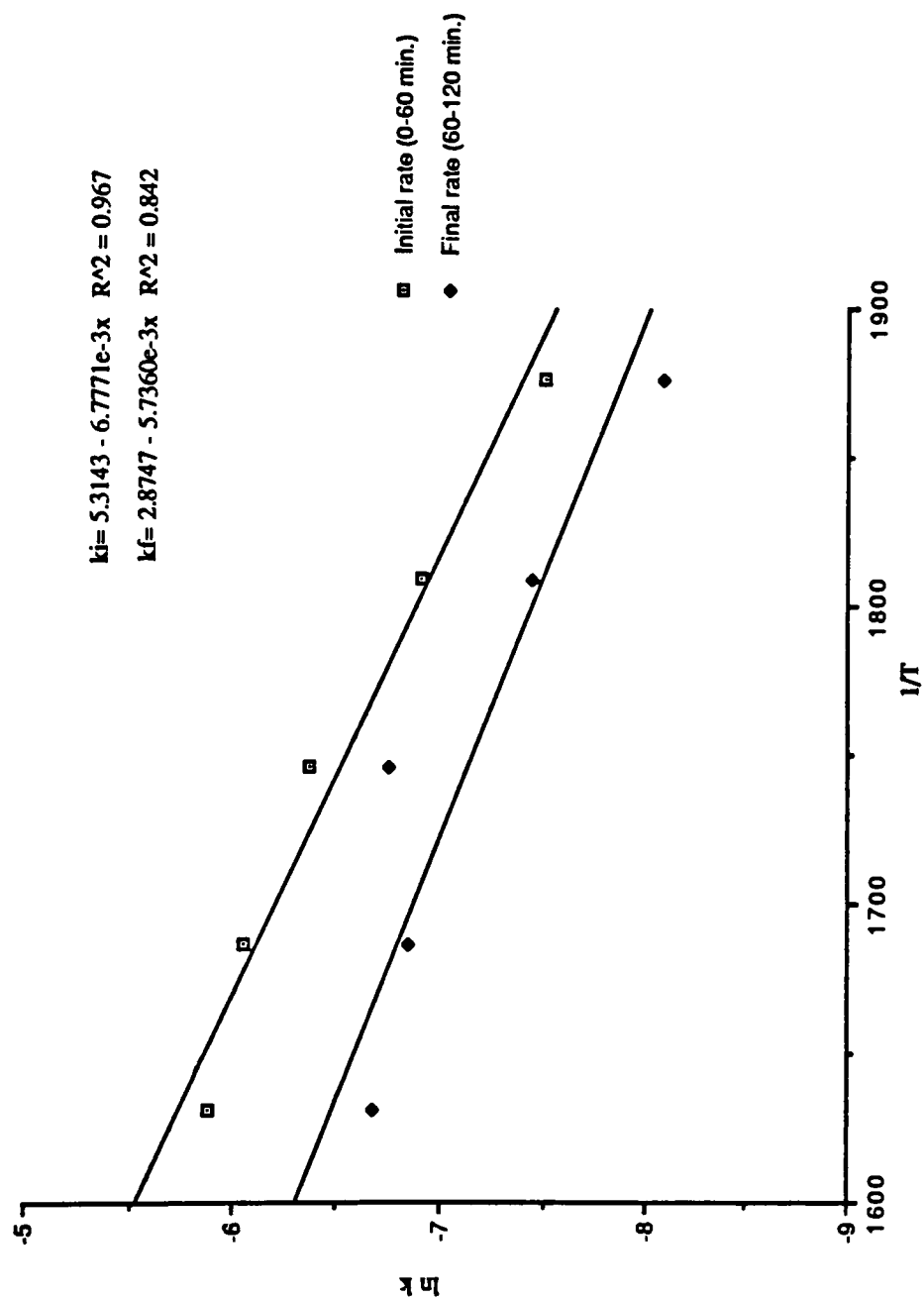
Figure 23.   Arrhenius plot for polyester **7** under air (Seiko).

y= 29.860 - 1.7963e-2x   R^2 = 1.000
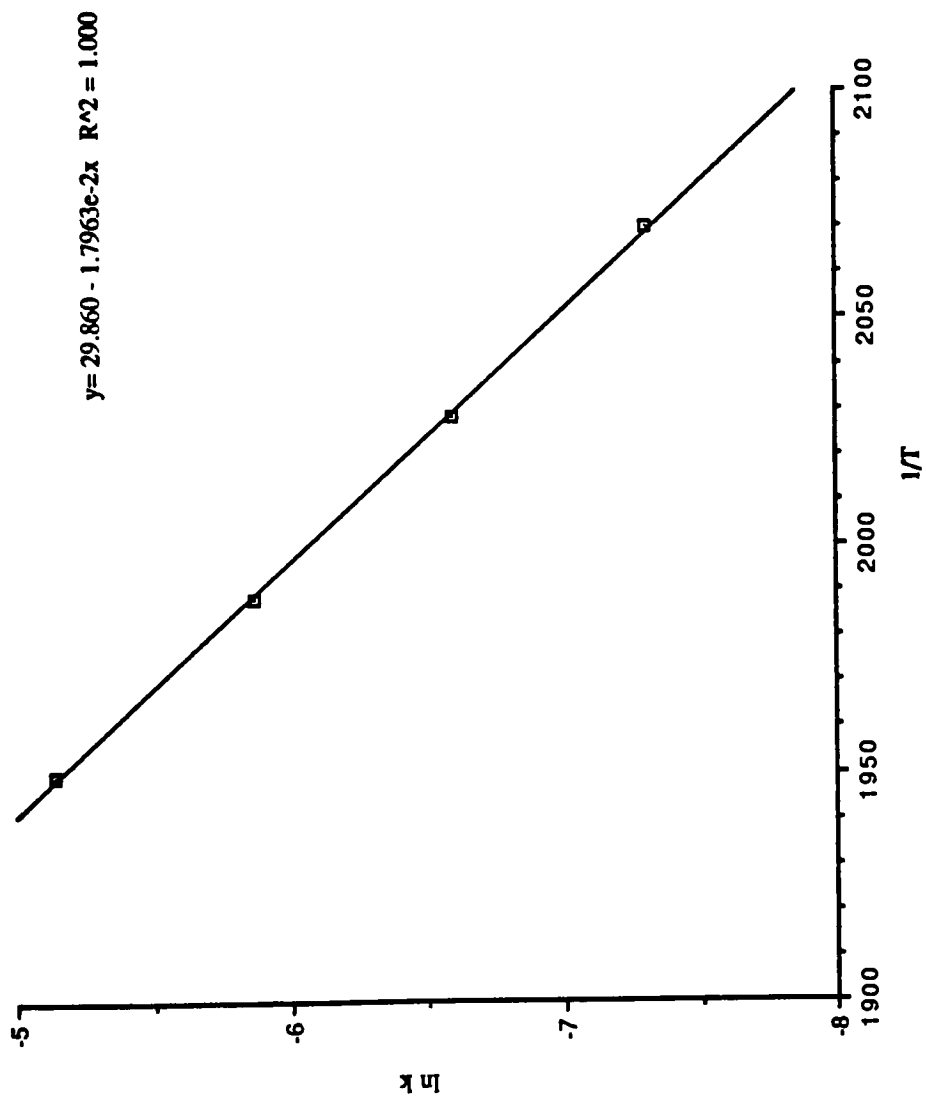
Figure 24.   Arrhenius plot for solution polymerized polyester 7
under air (Seiko).

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thermograms for polyesters **6, 7,** and solution polymerized polyester **7** are shown in Figure 25 - 27 respectively. The onset of polymer decomposition temperatures, taken from the thermograms are higher for polyesters **6** and melt polymerized polyester **7**, 446 and 447°C respectively, than for solution polymerized polyester **7** which had a decomposition temperature of 289°C.

From the dynamic TG thermograms, polyesters **6** had an inital weight loss of 35% which is close to the expected side chain weight loss of 37%. The 45% weight loss of the side chain observed for melt polymerized polyester **7** weight loss was greater than the expected side chain weight loss of 38%. This was believed to be due to the additional weight loss of acetic acid from the chain extension reaction. The weight loss of approximately 80% for the solution polymerized polyester **7** is unaccountable and unexplanable. The anomalous results observed for the solution polymerized polyester **7** suggests that its structure is unknown and is not a structure containing equal quantities of phenyl and α-methylstyryl side chains.

