KINETICS AND MECHANISM OF THE CARBONATE ROUTE TO PES

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To Sarah

'I couldn't have done it without you!'

'You may derive thoughts from others;
your way of thinking, the mould in
which your thoughts are cast, must be
your own'.
Charles Lamb, 'The Old and the New
Schoolmaster', Essays of Elia (1823)

ACKNOWLEDGEMENTS

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Finally, but most important of all, I would like to thank and reaffirm my love for my wife, Sarah, and my family. Their continual encouragement, understanding, love and belief in what I can achieve are the most important aspects of my life.

SUMMARY

The kinetics of the 'carbonate' route to poly(phenylene ether sulphone) (PES) was studied by three separate techniques.

The first involved the use of Fourier Transform Infra-Red (FTIR) Spectroscopy, and studied the melt polymerisation between 4,4'-dichlorodiphenyl sulphone (DCDPS) and the bis potassium salt of 4,4'-dihydroxydiphenyl sulphone (Bis-S). The polymerisation was followed by either measuring the loss of the C-Cl group or the formation of the aryl ether group. Both methods led to the activation energy for the polymerisation being calculated to be ~109 $kJmol^{-1}$.

The viscosity of the solution polymerisation medium was also monitored to determine the activation energy of the reaction. This work showed that as the extent of reaction increased from $p = 0.95$ to $p = 0.98$ the polymerisation moved from being kinetically to diffusion controlled, as the activation energy reduced from ~93.5 $kJmol^{-1}$ to 21.8 $kJmol^{-1}$.

The main kinetic study involved the use of a model compound, namely the potassium salt of 4-(p-chlorobenzenesulphonyl)-4'-(p-hydroxybenzenesulphonyl) diphenyl ether (chlorophenate dimer). Four concentrations of the model compound were studied in diphenyl sulphone (DPS), each yielding activation energies of ~109 $kJmol^{-1}$. Rate constants were extrapolated to both zero and commercial manufacture concentrations.

The mechanism of the 'carbonate' route to PES was also studied by three main techniques.

The first involved the use of High Pressure Liquid Chromatography (HPLC) to study the growth and subsequent decline in the concentration of the chlorine-ended monomers and oligomers. This showed that there was little polymerisation below ~265°C under normal operating conditions. The effective use of Field Desorption Mass Spectrometry (FDMS) to study the polymerisation was also demonstrated.

The carbon dioxide (CO_2) evolved during the polymerisation process was also monitored as a means of elucidating the mechanism. This showed three distinct phases of evolution. Although earlier work had suggested this to be due to partial potassium salt formation of Bis-S, it was found that DCDPS must also be involved as a consequence of the HPLC study. Two variants of PES were also studied for comparison.

Finally, the polymerisation was studied both by solid state and liquid nuclear magnetic resonance (NMR). This indicated that 50% of the Bis-S reacted immediately, which seemed to contradict the CO_2 evolution studies. A postulated reaction mechanism involving aryl carbonates is discussed.

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CHAPTER 1: COMPETITORS OF PES AND A HISTORY OF ITS MANUFACTURE

1.1 Introduction

Poly (oxy-p-phenylenesulphonyl-p-phenylene) (PES) is one of a class of materials collectively called high temperature engineering thermoplastics. These materials are able to withstand temperatures of at least 150°C for reasonable periods of time. Also, they can be used under load bearing conditions in a number of applications.

There are two basic types of thermoplastics, namely semicrystalline or amorphous. The underlying difference between the two classes is in the morphology of the polymer matrix. A semicrystalline polymer has ordered regions imbedded in an unordered, amorphous polymer matrix, whereas an amorphous polymer lacks any morphological regularity. The term semicrystalline is used, since no polymer is completely crystalline. Also, some polymers may be amorphous or semicrystalline, depending on the cooling conditions from the melt. The morphology of a polymer matrix has a tremendous effect on its thermal properties. There are two major types of thermal transition temperatures - the crystalline melting temperature (T_m) and the glass transition temperature (T_g). The T_m of a polymer is the melting temperature of the crystalline domains of a polymer sample, and is thus only applicable to semicrystalline polymers. The T_g is the temperature at which the amorphous domains of a polymer absorb sufficient thermal energy to permit segmental motion of the polymer chain due to bond rotation.

Amorphous polymers obviously exhibit T_g, but as a polymer specimen increases in crystallinity, the effect of the T_g becomes less pronounced.

PES is a totally amorphous high temperature engineering thermoplastic, which was first commercialised by ICI in 1972. The current commercial capacity is 7000 tpa. The structure comprises phenylene rings linked via the para position to alternate sulphone and ether groups (Fig 1).

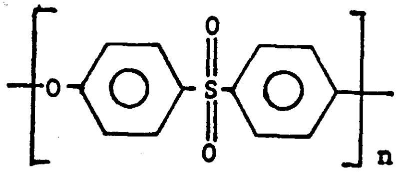


Figure 1: PES Repeat Unit

As a consequence of the amorphous nature of PES, despite its regular structure, the mechanical properties fall away rapidly once the glass transition temperature (T_g) has been exceeded.

The phenylene and sulphone groups are chain stiffening and enhance the T_g of the polymer. The ether linkage provides flexibility to the chain, reducing the T_g sufficiently such that the processing window between the T_g and the decomposition temperature of PES is large.

In general, the difference between the decomposition temperature and the T_g should be >130-150°C, and that between the decomposition temperature and the T_m for a semicrystalline polymer should be >30°C. This allows polymers, including PES, to be moulded by conventional means on conventional equipment.

Typical properties of PES and other polymers in this class are high heat distortion or continuous use temperatures, high mechanical properties including excellent flexural and tensile strengths and notched impact properties, good solvent resistance, especially if the material is partially crystalline, and low flammability.

Most of the polymers in this class of materials contain a largely aromatic or hetero ring backbone, with interlinking groups to give the chain sufficient flexibility to guarantee a large processing window.

Of the polymers in this class which have been successfully commercially manufactured, the most notable are the amorphous polyethersulphones (PES, UDEL, RADEL), polyetherimide (ULTEM) and polyarylates (ARDEL, DUREL), and the semicrystalline polyketones (PEEK, PEK) and polyphenylene sulphide (RYTON).

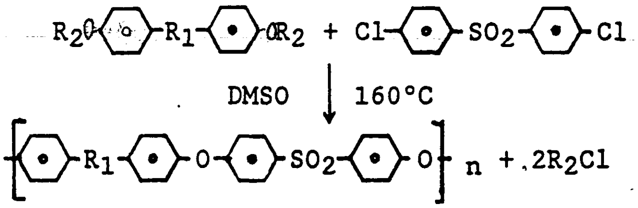
1.2 Competitors

1.2.1 Polysulphone (UDEL)

1.2.1.1 Synthesis And The Use Of The Polyetherification Process

Much of the early pioneering work on polyetherification to produce polyarylethers was conducted in the research laboratories of the Union Carbide Chemical Company. Farnham et al (1) were the first to document the preparation of polyarylethers by this method. Polymer was formed by the reaction of a preformed bisphenate with 4,4'-dichlorodiphenyl sulphone (DCDPS) in DMSO or tetrahydrothiophene-1,1-dioxide (sulpholane) at ~160°C for 1-2 hours;

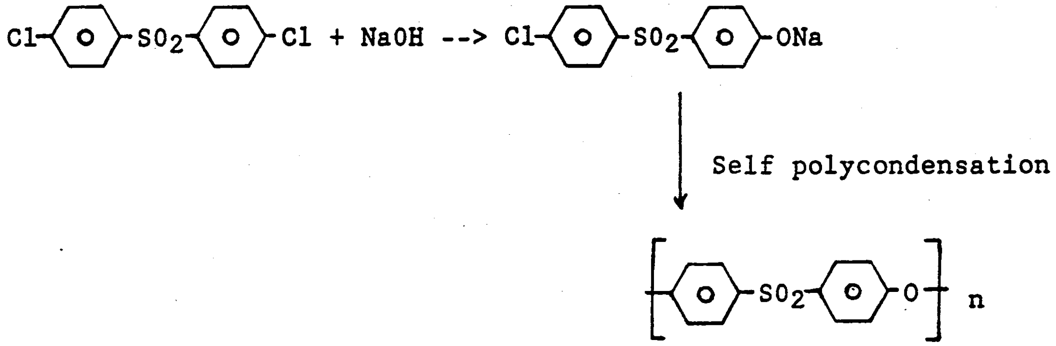
eg.



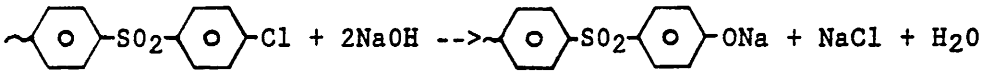
R_1 = $-C(Me)_2-$, $-SO_2-$, etc R_2 = Na, K, etc

The bisphenate is formed by the reaction of the dihydric phenol with aqueous KOH and azeotroping the water formed with chlorobenzene. Farnham et al found that only dipolar aprotic solvents were useful in obtaining high molecular weight polymer, and those solvents containing sulphone groups were particularly useful when high polymerisation temperatures were required. The main factors governing solvent choice were the need to dissolve the reactants under anhydrous conditions, the need for a facile reaction and the ability to keep the growing polymer in solution.

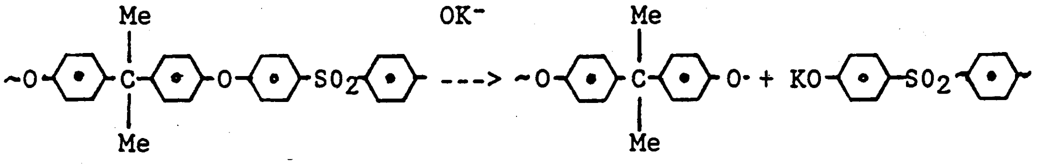
The presence of water had a marked effect on the ability to produce high molecular weight material. NaOH can be formed by the reaction of sodium bisphenate with water and this can lead to three damaging side reactions (2). The first is the partial hydrolysis of the dichloride monomer to yield the sodium salt of 4-chloro-4'-hydroxy-diphenyl sulphone, which can further react to form polymer by self polycondensation, eg;



Hydrolysis of polymer chloro end groups can also occur, eg;



Both processes would lead to low molecular weight polymer being formed due to stoichiometric imbalance. The base could also attack the polymer chain at the activated position para to the sulphone group, to give a Bis-A type phenolic end and a Bis-S type phenolic end, eg;

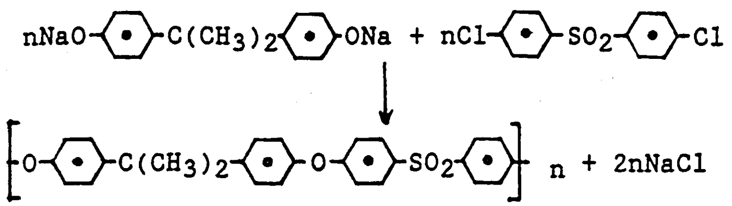


A number of polyethers were prepared by Farnham, and it was shown that the reactivity of the bisphenols varied inversely with acidity, and thus directly with the nucleophilicity of the bisphenates. This suggested a typical bimolecular reaction scheme, which was further substantiated by the fact that an all para structure was always formed. Potassium and sodium salts of the bisphenols were the only salts to give polymer, and the reactivity of the activated dihalides were as expected in that fluorine was more reactive than chlorine. The thermal properties of the various polyethers formed also followed normal theory, with the T_g of the final polymer depending to a certain extent on the linkages between the phenyl rings. Most of the polymers studied were amorphous, and all had excellent thermal stability.

Polysulfone of useful molecular weight was first successfully achieved in January 1962 by Dr R N Johnson in the Research Laboratories of Union Carbide Corporation, Bound Brook, New Jersey USA (3). It made use of Bisphenol A, which was a relatively cheap polymer intermediate, and 4,4'-dichlorodiphenyl sulphone (DCDPS).

The electron withdrawing character of the sulphone group strongly activated the chlorines toward displacement by nucleophiles such as phenoxide anions. The chosen polymerisation solvent was DMSO, presumably due to the ability of DMSO to complex cations leaving a free and very reactive anion. The bissodium salt was prepared first by reacting Bisphenol A with 50% caustic solution, the water formed being driven off with the aid of a chlorobenzene azeotrope. DCDPS was then charged to the vessel and the polymerisation took place at 160°C.

Summary:



The reaction was terminated by use of methyl chloride, to convert any remaining thermally unstable phenoxide ends to the more stable methoxy derivative.

1.2.1.2 Properties

Polysulfone has a T_g of 190°C and thus a continuous use temperature of ~150°C. It has good impact strength, excellent thermal stability for long periods in air at elevated temperatures and outstanding hydrolytic stability.

1.2.1.3 Commercial Activity

Amoco have a 6000 tpa plant at Marietta, Ohio USA. BASF have a small pilot plant at Fredrickshaven, West Germany.

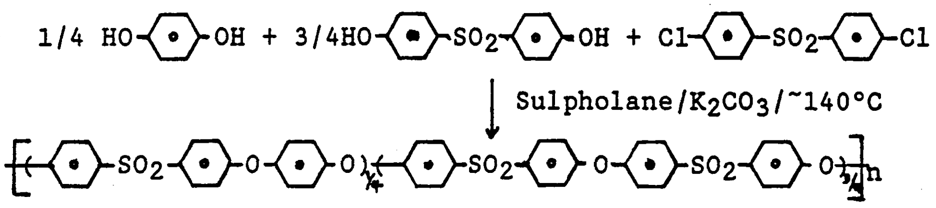
1.2.2 Polyarylethersulphone (RADEL)

1.2.2.1 Synthesis

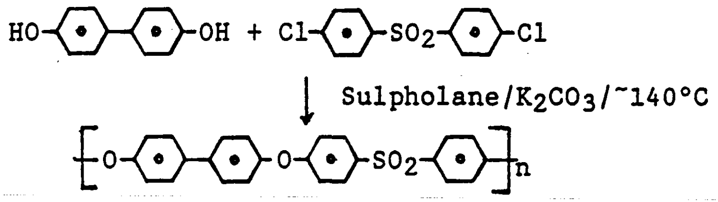
RADEL is a family of high temperature engineering thermoplastics based on polysulphone chemistry which are manufactured by Amoco. The process is believed to be based around 'carbonate' chemistry, with the main difference being that RADEL is probably made in sulpholane or NMP, and not DPS. There appear to be three types of RADEL (4).

The first is believed to be a terpolymer comprising 12.5% hydroquinone, 37.5% Bis-S and 50% DCDPS, and is termed RADEL A. RADEL B appears to comprise 50% biphenol and 50% DCDPS, and RADEL C is believed to be 50% biphenol and 50% bis(4-chlorobenzenesulphonyl) biphenyl. Therefore, the expected chemistry for each can be summarised;

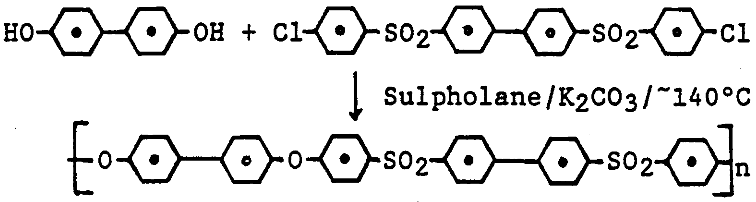
RADEL A:



RADEL B:



RADEL C:



1.2.2.2 Properties

The RADEL class of polyarylsulphones have high heat-deflection temperatures, are hydrolytically stable, and resist attack by common acids and bases over a wide range of temperatures. RADEL A is thought to be aimed at the medical market, whereas RADEL C is probably aimed at the high performance composite market.

1.2.2.3 Commercial Activity

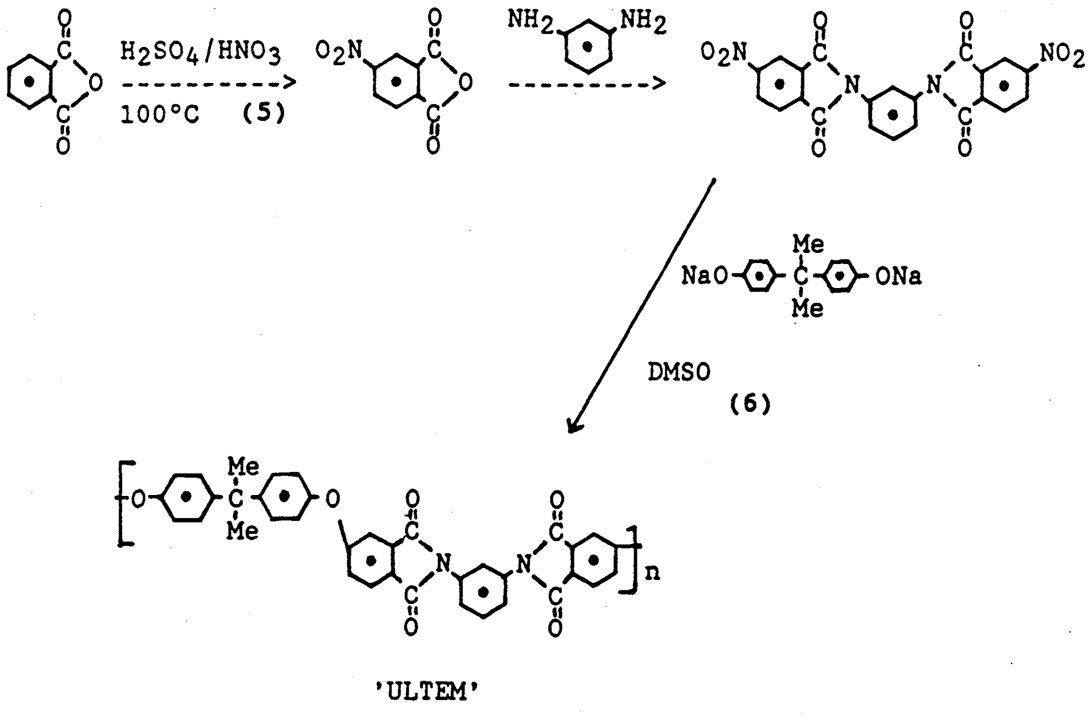
Amoco are currently the only producers of the RADEL class of thermoplastics. Tonnage is small at the moment, as the polymers have only recently entered the market.

1.2.3 Polyetherimide (ULTEM)

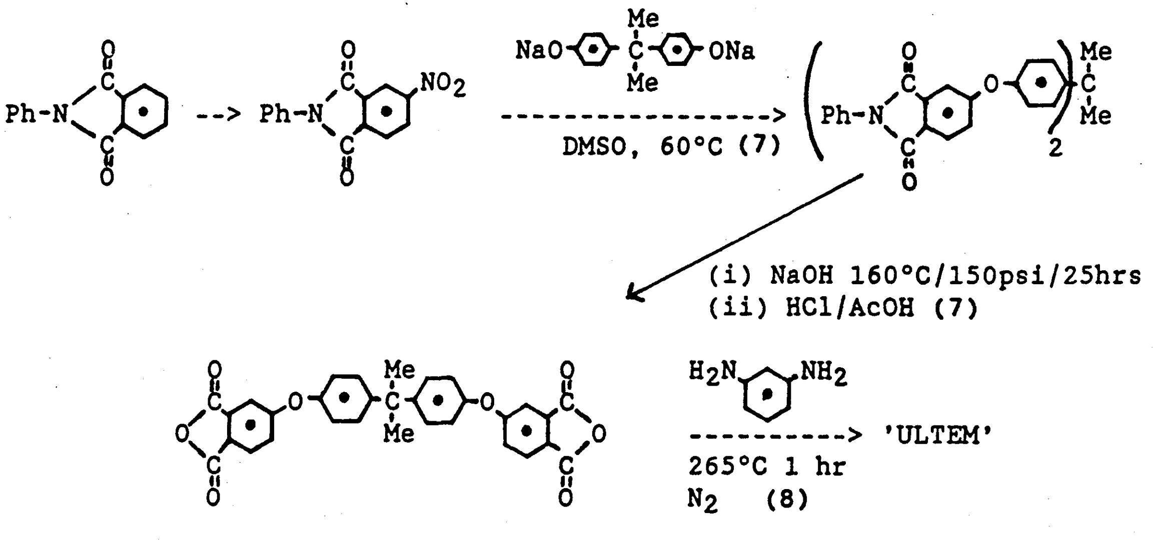
1.2.3.1 Synthesis

ULTEM was formally announced by General Electric Corporation in 1982, after years of research headed by J G Wirth in the laboratories at GEC. Three possible routes to ULTEM have been disclosed;

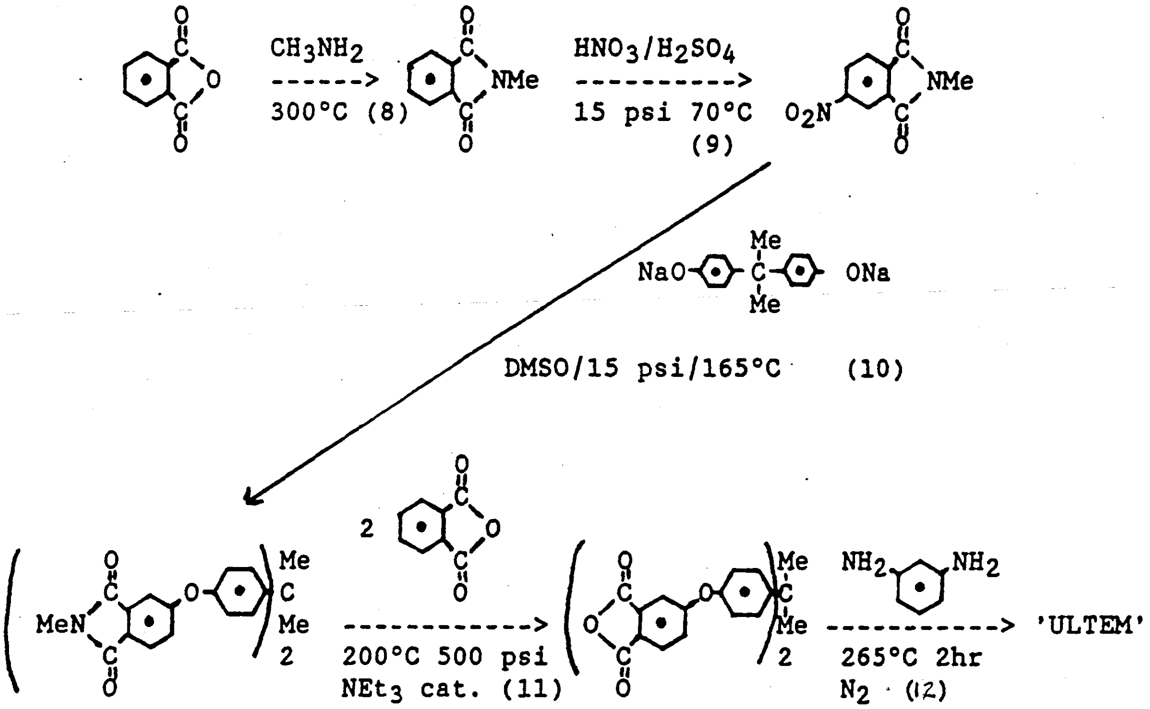
1 The first involves the nitration of phthalic anhydride to give the 3-nitro derivative which is further reacted with m-phenylenediamine to give the imide precursor. Reaction of this with the bissodium salt of Bisphenol A results in the formation of the polyetherimide.



2 In the second process, N-phenyl phthalimide is nitrated with nitric acid to give the N-phenyl nitrophthalimide which, on reaction with the bis sodium salt of Bis-A, yields the 'bis N-phenylphthalimide'. Hydrolysis of this intermediate, followed by acidification, dehydration and purification, leads to the 'bis anhydride'. Reaction of this with m-phenylenediamine again yields the polyetherimide.



3 The third possible route to polyetherimide is similar to the second. Phthalic anhydride is reacted with methylamine to yield the N-methyl phthalimide, which is nitrated with nitric acid to yield N-methyl nitrophthalimide (NMNP). This is then reacted with the bissodium salt of Bis-A in DMSO at 25°C to form the bis(etherphthalimide) in 86% yield. The bis(ether anhydride) is formed by reaction with a water/phthalic anhydride mixture at 200°C under 500 psi pressure for no more than 10 mins. Finally, the bis(ether anhydride) is reacted with m-phenylenediamine for 2 hours at 265°C under N_2 to give the product.



1.2.3.2 Properties

ULTEM has a T_g of 217°C and a heat distortion temperature of 200°C. It is inherently tough, is resistant to a wide range of chemicals and is inherently flame resistant. It has outstanding electrical properties and is readily processible on conventional equipment.

1.2.3.3 Commercial Activity

General Electric Corporation have the only commercial production facility, with a 5500 tpa plant at Mount Vernon, Indiana, USA.

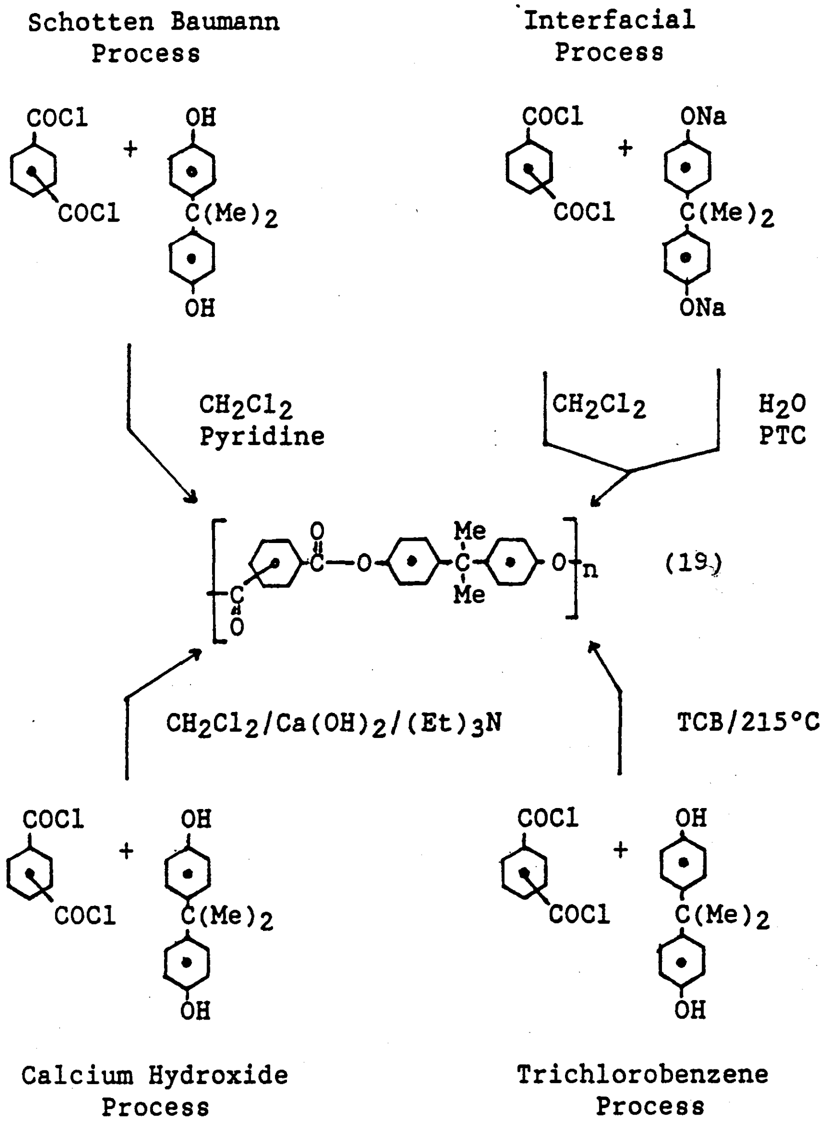
1.2.4 Polyarylates (ARDEL/DUREL)

1.2.4.1 Synthesis

1.2.4.1.1 Acid Chloride Processes

There are four basic acid chloride routes to polyarylate, all of which are solution processes. The first involves a Schotten-Baumann reaction, where a solution of the two monomers is reacted with at least a stoichiometric amount of an acid acceptor. The polymer is isolated by filtration and solvent evaporation or polymer coagulation (13).

An interfacial process involves reacting an aqueous solution of the dialkali metal salt of Bis A with a non-water soluble solution of the acid chloride. Phase transfer catalysts can be employed. Polymer isolation can be achieved by phase separation followed by solvent evaporation or polymer coagulation (14-16).

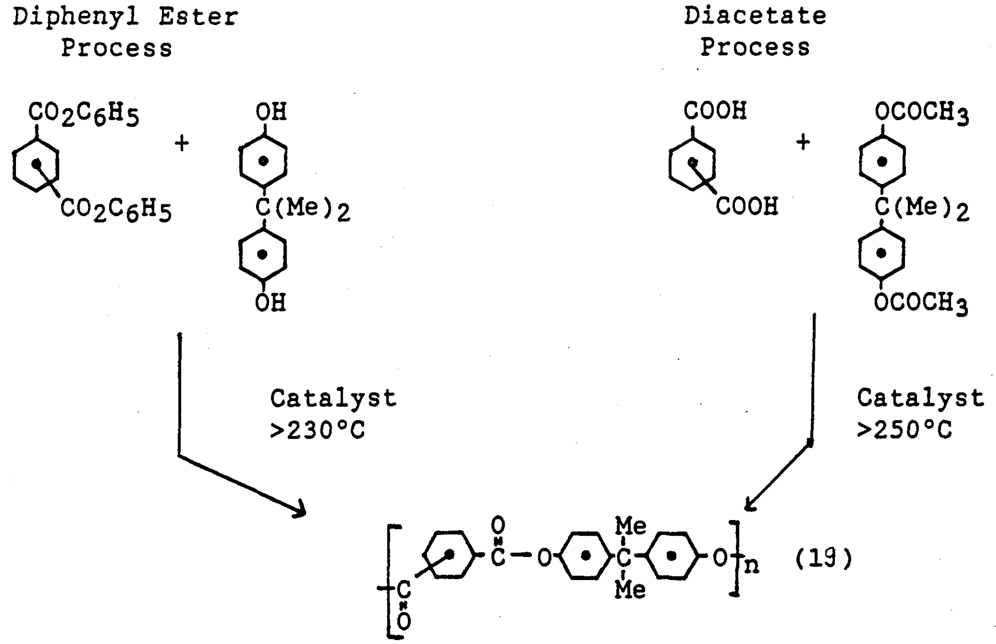

(19)

It is believed that the interfacial process is being used commercially to produce polyarylates. Another two phase system involves contacting a solution of the two monomers with solid calcium hydroxide, using triethylamine as the phase transfer catalyst. Polymer isolation is as before after filtering of the calcium chloride by-product (17). Use of high boiling solvents such as trichlorobenzene have been used to make polyarylates. Polymer isolation is achieved by coagulation or direct devolatilisation in a vented extruder (18).

1.2.4.1.2 Non-Acid Chloride Processes

The non-acid chloride processes are generally melt or slurry reactions, as the insolubility of some polyarylates prevents low temperature solution processes. The diphenyl ester process involves the polymerisation of diphenyl iso/terephthalates with Bis A at temperatures over 230°C.

Transition metal catalysts have been used to promote the reaction and phenol must be continually removed to drive the equilibrium to high molecular weight (20,21). The diacetate process involves reaction of the iso-and tere-phthalic acids with Bis A acetate. Acetic acid is again required to be removed constantly from the reaction to ensure high molecular weight polymer. Catalysts and heat transfer fluids have been used to promote the polymerisation (22-28).



(19)

1.2.4.2 Properties

Polyarylates are tough, amorphous, rigid thermoplastics exhibiting high heat distortion temperatures. Favourable properties include good flammability resistance, transparency to UV exposure, environmental stress rupture resistance and significant notched toughness after annealing.

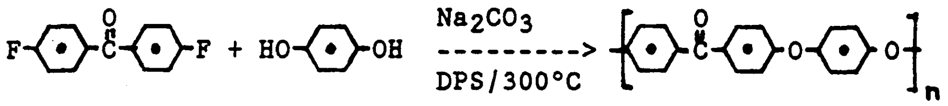
1.2.4.3 Commercial Activity

Amoco have begun work on a 6000 tpa plant at Marietta, Ohio USA. Hoechst/Celanese have a 250 tpa semiworks plant at Corpus Christi, Texas USA, and Unitika have a 1000 tpa plant in Japan with plans to increase to 4000 tpa.

1.2.5 Polyetheretherketone (PEEK)

1.2.5.1 Synthesis

PEEK was first synthesised in 1962. The current process involves the polyetherification of difluorobenzophenone with hydroquinone in DPS, using a mixture of sodium and potassium carbonates as the base;



1.2.5.2 Properties

PEEK is a tough, semicrystalline thermoplastic which can be used at high temperatures under load bearing conditions for significant periods of time. It has a T_g of 143°C and a T_m of 334°C. It has excellent chemical resistance - especially to organic solvents, low flammability and excellent fatigue properties.

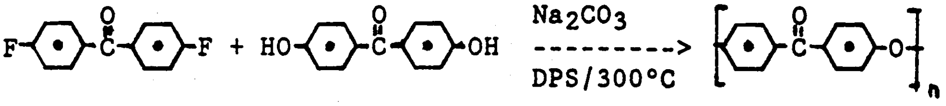
1.2.5.3 Commercial Activity

ICI Advanced Materials have a 1000 tpa plant at Thornton, Lancashire, England, and a smaller facility in Delaware, USA.

1.2.6 Polyetherketone (PEK)

1.2.6.1 Synthesis

Polyetherketone (PEK) was reported as early as 1962, although it has only recently achieved commercial production. The polymerisation procedure is similar to PEEK, with hydroquinone being replaced by 4,4'- dihydroxybenzophenone;



1.2.6.2 Properties

As for PEEK but with a T_g of 162°C and a T_m of 373°C.

1.2.6.3 Commercial Activity

ICI Advanced Materials is able to produce PEK at Thornton, Lancashire, England.

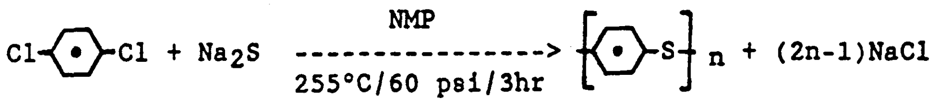
1.2.7 Polyphenylene Sulphide (RYTON)

1.2.7.1 Synthesis

Polyphenylene sulphide (PPS) was first reported as long ago as 1897, when Grenvesse prepared an amorphous insoluble resin by reacting benzene with sulphur in the presence of $AlCl_3$ (29). A material of similar chemical composition was also noted during the preparation of diphenyl sulphide (30-32). MaCallum was the first to systematically attempt the synthesis of PPS when he reacted 1,4-dichlorobenzene, sulphur and sodium carbonate in the melt (33).

The self polycondensation of cuprous salts of halobenzenethiols to form PPS was studied by Lenz et al in 1962 (34) at Dow Chemical Company, producing high molecular weight material by an Ullman type reaction. However, it was not until 1967 that PPS of useful molecular weight (15000-20000) and commercial viability was synthesised by Edmonds and Hill at Phillips (35). They patented a Wurtz Fittig reaction involving the nucleophilic displacement of chlorine from para dichlorobenzene with sodium sulphide in a polar organic solvent. Phillips commercialised the process in late 1972, after refining the laboratory procedure to enable scale-up to be feasible.

In 1975, PPS of high molecular weight was attained by using an alkali metal carboxylate as a polymerisation modifier (36).