Solution polymerized polyester **8** (containing only phenyl side chain groups) had an initial rate activation energy of 16 kcal/mole and a final rate of 12 kcal/mole. The results were unexpected because polyester structure **8** with the exception of carboxylic ester linakges contains only aromatic linkages and should have greater thermal stability than aliphatic linkages found in other polyesters studied. The polymer decomposition temperature obtained from the TG thermogram shows an onset temperature of 462°C. This value is the highest temperature observed for all the structures studied in this report and clearly shows that polyester **8** is the most stable. The low activation energy values determined for polyester **8** is believed to be a measure of the weight loss of residual solvent or moisture rather than the loss of side chain. The isotherm of polyester **8** (Fig. 11, pg. 26) shows a weight loss of only 4% at 340°C, the highest temperature studied. The Arrhenius plot and dynamic thermogram for polyester **8** are shown in Figures 28 and 29 respectively.
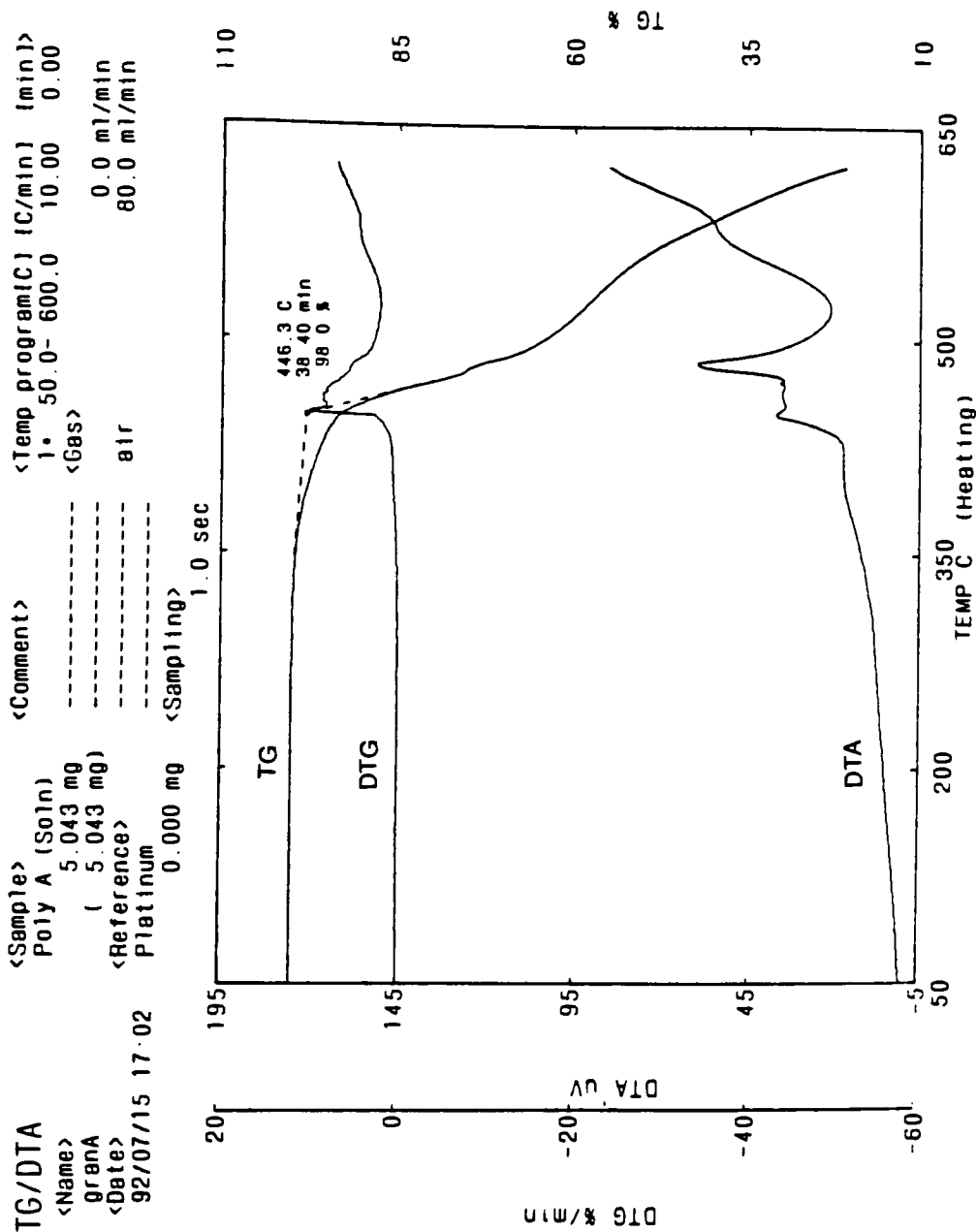
Figure 25. Dynamic TG thermogram for polyester 6 (Seiko, flowing air @ 80 cc/min).
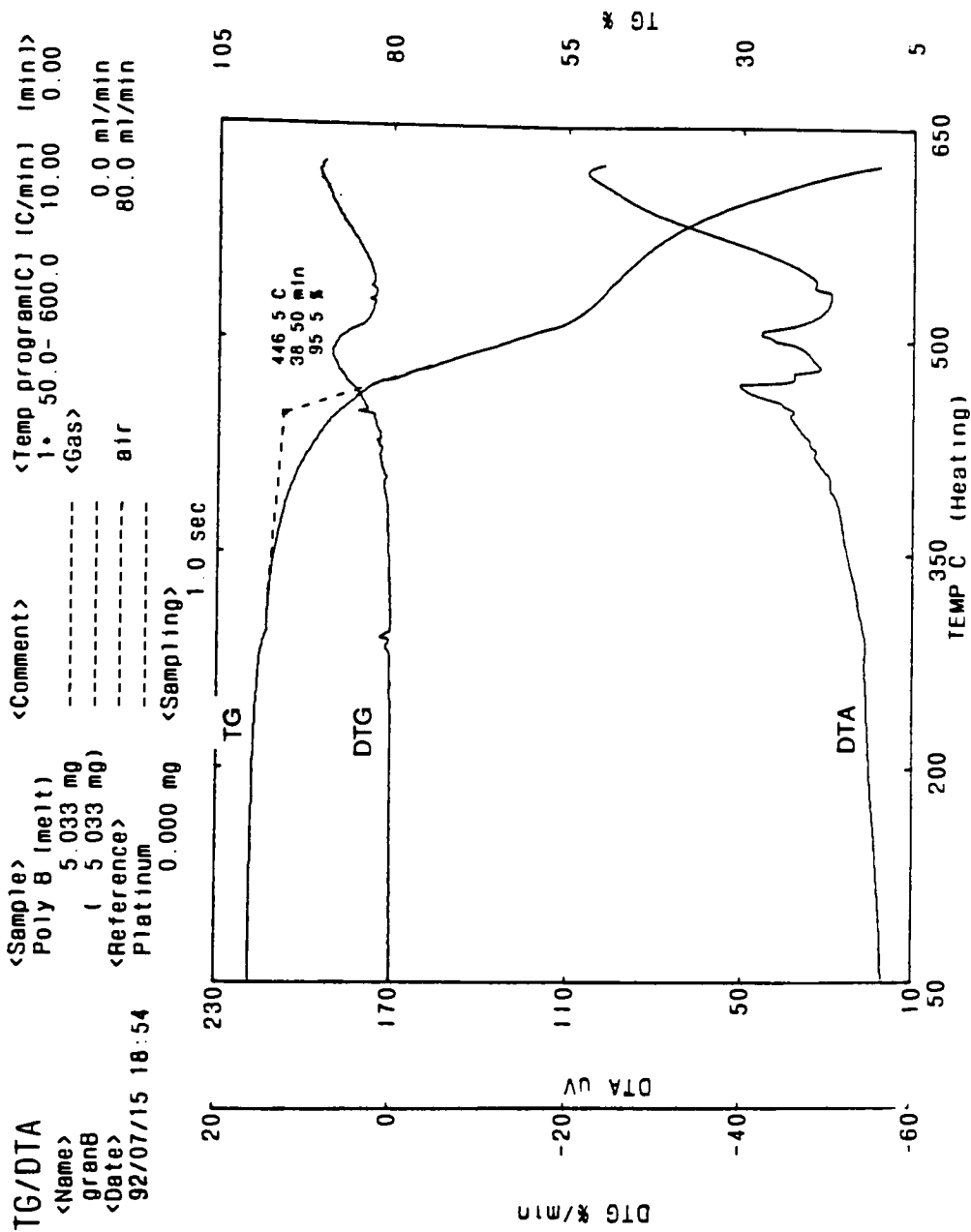
Figure 26. Dynamic TG thermogram for polyester **7** (Seiko, flowing air @ 80 cc/min).

TG/DTA

<Name>
granB
<Date>
92/07/15 18:54

<Sample>
Poly B (melt)
    5.033 mg
    (5.033 mg)
<Reference>
Platinum
    0.000 mg

<Comment>

<Sampling>
1.0 sec

<Temp program[C] [C/min] [min]>
1: 50.0- 600.0 10.00 0.00
<Gas>
air   0.0 ml/min
       80.0 ml/min

TG
DTG
DTA

446.5 C
38.50 min
95.5 %

TEMP C (Heating)

TG %

DTG %/min

DTA UV

TG/DTA

TG

DTG

DTA

289 2 C
98 7 %

TG %

110

80

50

20

-10

TEMP C (Heating)