1.2.7.2 Properties

PPS is unusual in that it possesses properties of both a thermoplastic and a thermoset. It can be moulded like any typical thermoplastic, but it can be cured under the correct conditions like a thermoset, by a process which is still not fully understood (37). PPS has a T_g of 83°C and a T_m of 283°C, and a maximum crystallinity of 65%. It possesses good thermal stability, chemical resistance, flame retardancy and unusual insolubility (38).

1.2.7.3 Commercial Activity

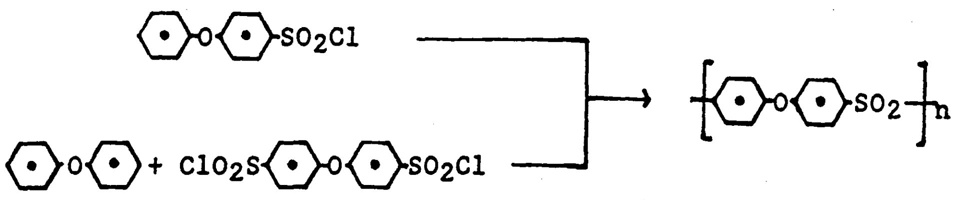
Phillips were the first company to produce PPS on a commercial scale at their 7000 tpa plant at Borger, Texas USA in 1972. Due to patent expiry, a number of companies have entered the market, including Bayer (8000 tpa plant in Antwerp, Belgium for 1990 start-up), Phillips/Toray (7500 tpa plant in Japan), Kureha (plans for 5500 tpa plant in near future) and Toto Kasei (plans for 3000 tpa plant in near future).

PROPERTY	UNITS	PES 4100G	UDEL P1700	RADEL A-400	ULTEM 1000	PEEK 450G	PEK 220G	RYTON R6
Density	Kg/m^3	1.37	1.24	1.37	1.27	1.32	1.30	1.34
Tensile Strength	MPa	84	70	82.7	105	92	105	67
Tensile Modulus	MPa	2500	2687	2655	3000	3600	4000	
Flexural Strength	MPa	129	106	110	145	170		
Flexural Modulus	MPa	2600	2600	2750	3300	2660	3700	3870
Notched Izod Impact	J/m	90	69	85	50	83		<27
Glass Trans. Temp.	°C	225	190	217	217	143	162	85
Melt Temperature	°C	-	-	-	-	334	373	285
Heat Distortion Temp	°C	203	174	204	200	160	186	135
Flammability	°C	VO(0.46)	V2(1.42)	VO(.023)	VO(0.41)	VO(0.057)	VO(0.03)	VO(0.38)
Limiting O_2 Index	%	38	30		47	35	40	46

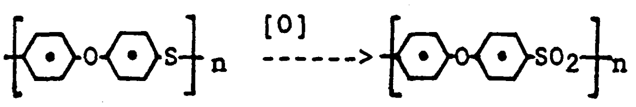
Table 1: Key Data of Competitors to PES

CHAPTER 2: ROUTES TO POLYETHER SULPHONE

There are three basic routes to PES. The first involves the formation of sulphone groups via an electrophilic aromatic substitution mechanism known as polysulphonylation, eg;

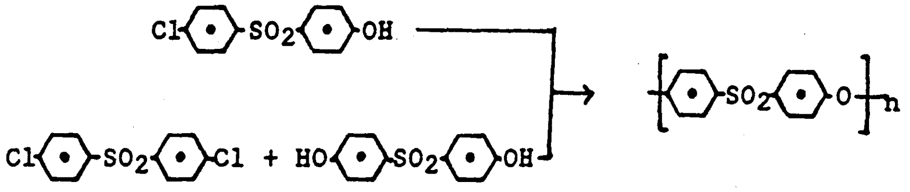


Another method of preparing PES is to oxidise the preformed polyether sulphide derivative, eg;



This method has received relatively little attention due to the difficulty in ensuring 100% oxidation.

The main alternative method of preparation involves a nucleophilic aromatic substitution process known as polyetherification, where the polymer is formed via the linking of aryl ether units, eg;



2.1 Polysulphonylation

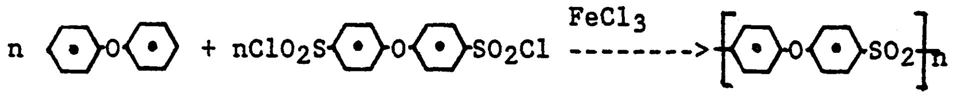
2.1.1 Ferric Chloride Catalysis

Preparation of PES via polysulphonylation involves electrophilic aromatic substitution using Friedel-Crafts chemistry. There are two basic routes, the first using two monomers and the second using one. Both routes use a catalytic quantity of a Friedel-Crafts catalyst.

The presence of the para aryl ether group enhances electrophilic aromatic substitution, and polymers of high molecular weight can be made using both processes.

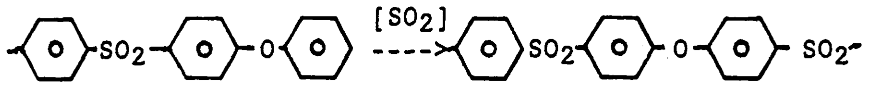
2.1.1.1 Two Monomer Route

The two monomer route involves the reaction between diphenyl ether and 4,4'-disulphonylchloride diphenyl ether, with $FeCl_3$ being used in catalytic quantities, eg:

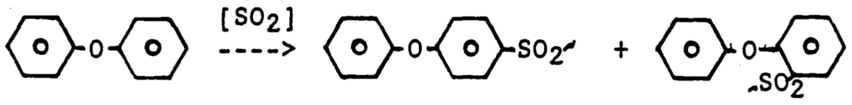


Using this method, it was difficult to obtain polymer of high molecular weight due to the loss of diphenyl ether in the exhaust gases along with the by-product HCl. Furthermore, the polymer produced from the two monomer route was lacking in toughness, due to the fact that it contained a significant proportion of ortho/para repeat units (~20%).

This substitution pattern resulted as only half of the sulphone links were formed by substitution at rings linked via oxygen to rings containing sulphone or sulphonyl chloride groups:



The remaining sulphone links result from monosulphonation of diphenyl ether where ortho and para substitution are possible:

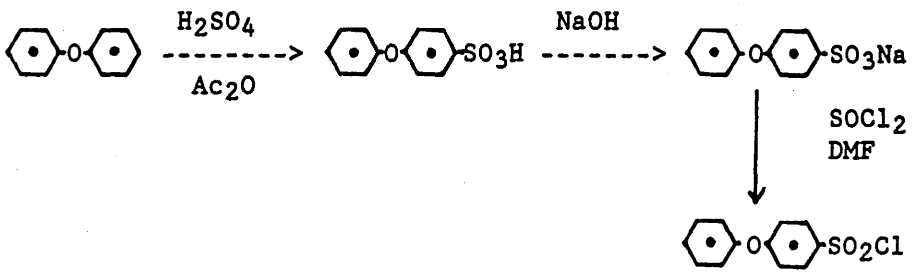


These findings are analogous to those documented for the nitration of diphenyl ether and 4-nitrophenyl phenyl ether (39).

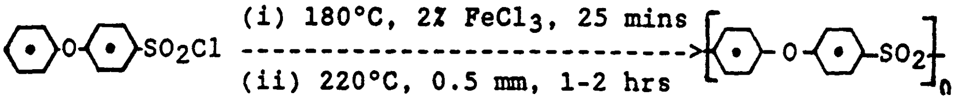
However, this route was initially favoured due to the availability and cheapness of the monomers.

2.1.1.2 Single Monomer Route

The single monomer route involved the self-condensation of diphenyl ether-4-sulphonyl chloride (40). This monomer was prepared via the following route;



The monomer was purified by two vacuum distillations and two recrystallisations from 40-60 petroleum ether (40). Solution and melt polycondensations were considered. Solution polymerisation, however, always gave polymer of poor colour and low molecular weight and so was discontinued. Melt polymerisation was performed in two distinct stages. The first involved the formation of pre-polymer by melting the monomer at 180°C for 10 minutes with 2% ferric chloride. The formation of HCl caused a large amount of foaming. The foamed mass was cooled, ground and the whole process was repeated with the mass being held at 180°C for 15 minutes. Grinding of the material was necessary, otherwise low molecular weight material would eventually be formed due to poor heat transfer. The second stage involved heating the ground pre-polymer at 200-240°C under 0.5 mm pressure for 1-2 hours.



Throughout the process, anhydrous conditions had to be rigorously maintained to prevent the catalyst deactivating and also to prevent the hydrolysis of the sulphonyl chloride ends. If 240°C was exceeded in the second phase, a significant portion of gel was formed.

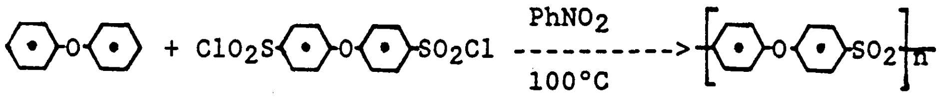
End group stabilisation was necessary due to the homolytic fission of the carbon-sulphur bond of terminal sulphonyl chloride groups which occurred at temperatures above ~240°C (41). This led to the formation of phenyl radicals which could then react with any unsubstituted position in the chain.

Stabilisation of end groups was achieved by treating a 10% solution of the polymer in DMF with aniline and shaking for half an hour to form the stable aryl sulphonamide derivative. Also, leaching of the polymer to isolate it from the catalyst was necessary and this was achieved by adding 8-hydroxyquinoline-5-sulphonic acid to a solution of the polymer in DMF to form the iron chelate. The dark green solution was then passed down a Spence Type H basic alumina column which retained the chelate, and the resulting polymer was recovered by precipitation in dilute hydrochloric acid.

The main problem with this process was the lack of reproducibility in the molecular weight of the resultant polymer. Various analyses failed to identify any monomer impurities and it was eventually thought that the problem was the result of chain branching due to the homolytic fission of the sulphonyl chloride groups. The polymer possessed a high yield stress and modulus, but had a relatively low notched impact strength. Also, thermal degradation during fabrication often occurred due to incomplete end group stabilisation (42).

2.1.2 Aluminium Chloride Catalysis

In 1967, Monsanto filed a patent describing the use of $AlCl_3$ catalyst in the preparation of PES via polysulphonylation (43). Diphenyl ether and bis(4-chlorosulphonylphenyl) ether were specified as the monomers, with nitrobenzene being the preferred polymerisation solvent, and reaction temperatures being 80-120°C to avoid oligomers and side reactions. However, no further development was conducted on this process.



2.1.3 Super Acid Catalysis

The first mention of the manufacture of PES via super acid catalysis was by Vogel in 1963, when in a 3M patent he explored the use of trifluorosulphonic acid and anhydrous HF for the condensation of aromatic disulphonyl chlorides and aromatic hydrocarbons (44).

Synthesis of PES via super acid catalysis was also investigated within ICI (45). Two basic routes were evaluated; the first involved the 'solvent' process where 4-phenoxy benzene sulphonic acid was polycondensed at 80°C for ~48 hours to form a solution of polymer in Triflic acid. The second 'catalytic' process involved the acid being converted to the chloride in situ, followed by polycondensation at 150°C for ~48 hours in DPS with ~1% Triflic acid.

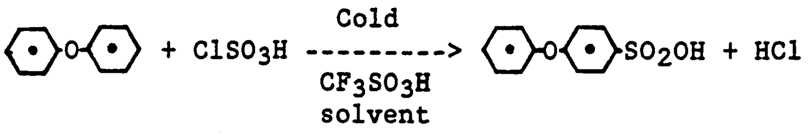
2.1.3.1 The 'Solvent' Route

The 'solvent' route involved a 'one-pot'/two stage process. The first stage was the sulphonation of diphenyl ether with chlorosulphonic acid in Triflic acid between 0-20°C. H_2SO_4 could also have been used as the sulphonating agent, but P_2O_5 would have had to have been added at a later stage to absorb the by-product water. Vigorous mixing was essential to ensure complete sulphonation. The resulting solution of 4-phenoxy benzene sulphonic acid in Triflic acid was polycondensed in the second stage by heating to ~80°C for ~48 hours.

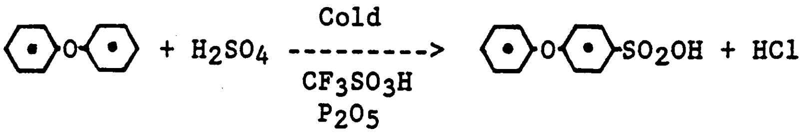
The product was isolated by pouring the solution into an excess of cold water, followed by milling to give a fine powder. This was then slurried in alkaline methanol and refluxed for several hours, before being vacuum dried at 140°C. The final polymer was relatively high in molecular weight (RV = 0.4-0.5), although the ortho content was typically 1-2% which consequently reduced the toughness of the polymer. The colour of the polymer produced was generally poor.

Stage 1: Sulphonation

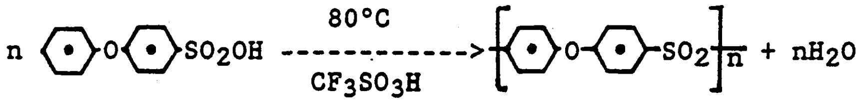
either



or



Stage 2: Polycondensation

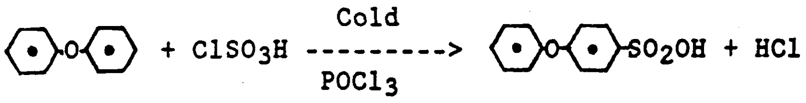


2.1.3.2 The 'Catalytic' Route

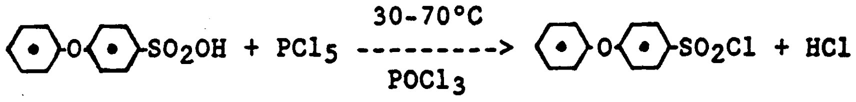
The 'catalytic' method superseded the above, mainly due to the excessive cost of the Triflic acid (£25000/te in 1983). It was a 'one-pot'/four stage process. In the first, a solution of $ClSO_3H$ in $POCl_3$ was fed over ~30 minutes to a stirred solution of diphenyl ether in $POCl_3$ between 0-30°C, yielding 4-phenoxy benzene sulphonic acid. In Stage 2 this was treated with PCl_5 at 30-70°C to form the sulphonyl chloride.

The third stage involved addition of DPS and distillation of the previous solvent $POCl_3$. The sulphonyl chloride was then polycondensed at 150°C over ~48 hours using 2.5% w/w Triflic acid as a catalyst in the fourth stage.

Stage 1: Sulphonation



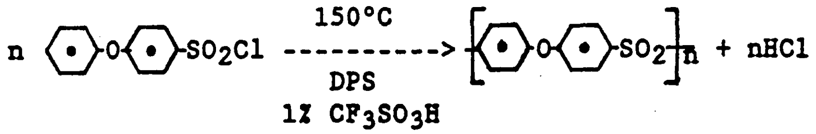
Stage 2: Chlorination



Stage 3: Solvent Exchange

Distil $POCl_3$ at 70-150°C, add DPS

Stage 4: Polycondensation



The product was isolated by refluxing the reaction crude in methanol for 6-20 hours, with periodic additions of alkaline methanol. The slurry was then filtered hot, and on cooling, the resultant cake was washed with methanol and water. It was then refluxed in methanol/acetone three times and finally vacuum dried at 130°C for ~4 hours. The polymer produced was again of relatively high molecular weight (RV = 0.4-0.5), although again the toughness of the polymer was affected due to the amount of ortho isomer present being ~3.5%.

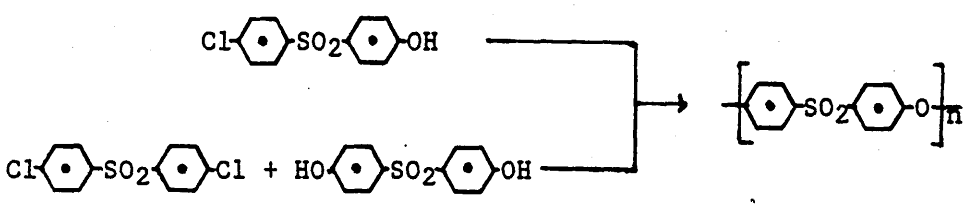
Other super acids, eg Diflic and Tetraflic acids, were also considered but were not commercially viable. Trifluoroacetic anhydride, although not a super acid, was also investigated at the same time, and PES of low molecular weight was obtained.

2.2 Oxidation Of Polysulphides

Oxidation of polysulphides (46,47) or partial oxidation of sulphoxide/sulphone/sulphide terpolymers (48) have also been described.

2.3 Polyetherification

Synthesis of PES using the polyetherification route can be achieved by using either one or two monomers, eg;



Both pathways have advantages and disadvantages. The single monomer route has a slow initial rate of reaction due to the adverse effect of the phenoxide on the reactivity of the halide. However, the two monomer process suffers due to the poor solubility of the bisphenoxide in most useful polymerisation solvents. The initial commercial process involved the one monomer route, because of the poor availability of Bis-S of sufficient purity. However, in recent years polymer grade Bis-S has become available from a number of suppliers and thus the two monomer route is now a viable alternative.

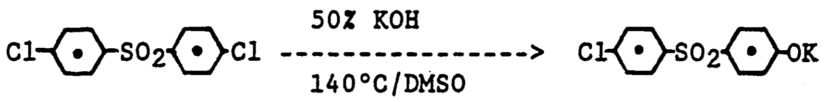
As noted above, the reactivity of the bisphenoxide of Bis-S is poor, not only due to its limited solubility in the polymerisation solvent, but also due to the presence of the para sulphone group which reduces the reactivity of the phenolate oxygen (4).

This poor reactivity necessitated the use of higher boiling dipolar aprotic solvents to produce polymer of high molecular weight, eg dimethyl sulphoxide, DPS, etc.

2.3.1 One Monomer Route to PES

2.3.1.1 The 'Hydrolysis' Route To PES

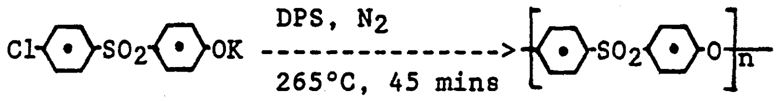
The 'hydrolysis' route had two distinct stages. The first involved the partial hydrolysis of DCDPS using 50% aqueous potassium hydroxide (KOH). The reaction occurred at 130-150°C in dimethyl sulphoxide (DMSO) (50). ie:



The reaction proceeded almost exclusively (~94%) to the potassium salt of 4-chloro-4'-hydroxydiphenyl sulphone, with ~3% remaining as DCDPS and ~3% reacting to give the bis potassium salt of Bis-S (51).

The polymerisation of the chlorophenate did not occur readily below 200°C. Because DMSO decomposes at its boiling point (190°C), giving products which could be incorporated into the polymer chain thus impairing its thermal stability (52), a solvent exchange process was necessary. Thus, the 'hydrosylate' was transferred to a polymerisation vessel, where DPS was added and the majority of the DMSO was removed at 140°C/10 mmHg.

The temperature was then increased to 200-220°C at 5-15 mmHg to further remove DMSO, and finally the temperature was increased to 240-250°C/ 25 mmHg where DPS began to distil off. The pressure was then raised to atmospheric under nitrogen. Polymerisation was performed at 260-270°C for 30-60 minutes.



Molecular weight control was established by the prior addition of the required molar excess of DCDPS. Finally, the polymer was end stopped with methyl chloride, so that any hydroxyl/phenate ends present were converted to the more thermally stable methoxy ends.

The reaction mixture was then poured onto a revolving steel band, milled, and leached with water and acetone to yield the free polymer. A more recently developed isolation process involves a totally closed process, whereby the 'toffee' is fed from the autoclave through vessels to separate the inorganic and the organic residue from the polymer before it is finally granulated.(53).

2.3.1.2 Other Solvents

Different sulphoxide and sulphone solvents have been tested during studies into PES manufacture, including dimethylsulphoxide, dimethylsulphone, diethylsulphoxide, diethylsulphone, diisopropylsulphone, tetrahydrothiophene-1,1-dioxide (sulpholane) (54).

However, for most of these solvents the halophenol monomer was not prepared in situ. Dimethyl sulphone was considered in detail as a variant of the 'hydrolysis' route (55). It was found that under well defined conditions, DCDPS could be hydrolysed with KOH to form the chlorophenate after 30 hours at 120°C. A 1/2 molar % excess base was required to overcome the loss of base due to side reaction with the solvent $DMSO_2$. Removal of the by-product water was effected by reducing the pressure to 10-20 mm, with a subsequent increase in the temperature to 140-150°C. Polymerisation occurred within 18 hours at 220°C to give polymer of high molecular weight. The use of $DMSO_2$ thus allowed the 'hydrolysis' route to be performed using a single solvent.

2.3.1.3 Melt Polymerisation

Melt polymerisation of a halophenate was described in the first ICI patent in this area (56), and was discussed in greater detail in a later report (57).

This later work showed that polymerisation was rapid at the melting point of the halophenate, and reasonable molecular weights could be achieved within 30 minutes. If the polymerisation temperature was increased above 360°C and/or the halophenol was not washed with water before regeneration of the salt, 'gel' material was formed due to cross-linking.

Polymerisations were also conducted on a heated moving metal band, which provided polymer of reproducibly high molecular weight, especially for the potassium salt of 4-chloro-4'-hydroxyphenyl sulphone.

2.3.1.4 Factors Affecting The 'Hydrolysis' Route To PES

The process involved in producing PES via the one monomer 'hydrolysis' route had several major problems. It involved two vessels and three distinct stages:

Hydrolysis vessel;	a)	Hydrolysis of 4,4'-dichlorodiphenylsulphone (DCDPS) by potassium hydroxide (KOH) in dimethyl sulphoxide (DMSO) as solvent.
Polymerisation vessel	b)	Removal of all the DMSO by distillation at low pressure and its replacement by the more thermally stable diphenyl sulphone (DPS). (Solvent Exchange).
	c)	Polymerisation in DPS

Great care had to be taken in the assaying and weighing of aqueous potassium hydroxide. Removal of the last traces of DMSO was vital but extremely difficult, otherwise the thermal stability of the resultant polymer would deteriorate. Furthermore, long cycle times were involved.

Due to these problems, work in the Research Laboratories of the ICI Plastics Division at Welwyn Garden City also concentrated on developing two monomer routes to PES.

2.3.2 Two Monomer Route to PES

2.3.2.1 Preformed Bisphenates

Spray dried and rotary evaporated samples of the bispotassium salt of Bis-S have been polymerised with DCDPS in DPS for ~24 hours at 285°C (58), resulting in polymers of high molecular weight (RV = 0.5-0.6).

Polymerisations involving the preformed bisphenate with a dihalo compound have been documented using solvents such as amides (59) or alkyl substituted amides or ureas (60).

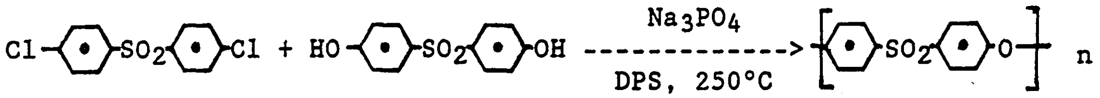
A number of patents filed by Denki describe the polymerisation of bisphenates and dihalo compounds in the melt (61-64).

2.3.2.2 In Situ Polymerisations

2.3.2.2.1 The 'Phosphate' Route

The successful development of the 'carbonate' route to PES led to other bases being tried in the polycondensation. These included sodium or potassium borates, formates, oxalates, phosphates, sulphites and meta-bisulphates, of which only the phosphates met with any success (65).

In particular, tri-sodium and tri-potassium orthophosphates (Na_3PO_4 and K_3PO_4) and tetra-potassium pyrophosphate ($K_4P_2O_7$) stood out. Two moles of the phosphate were required for each mole of Bis-S used, although as in the 'carbonate' route, small excesses of base tended to be incorporated. The temperature profile was similar to that used for the nucleophilic route, although the polymerisation temperatures were generally ~30°C lower than the equivalent carbonate;



Dimethyl sulphoxide was tested as a polymerisation solvent instead of the usual DPS, and, although it produced material of satisfactory molecular weight, rates were unacceptably low.

One difference between the 'phosphate' route and the 'carbonate' route was the large excess of DCDPS required in the former to produce polymer of high molecular weight. This was due to the fact that DCDPS reacted slowly with the phosphate to give various chlorinated oligomers.

The 'phosphate' route provided polymer of excellent colour and thermal stability, and also showed a much reduced high molecular size peak in GPC studies.

However, the process was not economically viable due to the large weight of phosphate required and the fact that the phosphates were more expensive than their carbonate analogues.

2.3.2.2.2 Copper Catalysis

The use of cuprous salts or cuprous salt complexes (eg CuCl/pyridine) in the polycondensation of di-alkali metal salts of dihydric phenols with dibromobenzenoid compounds have also been investigated (66).

2.3.3 The 'Carbonate' Route to Polyether Sulphone

There have been several modifications to the 'carbonate' route since it was first documented in 1975 (67,68). Plant manufacture of PES via the 'carbonate' route also went through several changes when it was introduced onto the Hillhouse plant in 1977 (69-71). Since then, both plant and laboratory procedures have changed slightly, as work in the research laboratories at ICI continued to find improvements in the process. The current laboratory polymerisation of PES is set out in detail in the experimental section, but a brief description is given below:

Laboratory PES polymerisations are normally conducted on the 0.25 mole scale in a glass reactor fitted with stirrer and N_2 inlet/outlet. Relevant quantities of DCDPS, Bis-S, K_2CO_3 and DPS are charged and manually mixed before the flask is placed in an oil bath. The contents are heated to 175°C and held at temperature for 30 minutes.

The temperature is then raised to 210°C and held for 90 minutes. The temperature is again raised to 265°C, where it is held for a further 90 minutes before finally being raised to the polymerisation temperature of 285°C for 90 minutes.

The 'toffee' is poured into water, milled, and leached with a methanol/water mixture, followed by a water leach, followed finally by a methanol/acetone leach to leave the polymer free of the DPS solvent and the inorganic salts.

2.3.3.1 The 'Carbonate' Route Using Other Polymerisation Solvents

2.3.3.1.1 N-Methyl-2-Pyrrolidone

PES can be prepared by the 'carbonate' route using N-methyl-2-pyrrolidone as the polymerisation solvent (72). The optimal reaction conditions were to charge all the reactants to the flask, purge with nitrogen and heat to 150°C. This was then increased to a contents temperature of 200-250°C and held for 4 hours. The polymerisation was end stopped with methyl chloride, before being passed hot through a sinter into a macerator containing demineralised water. The product was filtered, macerated and filtered again, before being washed four times in boiling water, once in boiling methanol and eventually dried at 80°C in vacuo for 24 hours. Polymer prepared by this route gave worse colour than that produced by the normal 'carbonate' route, and although several attempts were made to improve the situation, including slow addition of K_2CO_3 in the presence of chlorobenzene, use of sodium borohydride, lower temperature reaction with chlorobenzene azeotrope and the use of DFDPS, the colour did not improve greatly.

2.3.3.1.2 Dimethyl Sulphone

High molecular weight polymer can be made in dimethyl sulphone ($DMSO_2$) using 'carbonate' chemistry (58). One advantage of this polymerisation solvent was that polymer isolation only required a water wash, with potassium and $DMSO_2$ levels being reduced to 140 ppm and 0.35% respectively. However, milling the soft 'toffee' was a problem which was never really overcome. One approach was to hot filter a solution of the 'toffee' in dichlorobenzene to remove the potassium chloride, followed by distillation of the two solvents. This proved unsuccessful due to the solubility of KCl in $DMSO_2$, resulting in 3% of the KCl remaining in the final polymer.

2.3.3.1.3 Other Solvents

A patent due to BASF describes the use of a number of polar aprotic solvents in the synthesis of PES using 'carbonate' chemistry (74). The solvents named include N,N'-dimethylformamide, N,N'-dimethyl acetamide, N-methylpyrrolidone, dimethylsulphoxide, dimethylsulphone, sulpholane and diphenylsulphone, with N-methylpyrrolidone being the preferred solvent.

2.3.3.2 Factors Affecting The 'Carbonate' Route To PES

There are a number of curious features of the 'carbonate' route which this thesis attempts to explain.

The first area for investigation is the staggered evolution of CO_2 which is formed as a by-product in the reaction of phenols to form phenates. The CO_2 is evolved in three distinct phases, and each phase must proceed to completion if PES of good quality is to be made. Also, precipitation of material from the reaction solvent, DPS, occurs. It is known that the bispotassium salt of Bis-S is insoluble in DPS, but it is not thought that this species is ever present in significant concentrations. Partial salts of Bis-S may thus be formed, although this had never been investigated.

Thus, both the mechanism and the kinetics of the formation of PES by the 'carbonate' route were not fully understood, and the purpose of this work was to shed some light on both aspects of the chemistry.

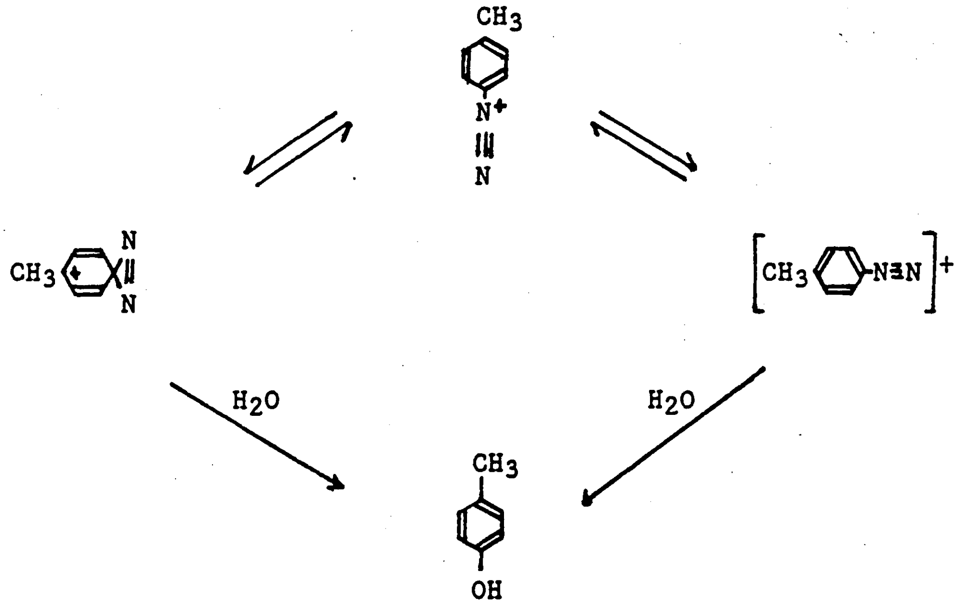
CHAPTER 3: NUCLEOPHILIC AROMATIC SUBSTITUTION REACTIONS AND PREVIOUS RELEVANT STUDIES TO PES KINETICS

3.1 Introduction

Synthesis of polyether sulphone by polyetherification is achieved via a nucleophilic aromatic substitution reaction. The first recorded reaction of this type was performed by Pisani in 1854, when he successfully displaced the chlorine group from picryl chloride to yield picramide and picric acid (75). There are four basic types of nucleophilic aromatic substitution.

3.1.1 The S_N1 Mechanism

The first type involves some form of S_N1 mechanism. Only a few of these reactions have been studied, and the best documented of these is the hydrolysis of diazonium salts, an example of which is the hydrolysis of the toluenediazonium salt. From various studies conducted on the mechanism, a postulated reaction scheme was constructed in terms of two intermediates, both of which still contained the two nitrogen atoms of the diazonium salt (76);



Evidence for the reaction proceeding via a unimolecular mechanism is on three counts (77). Firstly, the rate is unaffected by the identity or concentration of the anion of the diazonium salt (78). Secondly, the rate of reaction is virtually the same in D_2O as in H_2O (79) and finally, the kinetic effect of the aromatic substituents is completely different from bimolecular nucleophilic substitutions and can be readily understood on the basis of the unimolecular mechanism (79). Catalysis by copper (I) compounds also proceeds via an S_N1-like mechanism (80). The reactions are generally performed in aqueous solution and involve cuprous salt catalysed substitutions.

Other transition metal compounds have also been used, but the range of these reactions is smaller and the reaction conditions are more extreme. The absence of catalyst causes many of the systems to fail to react at all. A typical example is the halide displacement of the diazonium group. Without a catalyst, only the iodine reacts due to the kinetic nucleophilicity of the iodide ion in protic solvents being substantially greater than that of the other halides (76). With a cuprous salt, all the halides displace the diazonium group by a reaction mechanism that is still not fully understood. However, it has been shown that copper (I) complexes are formed with the aromatic substrate. This was illustrated in the study of the reaction between sodium trifluoroacetate and benzenoid or heterocyclic aromatic systems (81). In the presence of copper (I) iodide the trifluoromethyl group was shown to displace halogen. However, the addition of excess quantities of quinoline and iodide ions (both good ligands for copper) to the reaction involving iodobenzene yielded little product due to the formation of $[CuL_4]^+$ complexes.

3.1.2 The Radical Mechanism

The second mechanism involves a radical process (82). This mechanism has been postulated for the reaction of 5-iodo-1,2,4-trimethylbenzene with potassium amide in ammonia, which was found to be suppressed by the addition of radical scavengers. Nucleophilic aromatic substitutions occurring via this mechanism are termed $S_{RN}1$, and can be initiated either thermally (83), photochemically (84), electrochemically (85) or by solvated electrons.

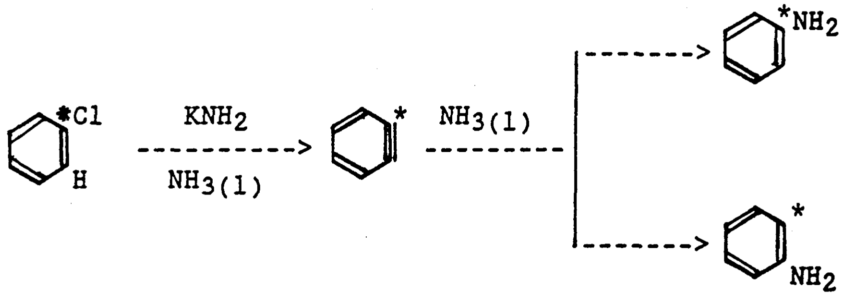
3.1.3 The S_N2 Mechanism

The vast majority of nucleophilic aromatic substitutions occur via a bimolecular, S_N2 mechanism. There are two distinct types of bimolecular mechanisms; the elimination-addition or benzyne mechanism, and the addition-elimination or activated mechanism.

3.1.3.1 The Benzyne Mechanism

Reactions involving the benzyne mechanism are generally catalysed by strong bases, and occur such that a proton ortho to the leaving group is eliminated, followed by the leaving group with its bonding electrons. The reaction proceeds via a benzyne intermediate, and thus substitution can occur either at the position previously occupied by the leaving group or ortho to it. An example of this type of mechanism is the reaction of chlorobenzene with amide ion in liquid ammonia to give aniline. Roberts (86-88) used chlorobenzene-1-^{14}C in this reaction, which yielded almost equal amounts of aniline-1-^{14}C and aniline-2-^{14}C.

The slight divergence from equality was ascribed to the small ^{12}C-^{14}C isotope effect on the symmetrical intermediate benzyne;

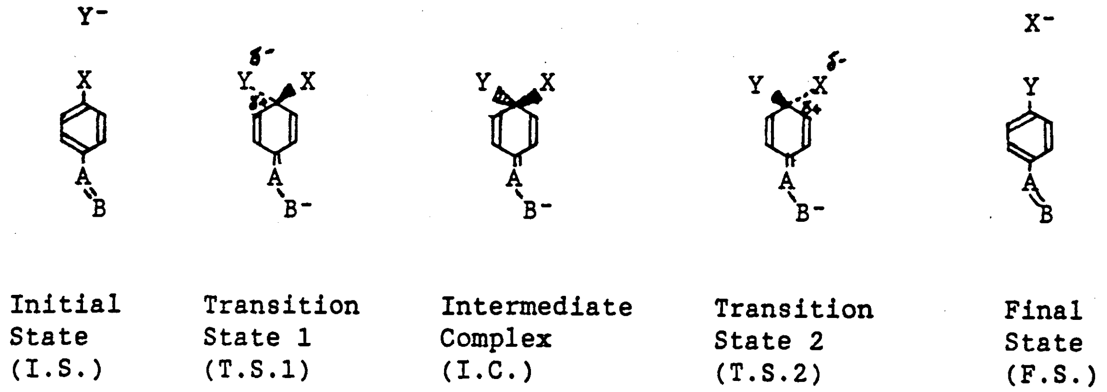


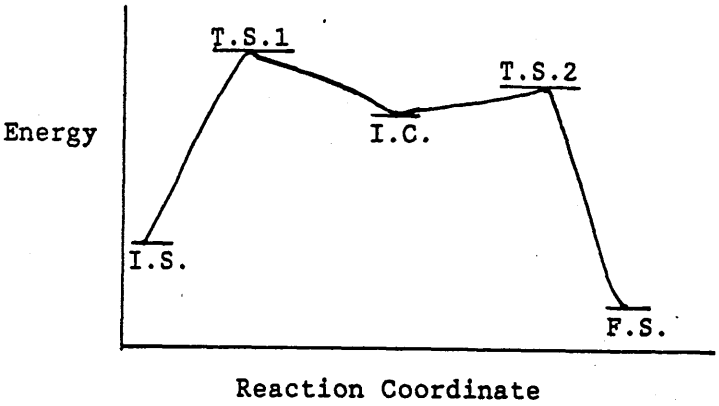
Thus the chloride is displaced prior to attack by the amide group, resulting in a two step, elimination-addition reaction mechanism. Further evidence for the mechanism came when it was found that compounds with no hydrogen atoms ortho to the leaving group were unreactive (88).

3.1.3.2 The Activated Mechanism

The most important mechanism with respect to this work is the activated or addition-elimination mechanism.

This reaction mechanism is predominant when there is a group readily replaceable with its bonding electrons at the point of substitution, as well as suitably placed electron withdrawing substituents (2- or 4-position) or ring hetero atoms (2- or 4- position) being present. The substituents help stabilise the transition state(s) and intermediate complex which are formed. These substitutions are overall second order when uncatalysed. A diagramatic representation of a typical reaction is shown below, showing the rate limiting step to be the formation of the first transition state (76);





Evidence for the first step being slow and thereby rate determining was the discovery that the reactivity of the halogens was in the order:

F >> Cl > Br > I

The carbon-fluorine bond is, however, the strongest and therefore the rupture of it cannot be in the rate determining step (89). However, Miller (76) showed that the above halogen order was correct only if the nucleophilic atom was from the first row of the periodic table. If the nucleophilic atom was from the second or higher rows, the mobility of the fluorine was reversed relative to the other halogens. This is due to the fact that for first row nucleophiles the main property of the replaceable group which affects its mobility is its electronegativity, whereas for heavier nucleophiles, additional factors such as strength of bond to the leaving group, its electron affinity and its heat of solvation as a displaced group are major considerations.

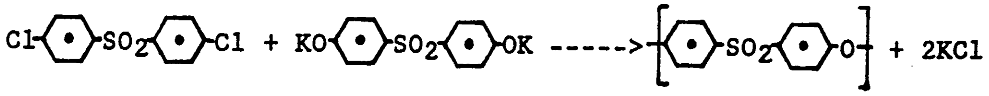
In the above scheme, the group AB needs to be electron withdrawing so that the group X is activated to nucleophilic displacement. The activating groups in S_NAr reactions must not contain an acidic proton, otherwise attack by phenoxide could deprotonate the group leading to deactivation (90). Useful activating groups include $-NO_2$, -CN, $-SO_2R$, etc. The presence of AB para to the leaving group provides the best results, as the presence of AB ortho to the leaving group may cause steric hindrance.

The stabilised intermediate complex is often referred to as the Meisenheimer complex, after the chemist who first isolated such species (91).

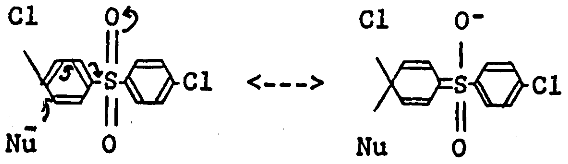
3.2 Mechanism With Respect To PES

Johnson et al, working for Union Carbide Corporation, were the first to report the synthesis of a high molecular weight polymer using the S_NAr mechanism, when they prepared an aromatic polyether using activated dihalo compounds with bisphenol salts (~~5~~10).

In ICI, production of PES moved away from the polysulphonylation process using Friedel-Crafts chemistry in favour of the more reproducible polyetherification system using S_NAr chemistry. As has already been discussed in this work, the 'carbonate' route was chosen which in its simplistic form is represented by;

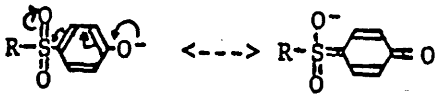


The presence of the electron withdrawing $-SO_2R$ group para to the activated halide leads to the smooth reaction due to the further stabilisation of the Meisenheimer complex, as the negative charge created on the ring is delocalised onto the sulphur oxygen(s) (92,93);



(Nu = Nucleophile)

However, with respect to the nucleophile, the more basic the phenolate (or the less acidic the phenol), the more reactive they are. Thus the presence of the $-SO_2R$ groups para to the phenolate oxygen reduces the reactivity (93);



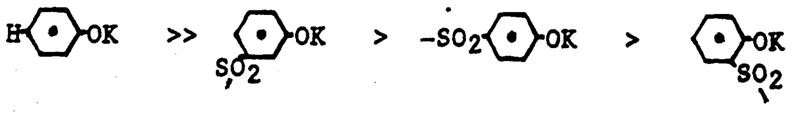
It is for this reason that Bis-A, with the electron donating $-CMe_2-$ group, is generally ~1000 times more reactive than Bis-S, with the electron withdrawing $-SO_2-$ group, towards 4-chlorodiphenyl sulphone (~~50~~1). Phenolate reactivity also depends on the alkali metal employed. Potassium salts are more reactive than sodium salts, due to the more electrovalent character of the O-K bond. Lithium, calcium and magnesium salts are not useful as they are insoluble in the solvents generally used (~~50~~1,94).

S_NAr reactions proceed readily in dipolar aprotic solvents (eg DMSO, DMF, DMAC, NMP). Anhydrous conditions are also required, and the greatest single factor governing solvent choice is the difficulty in dissolving the alkali metal bisphenolate under the anhydrous conditions. DMSO is the usual choice at moderate temperatures, but as the need for greater temperatures increases, solvents like DPS are used (95).

3.3 Previous Kinetic Studies Of Similar Systems

A number of studies into the kinetics of polyether sulphones have been undertaken by various workers, the first of which was by Schulze and Baron in 1968 (96). They found that when they polymerised a bisphenoxide with an activated dihaloaromatic compound, a higher rate of reaction was initially detected, indicating that the monomers were more reactive than the growing chain. They surmised that this was due to the highly unstable bisphenoxide monomer, where the proximity of the phenoxide salts promotes high reaction rate constants in the initial stages, with the more stable monophenoxide on the growing chain having a lower reaction rate constant.

The next study on PES kinetics was in 1972 when Newton and Rose discussed the relative reactivities of the functional group involved in the synthesis of PES from halogenated derivatives of diphenyl sulphone (93). Their study involved displacement of the halide by hydroxyl ion or phenoxide anion in DMSO or a DMSO/water mixture. They showed the order of halogen reactivity to be F>Cl~Br as was expected, with para isomers showing the greater reactivity and meta isomers showing rates of reaction comparable with the rate of sulphone bond fission. Phenolate reactivity was also found to vary in the order:



Newton and Rose found that there were two distinct effects which influenced the reactivity of the functional groups. The first were termed direct effects, when the substituent causing the effect was on the same ring as the reacting group, and the second were termed 'bridge' effects, where the substituents' influence was transmitted from an adjacent ring via the sulphone linkage.

Attwood studied the kinetics of PES as part of his Ph.D in 1972 (97). He considered the reaction of a number of different monomers in either DMSO or a DMSO/water mixture by using model systems to determine the variations in functional group reactivity due to the aforementioned 'bridge' effects.

An example of his findings was the fact that either of the two equivalent chlorines from 4,4'-dichlorodiphenyl sulphone was removed ~1.5 times faster than the single chlorine from 4-chlorodiphenyl sulphone. However, when the first chlorine had been replaced the second chlorine was removed over 30 times more slowly. These findings were attributed to the electronic effect of the chlorine in one ring being transmitted to the other via the sulphone bridge, ie the bridge effect.

Thus the halogen reactivity in one ring was enhanced by the para chloro substituent in the other, while the strongly electron donating phenoxide group in the salt of 4-chloro-4'-hydroxydiphenyl sulphone substantially reduced the halogen reactivity in the adjacent ring. Attwood went on to show that the effect of this was to cause markedly different initial rates of reaction depending on the monomer(s) chosen, such that the polymerisation of the potassium salt of 4-hydroxy-4'-fluorodiphenyl sulphone reached 95% reaction after ~460 minutes at 158°C in sulpholane, whereas the polymerisation between 4,4'-difluorodiphenylsulphone and the bispotassium salt of 4,4'-dihydroxydiphenyl sulphone reached 95% reaction under the same conditions in ~90 minutes.

In 1978, Shchori and McGrath described a spectrophotometric technique for determining the phenolic end group concentration in a variety of polymers including the polysulphone based on Bisphenol A (98). The technique was based on the fact that no distinct peak due to the phenolic end groups was seen in the UV absorbance spectrum of a solution of UDEL polysulphone in THF.

However, conversion of the phenolic groups to phenolates by the addition of a quaternary ammonium base caused a bathochromic shift in the absorption spectrum. The shift of 20-35nm in the absorption maxima allowed for the quantitative measurement of phenolic end groups in the polymer to be determined. The sensitivity of the technique was such that the workers estimated satisfactory accuracy up to M_n=200000.

In 1984, Yu et al also found that different rate constants were obtained depending on the monomers chosen (99). By discriminating between reactions between monomer/monomer, monomer/polymer and polymer/polymer, a set of multi-parameter kinetic equations was obtained which were in good agreement with experimental rate constants. DMSO was the reaction solvent and the chosen monomers were either the potassium salt of 4-chloro-4'-hydroxydiphenylsulphone or 4,4'-dichlorodiphenylsulphone and the bispotassium salt of 4,4'-dihydroxydiphenylsulphone.

Finally, Viswanathan, Johnson and McGrath published a paper in 1984 on the kinetics of polyethersulphones via the 'potassium carbonate/DMAC' process (100). A number of polyethersulphones were prepared by reacting 4,4'-dichlorodiphenylsulphone with a variety of bisphenoxides. Potassium carbonate was used as the base and dimethyl acetamide was used as the polymerisation solvent. In this system, excess potassium carbonate, unlike aqueous caustic, does not prevent the synthesis of high molecular weight polymer. It was observed that the system deviated from the expected simple second order kinetics usually found in S_NAr reactions. The apparent order of the reaction varied from 0.85 to 1.35, depending on the initial concentration of monomers used.

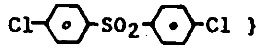
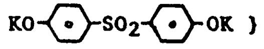
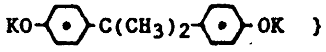
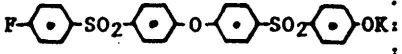
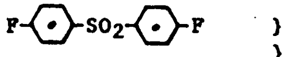
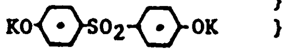
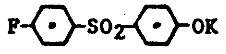
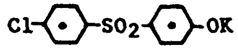
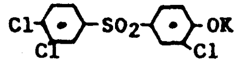
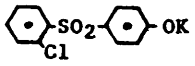
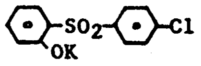
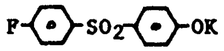
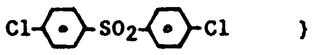
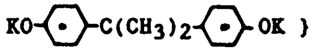
The use of model compounds again failed to produce the expected second order plot. Thus it was reasoned that the reactive species were present in nonstoichiometric amounts. This was thought to be due to either the incomplete formation of the phenoxide caused by the poor solubility of the base under the reaction conditions or the insolubility of the bisphenoxide formed, or both.

One would expect that the cation solvating power of DMAC would lead to a greater solubility of the bisphenate, but the presence of toluene as the azeotrope would undoubtedly reduce the solubility of the base.

3.3.1 Comparison of Data from Previous Studies

Table 2 compares the results generated by these previous studies against each other in terms of monomers, solvents and temperatures employed and either the calculated initial rate constants, or the time taken to achieve 50% reaction ($t_{\frac{1}{2}}$).

Table 2: Comparison of Data from Previous Work

REF.	MONOMERS	SOLVENT	TEMP (°C)	INITIAL RATE CONSTANT ($lmol^{-1}sec^{-1}$)	50% REACTION $t_{\frac{1}{2}}$ (Mins)
WU et al (99)	 	DMSO	120	16.4 x 10^{-5}	
VISWANA-THAN et al (100)	 	DMAC	140 150 157		130 45 25
ATTWOOD & NEWTON (97)		Sulpholane	158		70
	 	"	"		60
		"	"		330
NEWTON & ROSE (93)		DMSO	178		200
		"	"		375
		"	"		960 (40% reaction)
		"	"		960 (10% reaction)
		"	120		230
SHULTZE & BARON (96)	 	DMSO	80 90.1 100	4.67 x 10^{-3} 7.17 x 10^{-3} 12.5 x 10^{-3}	

CHAPTER 4: KINETIC INVESTIGATION USING FOURIER TRANSFORM INFRA-RED (FTIR) SPECTROSCOPY

4.1 Introduction

The kinetics of the polymerisation reaction to form PES were investigated by the use of FTIR spectroscopy. The technique involved monitoring the formation or disappearance of infra-red active groups, against a reference which remained unchanged during the polymerisation. The polymerisation route studied was the reaction between DCDPS and the bispotassium salt of Bis-S. Most of the work was based on the melt polymerisation between the two monomers mentioned, although one experiment was undertaken where the solution polymerisation was studied by adding DPS. Computer programs were developed to automate the IR scanning of the process as the polycondensation proceeded.

Three computer programs were also written to study certain kinetic parameters during the polymerisation of DCDPS and the bispotassium salt of Bis-S. The first program, 'AUTOTIME', was an 'obey' program which worked from the IR spectrometer operating system. In this, the commands normally used in obtaining and manipulating IR spectra were valid program commands. The 'obey' program recorded a spectrum and saved it with an identification that was a reading of the computer clock. The program then determined the absorbance at two specified frequencies on the spectrum.

The first frequency was the position of the peak which varied during the polymerisation. This was initially chosen to be the peak due to the carbon-chlorine stretching mode at ~732cm^{-1}, which gradually disappeared on polymerisation as the activated aryl halogen was displaced by the phenate ion during nucleophilic aromatic substitution. The second frequency was the position of the reference peak which remained unchanged during the reaction. The sulphone stretching frequency at ~1156cm^{-1} was used for this purpose. It was found possible to study the growth of the aryl ether band at ~1246cm^{-1} as well as the disappearance of the carbon-chlorine band at ~732cm^{-1}. This was useful due to the fact that C-Cl groups could still be present at the end of the reaction, which could therefore lead to irreproducible results being generated. Therefore, on completion of the experiment, another program was activated to calculate the ratio of the aryl ether band to the reference band. The ratio of the two peaks was calculated and 'AUTOTIME' then sent this ratio and the time to the second computer program.

The second computer program was a graphics routine written in BASIC, and plotted a graph of ratio against time for the duration of the experiment (Graph 1 for ~732cm^{-1} sample peak; Graph 3 for ~1246 cm^{-1} sample peak). When the specified number of spectra had been recorded, the data was sent to the third computer program.

This last program calculated the rate constant from the data that had been generated by the previous two programs.

It was written in BASIC and plotted a graph of ln(ratio) against time, and calculated the rate constant using a weighted least squares routine tailored for kinetic studies, which took less account of the points towards the end of the reaction, where the rate would be decreasing (Graph 2 for ~732 cm^{-1} sample peak; Graph 4 for ~1246 cm^{-1} sample peak). The error in the rate constant was also calculated using the weighted least squares routine. A pseudo first order reaction was assumed due to the insolubility of the bisphenate in DCDPS, and the fact that at the temperatures used DCDPS would have been molten, but the bisphenate would still have been solid.

4.2 Method

The experimental procedure was to weigh equimolar quantities of the two monomers to four decimal places (~40 mg). These were then mixed with ~2.25 g potassium bromide (KBr), also accurately weighed. The whole was manually ground to ensure complete mixing and was then compressed with 12 lbs pressure to form a 'KBr disc'. This was placed in a hot cell capable of maintaining the temperature of the disc at 250°C. An atmosphere of nitrogen was passed over the cell and an initial spectrum was recorded as the cell was reaching the target temperature. Under control of 'AUTOTIME', a spectrum was then recorded every five minutes and calculations made as previously discussed.

4.3 Results

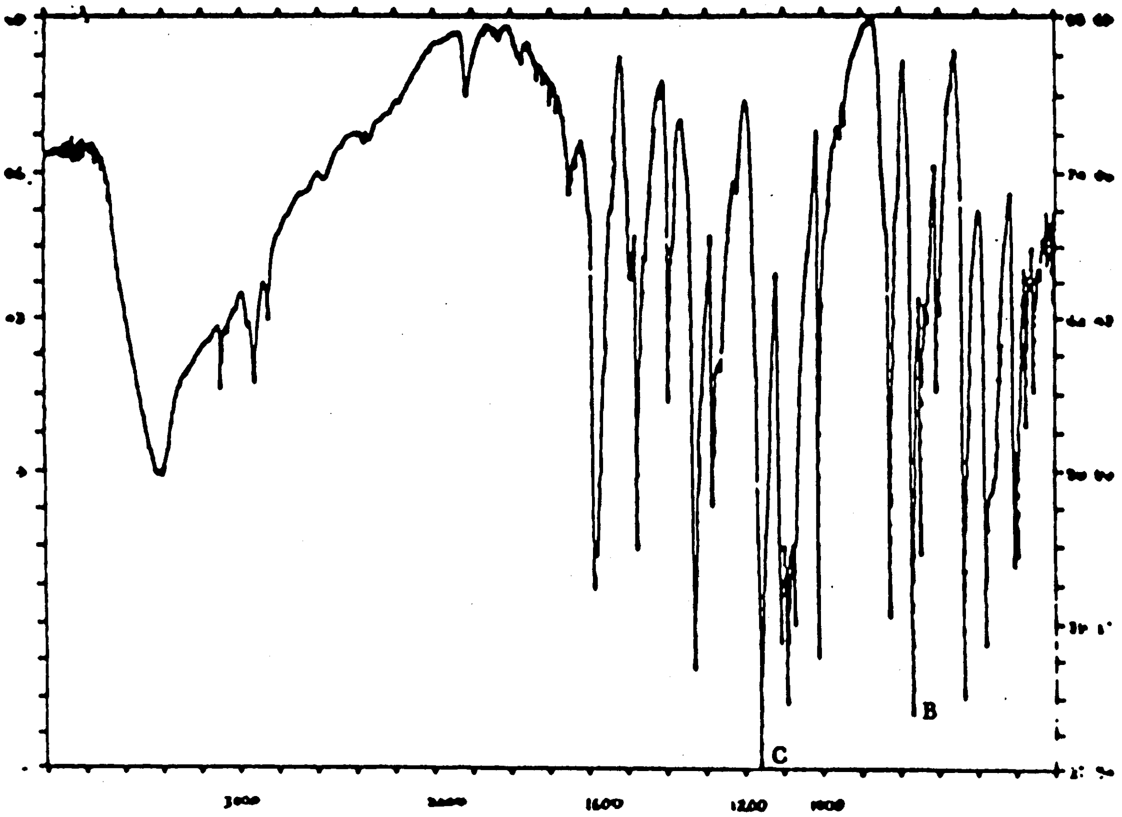
Initial and final spectra (Spectra 1,2) for a typical run are shown, and in each case the formation and growth of the aryl ether band (A), the decrease in the carbon-chlorine band (B), and the reference band due to the sulphone group (C) are indicated.

From the graphs of ratio (sample peak:reference peak) against time (Graphs 1 & 3), kinetic plots of ln (ratio) against time were drawn (Graphs 2 & 4). This gave graphs which approximated to linearity, which was expected from the assumption that the reaction followed pseudo first order kinetics. From these graphs the following results were obtained;

Table 3: Results for FTIR Kinetics

File Name + Temp. (°C)	Sample Peak (cm^{-1})	Reference Peak (cm^{-1})	Rate Constant k: $*10^{-4}$(s^{-1})	Error $*10^{-6}$ (s^{-1})	lnk	1/T $*10^{-3}$ (°K^{-1})
AT 250	731	1157	2.9516	8.2	-8.128	1.912
AT 250	1240	1157	3.2907	20.0	-8.018	1.912
AT 240	732	1157	1.7600	5.5	-8.644	1.949
AT 240	1243	1156	2.6422	9.0	-8.523	1.949
AT 230	732	1157	1.1220	2.8	-9.093	1.988
AT 230	1246	1156	1.1397	1.5	-9.078	1.988
AR 250*	1242	1157	1.4840	5.1	-8.816	1.912

Spectrum 1: Initial Spectrum Of Polymerisation Studied By FTIR



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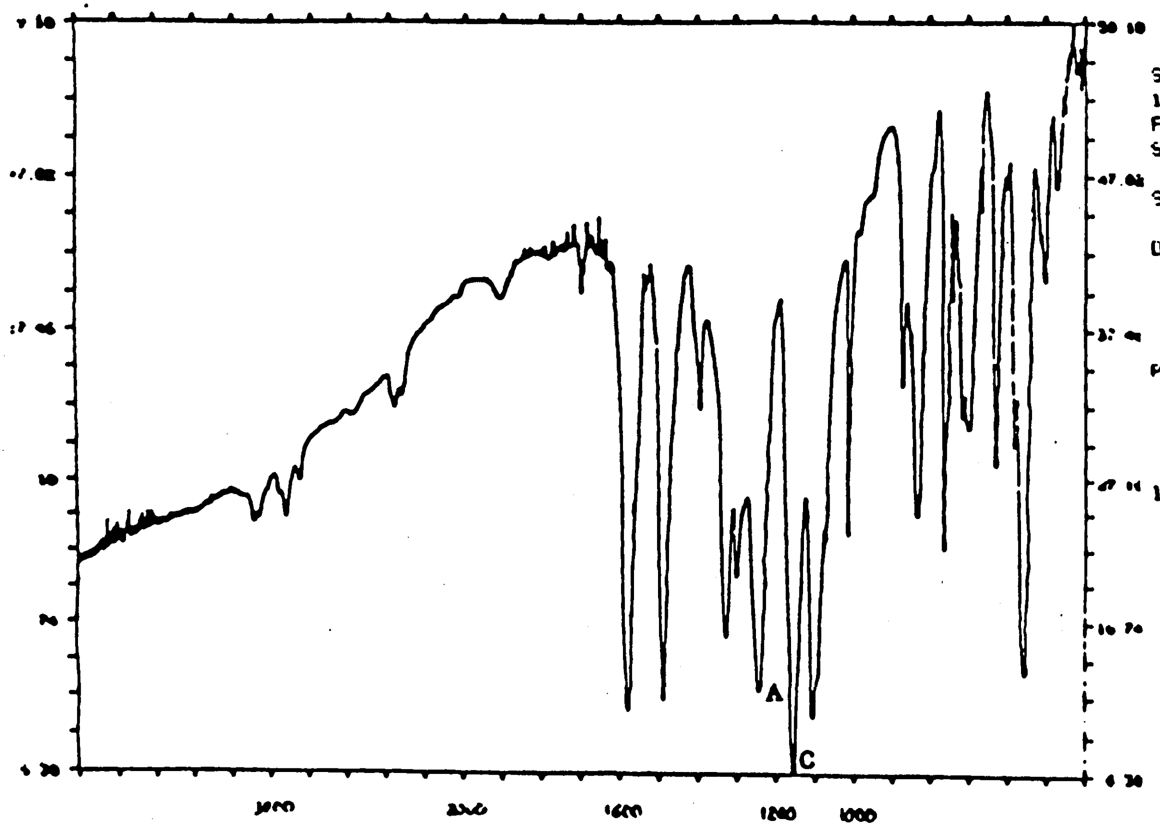
PERKIN-ELMER MODEL 1700                   SPECTRUM NUMBER: 2
                                          OPERATOR: ABT
STATUS: 3601 4000   -   400     1.00      27.54    85 71 T
00.602
FILID:   ST001                            DATE: 29-5-86
SAMPLE: INITIAL SPECTRUM OF [illegible]/FULL SALT
          RUN AT [illegible]
SAMPLE PREPARATION:   KBr DISC            SAMPLE THICKNESS:-

DATA PROCESSING:
  ABEX:          0.00                     DIFFERENCE:
  SMOOTH:  0                              FLAT:
  ENHANCE:       0.00      0.00           OTHERS:

PLOT PARAMETERS:
  ABSCISSA EXPANSION:      0.50           PLOT RANGE:  4000.00 -  400
  ORDINATE SCALE:     1 72                ORDINATE OFFSET:     27 54
  OTHERS:

INSTRUMENT PARAMETERS:
  SAMPLE
  NUMBER OF SCANS: 1
  RESOLUTION:    2.00                     APODIZATION: MEDIUM
  PHASE CORRECTION: SELF                  REAL
  ACQUIRE MODE: INTERLEAVED               GAIN: 1
  JACQUINOT STOP: 2                       SCAN SPEED 0.250
  DETECTOR: TGS
```

Spectrum 2: Final Spectrum Of Polymerisation Studied By FTIR



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PERKIN-ELMER MODEL 1700                         SPECTRUM NUMBER: 4
                                                OPERATOR: AGT
STATUS: 3601 4000    -   400      1.00      6.38    58.20 T
12.197
FILID:  ST148                                   DATE: 27-5-86
SAMPLE: Final spectrum of DCPE/full salt
        poly at 240°c
SAMPLE PREPARATION: KBr Disc                    SAMPLE THICKNESS: -

DATA PROCESSING:
  ABEX:          0.00                           DIFFERENCE:
  SMOUTH:  6                                    FLAT:
  ENHANCE:       0.00      0 00                 OTHERS:

PLOT PARAMETERS:
  ABSCISSA EXPANSION:      0.50                 PLOT RANGE:  4000.00 -
  ORDINATE SCALE:      1.93                     ORDINATE OFFSET:
  OTHERS:

INSTRUMENT PARAMETERS:
  SAMPLE          :
  NUMBER OF SCANS: 1
  RESOLUTION:    2.00                           APODIZATION: MEDIUM
  PHASE CORRECTION: SELF                        REAL
  ACQUIRE MODE: INTERLEAVED                     GAIN: 1
  JACQUINOT STOP: 2                             SCAN SPEED 0.250
  DETECTOR: TGS
```
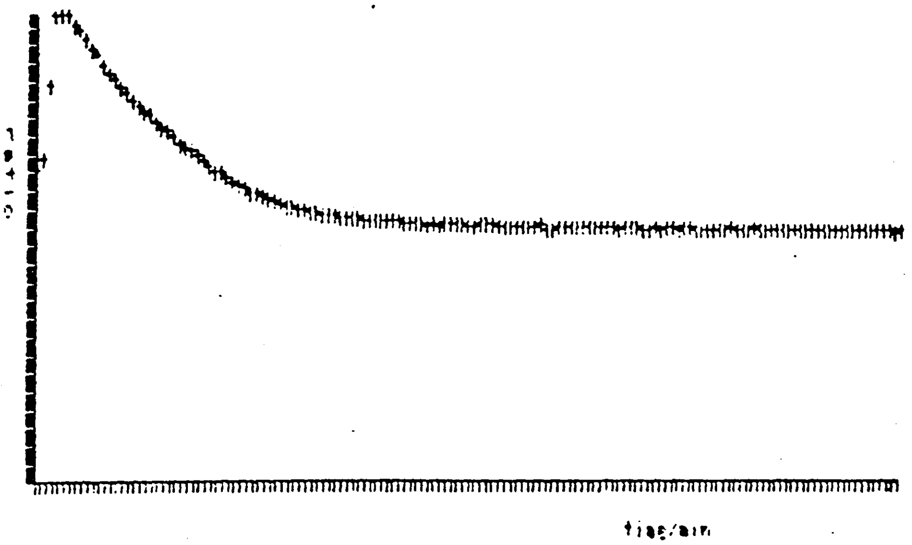
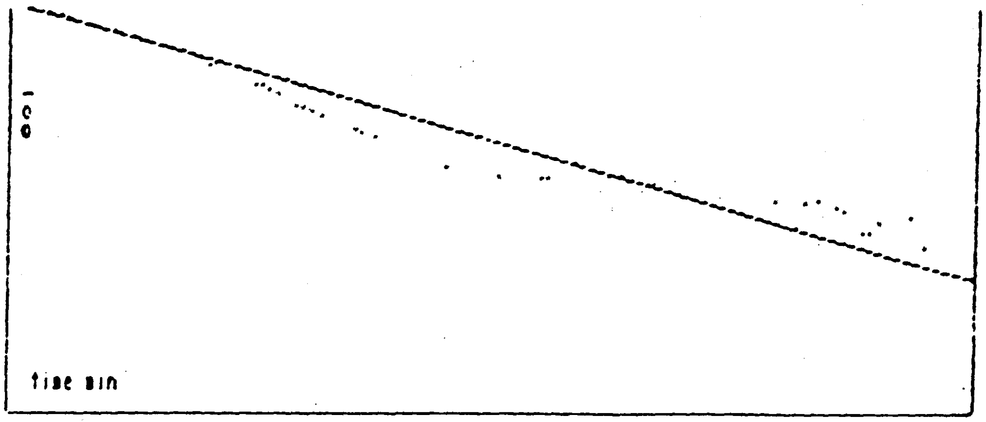

```
*
*
File Name: st (240deg)
*
*
Sample Peak: 732 cm-1
Reference peak: 1157 cm-1
*
*
rate constant: 0.010565 min-1 (dev: 0.000331)
*
```

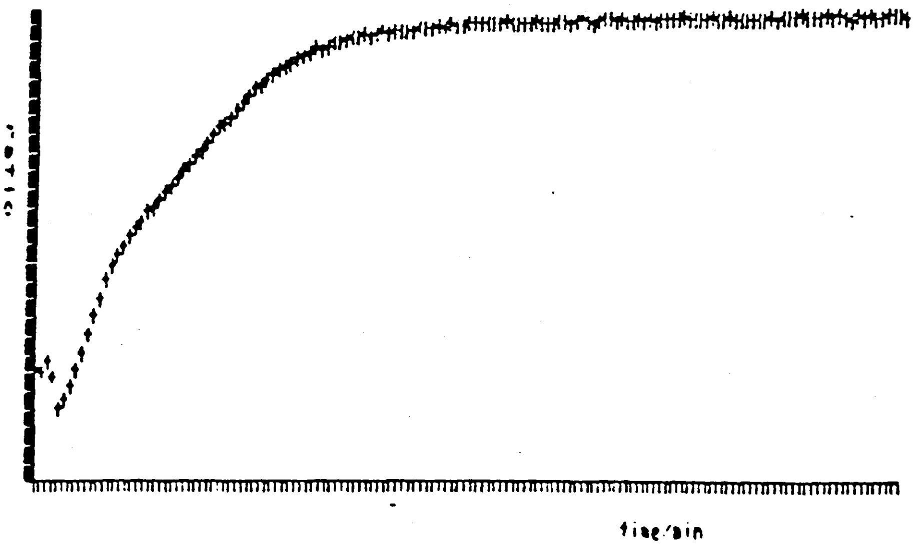


Graph 1: Ratio Of Sample/Reference Peak v. Time For 732cm-1 Peak

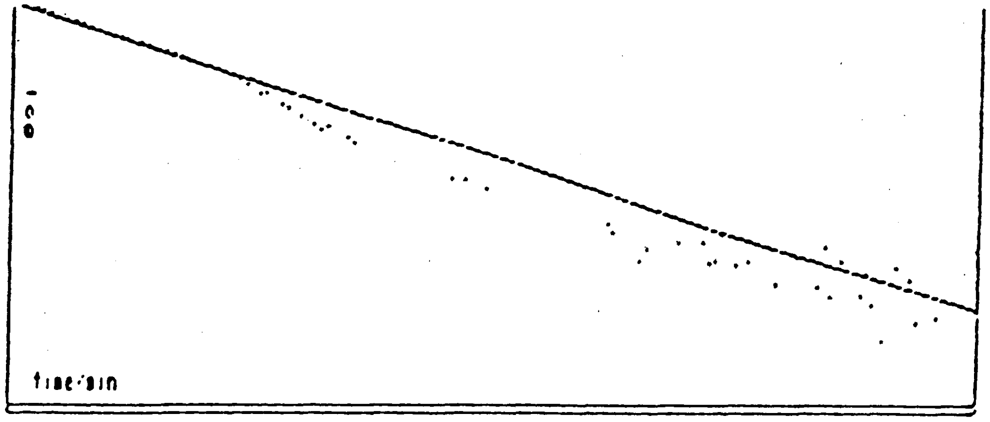


Graph 2: log(Ratio) v. Time For 732cm-1 Peak

```
*
file name: st (240deg)
*
*
sample peak: 1243 cm-1
reference peak: 1156 cm-1
*
*
rate constant: 0.015853 min-1 (dev: 0.000541)
*
*
```



Graph 3: Ratio Of Sample/Reference Peak v. Time For 1246cm-1 Peak



Graph 4: log(Ratio) v. Time For 1246cm-1 Peak

Arrhenius plots to determine the activation energy of this reaction were drawn for each sample peak. The following results were calculated from a regression analysis, with the error being estimated from the standard error of the coefficient.