150   350   550   750

-50

-5

15

35

55

75

DTG %/min

DTA UV

40   0   -40   -80   -120
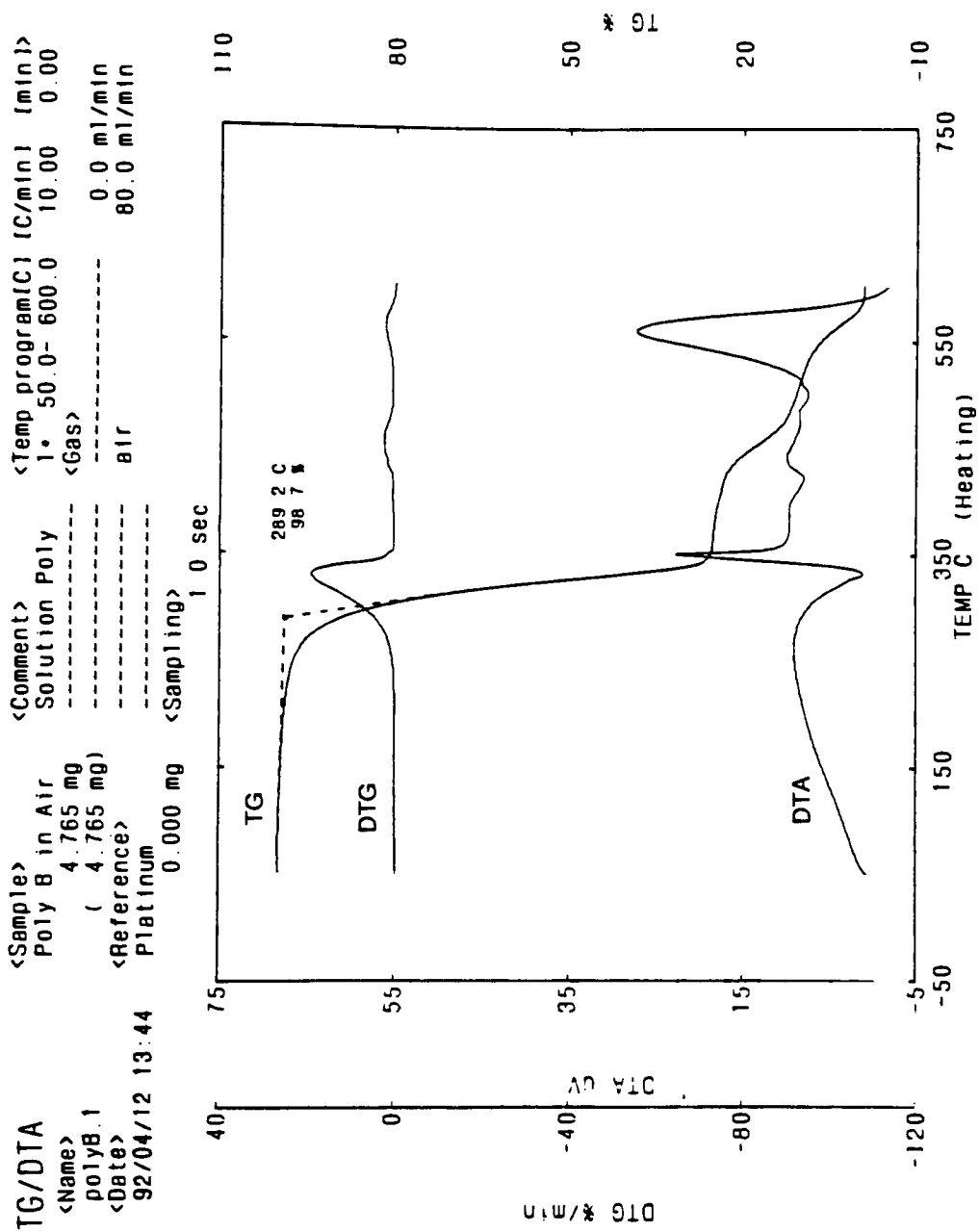
Figure 27. Dynamic TG thermogram for solution polymerized
polyester 7 (Seiko, flowing air @ 80 cc/min).

ki= 6.5321 - 7.9637e-3x   R^2 = 0.978

kf= 2.1026 - 5.8733e-3x   R^2 = 0.929

□ Initial rate (0-60 min.)

◆ Final rate (60-120 min.)

Figure 28. Arrhenius plot for polyester **8** under air (Seiko).

47
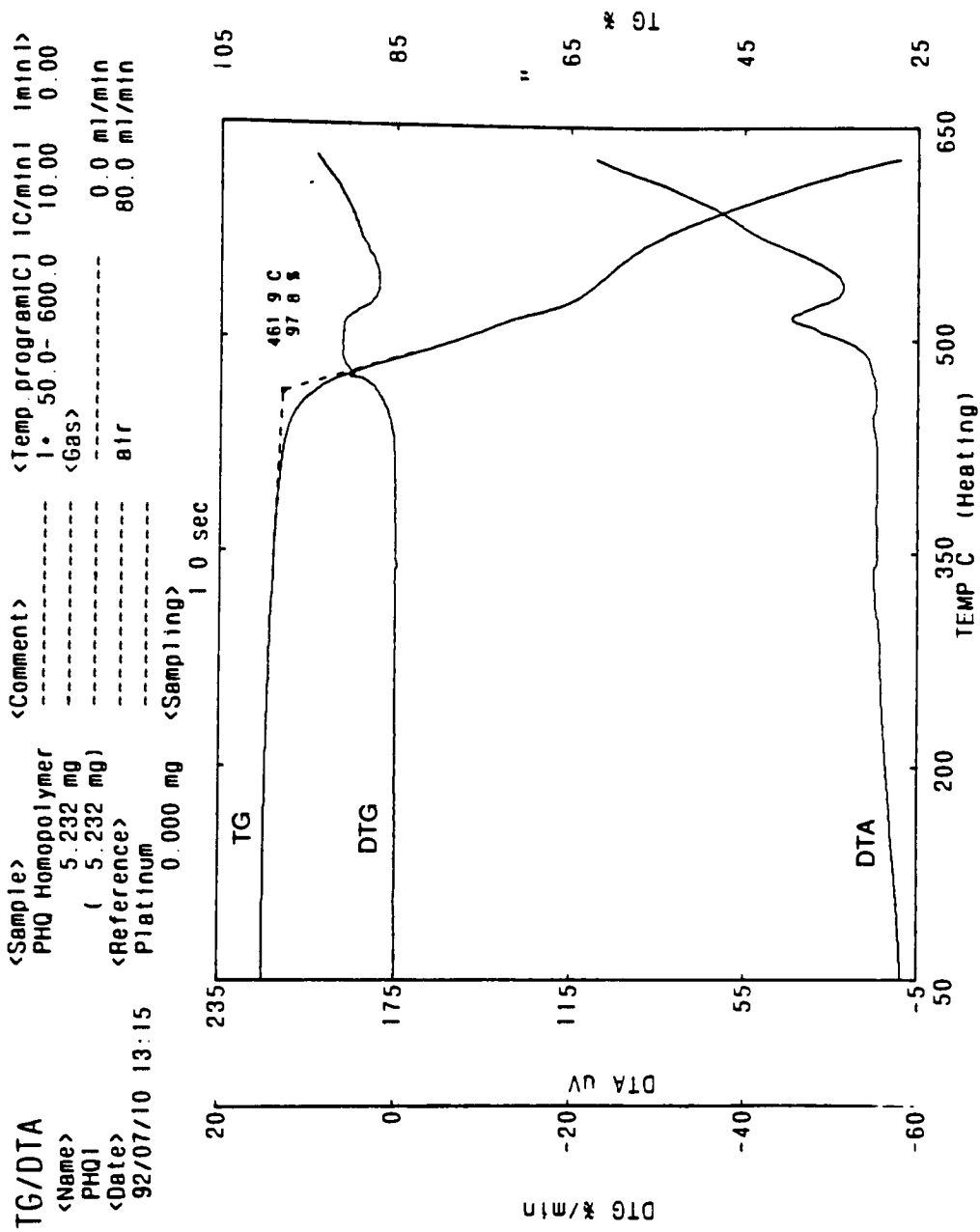
Figure 29. Dynamic TG thermogram for polyester 8
(Seiko, flowing air @ 80 cc/min).

Polyester **9** containing only α-methylstyryl side chain groups had an initial rate activation energy of 20 kcal/mole and a final rate activation energy of 16 kcal/mole. Arrhenius plot and dynamic thermogram for polyester **9** are shown in Figures 30 and 31 respectively. The onset for polymer decomposition, obtained from the dynamic thermogram was observed to be 436°C. The isothermogram (Fig. 12, pg. 27) showed a weight loss of 12% at 340°C.

ki= 10.876 - 9.9534e-3x   R^2 = 0.992

kf= 6.7917 - 7.9206e-3x   R^2 = 0.986

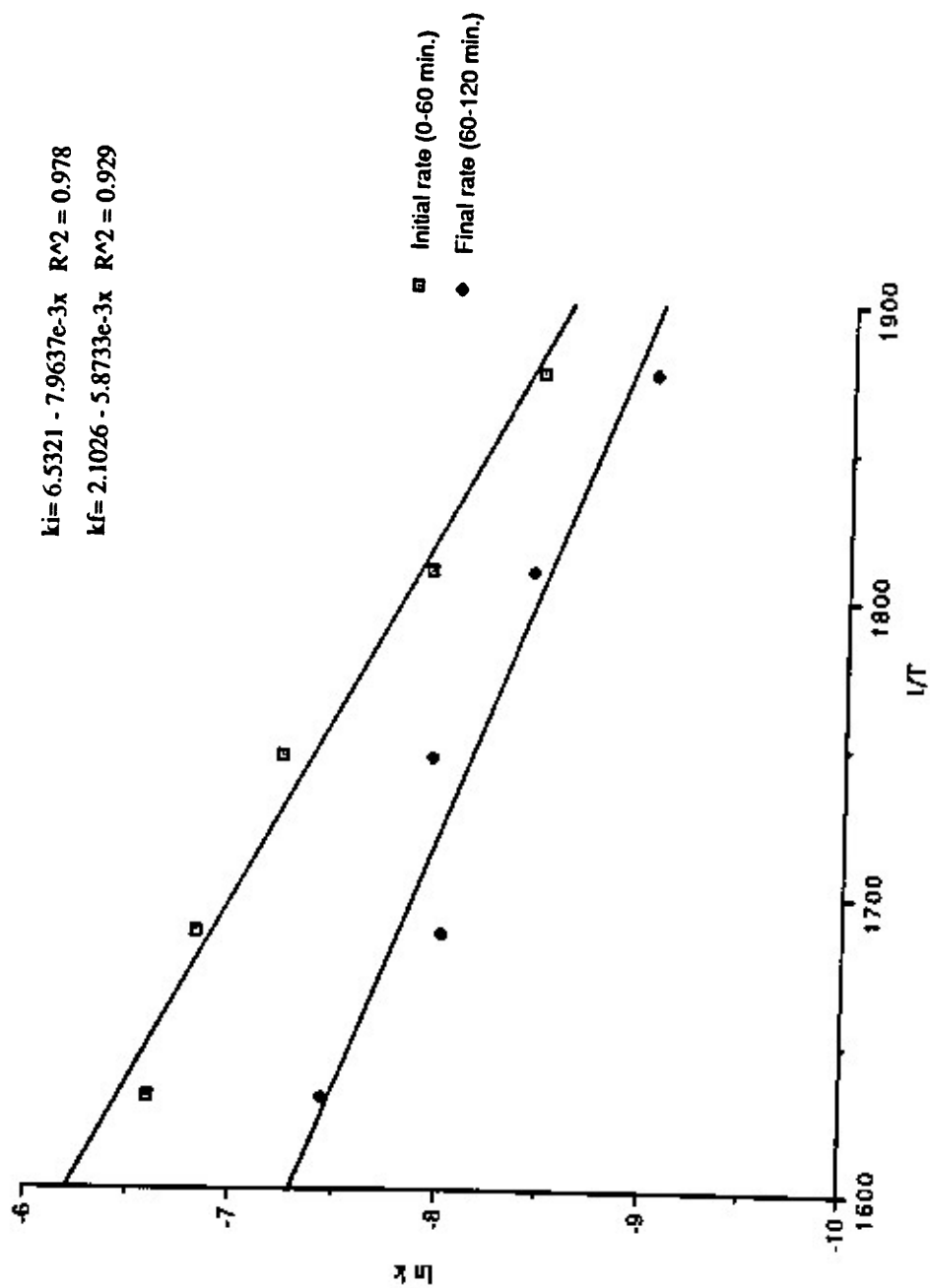□ Initial rate (0-60 min.)

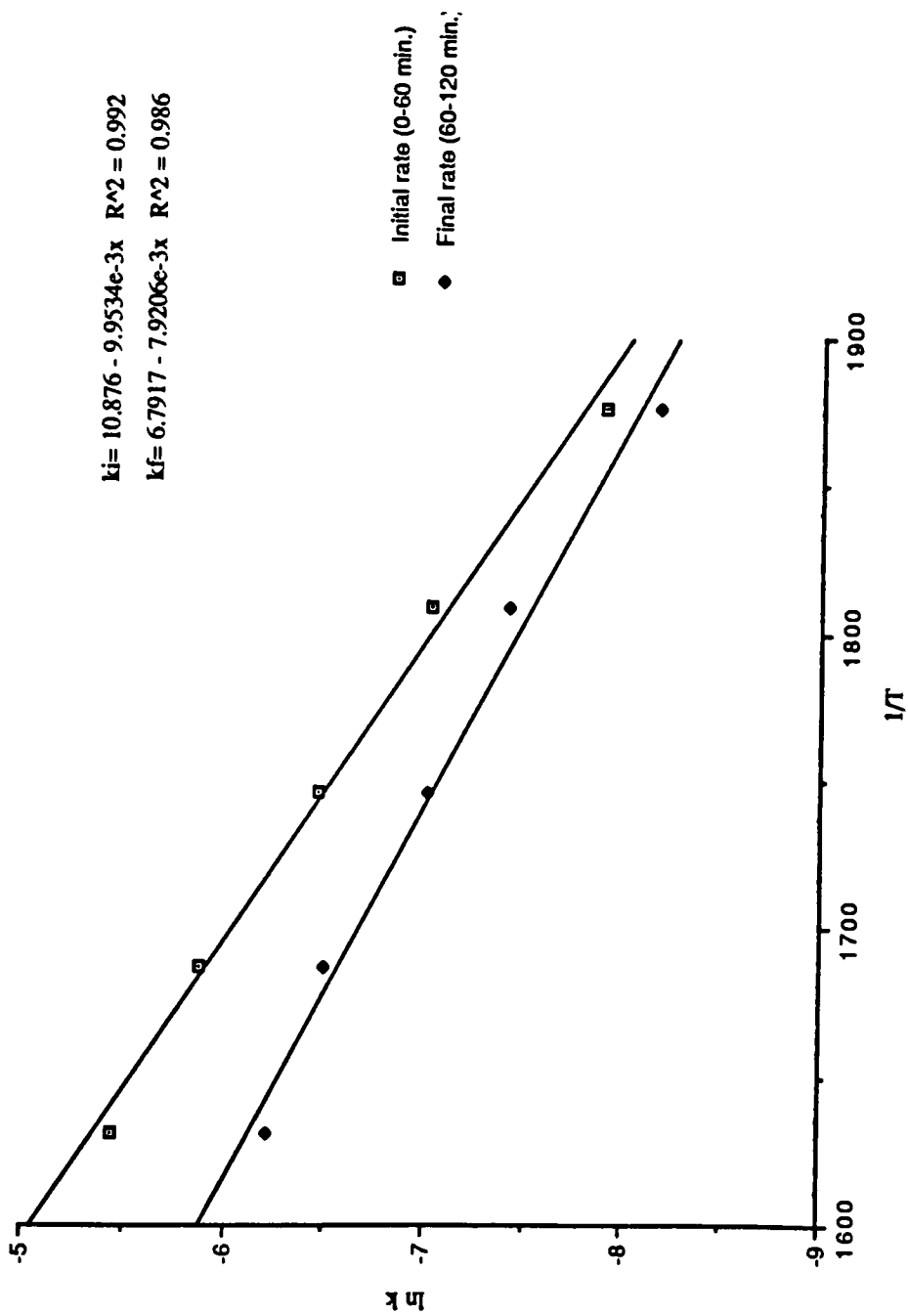♦ Final rate (60-120 min.)

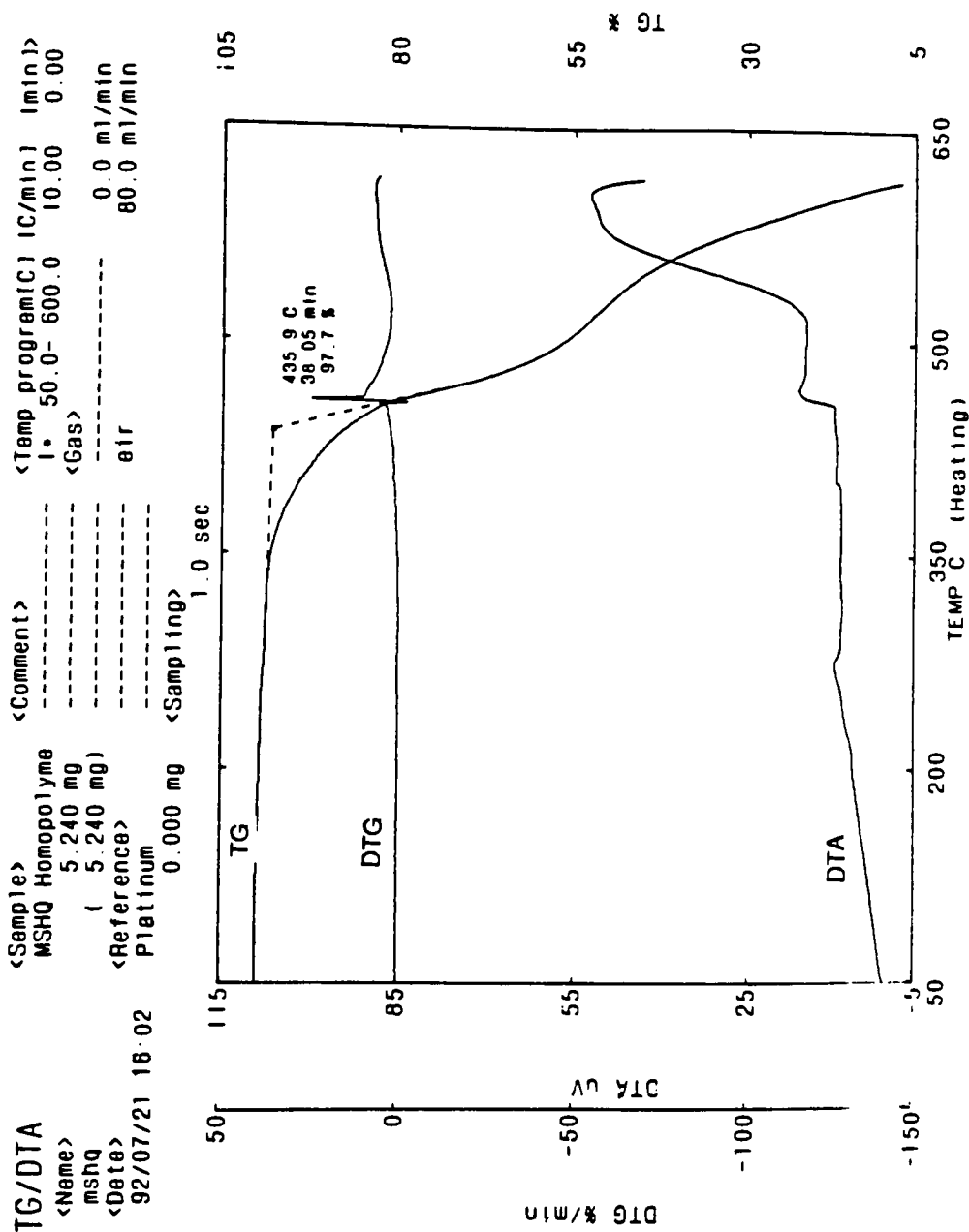Figure 30. Arrhenius plot for polyester 9 under air (Seiko).