For Sample Peak ~732 cm^{-1} (Graph 5)

$$dy/dx = -Ea/R \qquad R = \text{Gas Constant}$$

$$\Rightarrow \quad -12603.1 = -Ea/8.314$$

$$\Rightarrow \quad Ea = 104782.2 \text{ Jmol}^{-1}$$

$$= 104.8 \pm 5.9 \text{ kJmol}^{-1}$$

For Sample Peak ~1246 cm^{-1} (Graph 6)

$$dy/dx = -Ea/R \qquad R = \text{Gas Constant}$$

$$\Rightarrow \quad -13858.5 = Ea/8.314$$

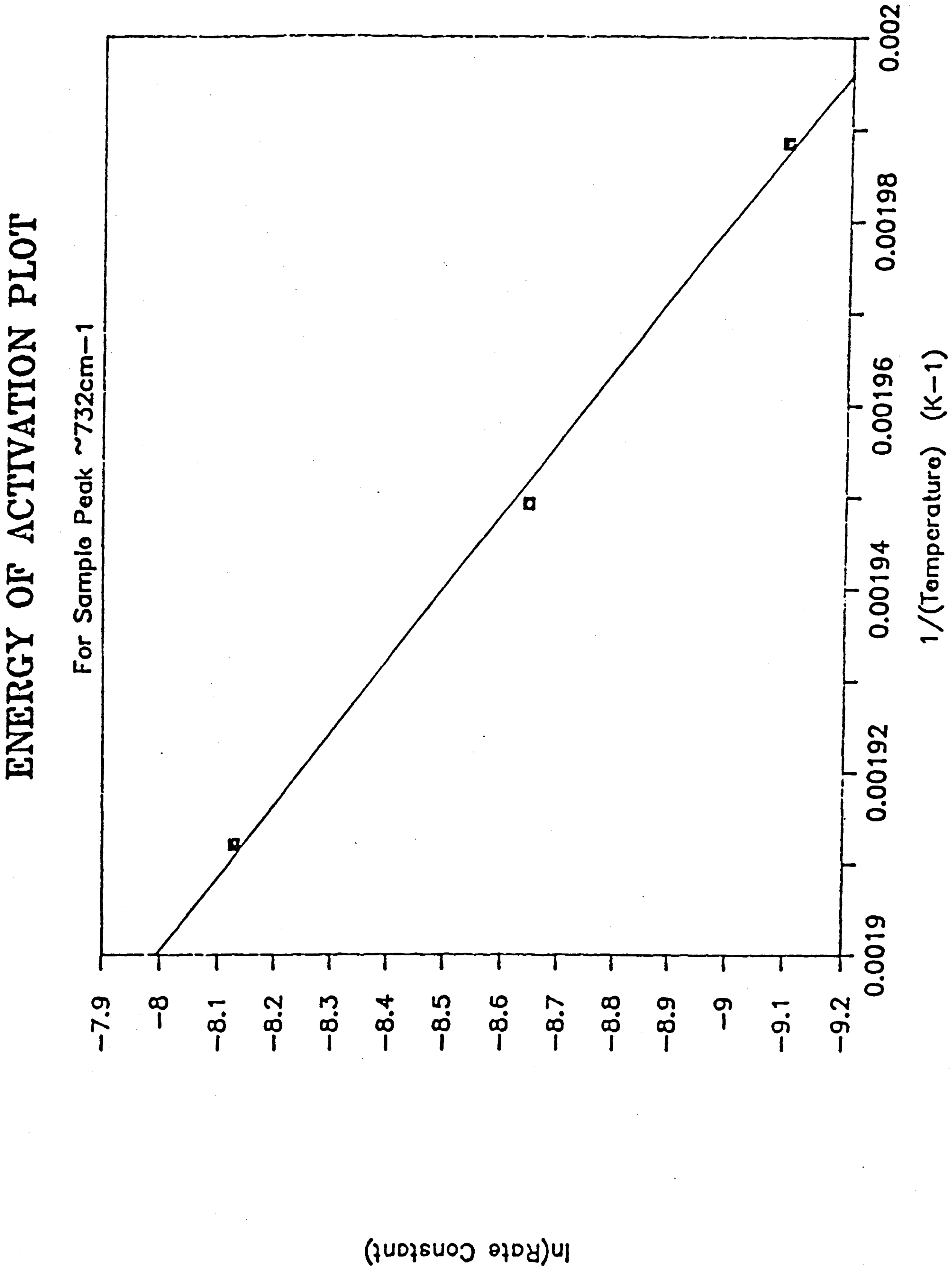
$$\Rightarrow \quad Ea = 115219.6 \text{ Jmol}^{-1}$$

$$= 115.2 \pm 1.2 \text{ kJmol}^{-1}$$

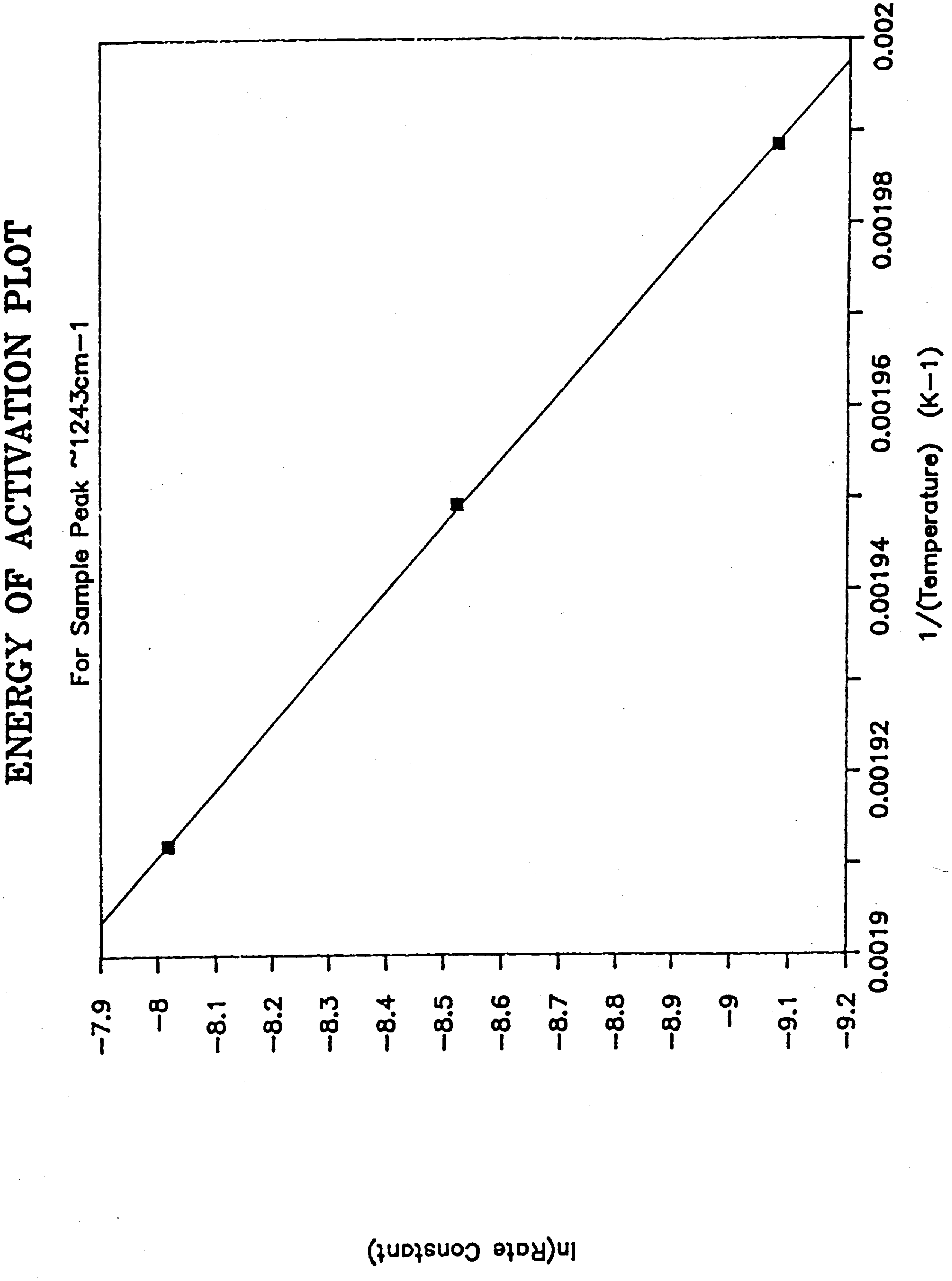
Therefore, the activation energy for the bulk polymerisation between DCDPS and the bispotassium salt of Bis-S was found to be much the same irrespective of which sample peak was monitored, the value being ~110 kJmol^{-1}. The closeness of the activation energies was encouraging. That they are not a closer fit is probably due to the different techniques used. Of the two approaches, the study of the formation of the aryl ether band is probably more accurate, due to the fact that a significant amount of carbon-chlorine groups could still be present at the end of the reaction if equimolar amounts of monomer were not present.

One experiment (AR 250 *) was also undertaken with the two monomers and DPS as polymerisation solvent.

Graph 5: Energy Of Activation Plot For 732cm-1 Peak



Graph 6: Energy Of Activation Plot For 1246cm-1 Peak



A temperature of 250°C was set, but this proved to be higher than required as the reaction was virtually complete before the cell had reached equilibrium temperature.

4.4 Discussion

Although the results from the kinetic investigation using FTIR were encouraging, the project was taken no further because the process was far removed from the 'carbonate' process under study. The major difference was that the melt reaction was being studied, rather than the solution reaction using DPS, and that the kinetics of the dimer formation rather than the polymerisation were being studied. Also, although a second order reaction is expected for this type of process, the actual order was almost certainly pseudo first order. This is due to the fact that DCDPS melts at 148°C, whereas the bispotassium salt of Bis-S is virtually insoluble in DCDPS and is stable to heat to at least 250°C, and thus the reaction studied was almost certainly one where the concentration of DCDPS in the melt was magnitudes greater than that of the bisphenate. Also, the graphs of ln (ratio) against time approximated to linearity, thus showing further evidence of pseudo first order kinetics.

Exact mass measurements could not be made due to the way in which the discs were formed, and so all concentration measurements were based on arbitrary values, although only relative concentrations are required to determine first order kinetics.

The solubility of the bisphenate in DCDPS would have increased with temperature, and thus the increase in rate of reaction with increasing temperature would not solely be a function of increasing thermal energy.

CHAPTER 5: KINETIC INVESTIGATION USING VISCOSITY MEASUREMENTS

5.1 Introduction

A preliminary investigation into the polymerisation of PES was conducted using the changing viscosity of the medium to determine the increase in polymer chain length. A Mark-Houwink equation was used which had been developed for PES polymers, relating the reduced viscosity (RV) of the polymer and the degree of the polymerisation (DP). This was used to determine the extent of reaction and consequently the activation energy of the polymerisation. The system used was an adapted laboratory polymerisation with the two monomers in equimolar amounts and a 2% molar excess of potassium carbonate. A small range of polymerisation temperatures was studied.

5.2 Method

A normal laboratory polymerisation was set up in the usual way and the standard procedure was adopted until the end of the 225°C hold. The temperature was then rapidly increased to the selected polymerisation temperature, ignoring the usual 265°C hold.

Samples were taken at regular intervals and the Reduced Viscosity (RV) of each was calculated by determining the time taken for a 1% w/v solution of the polymer to flow through an Ostwald Type A viscometer. To calculate the degree of polymerisation (DP) at a particular RV, an empirical relationship was used (101). This took the form of a Mark-Houwink equation, which related the DP (cf. molecular weight) to the RV (cf. intrinsic viscosity) of the polymer;

Mark-Houwink Equation: $[\mu] = KM^{a}$

Empirical Equation: $DP = 292RV^{1.508}$

A limitation of this empirical equation was that the constants K and a are fixed for a particular solvent/polymer pair at a fixed temperature. In this kinetic study a range of temperatures was studied. Also, the Mark-Houwink equation is only valid for polymers with the same molecular weight distribution, and as the rate of reaction was recorded at certain extents of reaction (p), the distribution was assumed to be constant. A graph of 1-(1/DP), (p), against time was plotted and from this, it was possible to draw a kinetic plot of ln (rate of change of p) versus reciprocal absolute temperature.

5.3 Results

a) Rate of Reaction at $p = 0.95$ (DP = 20, RV = 0.169)

Table 4: Results for $p = 0.95$

Temp. (°C)	1/(Temp) ($*10^{-3}$ $°K^{-1}$)	Increase in p ($k *10^{-5}$ sec^{-1})	lnk
255.0	1.8939	1.6834	-10.9921
261.0	1.8727	2.2059	-10.7218
266.0	1.8553	2.5925	-10.5603

From a plot of lnk against reciprocal temperature (Graph 7), a value for the activation energy for the polymerisation was determined for $p = 0.95$;

$$dx/dy = -11243.0$$

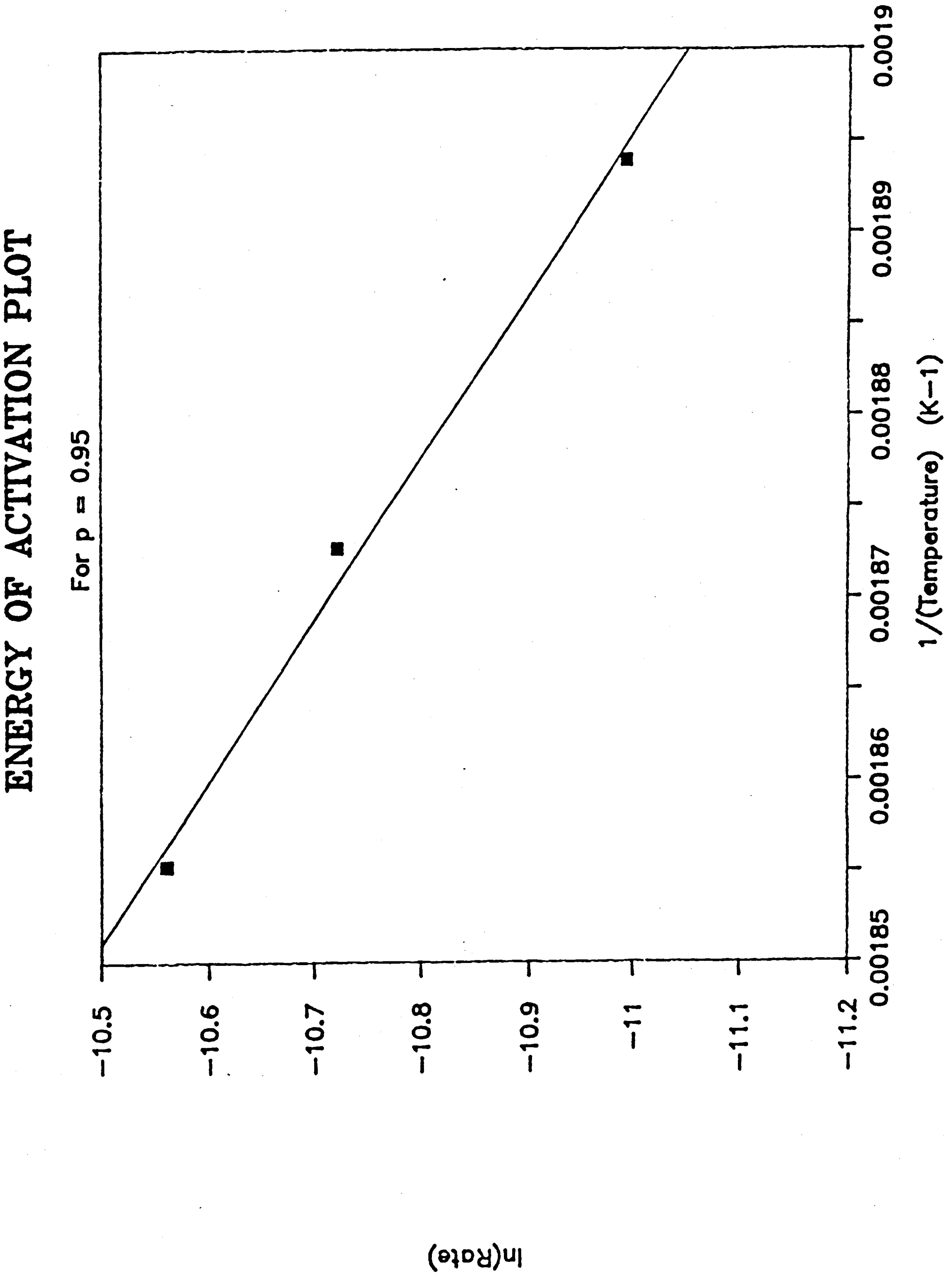
$$\Rightarrow \quad -Ea/R = -11243.0 \qquad R = \text{Gas Constant}$$

$$\Rightarrow \quad Ea = 93474.3 \text{ Jmol}^{-1}$$

$$\Rightarrow \quad = 93.5 \text{ kJmol}^{-1}$$

Therefore, the activation energy for the polymerisation between the two monomers was found to be 93.5 +/- 8.2 kJmol^{-1} (from regression analysis) for $p = 0.95$.

Graph 7: Energy Of Activation Plot For p = 0.95



b) Rate of Reaction at $p = 0.96$ (DP = 25, RV = 0.196)

Table 5: Results for $p = 0.96$

Temp. (°C)	1/(Temp) ($*10^{-3}$ °K^{-1})	Increase in p (k $*10^{-5}$ sec^{-1})	lnk
255.0	1.8939	1.3900	-11.1840
261.0	1.8727	1.5957	-11.0460
266.0	1.8553	2.1290	-10.7570
287.0	1.7857	3.6952	-10.2060

From a plot of lnk against reciprocal temperature (Graph 8), a value for the activation energy for the polymerisation was determined for $p = 0.96$;

$$dx/dy = -9167.8$$

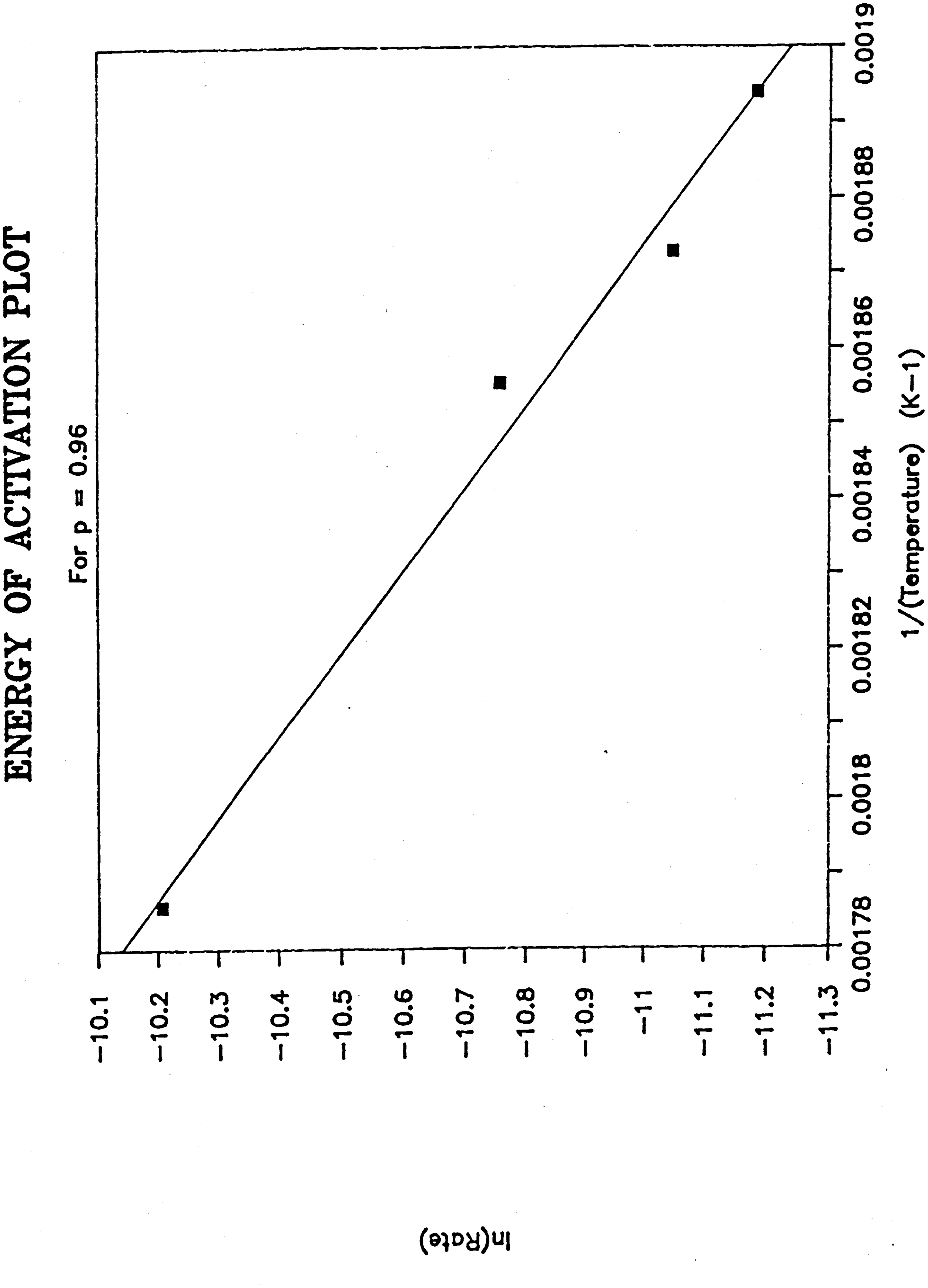
$$\Rightarrow \quad -Ea/R = -9167.8 \qquad R = \text{Gas Constant}$$

$$\Rightarrow \quad Ea = 76221.1\ Jmol^{-1}$$

$$\Rightarrow \quad = 76.2\ kJmol^{-1}$$

Therefore, the activation energy for the polymerisation between the two monomers was found to be 76.2 +/- 6.8 $kJmol^{-1}$ (from regression analysis) for $p = 0.96$.

Graph 8: Energy Of Activation Plot For p = 0.96



c) Rate of Reaction at p = 0.98 (DP = 50, RV = 0.310)

Table 6: Results for p = 0.98

Temp (°C)	1/Temp $(*10^{-3}{}^{\circ}K^{-1})$	Increase in p $(k *10^{-5} sec^{-1})$	lnk
261	1.8727	0.9750	-11.5382
266	1.8553	1.0050	-11.5079
287	1.7857	1.2185	-11.3153

From a plot of lnk against reciprocal temperature (Graph 9), a value for the activation energy for the polymerisation was determined for p = 0.98;

$$dx/dy = -2620.7$$

$$\Rightarrow \quad -Ea/R = -2620.7 \qquad R = \text{Gas Constant}$$

$$\Rightarrow \quad Ea = 21788.5 \text{ Jmol}^{-1}$$

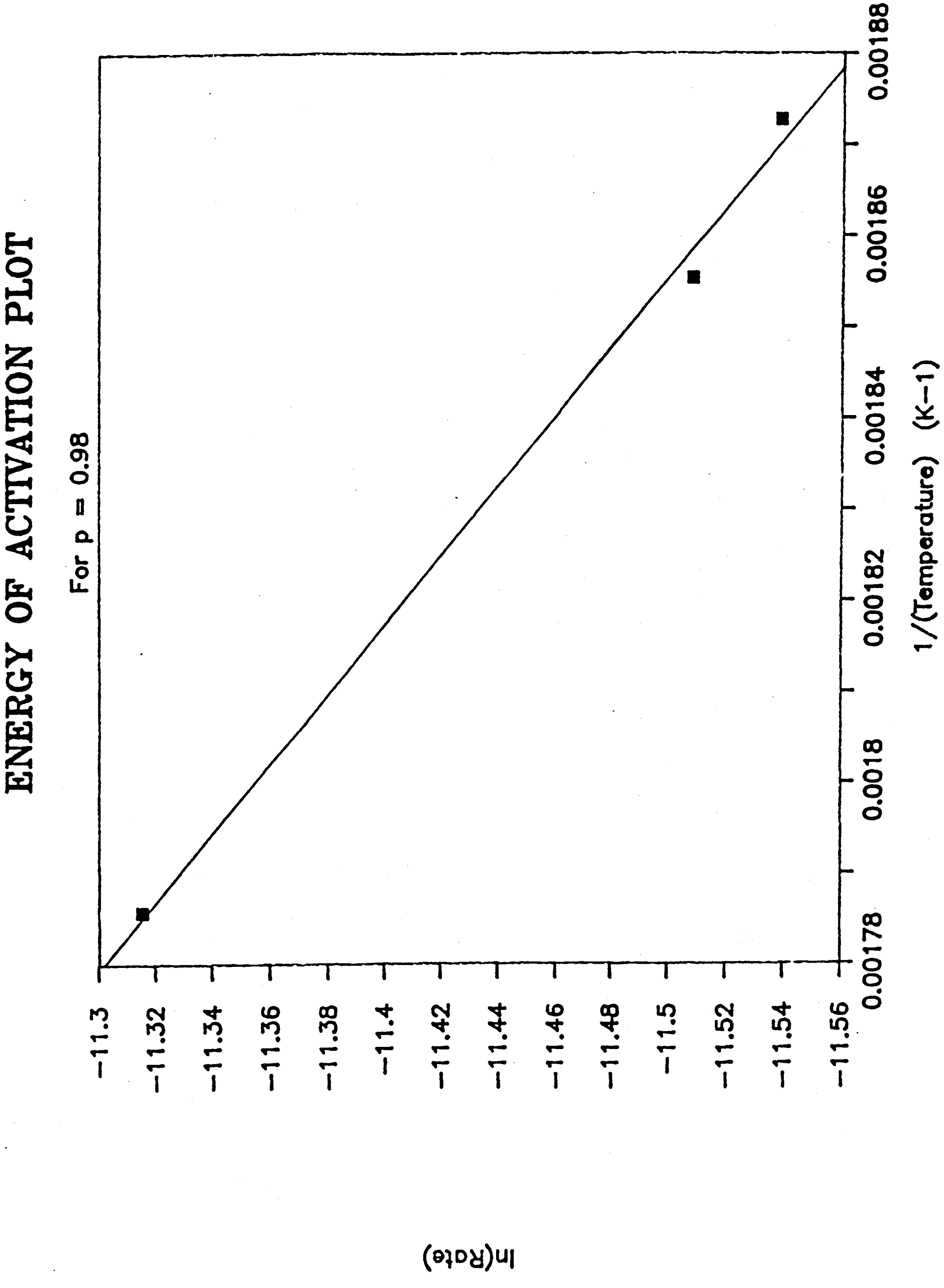
$$\Rightarrow \quad = 21.8 \text{ kJmol}^{-1}$$

Therefore, the activation energy for the polymerisation between the two monomers was found to be 21.8 +/- 1.4 kJmol^{-1} (from regression analysis) for p = 0.98.

5.4 Discussion

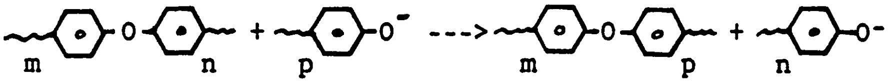
The activation energy for the polymerisation was found to decrease from 93.5 to 21.8 kJmol^{-1} as the extent of reaction increased from p = 0.95 to p = 0.98.

Graph 9 : Energy Of Activation Plot For p = 0.98



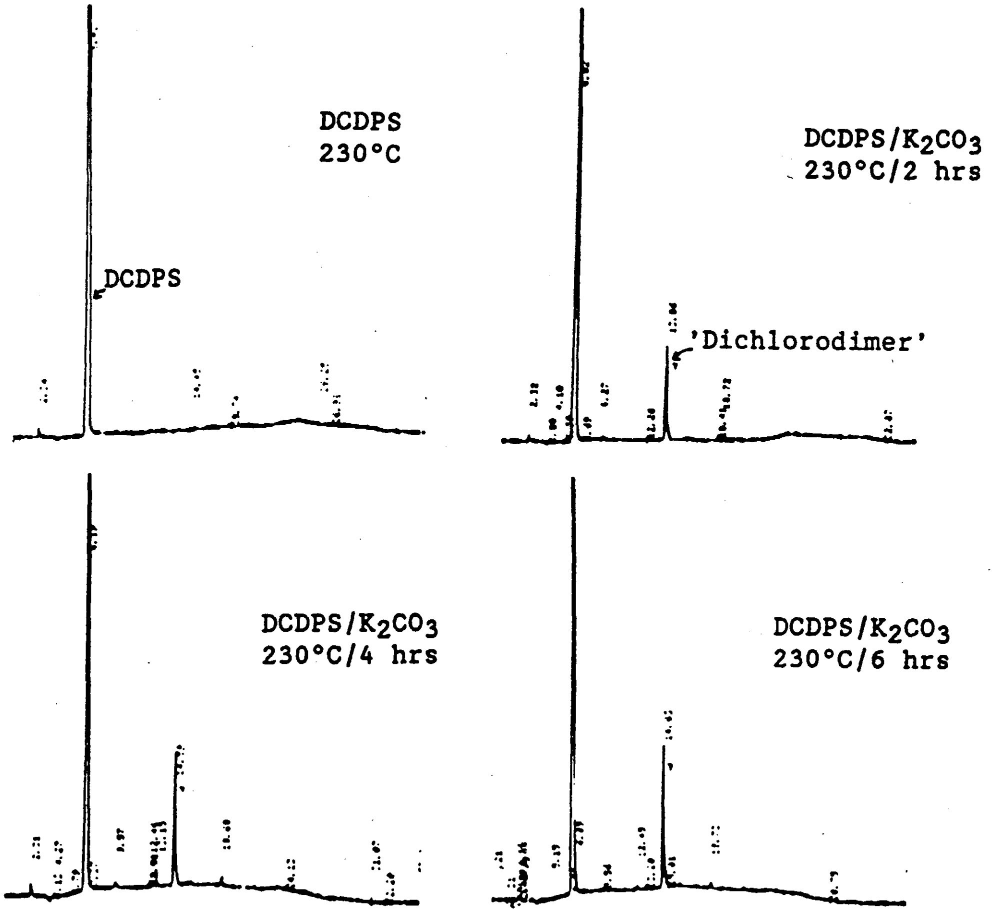
This would suggest that as the polymerisation proceeds, the rate of reaction moves from being kinetically controlled to being diffusion controlled. The value of 93.5 $kJmol^{-1}$ at $p = 0.95$ shows reasonable agreement with other work (see Chapter 6) which suggests that at this point in the reaction, the rate is limited by kinetic factors. However, as the reaction proceeds further, the activation energy decreases to a value of 21.8 $kJmol^{-1}$ at $p = 0.98$. This low value indicates that the reaction rate is now limited by diffusion factors. M_c is defined as the molecular weight at which chain entanglement can occur, and it is also an indication of when a polymerisation becomes diffusion rather than kinetically controlled. From previous work done on PES polymerisations (102), M_c has been calculated to be at $RV = 0.35$, or an extent of reaction of $p = 0.983$. This is in good agreement with the current study, as a lower activation energy would be expected for a system totally controlled by diffusion factors, and a gradual shift from kinetic to diffusion control is observed as M_c is approached.

The method was not further investigated as there were a number of problems associated with the reliability of the data. One of the main problems of the process was that there was more than one reaction occurring at any one time, making absolute kinetic measurements difficult. The main competing reaction which has been identified is that of the cleaving reaction between a phenate and the activated aryl ether on the polymer chain;



This leads to error immediately, as it is the exact reverse of the polymerisation procedure and thus affects the true rate of viscosity increase. As well as affecting the degree of polymerisation (DP), it also affects the molecular weight distribution, and the empirical relationship between RV and DP is only valid if the molecular weight distribution is the same each time.

Also, DCDPS has been shown to react slowly in the presence of potassium carbonate to form the 'dichlorodimer', as can be seen from the following HPLC traces (for reference see Chapter 8, Section 8.3.1);

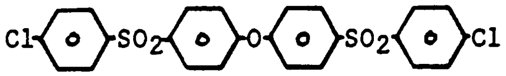


Thus this method of kinetic investigation is of limited value, although it is encouraging that the initial activation energy calculated by this method shows reasonable agreement with that calculated by other techniques.

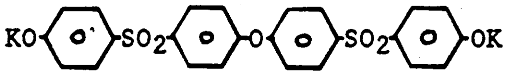
CHAPTER 6: KINETIC INVESTIGATION USING MODEL COMPOUNDS

6.1 Introduction

The use of model compounds formed the main study of the kinetics of the PES polymerisation process. Model compound studies enabled the reaction between a phenate and an activated aryl halogen to be determined without being masked by such effects as heterogeneity of the system and the varying reactivity of the functional groups during a normal polymerisation. Due to the insolubility of the bispotassium salt of Bis-S in DPS, its reaction with DCDPS in that solvent could not be studied using conventional solution kinetic methods. It was decided to study the reaction between bis(4-chlorobenzenesulphonyl) diphenyl ether (I) and the bispotassium salt of bis(4-hydroxybenzenesulphonyl) diphenyl ether (II), more commonly known as dichlorodimer and bisphenate dimer respectively;

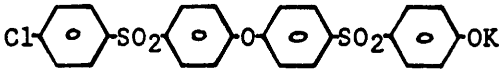


(I)



(II)

However, a solubility test on the bisphenate dimer proved that it was virtually as insoluble in DPS as the monomer analogue. Therefore, a one monomer route was investigated involving the potassium salt of 4-(chlorobenzenesulphonyl)-4'-(hydroxybenzenesulphonyl)diphenyl ether (III), more commonly termed the chlorophenate dimer.



(III)

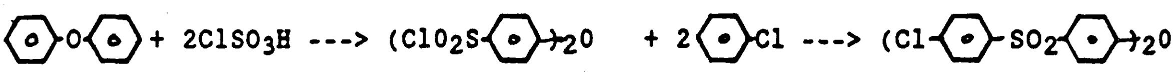
This proved to be soluble in DPS and so was used in the kinetic study. The chlorophenate monomer analogue is only sparingly soluble in DPS and would anyway be subject to sulphone bridge effects. This would lead to two distinct rates of reaction, the first involving the initial dimerisation of the monomer and the second involving the subsequent polymerisation to high molecular weight. The temperature range studied was between 180-220°C and the concentration range investigated was between 0.042 - 0.325 molar chlorophenate dimer in DPS (32 - 150g chlorophenate dimer per kg DPS). The polymerisation was followed by monitoring the reduction in phenate concentration using UV spectroscopy (98 ~~101~~) and the Arrhenius parameters were determined by conventional methods.

6.2 Preparation Of Model Compounds

Detailed experimental procedures for each of the model compounds used in this study can be found in the experimental section of the thesis. A brief outline of the main synthetic routes is given below.

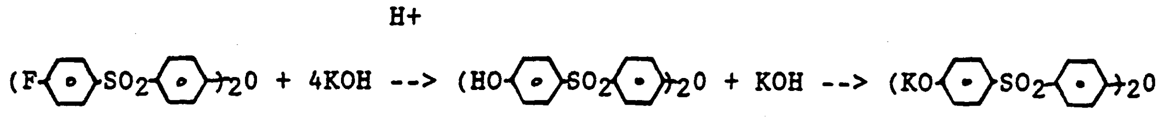
6.2.1 Bis(4-chlorobenzenesulphonyl)diphenyl ether

This was prepared by forming the bis(4-sulphonyl chloride) derivative of diphenyl ether and reacting this with two equivalents of chlorobenzene in the presence of a Friedel-Crafts catalyst ($AlCl_3$) to yield the 'dichlorodimer';



6.2.2 Bis(4-hydroxybenzenesulphonyl)diphenyl ether (bispotassium salt)

The 'bisphenate dimer' was prepared by reacting the bis(4-fluorobenzenesulphonyl) diphenyl ether (prepared by the above method using fluorobenzene) with four equivalents of potassium hydroxide (KOH) in DMSO. Cleavage of the activated aryl ether could easily occur if the reaction conditions were too vigorous, and thus temperatures just above ambient were used for long reaction times, such that dihydroxydimer formation was favoured. The product was acidified and isolated, before being further reacted with KOH to yield the bis potassium salt of bis(4-hydroxybenzenesulphonyl) diphenyl ether;

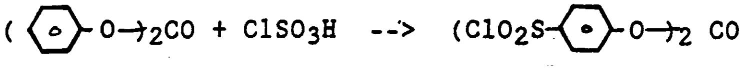


It was known that the bispotassium salt of Bis-S was sparingly soluble in DPS and it was hoped that the increase in chain length of the bisphenate dimer would markedly increase its solubility in the reaction solvent. However, a solubility test on the bisphenate dimer showed that the solubility was still not sufficient for a kinetic study to be undertaken, and thus the study of the polymerisation to PES was not possible using the two 'dimer' route.

The potassium salt of 4-chloro-4'-hydroxydiphenyl sulphone was known to be sparingly soluble in DPS and so the potassium salt of 4-(chlorobenzenesulphonyl)-4'-(hydroxybenzenesulphonyl) diphenyl ether was synthesised.