50

Figure 31. Dynamic TG thermogram for polyester 9
(Seiko, flowing air @ 80 cc/min).

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Conclusions

From the results of the isothermal degradation products obtained, they clearly showed that the benzene and oxygenated benzene degradation products obtained from polyester **6** (containing phenyl and styryl side chains) and polyester **7** (containing phenyl and α-methylstyryl side chains) do come from the decomposition of styryl or the α-methylstyryl pendant groups. This was evident because polyester **8** (containing only phenyl side chain) did not produce any benzene or oxygenated benzene products when studied under the same temperature range that polyesters **6** and **7** were exposed to. Under the same temperature range however, polyester **9** (containing phenyl and α-methylstyryl side chains) produced both benzene and oxygenated benzene products. This strongly indicates that the side chain aliphatic carbon bonds are weaker than the phenyl side chain carbon bonds.

Activation energies obtained through the use of isothermal techniques did not give clear evidence for the stabilities of the polymers. This was due to the fact that the isothermal method is a very time consuming technique. A fresh sample had to be used for each trial at each temperature increment. These factors make this technique more susceptible to error.

The Perkin-Elmer instrumentation showed that the activation energies for polyester **6** under flowing nitrogen was higher than under flowing air. This showed that polyester **6** was more stable under nitrogen than under air as expected. The comparison of the data obtained from the Perkin-Elmer instrument with the Seiko instrument was not possible because of their dissimilar thermobalance designs.

Polyester **8**, containing only phenyl side chains did not result in any decomposition products at the temperature range studied. Therefore, this polymer should be studied at higher temperatures to obtain the actual activation energies for the side chain scission reaction.

The Arrhenius plots that resulted in a non-linear curve

suggests that the initial assumption of a first order kinetics for the side chain decomposition reaction of the polyesters was false. The theoretical assumed value for the variable, m_f, used in the equation 2 (pg. 10), was a questionable value used in the determination of the activation energies. The GC/MS analysis showed that polyester **8** did not give any benzene related products under air. This suggests that the value of m_f used in equation 10 (pg. 23) for the calculation of E_a for polyesters **6** and **7** should not have included the phenyl side chain.

For polyester **6** and **7**, the two linear regions of the rate constant plots are showing simultaneous reactions that are taking place. The initial rate may be the result of depolymerization reaction or it may be the oxidation reaction. The final rate may be attributed to the result of secondary reactions. If the initial rate reaction only involves the depolymerization of the side chain for polyesters **6** and **7**. Then the calculation of m_f can not include the contribution of the phenyl side chain.

The atmosphere that the polyesters are exposed to also will have an effect on the reactions that are taking place. Figure 32 on page 54 is an overlay plot of polyester **8** under both nitrogen and air. The Differential Thermal Analysis (DTA) curve for polyester **8** under air shows that the decomposition reaction is an exothermic reaction (peak maximum). The DTA curve for polyester **8** under air shows that decomposition reaction is an endothermic reaction (peak minimum). The exothermic reaction under air suggests that the decomposition reaction is an oxidation or crosslinking reaction. The endothermic reaction is indicative of a melting process. In order to obtain the true side chain scission kinetics, these polymers should be studied under nitrogen atmosphere where only a single type of reaction should occur.
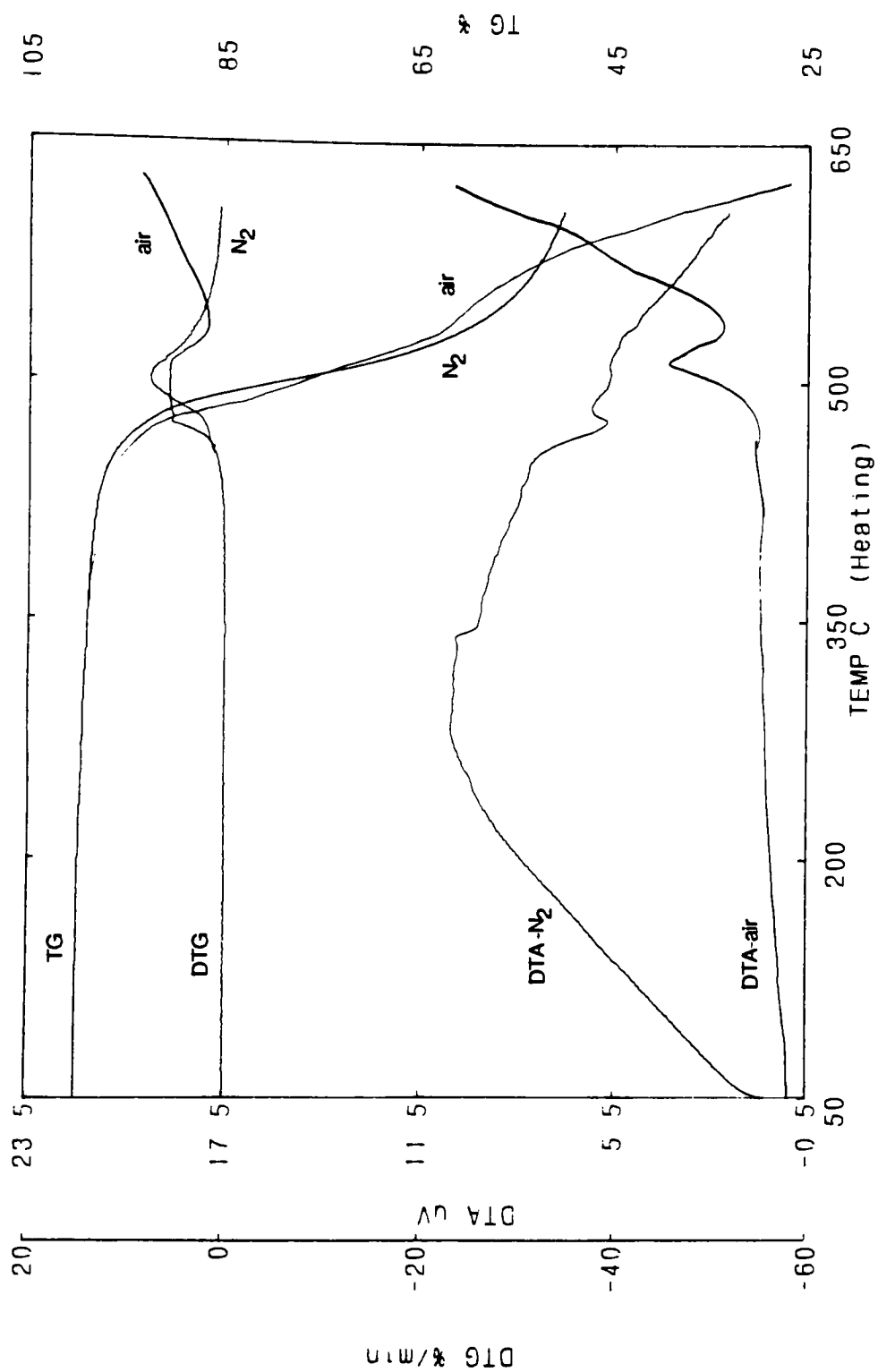
Figure 32. Overlay plot of dynamic thermograms for polyester **8** under both nitrogen and air.

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Experimental

General Information:

Polyesters **6, 7**, and α-methylstyrylhydroquinone (MSHQ) were provided by Granmont Inc. of the Montedison Group. Starting materials such as terephthaloyl chloride (TCl), phenylhydroquinone (PHQ), anhydrous methylene chloride were purchased from Aldrich Chemical Company.

Monomers MSHQ and PHQ were recrystallized from carbon tetrachloride prior to using. TCl was recrystallized from hexane. All recrystallized monomers were dried in a vacuum oven at room temperature overnight and used immediately.

TGA Sample Preparation:

The TGA samples were prepared by compressing the powder form of the polymer in a heated Carver hydraulic press between two Teflon™ coated aluminum sheets at 250° F and 30,000 PSI for ten minutes. The resulting film was cut into 5 ± 0.1 mg pieces weighed on a Mettler AJ100, 4 decimal places balance.

Instrumental:

The TGA thermograms were obtained from Perkin-Elmer TGS-2 TGA with a single hang-down balance and a Seiko TG/DTA220 with dual horizontal beam balance balance with a 20 MB Seiko SSC5200 Diskstation. Infrared scans were performed on a Perkin-Elmer 1760X FTIR with a 5 mW He-Ne laser and a PE Series 7000 Professional Computer workstation. Degradation products were analyzed on a Hewlett-Packard 5995 GC/MS with a 50 MB workstation. The gas chromatographic column used was a 30m X 0.32 mm I.D., non-polar, SPB-1 fused silica capillary.