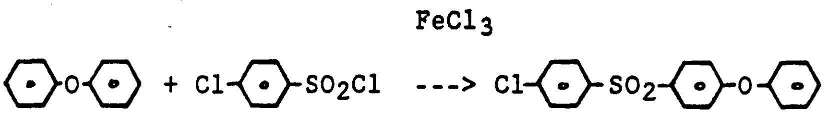
6.2.3 Potassium salt of (4-chlorobenzenesulphonyl)-4'-(hydroxybenzene- sulphonyl)diphenyl ether

This was prepared by first reacting diphenyl carbonate with chlorosulphonic acid to yield the 4,4'-disulphonyl chloride derivative (A);



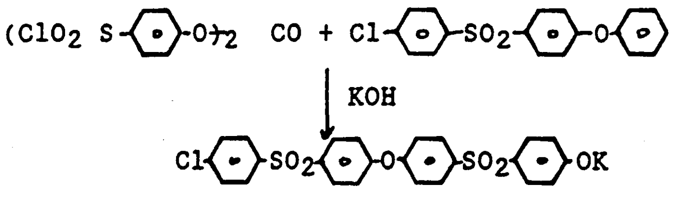
A

4-(p-chlorobenzenesulphonyl) diphenyl ether (B) was also prepared in a typical Friedel-Crafts reaction involving diphenyl ether and p-chlorobenzene sulphonyl chloride, using ferric chloride as catalyst;



B

Compounds (A) and (B) were reacted together to form the 'chlorophenol' dimer, again using a Friedel-Crafts reaction involving ferric chloride as catalyst. The product was isolated by hydrolysing the carbonate using potassium hydroxide.



6.3 The Use Of Ultra Violet Spectroscopy In The Kinetic Study

The use of UV spectroscopy to study the kinetics of the polymerisation of a polyaryl ether containing at least one hydroxy group was a novel approach and one that was both quick and accurate. It was developed from a method first recorded by Shchori and McGrath (98), who used UV spectroscopy as a means of determining the degree of polymerisation in a system that had at least one hydroxyl group. As discussed in the introduction to this chapter, the addition of a quarternary ammonium salt to a solution of the polymer in a suitable solvent shifted the UV absorbance due to the hydroxyl ends away from the absorbance due to the polymer backbone, such that the concentration of hydroxyl ends could be determined.

The success of this method depended crucially both on the molar absorptivity of the hydroxyl or complexed hydroxyl group remaining constant as the length of the polymer chain increased and the Beer-Lambert law being obeyed over the range of concentration used. Bis-S forms a number of partial potassium salts by reaction with varying levels of KOH, and thus the former assumption was proved by measuring the molar absorptivities of a number of potassium salts of Bis-S which contained a variety of hydroxyl groups per mole, both before and after complexation with the quarternary ammonium salt;

Table 7: Molar Absorptivities for a Range of Hydroxyl-Ended Compounds

Compound	$[O^-]$per mole	E_1 ~270 nm	E_1/ Aryl	E_2 ~320nm	E_2 $[O^-]$
Bis-S	2	14182	7091	25094	12547
K_2(Bis-S)	2	15686	7843	22353	11177
K(Bis-S)	2	11756	5878	23776	11888
K(Bis-S)$_2$	4	34727	8682	165625	16406
K(Bis-S)$_4$	8	64286	8034	120000	15000
Dihydroxydimer	2	27667	6917	24500	12250
Chlorophenate dimer	1			15044	15044

All molar absorptivity values were measured in litres cm^{-1} mole^{-1}. E_1 was the molar absorptivity of the compound, and E_2 was that of the complex with tetramethylammonium hydroxide pentahydrate. From the E_2 values the technique for measuring hydroxyl concentration was consistent both for the analysis of a number of partial salts of Bis-S, but more importantly it was consistent as the chain length increased from one to two units. Thus it could be assumed that the molar absorptivity of the hydroxyl group would be unaffected by polymer chain length. The graph of absorbance against concentration produced a straight line over the relevant concentration range, providing evidence that the Beer-Lambert law was indeed being obeyed over the range studied. (Graph 34)

6.4 Experimental Procedure

A known amount of DPS (~10g) was weighed into a 25ml round bottomed flask fitted with N_2 inlet/outlet and thermometer. It was placed in an oil bath and heated to the required temperature under nitrogen and maintained at that temperature with the use of a thermostat to +/- 0.1°C. A sample (~0.3g) was taken with a pipette and used as a control. A preweighed sample of the potassium salt of 4-(chlorobenzenesulphonyl)-4'-(hydroxybenzenesulphonyl) diphenyl ether, correct to four decimal places, was added and the time started. The amount of 'chlorophenate dimer' added depended on the concentration being studied. Samples of approximately ~0.3g were taken at regular intervals over an 8 hour period, and each sample was prevented from further reaction by pouring the mixture onto cooled aluminium foil to form a thin film. The samples were weighed to four decimal places and dissolved in 25 ml dimethyl formamide (DMF) in a volumetric flask. 0.5 ml of this solution was further diluted with 3.0 ml DMF and two drops of a 0.1M solution of tetramethylammonium hydroxide pentahydrate (QAS) in methanol were added. A UV scan of this solution between 260-400 nm was taken, using a reference of DMF and two drops of QAS.

A computer program was written (Appendix 1) which required an input of sample mass, sample time and the maximum absorbance detected at ~320 nm, and whose output was the reciprocal concentration of monomer left at the sample time. From the data produced, a graph of reciprocal concentration against time was plotted from which the rate constant was determined. (Graphs 10-29). (Appendix 2)

The polymerisation was performed at different temperatures at the same concentration of monomer in DPS, so that the Arrhenius parameters could be calculated (Graphs 30-33). The concentration of the monomer was then altered so that the effect of concentration could be studied.

6.5 Results

The results are tabulated in Table 9

6.5.1 Arrhenius Parameters

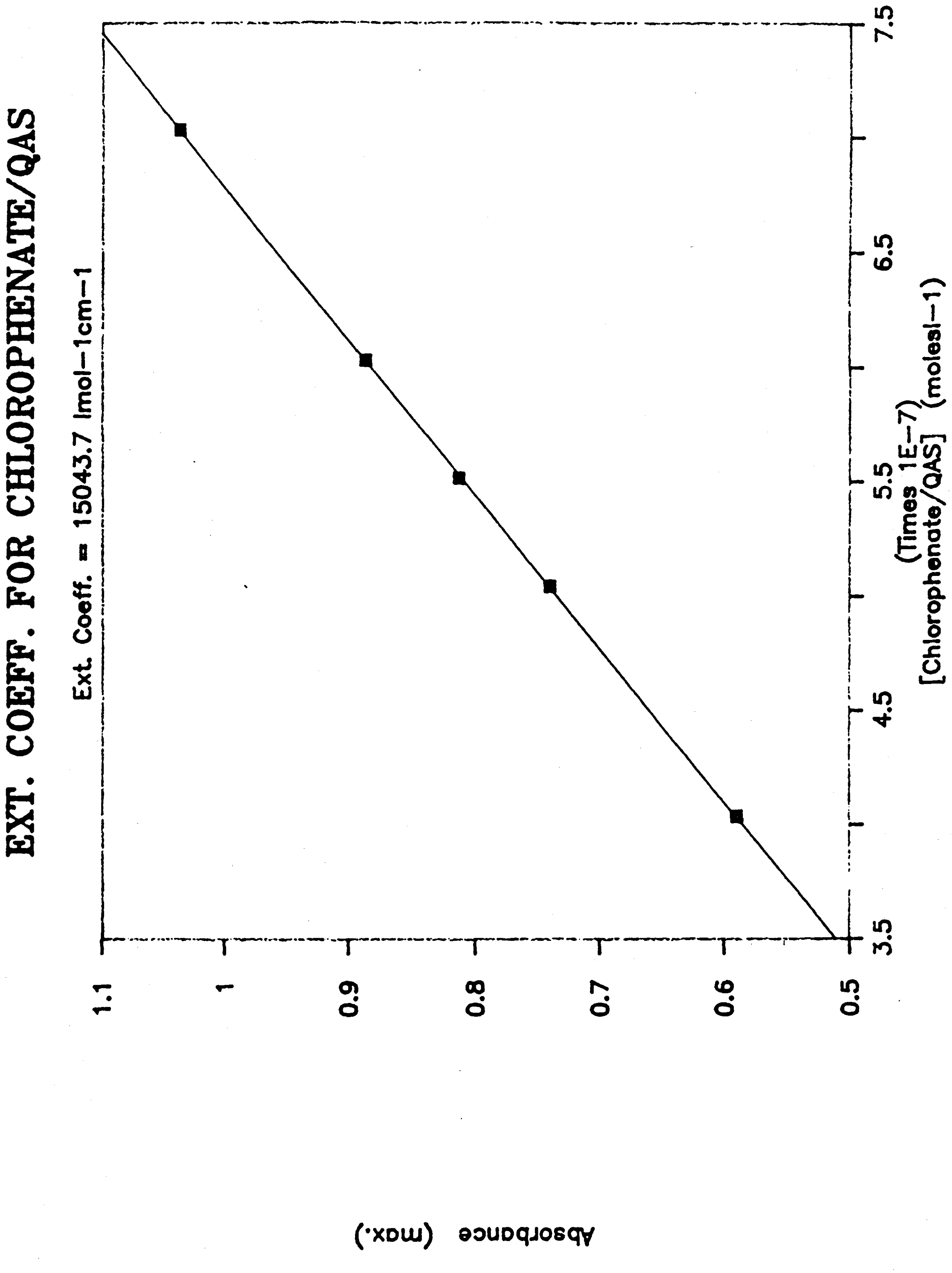
Table 8: Arrhenius Parameters Calculated for Dimer Kinetics

Monomer Concentration (moles monomer/kg DPS)	Activation Energy Ea ($kJmol^{-1}$)	Pre-Exponential Factor A ($lmol^{-1}sec^{-1}$)
0.042	113.4	1.49×10^{12}
0.138	123.6	7.67×10^{12}
0.203	97.3	8.65×10^{8}
0.325	103.4	2.01×10^{10}

Table 9: Data for Dimer Kinetic Study

Run	[Mono] moles/kg DPS	Temp °C	1/Temp °K^{-1} (*10^{-3})	Rate Constant k (lmol^{-1}sec^{-1})	lnk
1	0.04454	200	2.1142	0.424138	-0.85770
2	0.04359	209.5	2.0725	0.693099	-0.36658
3	0.04251	204	2.0964	0.554983	-0.58882
4	0.04232	195	2.1368	0.301825	-1.19791
6	0.04220	220	2.0284	1.290003	0.25464
7	0.04000	189	2.1645	0.207641	-1.57194
8	0.13976	200	2.1142	0.207125	-1.57443
9	0.13663	190	2.1598	0.103595	-2.26727
10	0.13735	208	2.0790	0.288294	-1.24377
11	0.14021	181	2.2026	0.049571	-3.00435
12	0.32364	200	2.1142	0.075394	-2.58503
13	0.32825	210	2.0704	0.134926	-2.00303
14	0.32630	190	2.1598	0.049152	-3.01284
15	0.32473	181.5	2.2002	0.024501	-3.70904
16	0.32497	213.75	2.0544	0.156918	-1.85203
18	0.20355	197.75	2.1243	0.148221	-1.90905
19	0.20425	190	2.1598	0.082664	-2.49297
20	0.20289	185	2.1834	0.072271	-2.62733
21	0.20393	213.25	2.0566	0.300540	-1.20217
22	0.20469	206	2.0877	0.204103	-1.58913

Graph 34: Extinction Coefficient For Chlorophenate/QAS Complex



6.6 Discussion

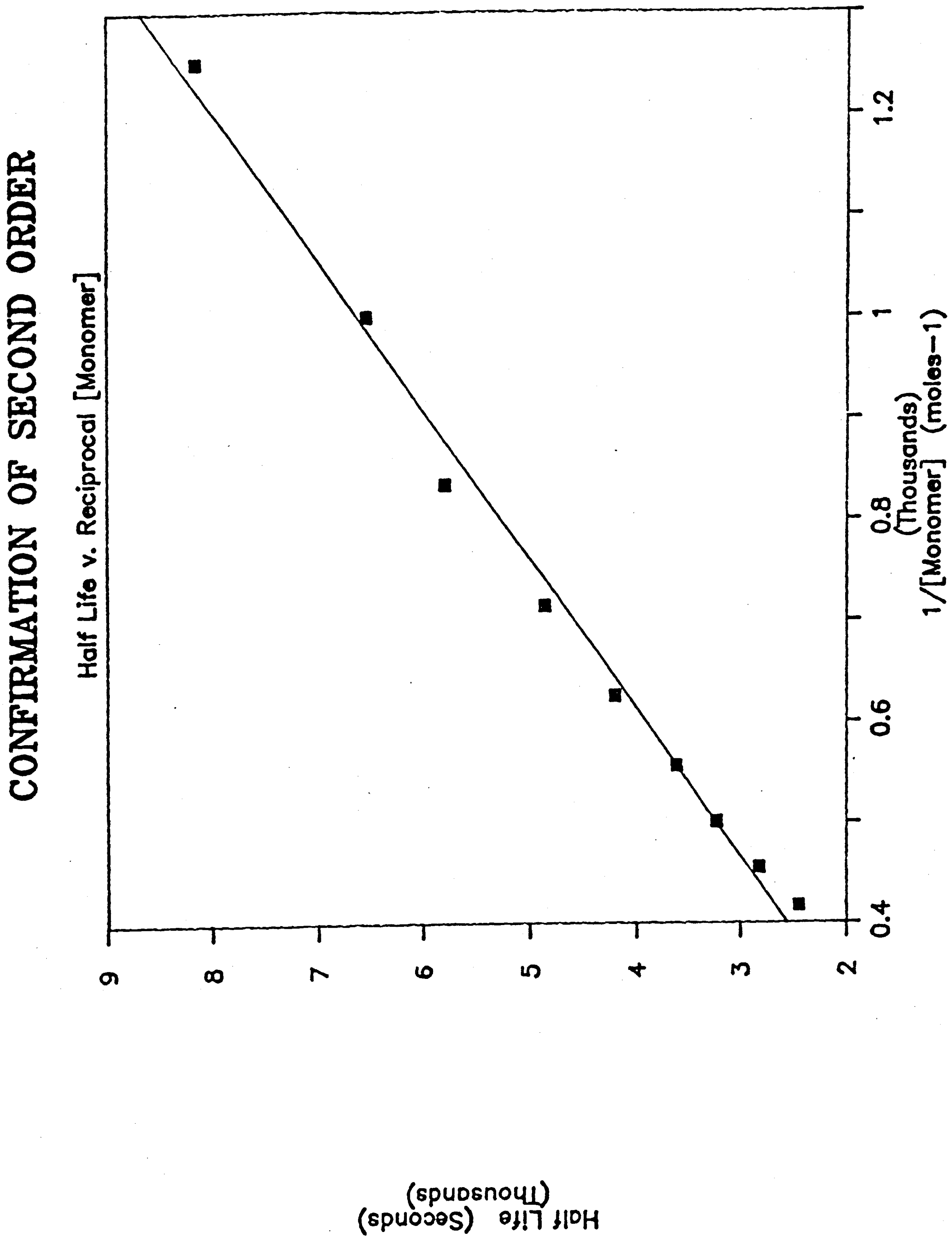
The extinction coefficient of the chlorophenate dimer/QAS complex was found to be 15043.7 $lmol^{-1}cm^{-1}$. It was shown to obey the Beer-Lambert law over a similar range of concentrations to that used in the kinetic study (Graph 34). From the study of the extinction coefficients for a series of compounds containing hydroxyl groups and increasing chain length, it was assumed that the extinction coefficient of the complexed hydroxyl would remain constant throughout the polymerisation.

The self polycondensation of the potassium salt of 4-(chlorobenzenesulphonyl)-4'-(hydroxybenzenesulphonyl) diphenyl ether was expected to follow conventional second order kinetics. Schulze and Baron (98) had demonstrated that polyether synthesis occurred via second order kinetics, although functional group reactivity and sulphone bridge effects have been shown to affect the initial rate of reaction (99). Also, since a model compound was used, there were no side reactions due to potassium carbonate and no solubility effects. Second order kinetics was confirmed during each run, where a plot of reciprocal concentration against time produced a straight line (Graphs 10-29). Further proof was seen from the plot of half life against reciprocal monomer concentration, which again produced a straight line relationship over the majority of the reaction (Graph 35).

Thus, as both functional groups were on the same monomer, the order of the reaction was defined as the square of the monomer concentration, or;

$$\text{Rate of reaction} = k[\text{Chlorophenate}]^2$$

Graph 35 : Confirmation Of Second Order Kinetics

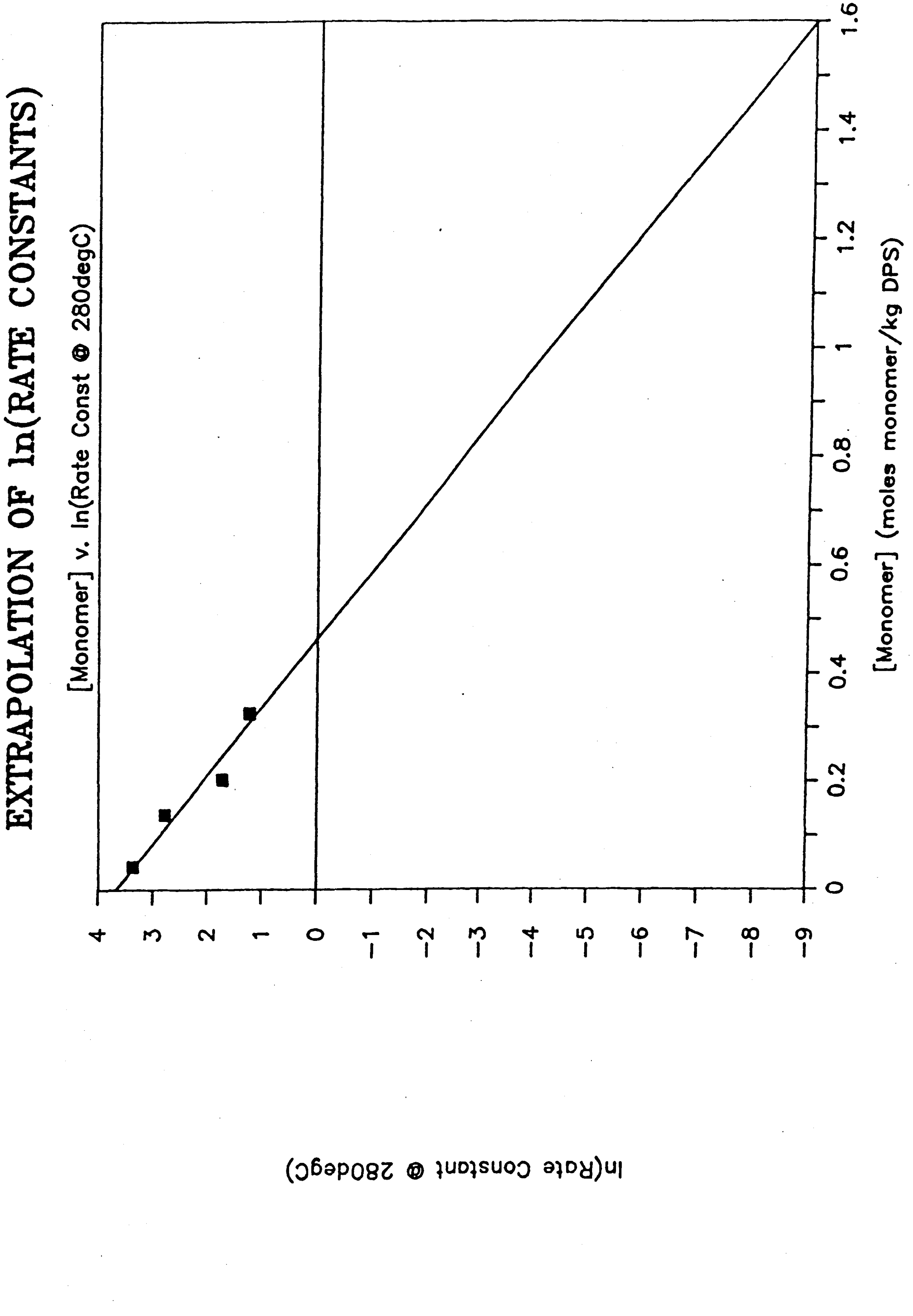


Four concentrations were studied over a 40°C temperature range. The concentration of the monomer was varied for two reasons. The first reason was to study the salt effect on the rate of reaction and the second was to use this information with the aim to extrapolate the results to the concentration and temperatures used in a typical laboratory reaction to produce PES by the two monomer 'carbonate' route. In this, the concentration of monomer (DCDPS and Bis-S) used is 1.505 1.518 moles monomer/kg DPS and the final polymerisation temperature is 280°C. For each concentration studied, the Arrhenius equation was used to determine the rate of reaction at 280°C. The natural logs of the extrapolated rates were then plotted against monomer concentration to determine the rate of reaction at the above conditions (Graph 36). This was found to be;

$k = 2.315 \times 10^{-4}\ \mathrm{lmol^{-1}sec^{-1}}$ (at 1.518 moles monomer/kg DPS and 280°C)

This is lower than expected. In the model compound work, 90% completion of reaction took in the region of 8-9 hours at ~200°C, whilst in typical laboratory reactions, polymerisation temperatures are held for ~2 hours at ~280°C, and so by that time, the polymerisation is ~95-99% complete. However, the extrapolation is tenuous, in that both the concentration and the temperature used in a normal laboratory preparation of PES are far from those used in the kinetic study and there is obviously a limit to the extent of extrapolation. Also, in this study a homogeneous reaction was investigated, whereas the 'carbonate' process is heterogeneous and therefore the kinetics are much more complicated.

Graph 36 : Extrapolation Of Rate Constants At 280°C



However, the above rate coefficient was calculated on the assumption that the salt effect was evident in the 'carbonate' process to PES. The poor solubility of the phenate ended oligomers in DPS has already been established, and thus a postulated reaction scheme could involve the rate limiting step to be the formation of the phenate by the reaction of the soluble hydroxyl with the insoluble carbonate, followed by immediate reaction of the phenate with the activated halide. Thus the concentration of phenate ends in DPS at any time would approximate to zero, and consequently the salt effect would become neglible. If the rate constants were extrapolated back to zero concentration of chlorophenate (cf zero concentration phenate ends, Graph 36), this would yield the expected rate constant at zero salt effect at 280°C. Thus, at zero moles monomer/kg DPS at 280°C;

$$k = 39.707 \ \mathrm{lmol^{-1}\ sec^{-1}}$$

This extrapolation, being closer to the concentrations studied, is more informative than the one at 1.518 moles monomer/kg DPS. Also, the larger rate constant is more realistic, in that polymerisation is essentially complete after ~2 hours at 280°C, as discussed previously.

The salt effect in this study is clearly demonstrated by comparing rates of reaction at constant temperature but varying the concentration (Graphs 37 - 41). Although no direct correlation was observed, there is a definite reduction in rate of reaction as the concentration is increased at any given temperature.

The effect of temperature on the rate of reaction at constant concentration is shown in Graphs 42 - 45. As expected the rate of reaction increases by a factor of approximately two as the temperature is increased by 10°C.

The energy of activation for the polymerisation was found to vary between 97.3 and 123.6 kJmol^{-1}, depending on the monomer concentration used. The activation energy did not vary directly with the concentration of monomer used, and indeed thus the effect of concentration (over the range studied) on the activation energy was found to lie within the experimental error.

The activation energy was in good agreement both with other methods of analysis in this thesis and with previous studies (97). Of particular importance is the correlation between the activation energy as measured by this technique and that found by monitoring the extent of reaction in a normal laboratory polymerisation. Although it has been stated that the 'carbonate' process is heterogeneous, by the time the degree of polymerisation has reached DP $\sim$10 the CO_2 evolution has ceased (and thus all the hydroxyl groups have been converted to the phenate derivative) and the decamer is believed to be soluble in DPS whatever the end groups. Thus at this stage the process has become pseudo homogeneous, in the sense that the species involved in the polymerisation process are all in solution. If it is assumed that a decamer has one chlorine group and one phenate group, then the concentration of phenate groups can be calculated;

At DP = 0 there are two hydroxyl (phenate) groups per molecule (from Bis-S), and thus in a normal laboratory polymerisation there are 3.164 phenates/kg DPS.

At DP = 10 there is one phenate group per molecule (nine aryl ether groups having been formed), and therefore the concentration of phenates is reduced to 0.3164 phenates/kg DPS.

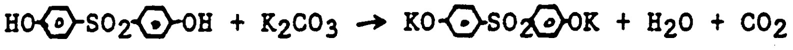
At DP = 80 there is one phenate group per molecule (seventy nine aryl ether groups having been formed), and therefore the phenate concentration is reduced to 0.03954 phenates/kg DPS.

Therefore, the range of phenate concentration in going from DP = 10 to DP = 80 (0.3164 - 0.03954 phenates/kg DPS) is almost identical to the range of concentrations studied using the model compound (0.325 - 0.042) and thus it is expected that the activation energies for the two studies should be similar.

CHAPTER 7: STUDY OF THE PES POLYMERISATION BY CO_2 EVOLUTION

7.1 Introduction

The study of the condensation by-products in a polycondensation reaction can be a useful method of following the extent of a particular polymerisation. In the 'carbonate' route to PES the condensation by-product is KCl, formed by the reaction of the activated chloro group with the phenate to form an aryl ether bond. There are, however, two pre-condensation by-products which can be studied in order to monitor the extent of the reaction. More importantly, the study of the kinetics of these reactions could help to indicate which process is rate determining in the 'carbonate' process, formation of the phenate group or formation of an aryl ether bond. The two by-products are water and carbon dioxide. Both are evolved in the reaction between potassium carbonate (K_2CO_3) and Bis-S. A general reaction scheme can be represented by;



Therefore, for every mole of K_2CO_3 consumed, one mole of CO_2 is generated. The solubility of CO_2 in the polymerisation solvent, DPS, is negligible within the range of temperatures used in the polymerisation process, and so its evolution from the reaction medium can be studied. The technique used to monitor the flow of CO_2 was by the use of a dry gas meter.

7.2 Earlier Work

Previous work on the study of the evolution of CO_2 during a PES polymerisation concentrated on using titrimetry (103). This involved passing the exhaust gases from a polymerisation through an aqueous solution of KOH at pH=11. The CO_2 in the exhaust gases reacted with KOH to form carbonic acid;

$$CO_2 + OH^- \rightarrow HCO_3^-$$

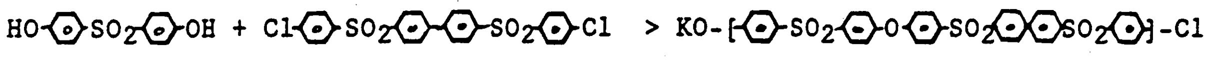
This reduced the pH of the solution over a period of time, and the amount of KOH needed to restore the pH to 11, added from a burette, was plotted as a function of time. The results using this method were varied, but a typical plot of CO_2 evolution against time was similar to those found in this study. The kinetics of the process were not determined, as the purpose of the exercise at that time was to ensure that CO_2 evolution remained at safe levels throughout the polymerisation.

7.3 Exact Procedure

The experimental procedure was to charge molar quantities of DCDPS, BIS-S, an excess of K_2CO_3 (4% molar excess) and the appropriate amount of DPS (~500g) into a 2l round bottomed three necked flask, fitted with nitrogen inlet/ outlet, thermocouple and stirrer. Nitrogen was passed through the medium to allow complete purging of air from the system. The whole was lowered into an oil bath at ~170°C, and at this point the nitrogen flow was stopped so that any exhaust gases detected would be due to reactions from within the flask.

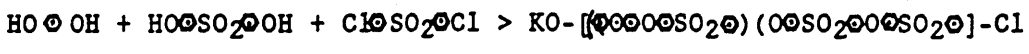
The outlet was connected via a cold trap to an American Dry Gas Meter. The stirrer was started once the reaction mass started to melt. The temperature was held for a further 1/2 hour before following an adapted laboratory polymerisation process. Various hold temperatures were studied for each plateau temperature which is normally incorporated into the 'carbonate' route, although the hold periods were longer to ensure that either the gas evolution had ceased or remained constant for a reasonable period of time. The total volume of CO_2 evolved was plotted against time, and the rate of CO_2 evolution at any point was calculated from the tangent of the slope at the relevant time.

Two other PES variants were studied at the same time. The first was the polymer prepared from bis(4-chlorobenzenesulphonyl)biphenyl (I) and Bis-S, which has a higher T_g than PES due to both the biphenyl linkage in (I) and the increased ratio of sulphone:ether groups, which increase the rigidity of the polymer backbone.



Bis-S (I) PES 1

The second PES variant to be studied was the copolymer formed by the reaction of hydroquinone (HQ), Bis-S and DCDPS, which has a lower T_g than PES due to the decrease in sulphone:ether ratio, but has a higher hydrolytic resistance;



HQ Bis-S DCDPS PES 2

7.4 Results

7.4.1 PES

A plot of the typical CO_2 evolution against time and temperature for a PES polymerisation can be seen in Graph 46. Two periods of the PES polymerisation gave reproducible CO_2 evolution rates. The first was the second hold temperature, which was measured between 215-249°C, and the second period was the final hold temperature, which was measured between 267-297°C.

Second Hold Temperature

Table 10: Results for PES Second Hold Temperature

Temp °C	1/Temp $*10^{-3}$°K^{-1}	Rate $lmin^{-1}$	lnRate
224	2.012	0.0115	-4.465
222	2.020	0.0103	-4.574
220	2.028	0.0061	-5.101
215	2.049	0.0022	-6.114
243	1.938	0.0211	-3.860
249	1.916	0.0308	-3.481
235	1.969	0.0198	-3.921
230	1.988	0.0145	-4.234
221	2.024	0.0103	-4.576
240	1.949	0.0200	-3.912

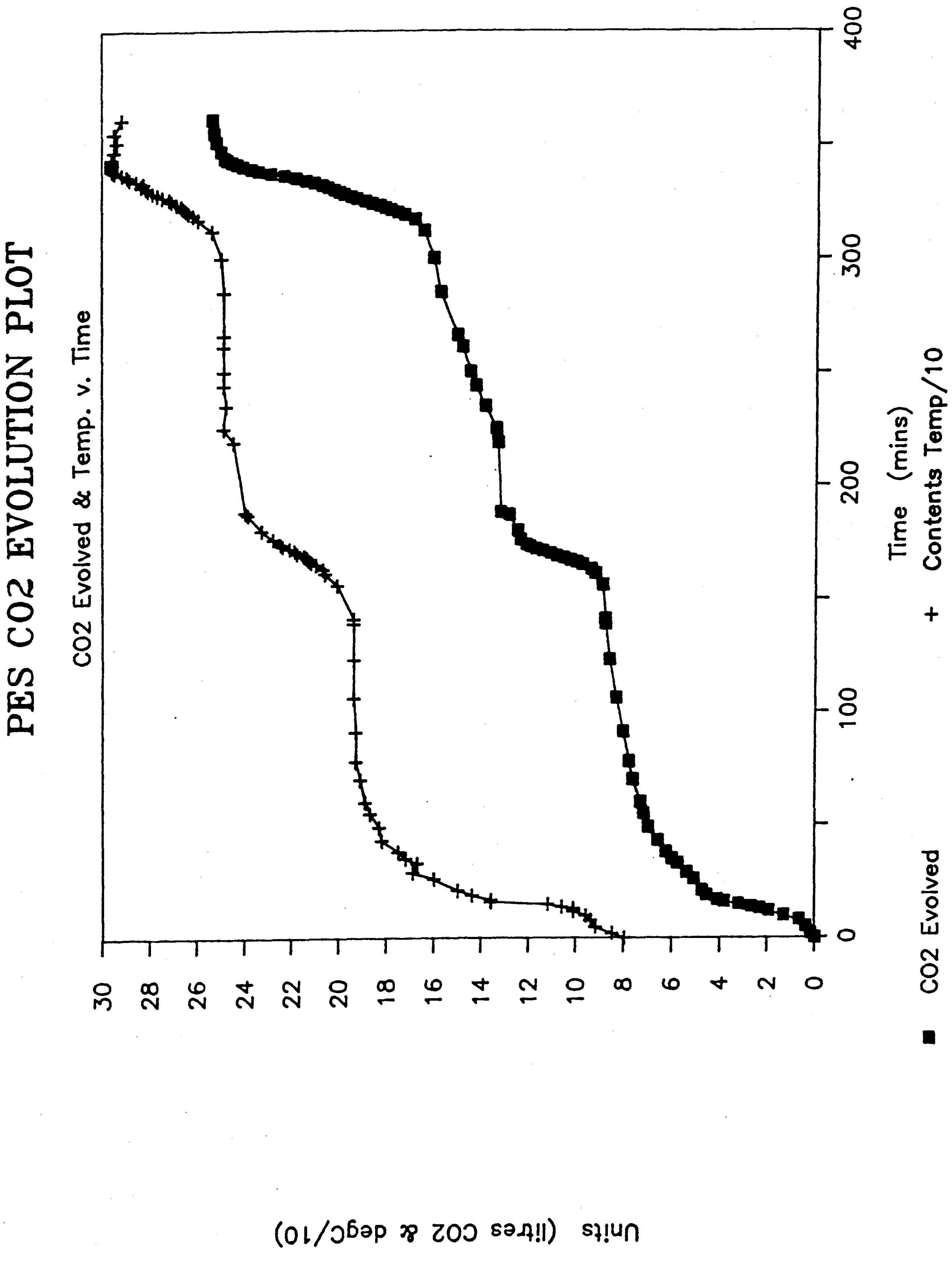
From a plot of reciprocal temperature (Kelvins) against the natural log of the rate of CO_2 evolution, the activation energy for the reaction could be determined, using a least squares routine;