Viscosity Measurements:

Viscometry was performed @ 30° C in a constant

temperature bath using a size 1C Ubbelohde viscometer with a 0.02933 centistokes/second constant and 3:2 phenol:tetrachloroethane as the solvent. All samples were prepared using a concentration of 0.5 g/dL.

TGA Measurements:

Polyester **6** was tested under nitrogen atmosphere using the PE TGS-2 TGA from the temperatures ranging from 320°C - 400°C for one hour period in 10°C increment. Then polyester **6** was run under air atmosphere for two hour period from the range of 320°C - 400°C in 10°C increments. The runs were for two hour period from the range of 320°C - 400°C in 10°C increments. Initially, the plan was for running the polymer at each temperature five times to obtain a good statistical average, but due to the replacement of the PE TGS-2 TGA, only three runs were performed.

Using the Seiko TG/DTA 220 instrumentation, polyester **6** under air was repeated. Samples of polyester **6** were analyzed five times at each temperature for two hour period at temperatures ranging from 260°C - 340°C in 20°C increments. Polyesters **8** and **9** were analyzed under the same conditions as polymer **6**. Solution polymerized polyester **7** was studied at temperatures ranging from 210°C - 240°C in 10°C increments.

Decomposition Product Analysis Using GC/MS:

Polyesters **6**, **7**, **8**, and **9** were isothermally degraded from 260°C - 340°C in 20°C increments. Approximately 10 grams of polymer was placed into a three-necked, 250 ml round bottomed flask fitted with a nitrogen inlet, a mechanical stirrer and a gooseneck fitting leading to two or three cold traps depending on the coolant used. Two traps were used for liquid nitrogen and three traps were used for isopropanol/dry ice mixture. The degradation apparatus is shown in Figure 32 on the following page.
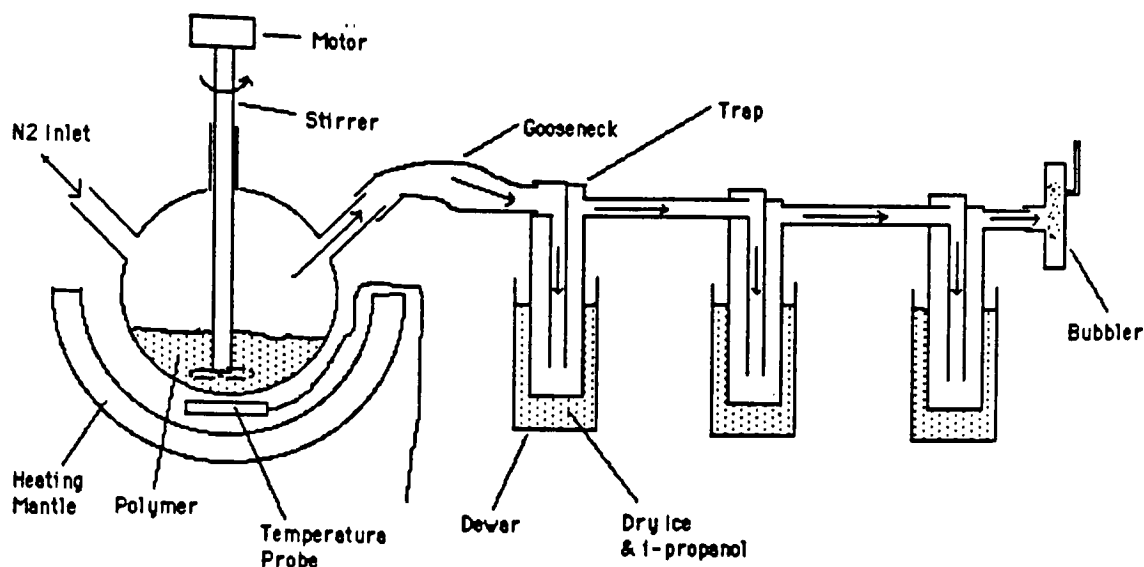
Fig 33. Isothermal decomposition setup diagram.

The degradation at each temperature was allowed to run for two hours and the degradation products in the cold traps were washed into scintillation vials with a minimal amount of acetone. The samples collected were then analyzed on the GC/MS with the oven temperature program from 70°C - 200°C in 10°C/min with the injection port set at 180°C. Only one microliter samples were injected manually.

Preparation of Poly(phenyl-p-phenyleneterephthalate), (PHQ-TP), 8:

Polyester 8 was prepared using solution polymerization. PHQ, 72.94 g (0.389 mol) plus 2.64 g (1.3 wt. % excess) was placed in a 5 L, 3 necked round bottom flask equipped with an addition funnel, a nitrogen gas inlet and a mechanical stirrer. Pyridine, 62 ml (0.785 mol, 2 eq.) was added to the flask along with 500 ml of anhydrous methylene chloride (CH_2Cl_2). TCl, 81.65 g (0.402mol) was dissolved in 420 ml of CH_2Cl_2 and placed in the addition funnel.

While stirring and nitrogen purging, the first 25% of the TCl solution was added slowly to the reaction mixture over a 10 minute period and then held for 20 minutes. The second 25% was also added in 10 minutes and then held for 10 minutes. The remainder in the addition funnel was added in 15 minutes and then allowed to stir for 40 minutes. The reaction flask was then chilled with an ice bath for 30 minutes and then allowed to stir overnight.

The next day, a gray polymer precipitate appeared in the flask. Distilled water was added (5:1 ratio) and the solution was heated with a steam bath to remove the CH_2Cl_2. After 30 minutes, the resulting solid was filtered and rinsed with acetone. Then the solid was placed back into the flask and acetone was added. The mixture was boiled for 30 minutes and then the polymer filtered off. The wet polymer was dried in a vacuum oven overnight @ 80°C. The dried polymer appeared light brown and weighed 129.2 g (88.7% yield) with a m.p. of 338-340°C. The inherent viscosity of the polymer was determined to be 0.78 dL/g.

Infrared spectrum:

Peaks were observed at 3054 cm^{-1} (aromatic C-H stretch) and 1737 cm^{-1} (ester carbonyl stretch). The infrared spectrum obtained is consistent with polyester **8**, (Fig. 34, pg. 59). A DSC endotherm is observed at 338°C (Fig. 35, pg. 60).

Preparation of Poly(1-methyl-1-phenylethyl-p-phenyleneterephthalate), (MSHQ-TP), **9**:

Using the same procedure as above, but using MSHQ, 80.0 g (0.349 mol) in 450 ml CH_2Cl_2, 73.6 g (0.363 mol) TCl in 400 ml CH_2Cl_2, and pyridine, 55 ml (0.698 mol, 2 eq.). The resulting polymer appeared white and weighed 114.6 g (87% yield) with a m.p. of 294 - 298°C. The inherent viscosity was determined to be 0.21 dL/g. Due to the low molecular weight of the polymer obtained the polymer was placed in a oven and heated @ 210°C for 24 hours to allow chain extension to occur. Then the polymer's viscosity was repeated and determined to be 0.46 dL/g.
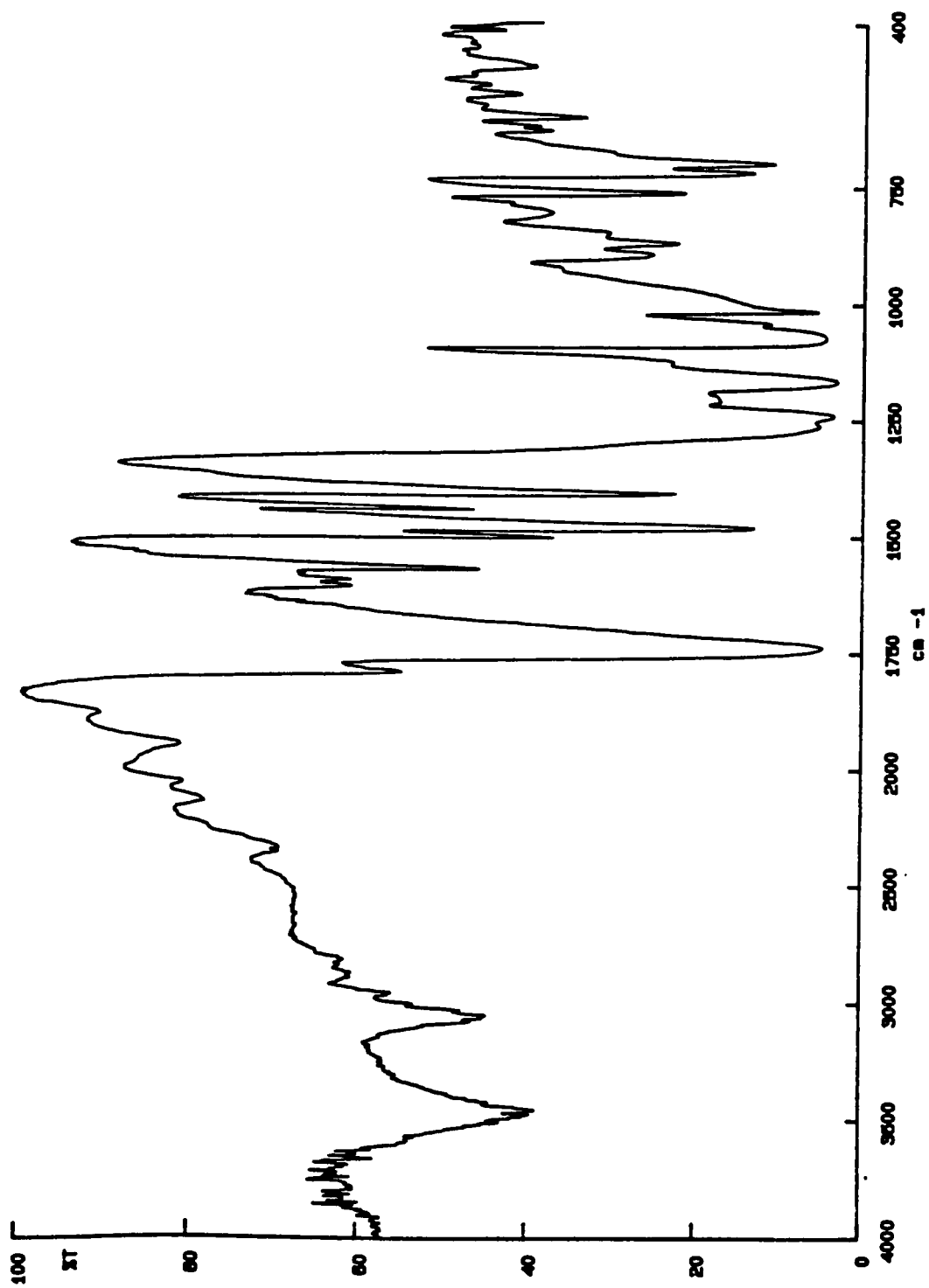
Figure 34. Infrared spectrum of polyester 8.