$$dy/dx = -Ea/R = -16168.3 \pm 1173.9 \text{ K} \qquad R = \text{Gas Constant}$$

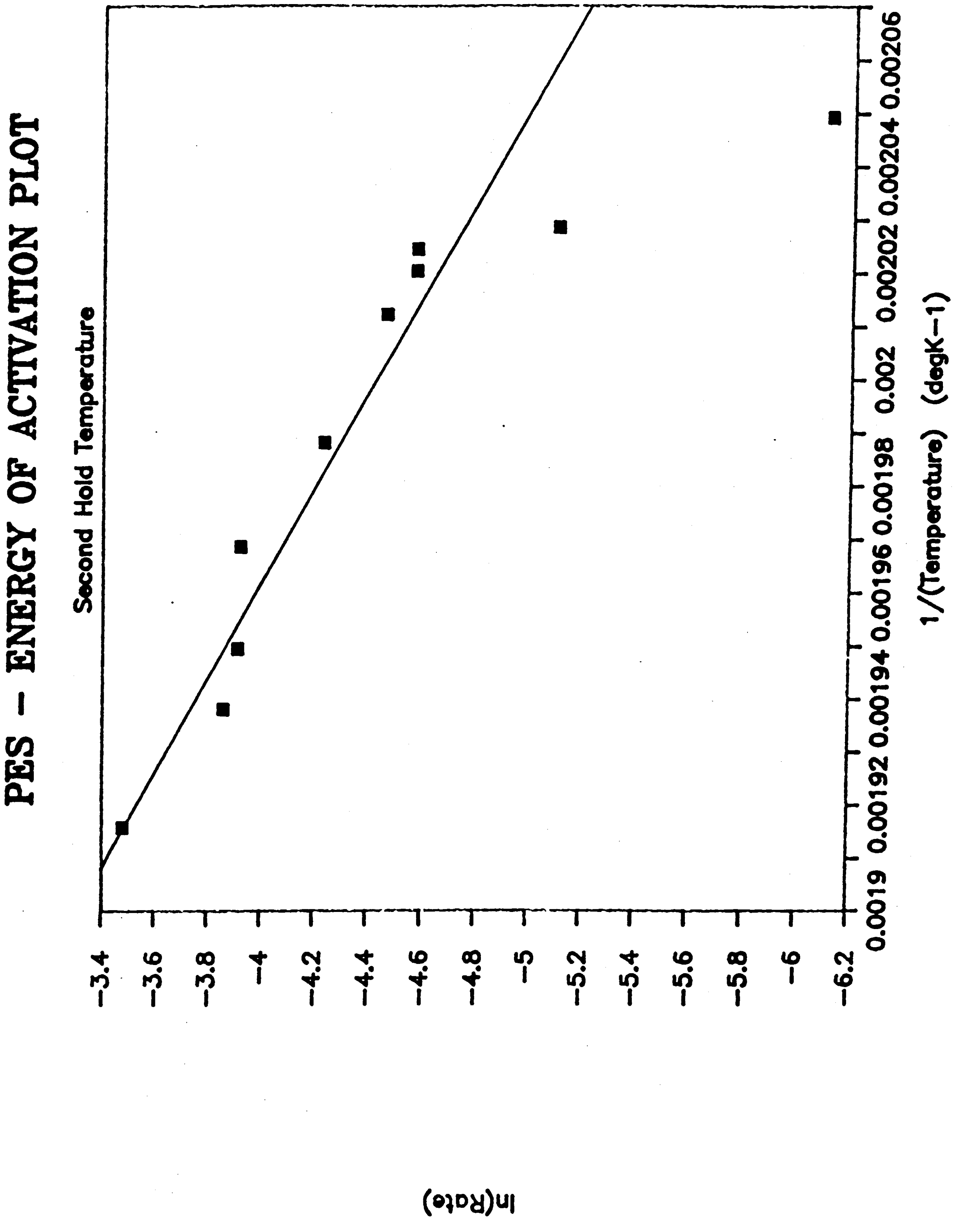
$$\Rightarrow \qquad -Ea = -134423.2 \pm 9759.8 \text{ Jmol}^{-1}$$

$$\Rightarrow \qquad Ea = 134.4 \pm 9.8 \text{ kJmol}^{-1}$$

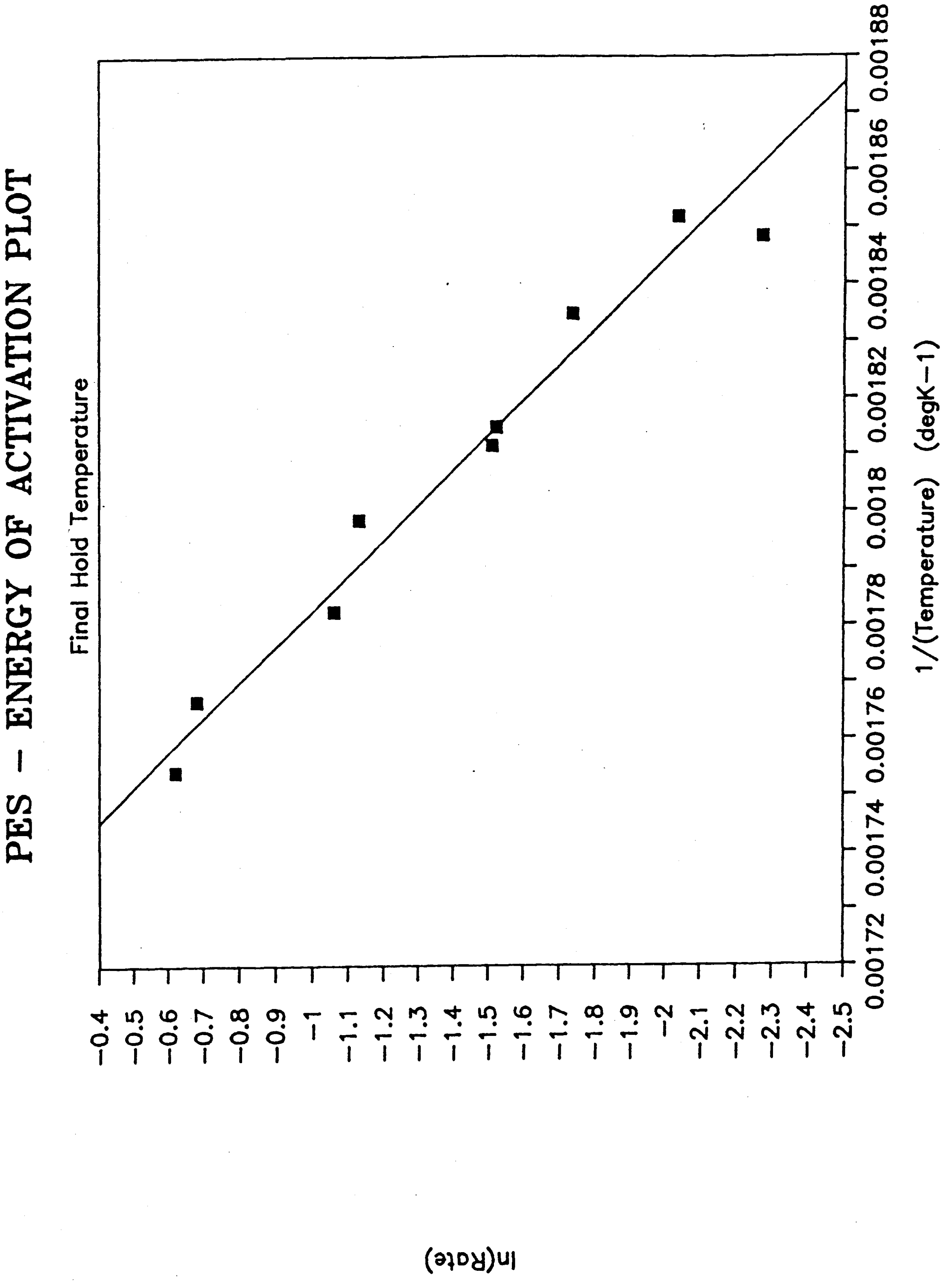
Graph 46: CO2 Evolution Against Time/Temperature For PES



Graph 47: Activation Energy Plot For PES Second Hold Temperature



Graph 48: Activation Energy Plot For PES Final Hold Temperature



Final Hold Temperature

second.

Table 11: Results for PES Final Hold Temperature

Temp °C	1/Temp $*10^{-3}\,°K^{-1}$	Rate $lmin^{-1}$	lnRate
297	1.754	0.5378	-0.620
293	1.767	0.5066	-0.680
288	1.783	0.3465	-1.060
283	1.799	0.3230	-1.130
279	1.812	0.2216	-1.507
278	1.815	0.2187	-1.520
272	1.835	0.1764	-1.735
268	1.848	0.1033	-2.270
267	1.852	0.1306	-2.036

As before;

$$dy/dx = -Ea/R = -14980.2 \pm 2778.2\ K \qquad R = \text{Gas Constant.}$$

$$\Rightarrow \qquad -Ea = -124547.9 \pm 23098.0\ Jmol^{-1}$$

$$\Rightarrow \qquad Ea = 124.5 \pm 23.1\ kJmol^{-1}$$

7.4.2 PES1

A plot of the typical CO_2 evolution against time and temperature for a PES1 polymerisation can be seen in Graph 49. Three periods of the PES1 polymerisation gave reproducible results; the first ramp temperature, studied between 202-212°C, the middle hold temperature, studied between 220-244°C, and the final ramp temperature, studied between 265-279°C.

First Ramp Temperature

Table 12: Results for PES1 First Ramp Temperature

Temp °C	1/Temp $*10^{-3} °K^{-1}$	Rate $lmin^{-1}$	lnRate
212	2.062	0.3740	-0.984
206	2.088	0.2590	-1.351
201	2.110	0.1775	-1.729
209	2.075	0.3488	-1.053
205	2.092	0.2479	-1.398

As before;

$$dy/dx = -Ea/R = -16245.7 \pm 1675.9 \text{ K} \qquad R = \text{Gas Constant}$$

$$\Rightarrow \qquad -Ea = -135066.7 \pm 13933.4 \text{ Jmol}^{-1}$$

$$\Rightarrow \qquad Ea = 135.1 \pm 13.9 \text{ kJmol}^{-1}$$

Middle Hold Temperature

Table 13: Results for PES1 Middle Hold Temperature

Temp °C	1/Temp $*10^{-3} °K^{-1}$	Rate $lmin^{-1}$	lnRate
230	1.988	0.0081	-4.812
237	1.961	0.0148	-4.216
220	2.028	0.0057	-5.166
227	2.000	0.0080	-4.832
244	1.934	0.0258	-3.658

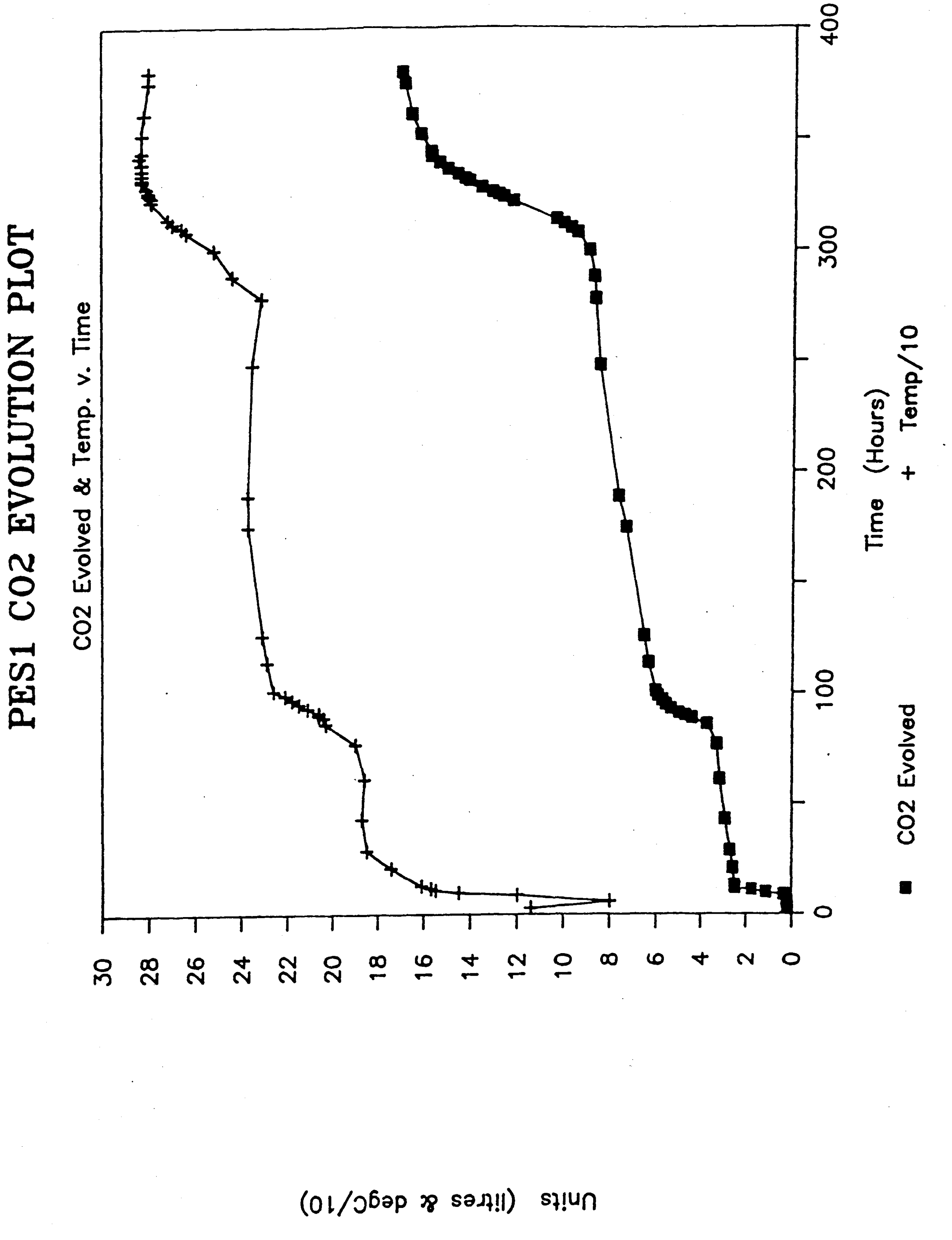
As before;

$$dy/dx = -Ea/R = -16203.2 \pm 1914.2 \text{ K} \qquad R = \text{Gas Constant}$$

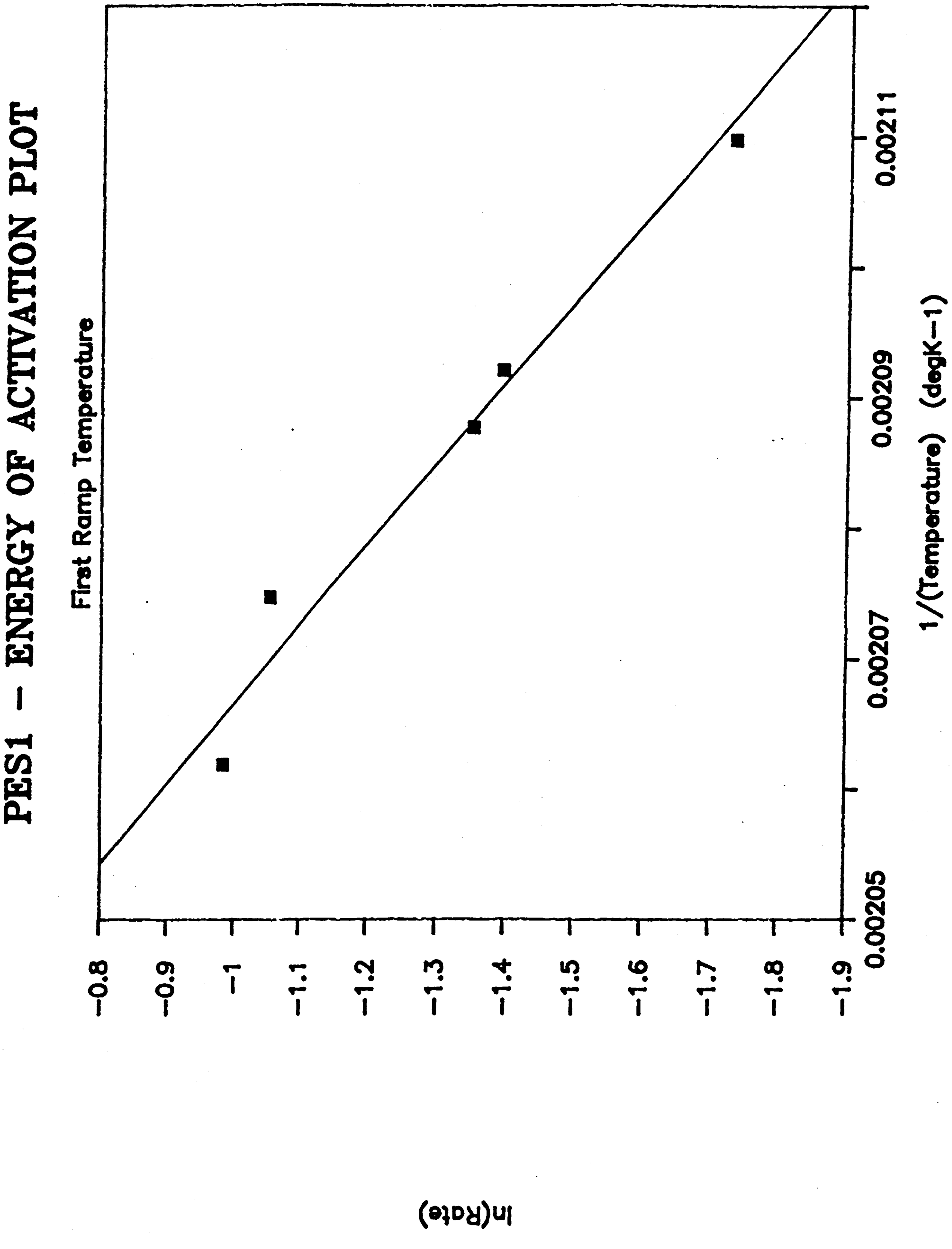
$$\Rightarrow \qquad -Ea = -134713.4 \pm 15914.7 \text{ Jmol}^{-1}$$

$$\Rightarrow \qquad Ea = 134.7 \pm 15.9 \text{ kJmol}^{-1}$$

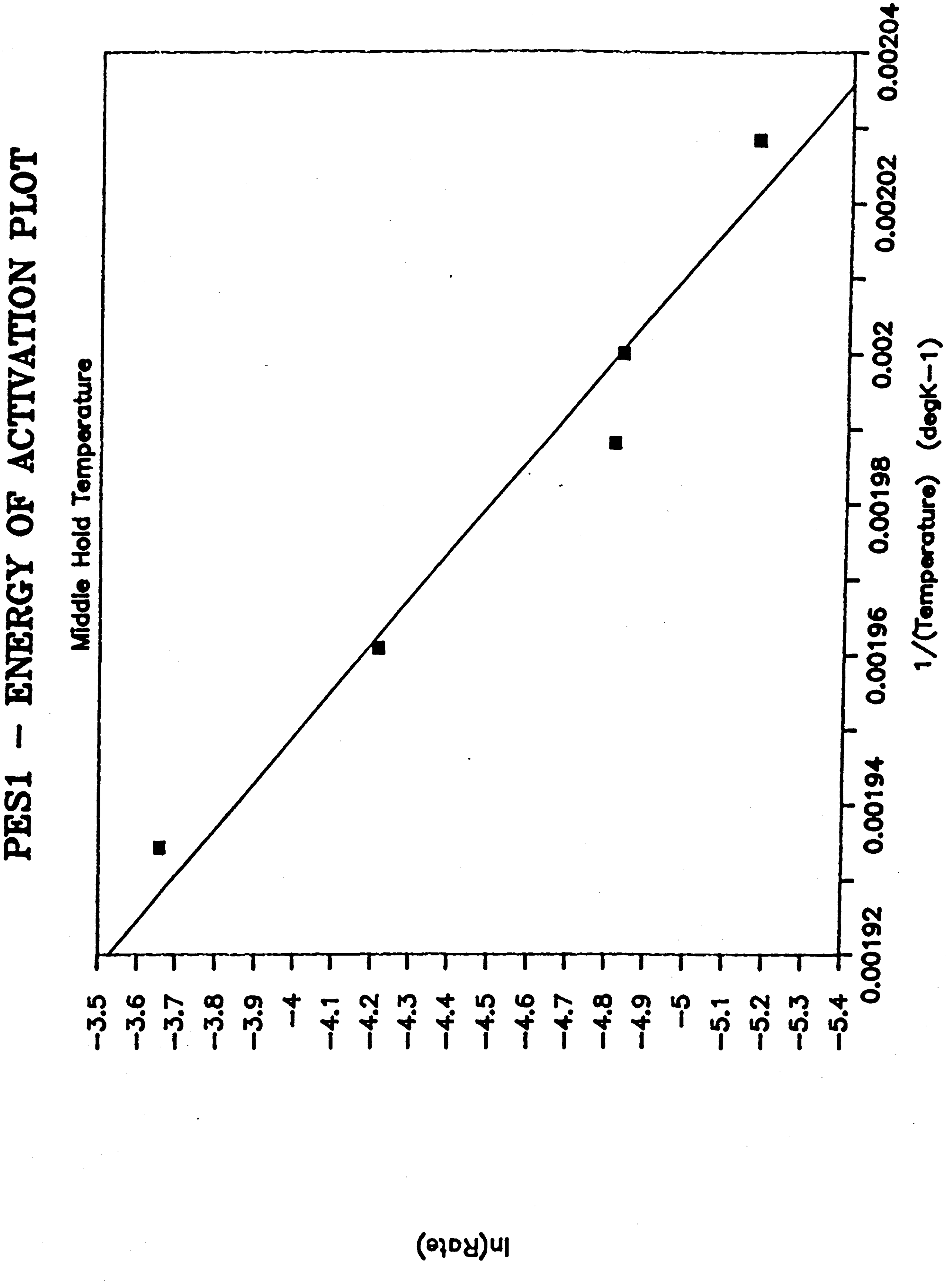
Graph 49: CO2 Evolution Against Time/Temperature For PES1



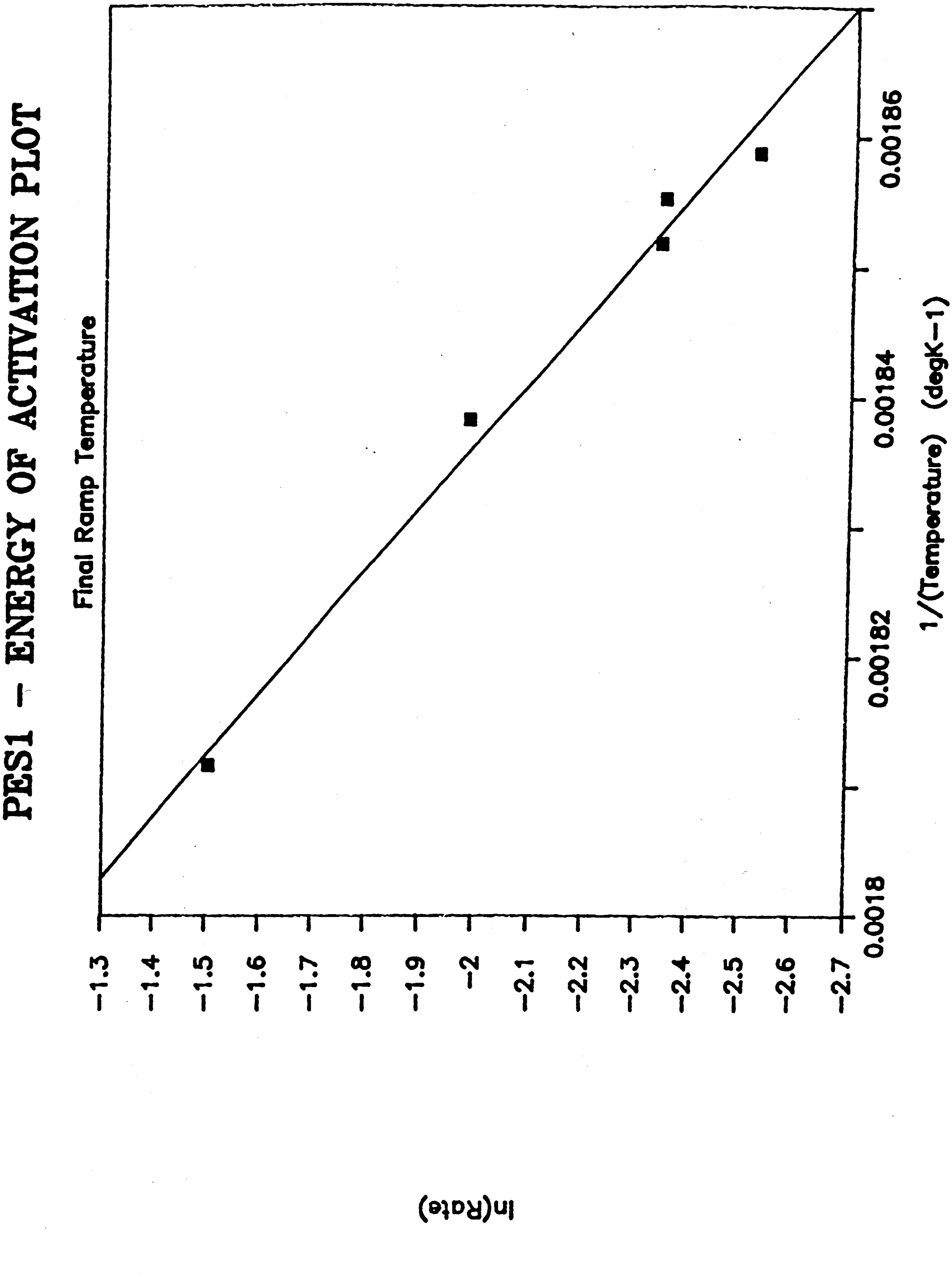
Graph 50: Activation Energy Plot For PES1 First Ramp Temperature



Graph 51: Activation Energy Plot For PES1 Middle Hold Temperature



Graph 52: Activation Energy Plot For PES1 Final Ramp Temperature



Final Ramp Temperature

Table 14: Results for PES1 Final Ramp Temperature

Temp °C	1/Temp $*10^{-3}°K^{-1}$	Rate $lmin^{-1}$	lnRate
271	1.838	0.1371	-1.987
279	1.812	0.2222	-1.504
265	1.859	0.0804	-2.521
266	1.855	0.0959	-2.345
267	1.852	0.0965	-2.339

As before;

$$dy/dx = -Ea/R = -20840.0 \pm 1401.4 \text{ K} \qquad R = \text{Gas Constant}$$

$$\Rightarrow \qquad -Ea = -173263.8 \pm 11651.2 \text{ Jmol}^{-1}$$

$$\Rightarrow \qquad Ea = 173.3 \pm 11.7 \text{ kJmol}^{-1}$$

7.4.3 PES2

A plot of the typical CO_2 evolution against time and temperature for a PES 2 polymerisation can be seen in Graph 53. Two periods during the PES2 polymerisation gave reproducible CO_2 evolution rates; the initial ramp temperature, studied between 197-209°C, and the second ramp temperature, studied between 227-251°C.

Initial Ramp Temperature

Table 15: Results for Initial Ramp Temperature

Temp °C	1/Temp $*10^{-3}$°K^{-1}	Rate lmin^{-1}	lnRate
201	2.110	0.2000	-1.609
209	2.075	0.5055	-0.682
198	2.123	0.1435	-1.941
204	2.096	0.3448	-1.065
197	2.128	0.1240	-2.088
198	2.123	0.1333	-2.015
207	2.083	0.4308	-0.842
206	2.088	0.4275	-0.850

As before;

$$dy/dx = -Ea/R = -15840.4 \pm 552.1\ K \qquad R = \text{Gas Constant}$$

$$\Rightarrow \qquad -Ea = -131697.1 \pm 4590.2\ Jmol^{-1}$$

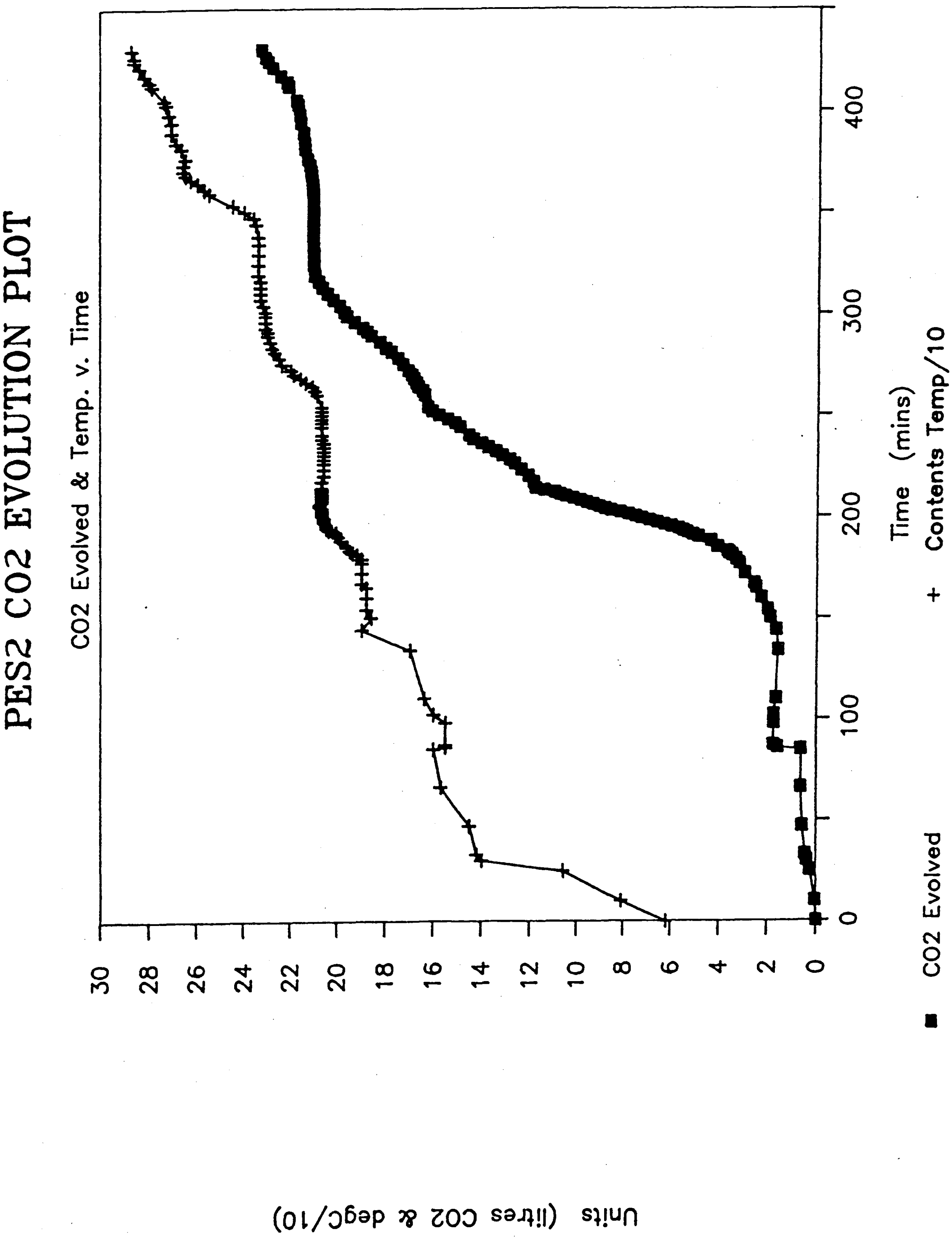
$$\Rightarrow \qquad Ea = 131.7 \pm 4.6\ kJmol^{-1}$$

Second Ramp Temperature

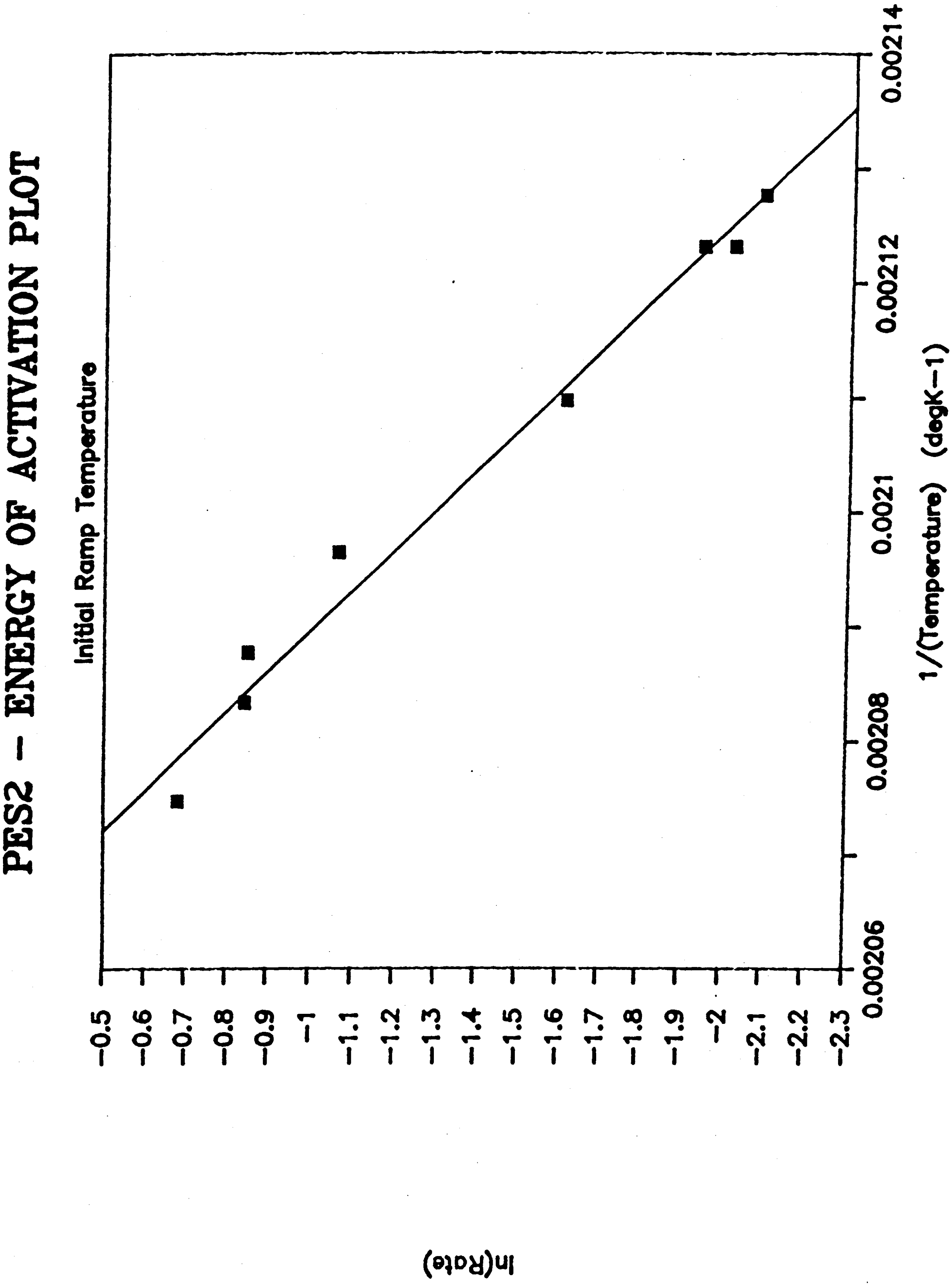
Table 16: Results for PES2 Second Ramp Temperature

Temp °C	1/Temp $*10^{-3}$°K^{-1}	Rate lmin^{-1}	lnRate
246	1.927	0.0871	-2.441
237	1.961	0.0485	-3.026
231	1.984	0.0329	-3.416
242	1.942	0.0646	-2.739
247	1.923	0.0880	-2.431
251	1.908	0.1017	-2.286
227	2.000	0.0250	-3.689

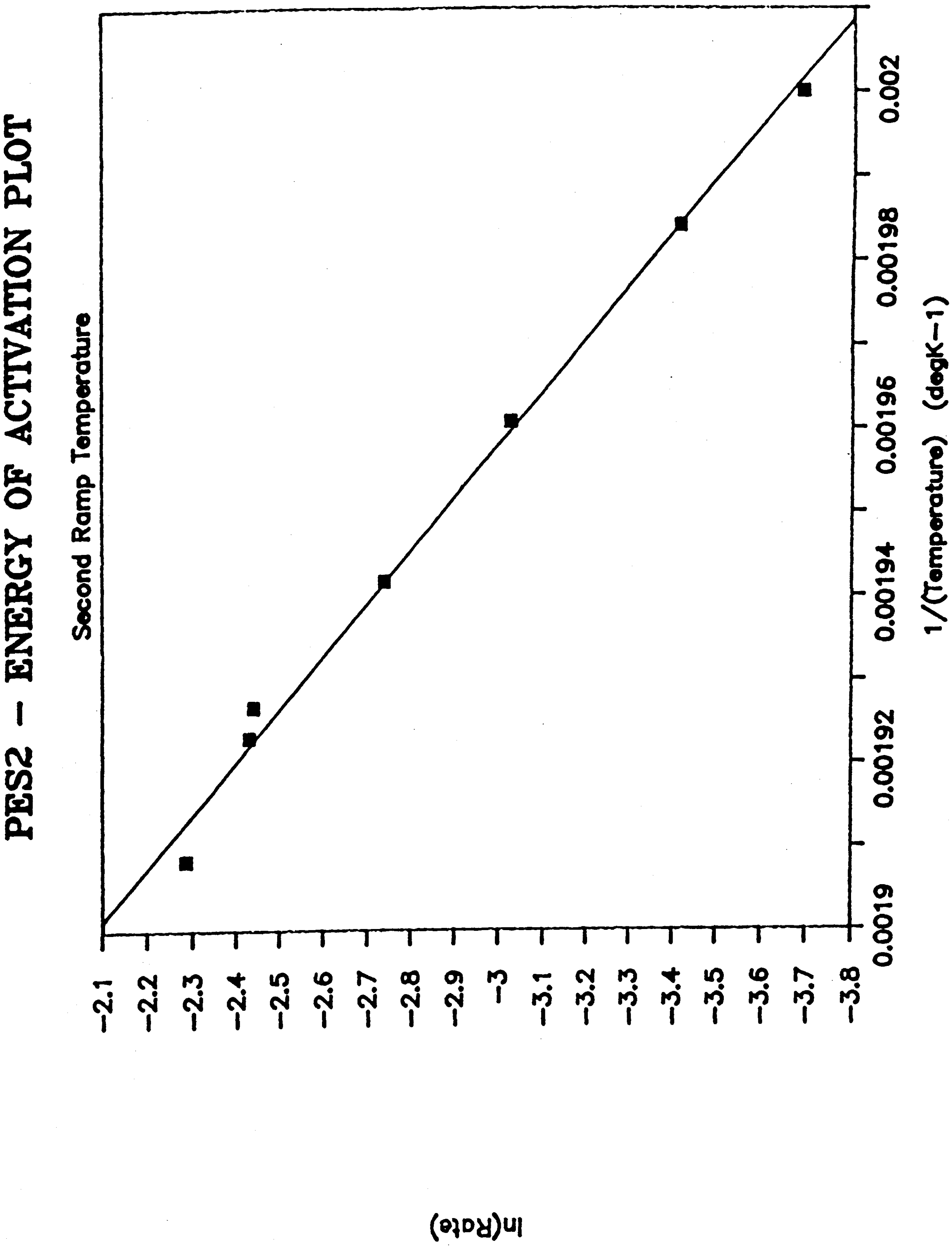
Graph 53: CO2 Evolution Against Time/Temperature For PES2



Graph 54: Activation Energy Plot For PES2 Initial Ramp Temperature



Graph 55: Activation Energy Plot For PES2 Second Ramp Temperature



As before;

$$dy/dx = -Ea/R = -28529.9 \pm 1563.3\ K \qquad R = \text{Gas Constant}$$

$$\Rightarrow \qquad -Ea = -237197.6 \pm 12997.3\ Jmol^{-1}$$

$$\Rightarrow \qquad Ea = 237.2 \pm 13.0\ kJmol^{-1}$$

7.5 Discussion

7.5.1 PES

From CO_2 evolution studies, the activation energy for the reaction between K_2CO_3 and the hydroxyl groups originating from Bis-S during the second hold temperature was $134.4 \pm 9.8\ kJmol^{-1}$, and the activation energy for a similar reaction during the final hold temperature was $124.5 \pm 23.1\ kJmol^{-1}$.

Work undertaken in the past (104) led to a postulated reaction scheme as follows:

[Ø = ]

(a) 170-180°C

$$HOØSO_2ØOH + 1/4K_2CO_3 \text{ ---------> } 1/2HOØSO_2ØOH.HOØSO_2ØOK + 1/4H_2O + 1/4CO_2$$

(b) 208-225°C

$$1/2HOØSO_2ØOH.HOØSO_2ØOK + 1/4K_2CO_3 \text{ ---------> } HOØSO_2ØOK + 1/4H_2O + 1/4CO_2$$

$$(c)\ HO\phi SO_2\phi OK + Cl\phi SO_2\phi Cl \xrightarrow{260\text{-}265^\circ C} HO\phi SO_2\phi O\phi SO_2\phi Cl + KCl$$

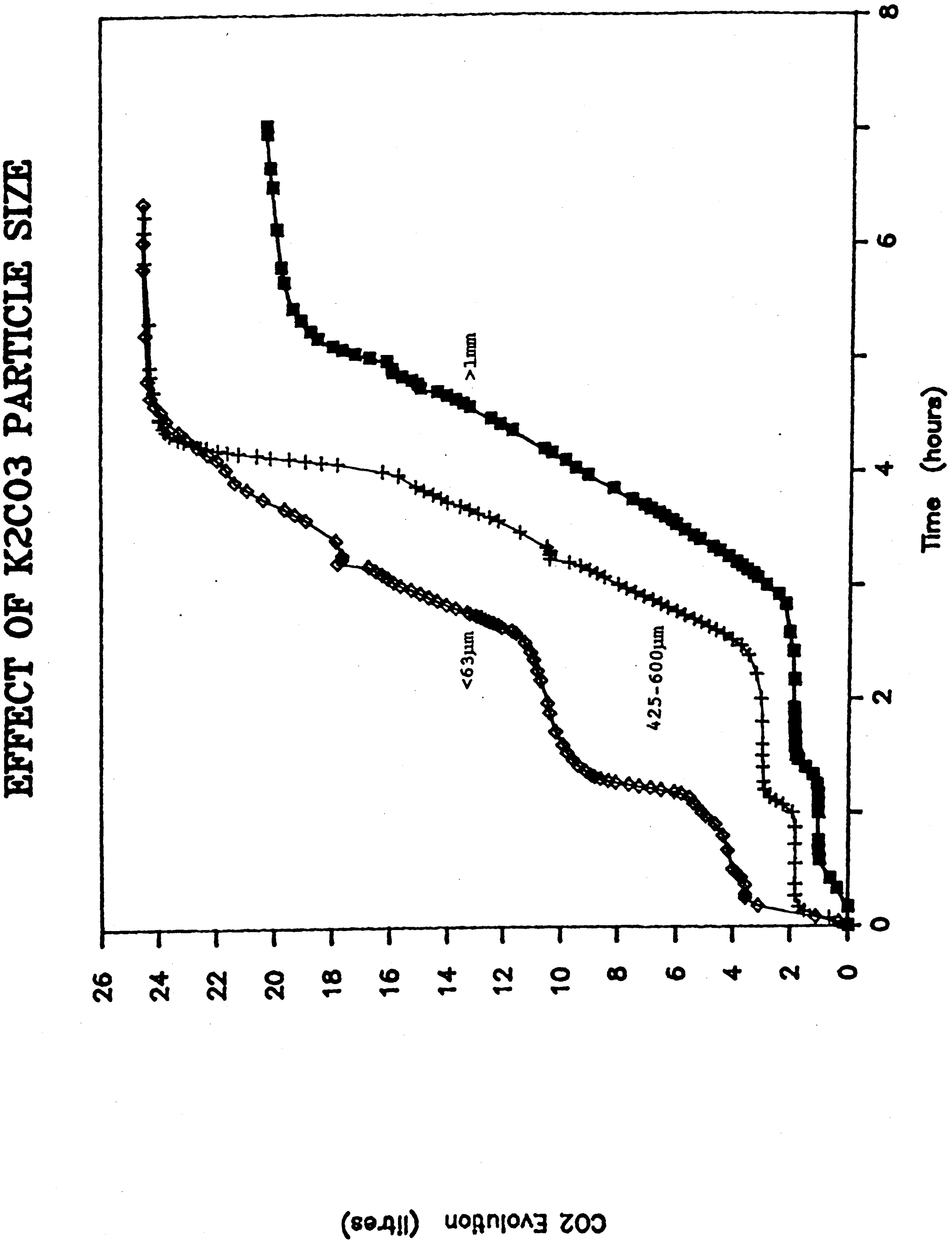
$$(d)\ HO\phi SO_2\phi O\phi SO_2\phi Cl + 1/2K_2CO_3 \xrightarrow{\sim 265^\circ C} KO\phi SO_2\phi O\phi SO_2\phi Cl + 1/2H_2O + 1/2CO_2$$

$$(e)\ nKO\phi SO_2\phi O\phi SO_2\phi Cl + Cl\phi SO_2\phi Cl \xrightarrow{\sim 285^\circ C} Cl(\phi SO_2\phi O)_{2n}\phi SO_2\phi Cl + KCl$$

It has been shown that the rate of CO_2 evolution is dependent on the particulate size of the K_2CO_3 (105 + graph 56), and the above series of reactions were thought to go to completion only if K_2CO_3 of less than 70µm was used, unless excessively long hold periods were incorporated. This proves that the system is heterogeneous, and that any kinetic study has to be conducted using a constant K_2CO_3 particulate size for the results to be reproducible. Each polymerisation undertaken in this study used K_2CO_3 sieved to less than 250µm.

From analysis of various polymerisation samples by ^{13}C solid state NMR it has been discounted that the polymerisation proceeds via the bis potassium salt of Bis-S (see later), and thus partial salts are formed which either react with DCDPS to form a chlorophenol(ate) oligomer or precipitate from solution and only further react at higher temperatures and under heterogeneous conditions.

Graph 56 : Effect Of K2CO3 Particulate Size On CO2 Evolution For PES



7.5.2 PES1

The first ramp temperature in PES1 was found to have an activation energy of 135.1 ± 13.9 $kJmol^{-1}$, the middle hold temperature was found to have an activation energy of 134.7 ± 15.9 $kJmol^{-1}$, whilst the final ramp temperature has an activation energy of 173.3 ± 11.7 $kJmol^{-1}$. The polymer is characterised by the inclusion of compound I rather than DCDPS, which results in a biphenyl linkage being incorporated into the polymer chain. This has the effect of reducing the initial reactivity of the activated chloro group due to the sulphone bridge effect being negated by the biphenyl linkage.

However, the difference in reactivity is expected to be minimal, as the difference in reactivity between 4-chlorodiphenyl sulphone and the first chlorine group in DCDPS has been shown to be in the ratio 1.5:1 (97). phenol/phenoxide base This reduction in reactivity has no noticeable effect on the evolution of CO_2, and thus it would suggest that the rate determining step is the formation of the phenoxide rather than its subsequent reaction with the activated chloro substituent. It would also suggest that I is not involved in the reactions leading to the evolution of CO_2, which is to be expected. However, the activation energies seem slightly higher than for PES, especially that of the final ramp temperature, which possibly suggests involvement by compound I, which causes increased solution viscosity at similar molecular weights to PES. which perhaps restricts CO_2 evolution.

7.5.3 PES2

The activation energy for the initial ramp temperature for PES2 was found to be 131.7 ± 4.6 $kJmol^{-1}$, whilst that of the second ramp temperature was found to be 237.2 ± 13.0 $kJmol^{-1}$. PES2 is a copolymer comprising 50 mol% DCDPS, 40 mol% HQ and 10 mol% Bis-S. The incorporation of the HQ moiety has a profound effect on the CO_2 evolution profile. The vast majority (~80%) of the CO_2 is evolved at a temperature of ~210°C, compared with the PES or PES1 CO_2 profile which would have evolved ~40-50% by the same stage. This could be due to the pKa's of the hydroxy protons in HQ and Bis-S being substantially different;

Sample	pKa_1	pKa_2
Bis-S	8.70	9.93
HQ	10.16	10.64

The Bis-S values do not have a correction for the activity of the sample, which would be expected to decrease each pKa by ~1 unit. The pKa's for Bis-S were measured by a method developed specifically for Bis-S due to its insolubility in water. An auxiliary solvent (acetone) was required, together with a surfactant (106). The HQ pKa's were measured by a published method (107).

The pKa values for Bis-S and HQ seem to contradict the CO_2 evolution studies. As the pKa's of the HQ protons are higher, and therefore less acidic, than the Bis-S protons, it would be expected that the Bis-S protons would be the first to react to form the phenate derivative.

It would therefore seem that although the pKa's of the hydroxy protons in HQ and Bis-S are substantially different, other factors such as solubility of the resulting phenoxides, the kinetics of the proton transfer and the fact that the pKa's were measured in a water based system and not in DPS, must cause the CO_2 to be evolved earlier in PES2 manufacture than in PES manufacture. The closeness of the HQ pKa's would cause the two hydroxyl groups to react almost at the same time, which would account for the large amount of reaction that is seen at ~210°C in the PES2 process.

CHAPTER 8: STUDY OF CHLORINE-ENDED OLIGOMERS BY HPLC

8.1 Introduction

No mechanistic studies have been performed to date on PES by the various polymerisation routes already discussed. It was decided to follow the formation of chlorine ended oligomers by HPLC in an attempt to deduce the mechanism of the polymerisation.

8.2 Method

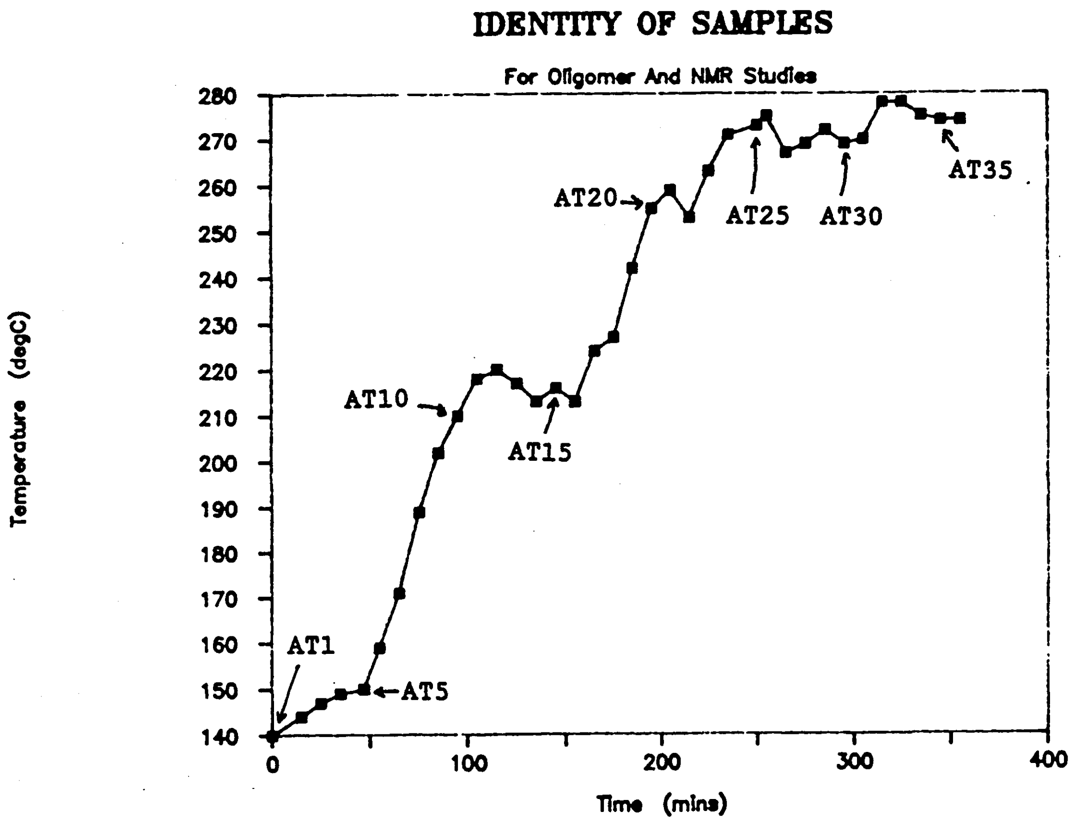
A normal laboratory polymerisation was performed with samples taken approximately every 15 minutes. The samples were spread thinly on aluminium foil to cool quickly and thus quench the reaction. A portion of the sample was then dissolved in dichloromethane. A detailed summary of the identity of the samples can be seen in Table 17 and in Graph 57. Complete dissolution did not occur due to the insolubility of the alkali metal salts and the phenate ended oligomers in the solvent. The solution was filtered and used in the analysis of chlorine-ended oligomers by HPLC.

The HPLC system used incorporated a Spectra-Physics SP8700XR LC pump interfaced via a dynamic mixer, autosampler and column to a Spectra-Physics SP8440XR UV/VIS detector.

Table 17: Identity of Samples for HPLC and NMR Studies

Sample	Time (mins)	Temp (°C)
AT1	0	140
AT2	15	144
AT3	25	147
AT4	35	149
AT5	47	150
AT6	55	159
AT7	65	171
AT8	75	189
AT9	85	202
AT10	95	210
AT11	105	218
AT12	115	220
AT13	125	217
AT14	135	213
AT15	145	216
AT16	155	213
AT17	165	224
AT18	175	227
AT19	185	242
AT20	195	255
AT21	205	259
AT22	215	253
AT23	225	253
AT24	235	271
AT25	250	273
AT26	255	275
AT27	265	267
AT28	275	269
AT29	285	272
AT30	295	269
AT31	305	270
AT32	315	278
AT33	325	278
AT34	335	275
AT35	345	274
AT36	355	274

Graph 57: Identity Of Samples For HPLC And NMR Studies



A Spherisorb S5CN (250cm x 4.9mm) reverse phase column was used together with a flow rate of 2ml/min, a 50μl loop, a block temperature of 40°C and the wavelength set at 268nm. A gradient system was used with three solvents - hexane, dichloromethane and methanol, all with 1% v/v glacial acetic acid (Graph 58). Each sample was studied so that the increase and subsequent decrease in chlorine-ended oligomer concentration could be monitored.

A limited set of standards were used so that qualitative and quantitative data could be recorded.

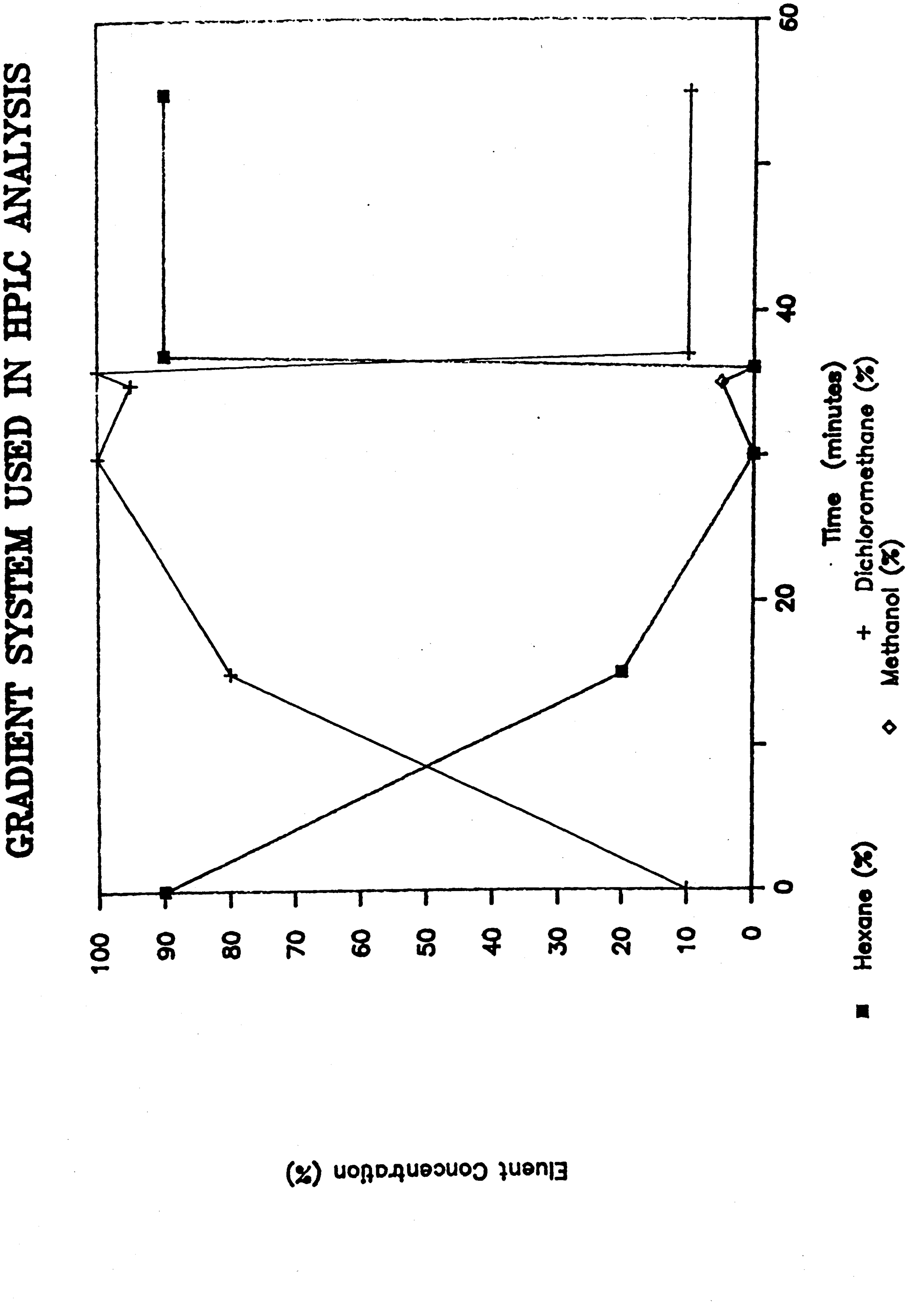
8.3 Results

8.3.1 Standards

Table 18: Results for Standards

Compound	Concentration $(*10^{-4}mol^{-1})$	Retention Time (mins)	Peak Height
DPS	12.792	5.54	33.7191
DCDPS	6.6027	4.13	42.3295
Cl-Dimer-Cl	4.1124	11.65	69.5534
Cl-Trimer-Cl	2.7991	16.52	294.8700
Cl-Tetramer-Cl	(1.8376)	19.08	44.6578
Cl-Pentamer-Cl		21.16	36.0291
Cl-Sexamer-Cl		22.57	25.9987
Cl-Septamer-Cl		23.81	18.7802
Cl-Octamer-Cl		24.77	12.7836

Graph 58: Gradient System Used For HPLC Study



The first four standards all produced chromatograms with a single strong peak, whereas the Cl-Tetramer-Cl gave a chromatograph which indicated a mixture of compounds. Field Desorption (FD) was used to separate the individual compounds in the Cl-Tetramer-Cl standard and thus facilitate their identification. By using this 'soft' mass spectrometric technique, the species of higher molecular mass could be identified before they fragmented during decomposition. The results showed that the standard was indeed a mixture of compounds whose molecular masses were identical to those calculated for the chlorine ended oligomers from the trimer through to the septamer. This meant that several of the peaks present in the HPLC chromatographs of the later samples from the laboratory polymerisation were able to be characterised. As the chain length of the oligomer increased, so it was retained longer on the column and thus oligomers up to and including the chlorine ended octamer were identified.

8.3.2 Samples

In all the samples the concentration of DPS should remain constant, as this is the polymerisation solvent and as such its concentration should remain unchanged throughout the reaction. However, due to the variation in sample size the peak height (PH) of the DPS signal in successive samples was not constant and so it was decided to standardise on a constant peak height of 60 for DPS. Also, the actual peak height of the DPS signal varied by ± 8% of the calculated value, and so all other peak heights were adjusted accordingly by taking into account the variance in the signal for each sample.

Table 19: Results for DPS and DCDPS

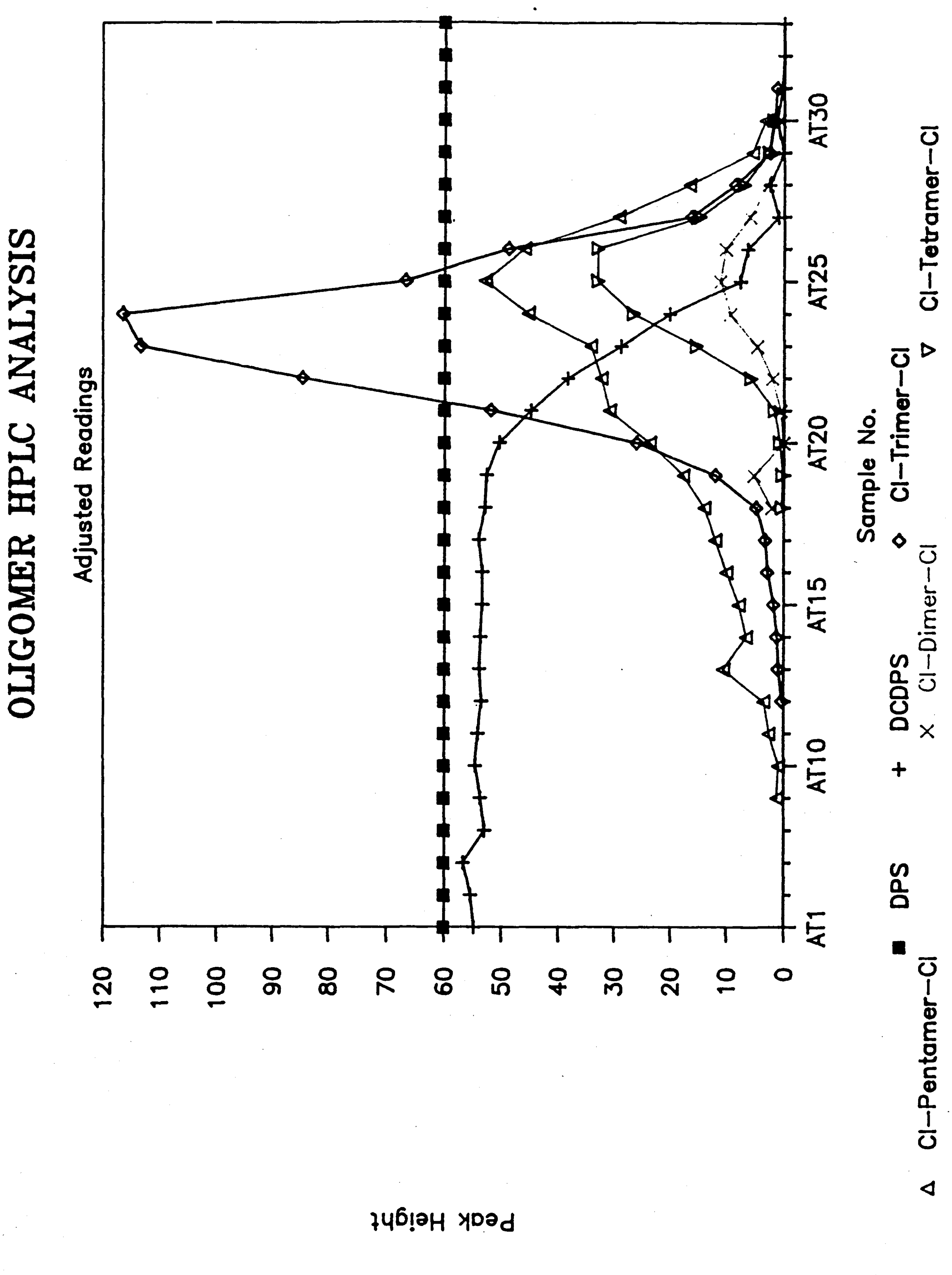
Sample	Time min	Temp. °C	Conc. g/l	Actual DPS PH	Adj DPS PH	Actual DCDPS PH	Adj DCDPS PH
AT1	0.00	140	0.292	16.1577	60	14.7522	54.7808
AT3	0.25	147	0.740	37.3648	60	34.4521	55.3228
AT5	0.47	150	0.684	36.7244	60	34.6188	56.5599
AT7	1.05	171	0.460	30.3975	60	26.8017	52.9024
AT9	1.25	202	0.348	18.9331	60	16.9090	53.5855
AT10	1.35	210	0.452	26.2033	60	23.8253	54.5570
AT11	1.45	218	0.346	19.4450	60	17.5080	54.0231
AT12	1.55	220	0.554	28.5834	60	25.4783	53.4820
AT13	2.05	217	0.441	22.5393	60	20.2171	53.8183
AT14	2.15	213	0.623	31.1483	60	27.8342	53.6162
AT15	2.25	216	0.467	22.7077	60	20.1687	53.2913
AT16	2.35	213	0.632	34.3695	60	30.5649	53.3582
AT17	2.45	224	0.794	45.1812	60	40.6285	53.9541
AT18	2.55	227	0.501	31.2472	60	27.5253	52.8533
AT19	3.05	242	0.850	56.0964	60	49.1781	52.6003
AT20	3.15	255	0.449	24.5997	60	20.6693	50.4135
AT21	3.25	259	0.641	32.1219	60	24.0716	44.9630
AT22	3.35	253	0.828	48.2015	60	30.8888	38.4496
AT23	3.45	263	0.882	44.9300	60	21.6640	28.9303
AT24	3.55	271	0.811	43.6894	60	14.6921	20.1771
AT25	4.10	273	0.658	33.0418	60	4.2341	7.6886
AT26	4.15	275	0.720	38.4569	60	4.0855	6.3741
AT27	4.25	267	0.704	36.0237	60	0.6043	1.0065
AT28	4.35	269	0.846	46.2966	60	1.9927	2.5825
AT29	4.45	272	0.790	44.3843	60	0.0000	0.0000
AT30	4.55	269	0.866	52.2494	60	1.0745	1.2339
AT31	5.05	270	0.741	41.2742	60	0.1497	0.2176
AT32	5.15	278	0.717	39.4100	60	0.0000	0.0000
AT33	5.25	278	0.682	35.07	60	0.0000	0.0000

From the chromatographs it was clear that dichloro-oligomer formation was not occuring before Sample AT9 after t = 1'25" when the contents temperature had reached 220°C, although the 'chlorohydroxy dimer' was presumably formed before this.

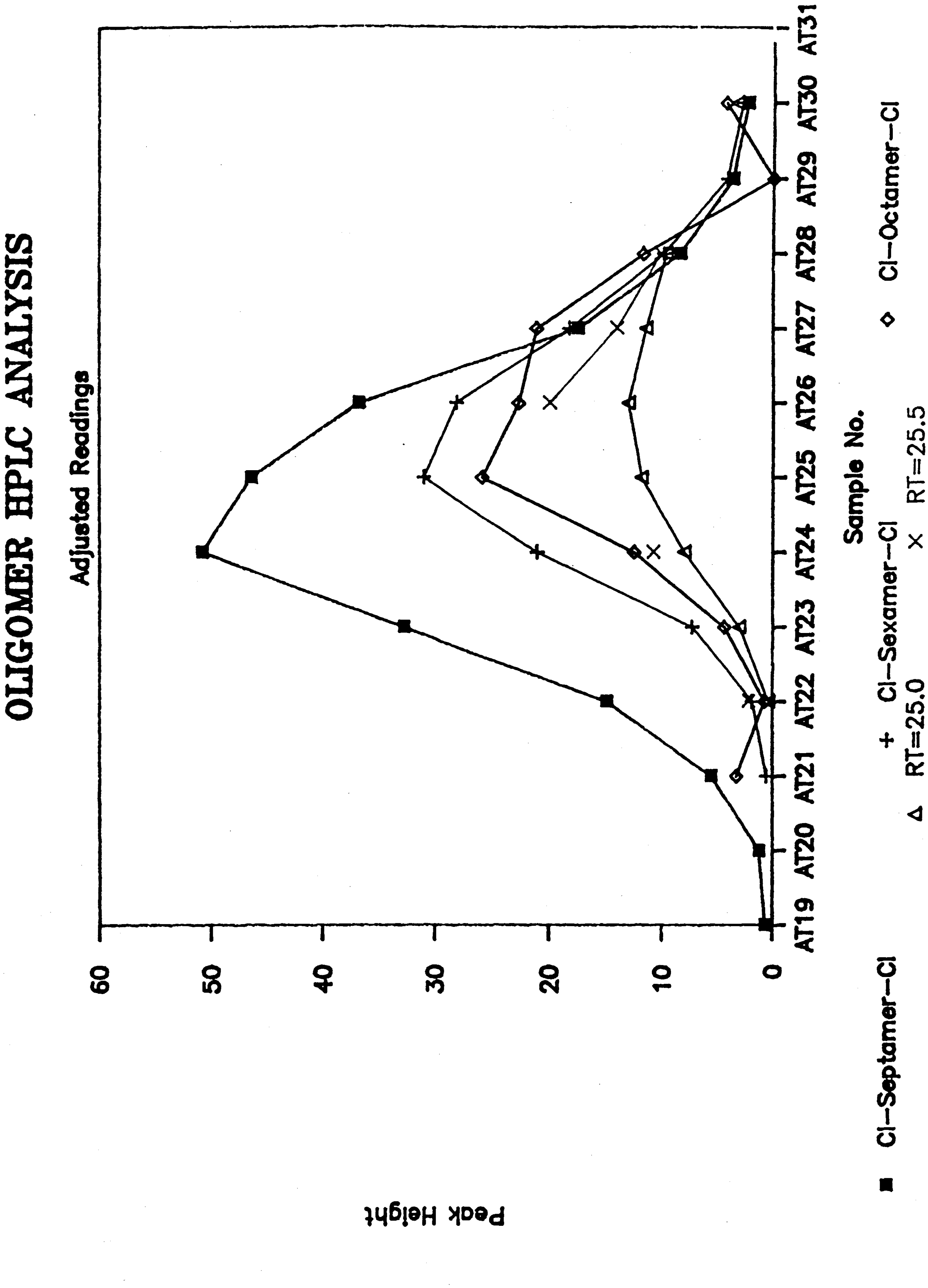
Table 20: Results for Oligomers

Sample	Dimer PH	Trimer PH	Tetramer PH	Pentamer PH	Sexamer PH	Septamer PH	Octamer PH
AT1							
AT3							
AT5							
AT7							
AT9				1.2242			
AT10				0.9546			
AT11				2.6070			
AT12		0.3016		3.5269			
AT13		0.9056		10.5903			
AT14		1.2230		6.5900			
AT15		1.7727		7.8954			
AT16		2.8620		10.0420			
AT17		3.2892		11.9948			
AT18	2.0740	4.8521	0.3061	13.9255			
AT19	5.2118	11.8961	0.2469	17.7481		0.6943	
AT20		26.0689	0.6771	23.7776		1.2361	
AT21	0.5473	51.8766	1.7015	31.0526	0.5865	5.6266	3.336
AT22	1.9614	84.5401	5.8253	32.4708	1.9188	14.9343	0.7429
AT23	4.6906	113.3093	15.3843	34.3580	7.3645	32.8868	4.4628
AT24	9.3480	116.3637	26.7171	45.5262	21.0754	50.8893	12.5794
AT25	11.0591	66.5332	33.1028	53.0023	31.0903	46.4237	25.7946
AT26	10.1570	48.8833	33.1178	46.0913	28.0913	36.9019	22.6747
AT27	5.9862	16.1565	14.7138	29.2979	18.2730	17.4981	21.1246
AT28	2.8075	8.4771	7.0594	16.6251	9.8907	8.4029	11.7631
AT29	1.0705	2.5174	2.6107	5.5357	4.2488	3.7382	
AT30	0.8107	1.5593	1.8551	3.2558	2.8946	2.3763	4.4088
AT31		1.1605					
AT32							
AT33							

Graph 59: Graph Of Peak Height v. Sample Number For
$\mathrm{Cl0SO20(O0SO20)_nCl}$ For n = 0-4



Graph 60 : Graph Of Peak Height v. Sample Number For $Cl0SO_20(O0SO_20)_nCl$ For n = 5-7, RT=25.0 & 25.5



8.4 Discussion

The first surprising result from this work was that the concentration of DCDPS had fallen from 100% to approximately 80% of the theoretical value by the time the first sample was taken at t=0'00", which was when the mixture was able to be stirred due to the melting of the DPS. At this temperature (140°C), there is appreciable reaction between Bis-S and K_2CO_3, as has been documented before in this work. From the work on CO_2 evolution it would appear that 20-25% of the theoretical volume of CO2 is evolved by the time the first temperature hold is complete, and this seems to correlate with the loss of ~20% DCDPS.