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Figure 35. DSC endotherm of polyester **8** (Seiko, flowing nitrogen @ 200 cc/min).

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Infrared spectrum:

Peaks were observed at 3060 cm^{-1} and 2990 cm^{-1} (aromatic and aliphatic C-H stretches), and 1745 cm^{-1} (ester carbonyl stretch). The infrared spectrum is consistent with polyester **9** (Fig. 36, pg. 62). A DSC endotherm is observed at 270°C (Fig. 37, pg. 63).

<u>Preparation of Solution polymerization of Poly(phenyl-p-phenyleneterephthalate)-co-(1-methyl-1-phenylethyl-p-phenyleneterephthalate), (PHQ-MSHQ-TP), 7:</u>

Using the same general procedure as above, MSHQ, 6.29 g (0.0275 mol) and PHQ, 5.15 g (0.0275 mol) were dissolved 80 ml of CH$_2$Cl$_2$ placed in a 300 ml 3 necked round bottomed flask along with pyridine, 4.35 g (0.055 mol). Then TCl, 11.31 g (0.0557 mol) dissolved in 30 ml of CH$_2$Cl$_2$ was added in the same fashion as in the previous procedure. The resulting polymer appeared light brownish and weighed 12.5 g (89.1% yield) with a m.p. of 352 - 356°C. The inherent viscosity was determined to be 0.70 dL/g.

Infrared spectrum:

Peaks were observed at 3065 cm^{-1} and 2980 cm^{-1} (aromatic and aliphatic C-H stretches), and 1740 cm^{-1} (ester carbonyl stretch). The infrared spectrum is consistent with polyester **7**, (Fig. 38, pg. 64). A DSC endotherm was observed at 354°C (Fig. 39, pg. 65).
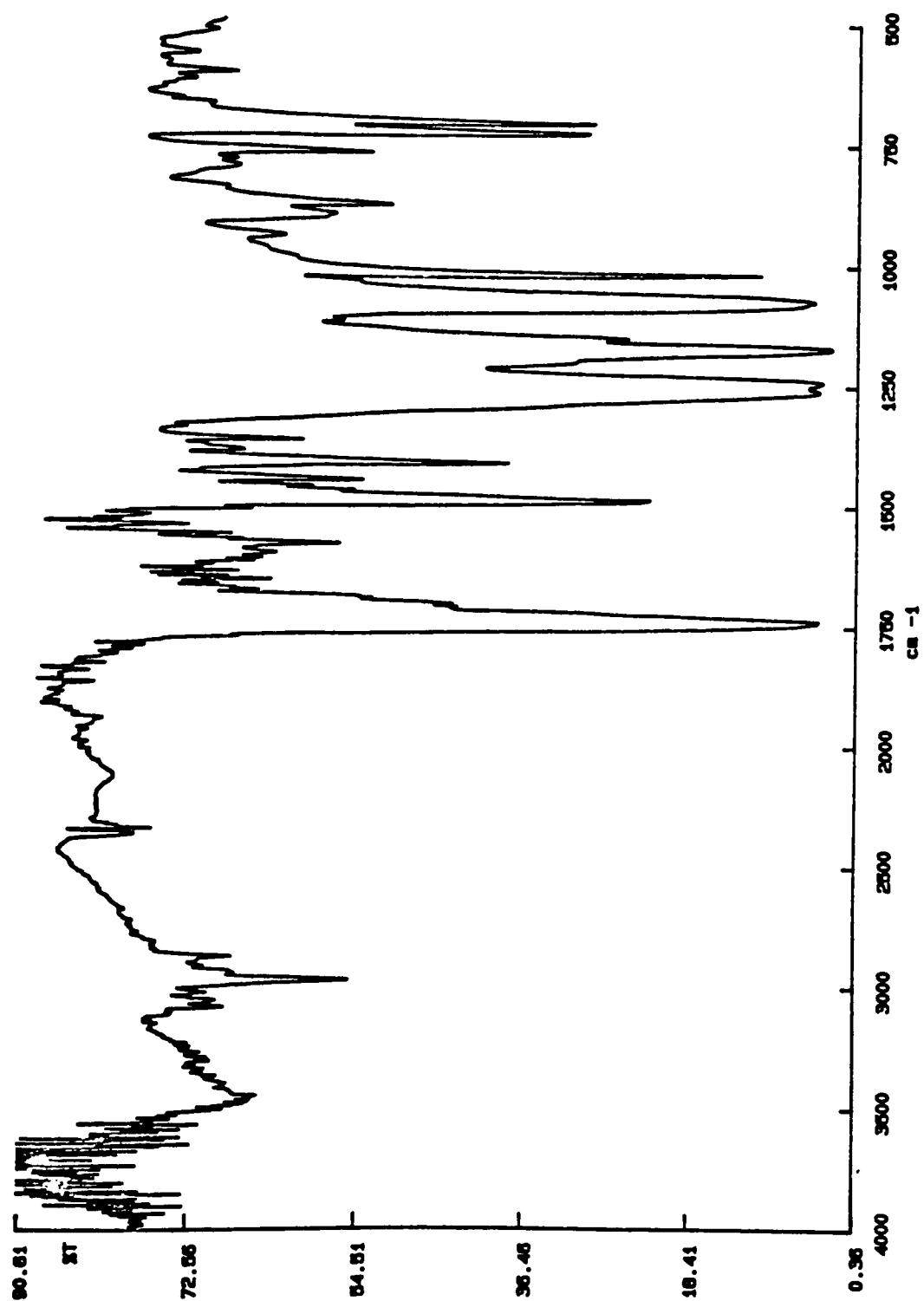
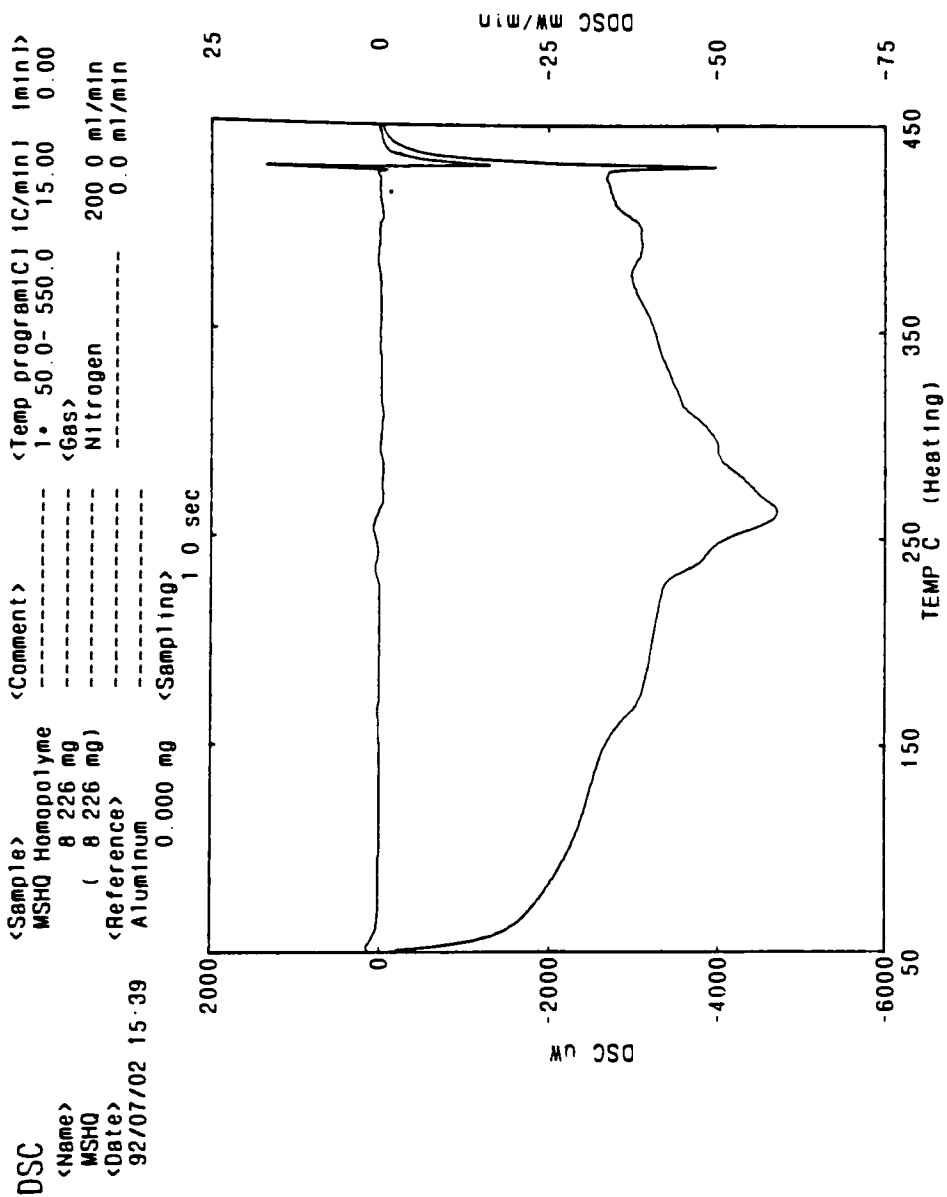Figure 36. Infrared spectrum of polyester 9.

62

Figure 37. DSC endotherm of polyester **9**
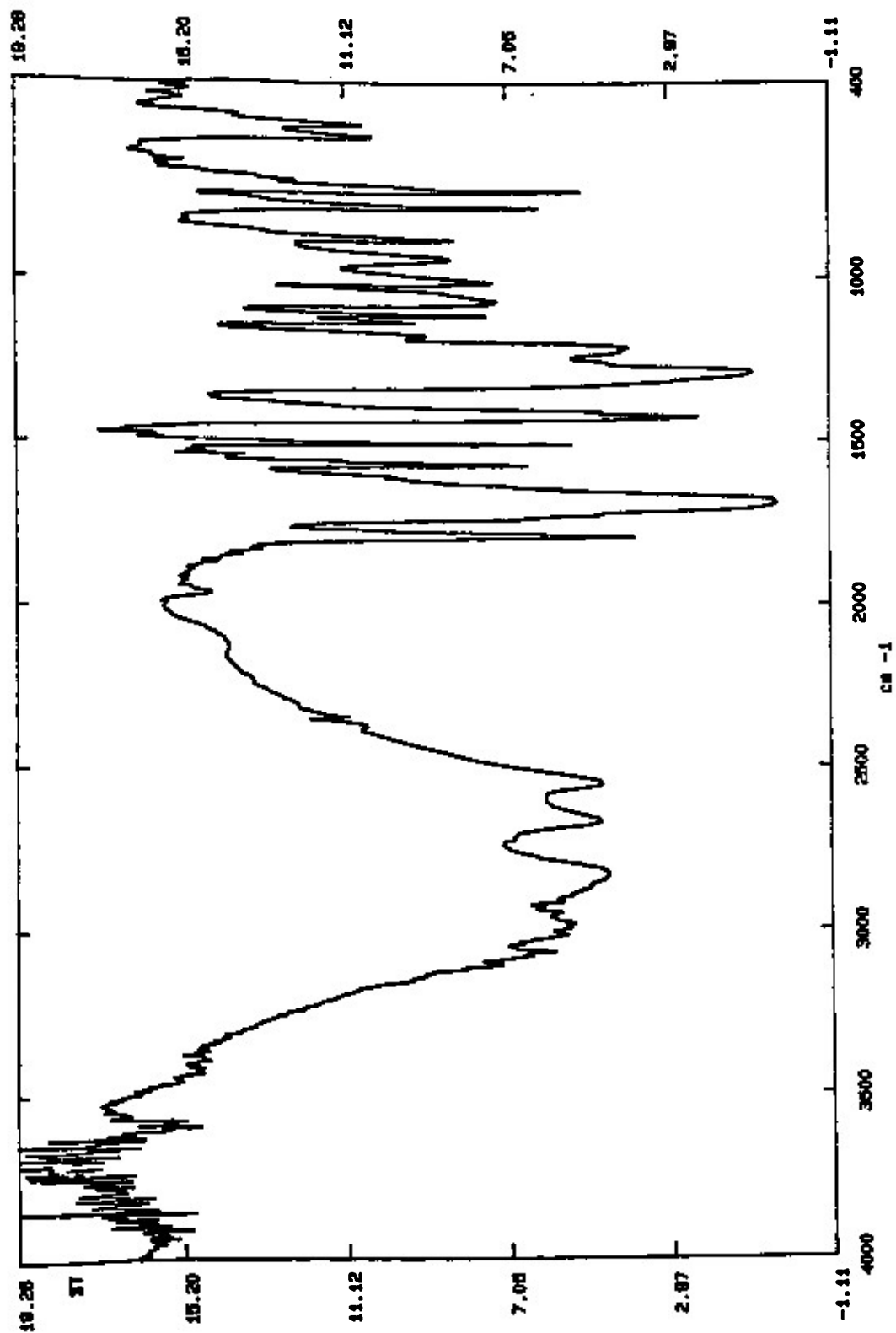(Seiko, flowing nitrogen @ 200 cc/min).

Figure 38. Infrared spectrum of solution polymerized polyester 7.
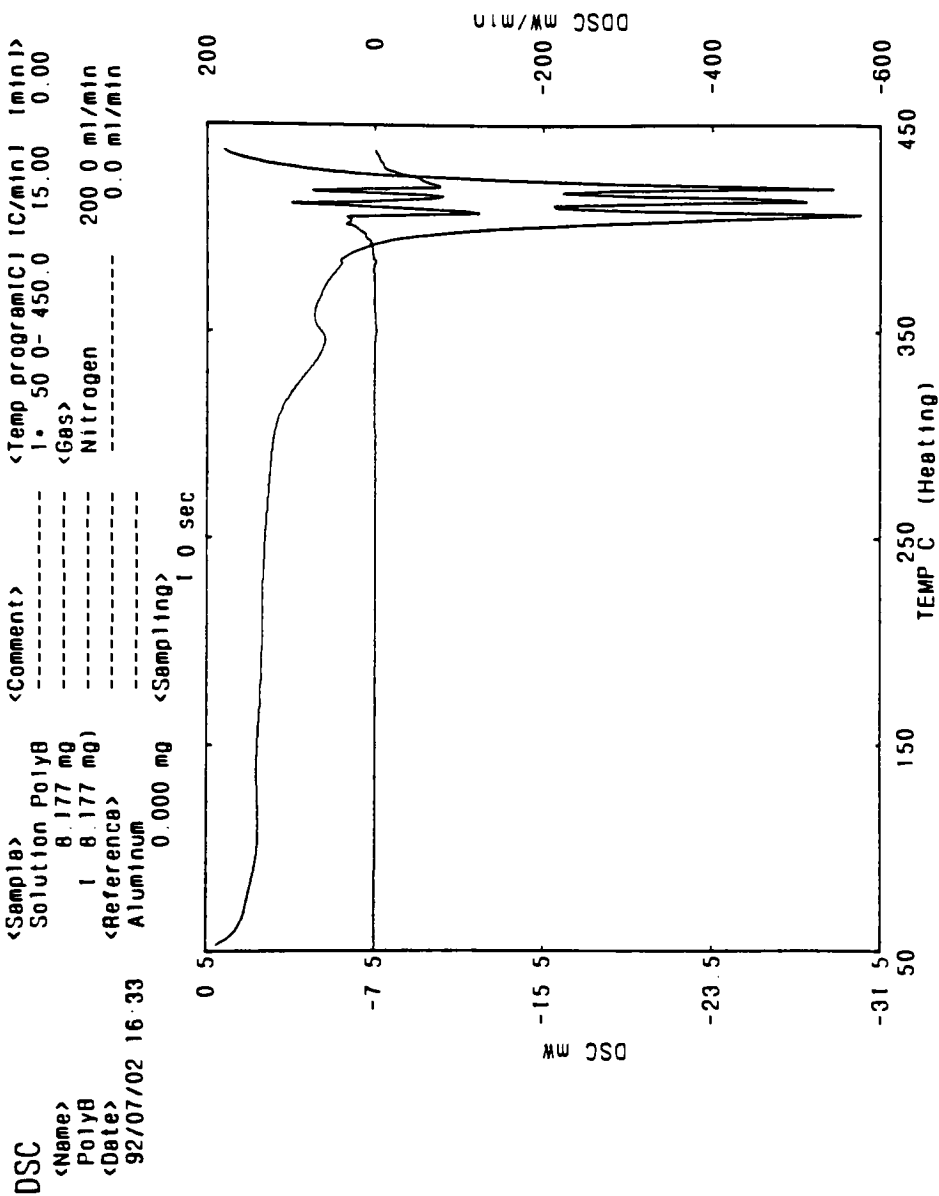
Figure 39. DSC endotherm of solution polymerized polyester 7 (Seiko, flowing nitrogen @ 200 cc/min).

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