It therefore seems that one in four or one in five hydroxyl ends react to give the phenate derivative, which further react with an activated chloro end, with the rate determining step being the formation of the phenate. The actual species that is formed is not clear. It has been documented in the past (104), that the 25% evolution of CO_2 is due to the formation of a 'quarter salt' where one in four hydroxyls is converted to the phenate;

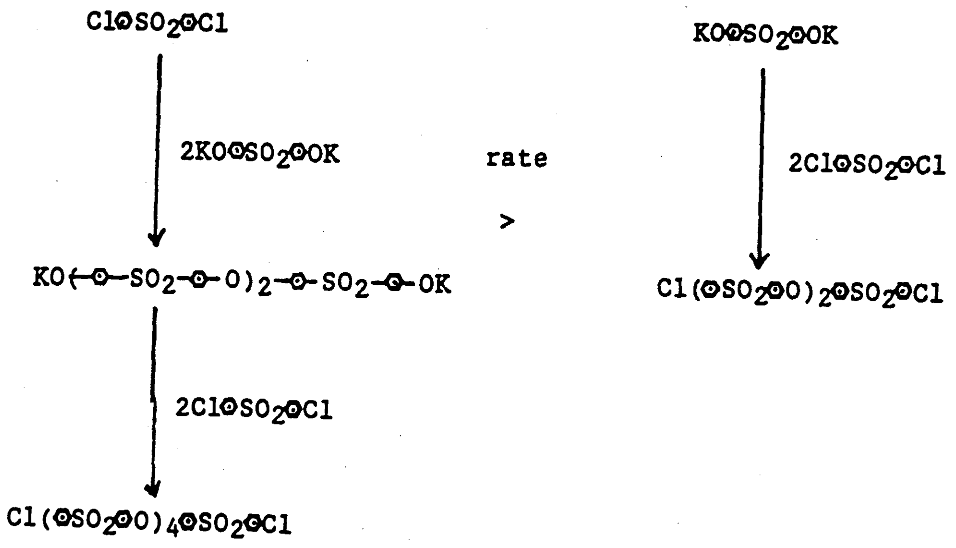
$$HO\odot SO_2\odot OH + 1/4K_2CO_3 \quad > 1/2HO\odot SO_2\odot OK.HO\odot SO_2\odot OH + 1/4CO_2 + 1/4H_2O$$

The 'quarter salt' complex would presumably be held together by some form of hydrogen bonding. This theory would explain the evolution of CO_2 but would not account for the apparent loss in DCDPS. The loss of DCDPS could be partially explained either by the formation of the 'chlorohydroxy dimer', or the formation of the dihydroxytrimer if two 'quarter salt' complexes reacted with one DCDPS, although it is unclear why the reaction ceases after only 20-25% conversion.

After the initial loss of DCDPS, however, the concentration of the dichloride remains constant until sample AT20, after 3'15" and at a temperature of 255°C. At this point DCDPS is consumed rapidly to the point where little or none is detected. Thus DCDPS is unaffected by the second period of CO_2 evolution, where again approximately 25% of the theoretical CO_2 is evolved.

Oligomer formation was shown to occur at significantly lower temperatures than previously thought. The presence of chlorine-ended oligomers was detected as early as sample AT9, which was taken after 1'25" when the temperature was only 202°C. This contrasts markedly with previous theories, where chlorine-ended oligomers were not expected below 260°C (104). However, oligomer formation is slow until ~255°C, where a rapid increase in the rate of formation is seen.

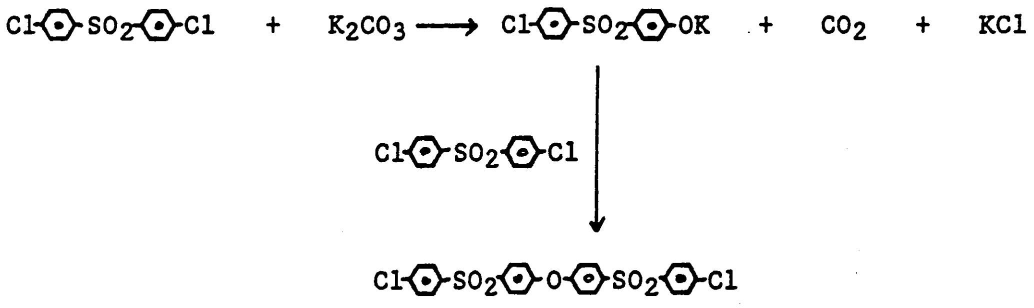
It is also evident from these results that formation of the Cl-Pentamer-Cl occurs before that of the Cl-Trimer-Cl. Thus, the initial reaction involving DCDPS is faster than the initial reaction involving Bis-S. The pictorial representation of this is given below, although the bispotassium salt of Bis-S is not thought to be formed per se, and the intermediate species may not be as depicted;



Further confirmatory evidence is that, from solubility studies performed on the potassium salts of Bis-S and other longer chain bisphenates, it is evident that the solubility of the phenate-ended oligomers in DPS increases with increasing chain length, to the extent that phenate-ended polymers of high molecular weight are totally soluble in the solvent.

Thus although DCDPS does not seem to be involved in any way with the evolution of CO_2 at ~210-225°C, it is evident that oligomer formation is a consequence of this reaction.

The appearance of the even numbered oligomers (Cl-Dimer-Cl, Cl-Tetramer-Cl, etc) could be explained by the work presented earlier in this thesis (Section 5.4) that hydrolysis of the activated halide on both the monomer and indeed the oligomer can occur via the interaction with potassium carbonate, eg;



However, the rate of hydrolysis is slow and thus the effect on the stoichiometry is limited and relatively large excesses of alkali can be employed. This compares markedly with the effect of adding excess alkali in the 'hydrolysis' route, where even a small excess caused the hydrolysis side reaction, precluding~~,~~ high molecular weight polymer being formed.

Hydrolysis of DCDPS is first detected by the appearance of Cl-Dimer-Cl at AT18, after t = 2'55" whilst the temperature is increasing to ~270°C, although at that stage it was only 227°C. Hydrolysis of the Cl-Trimer-Cl began at the same time, indicating that the reactivity of a chlorine end on a monomer is comparable to that on a oligomer/polymer. However, it has been shown in the past that the reactivity of one chlorine in DCDPS is complimented by the presence of the other, resulting in an increase in the rate of reaction of up to 60% (9~~5~~7). It is therefore surprising that the hydrolysis of the monomer does not occur appreciably before the hydrolysis of the Cl-Trimer-Cl. However, the reactivity of a chlorine group in DCDPS was compared against the chlorine group in 4-chlorodiphenyl sulphone and not a chlorine group at the end of a polymer chain. The presence of the aryl ether would be expected to reduce the reactivity of the chlorine group by its electron donating properties through the sulphone bridge. It is therefore not clear why hydrolysis of DCDPS occurs at the same time as hydrolysis of the Cl-Trimer-Cl.

The two compounds at retention time RT = 25.0 and RT = 25.5 (Graph 60) have not been identified, but they do follow a similar formation and consumption pattern as the other identified oligomers.

8.5 Field Desorption Mass Spectrometry

Field Desorption (FD) mass spectrometry was also conducted on the samples taken from the laboratory polymerisation discussed above. Oligomer formation has been studied in the past by this technique (108, 109), although this was the first study for the polyarylether sulphone family of thermoplastics.

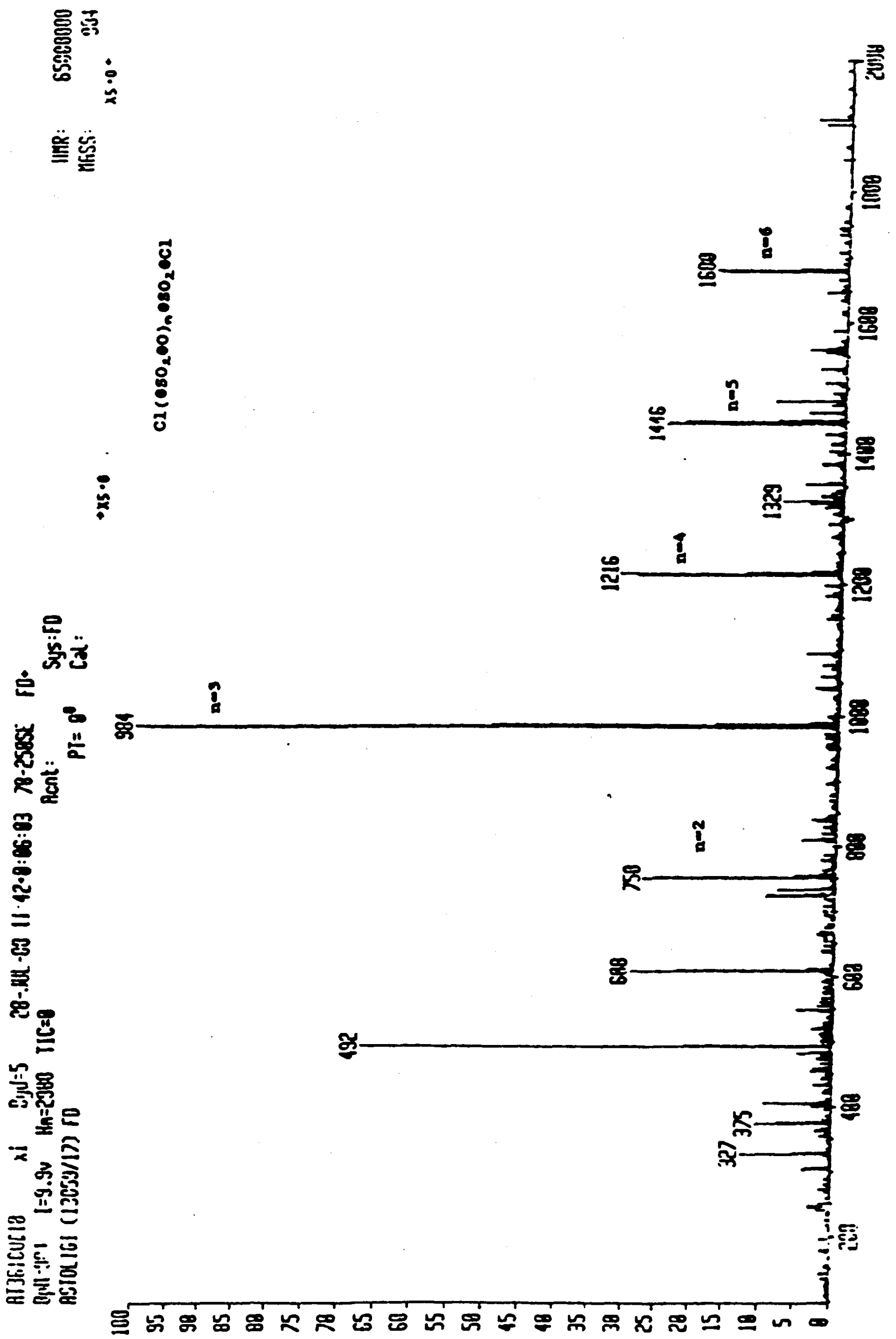
8.5.1 Method

FD analysis was performed on a ZAB2E mass spectrometer operating in the field desorption mode at an accelerating voltage of 8KV with an extraction voltage of 5KV. The mass spectrometer was scanned from mass 2000-100 exponentially with a scan speed of 10 seconds/decade. The data was acquired in the multi-channel analysis (MCA) mode, averaging all the scans together. The mass spectrometer was calibrated in the FAB ionisation mode using CsI. The emitter used for the analysis were carbon emitters grown on 10μm tungsten wire and the samples were loaded onto the emitters by syringe.

8.5.2 Results

Due to the minimal use of this technique in monitoring the formation of oligomeric species and also the limited availability of the instrument, the data obtained is less detailed than the previous study using HPLC. It does, however, demonstrate that FD can be usefully used in the study of oligomer formation and the kinetic considerations thereof, which is an original use of the technique.

Spectrum 3: FD Spectrum Of Sample AT25



Sample AT25 from the oligomer study was shown to have the greatest proportion of chlorine-ended oligomers by HPLC, and so this sample was studied in more detail than the others. Spectrum 3 shows there to be peaks at 750, 984 and 1216, 1446 and 1680 which correspond to the dichloro-trimer, tetramer, pentamer, sexamer and septamer respectively.

The peak at 1329 cannot be identified as an expected oligomer, although the peak height is abnormally high. A normal molecular weight distribution can be drawn to incorporate the five chlorine-ended oligomers; As the reaction proceeds the polymeric molecules tend to decompose in the mass spectrometer before detection, and thus it is not possible to follow the reaction beyond the septamer.

CHAPTER 9: STUDY OF THE PES POLYMERISATION BY NMR SPECTROSCOPY

9.1 Use Of NMR To Study A Typical Laboratory PES Polymerisation

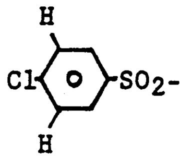
NMR was also used to study the polymerisation reaction to form PES. The study was undertaken to complement the chlorine-ended oligomer study using HPLC. Without isolating the polymer from the solvent, the chemical shift of the chlorine next to the ipso carbon is masked by the presence of DPS due to the resonances of the protons ortho and meta to the C-Cl bond both being masked by the resonances of the protons ortho, meta and para to the $-SO_2-$ group in DPS.

Isolating the polymer by traditional solvent extraction techniques could have led to water soluble oligomers (eg very low molecular weight bisphenates), or methanol/acetone soluble oligomers (eg low molecular weight chlorine-ended oligomers) being lost in the effluent.

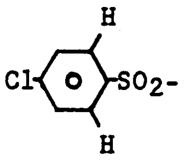
It was therefore decided to analyse the samples taken during a laboratory polymerisation by both solution and solid state NMR without isolating the polymer. The same laboratory polymerisation was analysed as in the chlorine-ended oligomer study, although the samples were taken at different times into the reaction.

9.1.1 Solution NMR Study

A series of standards was initially studied to determine the chemical shift of particular groups. Standards of the dichlorodimer and dichlorotrimer yielded resonances at ~7.7ppm and ~8.0ppm, characteristic of protons ortho and meta to a para-chloro substituted phenylsulphone:



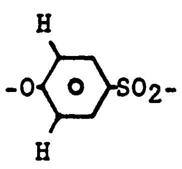
~7.7ppm



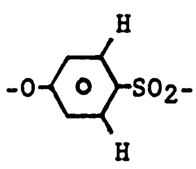
~8.0ppm

A series of partial potassium salts of Bis-S was interesting in that the chemical shift of the protons ortho and meta to the para O^- substituted phenyl sulphone shifted to a higher field as the ratio of OK:OH ends increased. The chemical shift of the protons ortho to the -OR group (where R = H or K) reduced from ~6.9 --> ~6.4 ppm as the percentage of ends as -OK increased from 0-100%.

Similarly, the chemical shift of the protons meta to the -OR group reduced from ~7.7-~7.4ppm as the percentage of ends as -OK increased from 0-100%.



~6.9-~6.4ppm



~7.7-~7.4ppm

A graph of chemical shift plotted against % ends as -OK yielded a gradual linear decrease of the chemical shifts of both the ortho and meta protons (Graph 61). This discovery allowed for an estimation of the percentage of ends as -OK in an oligomeric/polymeric system to be determined, as an integral of the peak area would previously have only yielded the total number of -OR groups.

9.1.1.1 METHOD

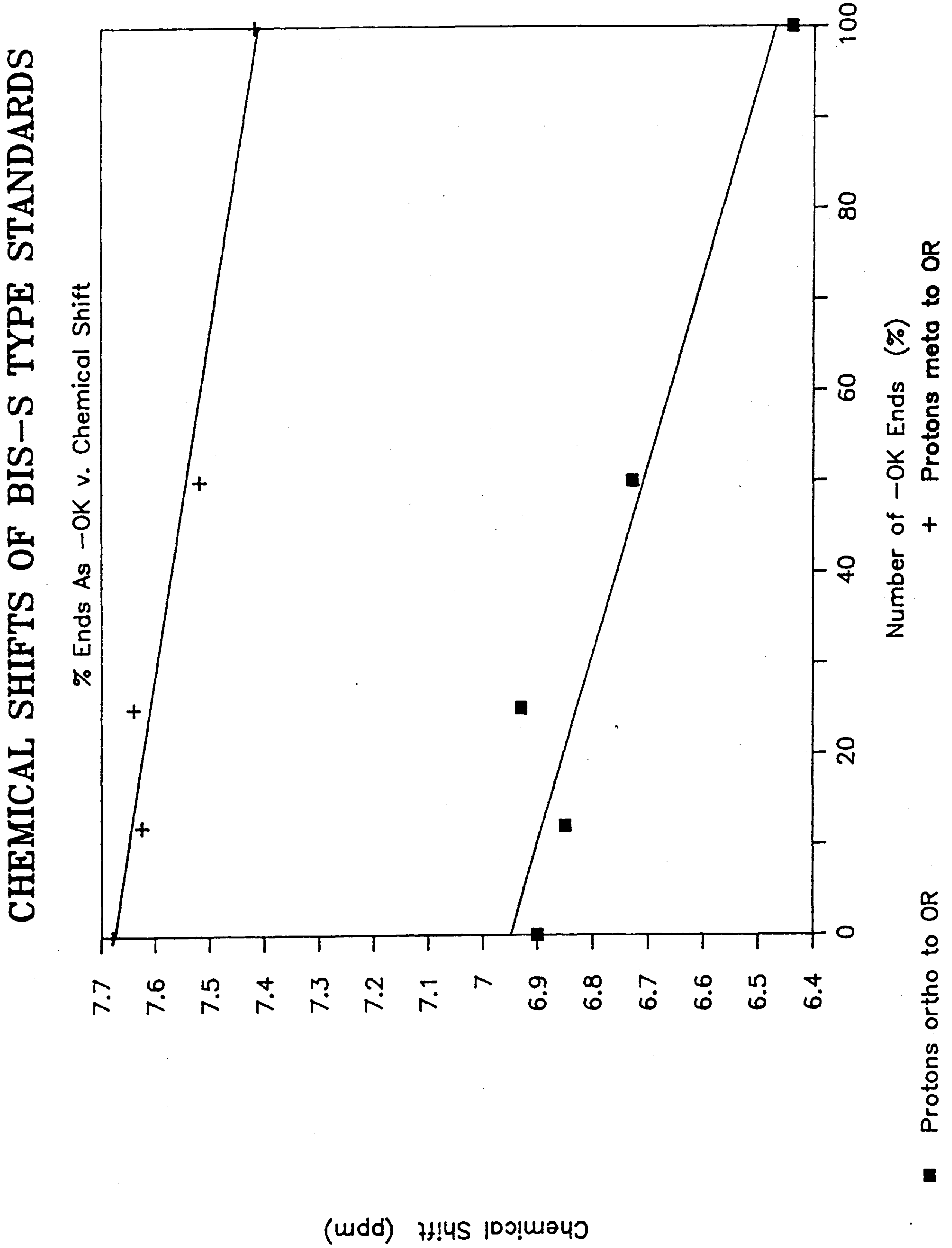
A series of samples was studied by accumulating 100 scans on a Jeol GX400MHz NMR at 80°C in DMSO. The reference for chemical shifts was taken as the central resonance of the d_6-DMSO solvent, pinpointed at 2.49ppm.

9.1.1.2 RESULTS

Table 21: Results for Normal PES Polymerisation Studied by Solution NMR

Sample	Int.@ 8.0ppm	Int.@ 7.85ppm	Int.@ 7.70ppm	Int. @ 7.40ppm	Int.@ 7.2ppm ether ?		Int. @ 6.50ppm	Int. @ 6.40ppm
4	51.2	1.3	68.2	17.0	0.4	3.4	16.6	1.7
6	49.9	3.3	65.1	17.1	0.7	6.7	14.5	2.8
10	51.7	3.5	66.0	15.0	1.1	7.4	11.7	3.3
14	51.3	4.2	62.7	15.7	1.4	8.5	12.0	3.6
20	51.0	3.0	63.0	17.5	2.3	6.6	13.8	2.6
22	52.8	3.5	60.4	15.0	6.4	8.1	10.7	2.8
26	64.6	2.4	52.0	5.1	23.6	6.2	3.0	3.0
28	71.0	low	48.0	0.5	38.6	low	0.5	0.6
33	70.2	low	46.5	0.7	41.0	low	0.5	0.4
Theo. Start	54.4		73.4	16.0	0		0	16.0
Theo. End	70.4		57.0	0	32		0	

Graph 61: Graph Of Chemical Shift v. % Ends As -OK



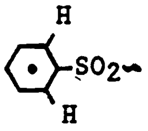
9.1.1.3 DISCUSSION

The polymerisation used 0.095 moles DPS, 0.0409 moles DCDPS and 0.040 moles Bis-S. These values were multiplied by 100 for ease of calculation and further multiplied by the number of aromatic protons per molecule in the polymerisation which gave a final total of 159.8.

The total area of the aromatic region of the spectrum was then subdivided so that the calculated area was 159.8. The relative intensity of the resonances at various chemical shifts could then be monitored as the polymerisation proceeded (Graphs 62, 63). Also, the theoretical initial and final intensities could be calculated and compared with the experimental results.

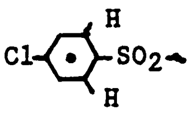
Even the very early samples taken at 149°C (Sample 4) and 159°C (Sample 6) showed evidence of aryl ether formation, with the chemical shift of the protons ortho to the aryl ether being detected at ~7.26ppm.

The resonances at ~8.0ppm are due to the protons ortho to the $-SO_2-$ group in DPS, the protons meta to a p-chlorosubstituted phenylsulphone and the protons ortho to the sulphone group in the polymer, as indicated below:

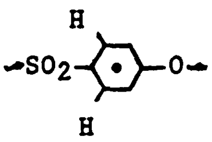


from DPS

~8.0ppm



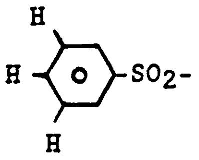
~8.0ppm



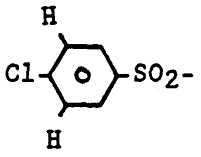
~8.0ppm

As can be seen from Table 21 the relative intensity of the peaks at ~8.0ppm rise from approximately the initial value of 54.4 to approximately the theoretical final value of 70.4 (Graph 62). However, a substantial rise is only detected in the last three samples which must be due to significant formation of aryl ether groups. This suggests that polymer formation only occurs to any great extent at temperatures above ~250°C.

Also plotted on the same graph is the reduction in intensity of the resonances at ~7.70ppm, which have been attributed to the two meta and one para protons relative to the $-SO_2-$ group in DPS and the two protons ortho to the chlorine group in the p-chloro substituted phenylsulphone:



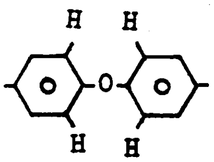
~7.70ppm



~7.70ppm

Again, early samples indicated little change in the relative intensity of the resonances from the theoretical start point, but a significant drop occurs over the last three samples, when the activated chloro group is displaced to form polymer by polyetherification.

A resonance not masked by the presence of DPS is the peak due to the protons ortho to an aryl ether within the polymer:

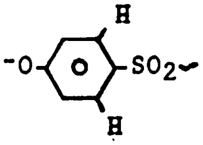


~7.2ppm

This is located at ~7.2ppm and is also tabulated in Table 21. As can be seen from Graph 62 , aryl ether formation becomes rapid, quickly rising to, and indeed above, the theoretical maximum relative intensity of 32.0.

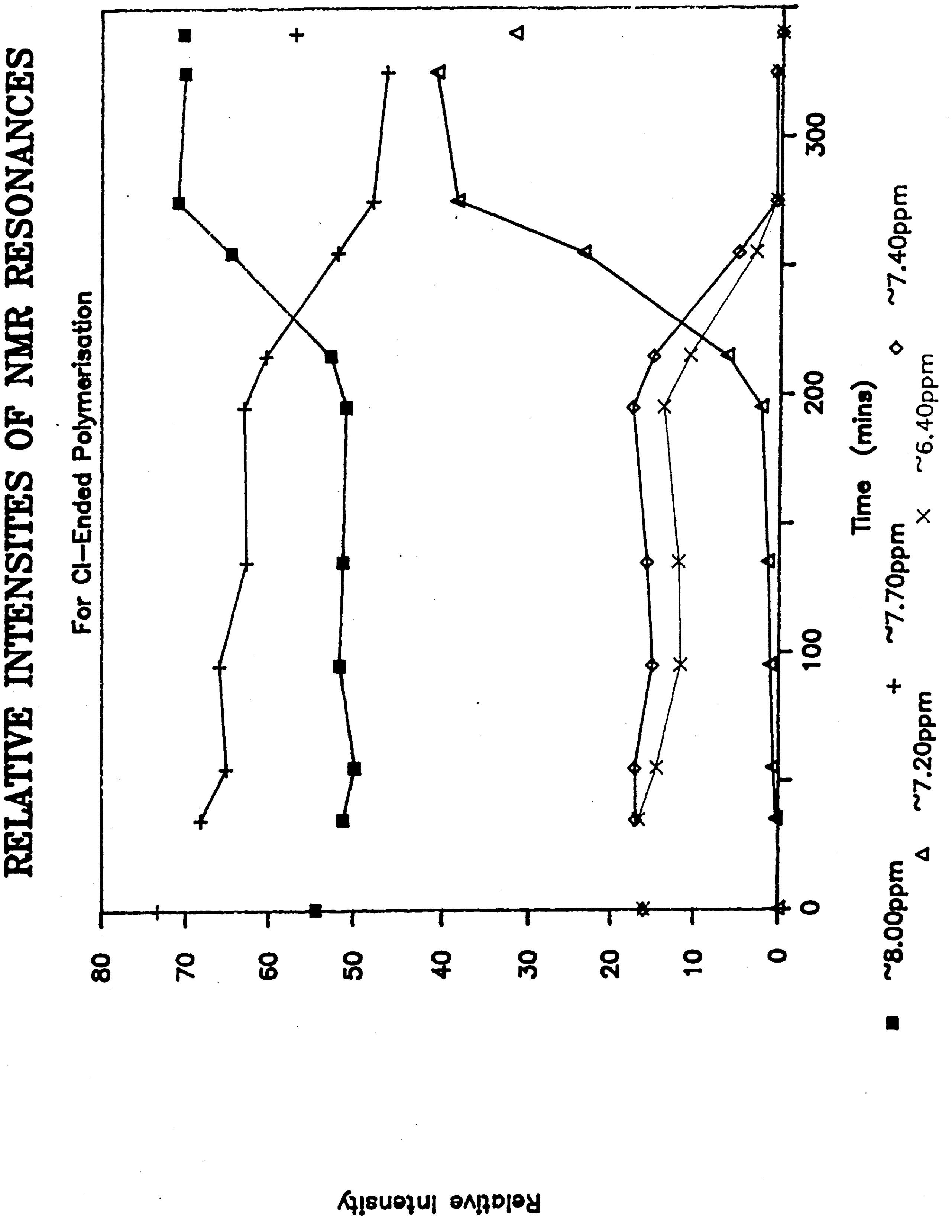
There is a further resonance located at ~7.2ppm which has not been characterised. It is a discrete compound which is present in Sample 4 and remains effectively unchanged until Sample 28 where the intensity drops markedly and remains low for the following, last sample. However, its presence in the last sample raises some questions, as in previous studies of PES polymer by NMR a similar species has not been detected. It therefore seems to be a species that is water, methanol or acetone soluble, and thus is removed during the normal isolation procedure.

A second resonance which is not masked by DPS resonances is the peak due to the protons meta to a p-O⁻ substituted phenyl sulphone:

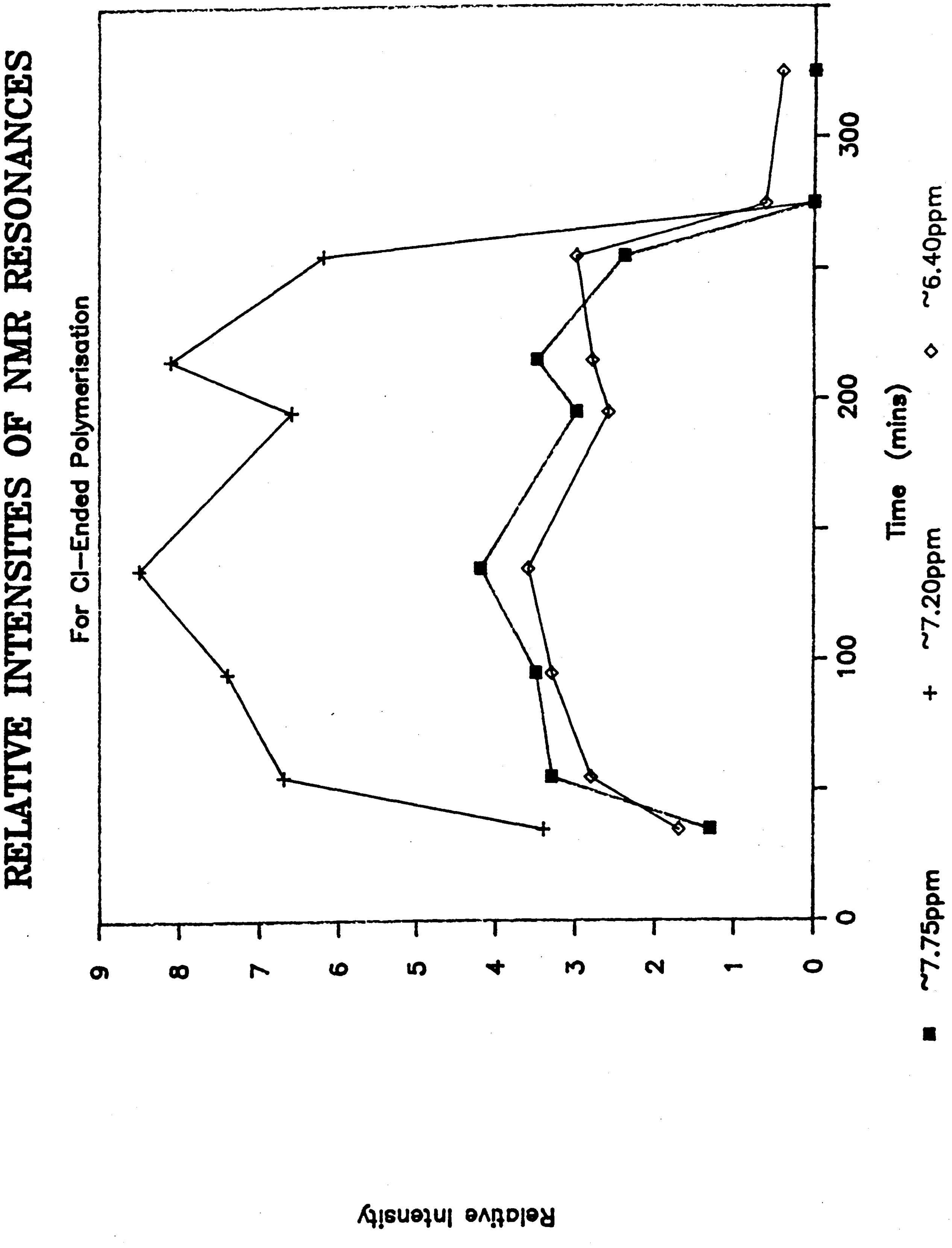


~7.4ppm

Graph 62 : Graph Of Relative Intensity Of Resonances v. Time For Normal PES Polymerisation

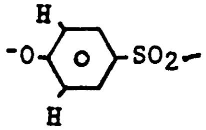


Graph 63 : Graph Of Relative Intensity Of Resonances v. Time For Normal PES Polymerisation (For Unknowns)



This has a chemical shift of ~7.4ppm, has a relative intensity of ~16 (the theoretical start point) during the early samples, and again shows little reduction until Sample 22 when the relative intensity falls rapidly to approximately zero.

The protons ortho to a p-O⁻ substituted phenyl sulphone have a chemical shift of ~6.5ppm, depending on the nature of the -OR group:

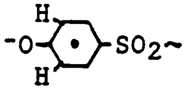
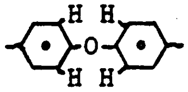
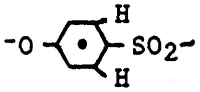
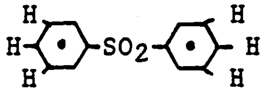
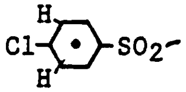
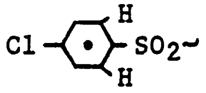
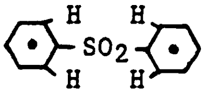
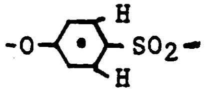


~6.5ppm

The relative intensity again is seen to drop off rapidly during the last three samples to approximately zero. The relative intensity in the first sample is close to the theoretical value of 16, with further samples indicating a slow reduction in the relative intensity to 10.7 before the rapid reduction as discussed above.

All five sets of resonances at ~8.00ppm, 7.70ppm, ~7.2ppm, ~7.4ppm and ~6.5ppm, tabulated in Table 22, indicate that polymerisation occurs rapidly above 260°C, and below that temperature, little chain lengthening takes place.

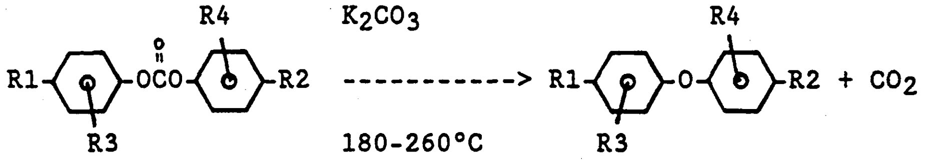
Table 22: Chemical Shifts for Various Structures

Structure	Chemical Shift (ppm)
	~6.9 - ~6.4
	~7.2
	~7.7 - ~7.4
	~7.7
	~7.7
	~8.0
	~8.0
	~8.0

Also, all five sets of resonances show no real change over the temperature range 200-250°C, whereas a considerable amount of CO_2 is evolved at ~210°C, as has been demonstrated by the CO_2 evolution studies discussed earlier. This suggests that the reaction(s) occurring at ~210°C which lead to the evolution of CO_2 do not consume or form species which are NMR active.

What is also evident in the early samples is that from the intensity of the resonances at ~7.40ppm and ~6.5ppm, due to protons meta and ortho to an aryl ether respectively, it seems that approximately half of the Bis-S hydroxyl groups have been reacted to form phenates, indicating that half of the potassium carbonate and indeed half of the CO_2 has been reacted or formed respectively. This obviously contradicts the previous CO_2 evolution study in Chapter 7 in that 20-25% of the theoretical CO_2 is evolved initially and then CO_2 evolution effectively ceases until the temperature is increased to 210-225°C where a further 30-25% of the theoretical CO_2 is evolved.

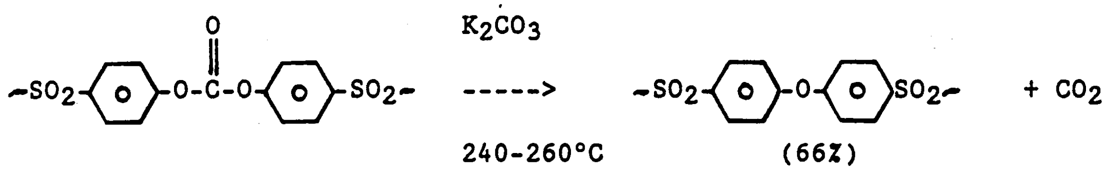
One possible explanation of this anomaly is that aryl carbonates are being formed which decompose as the temperature is increased. Witt, Holtschmidt and Muller documented in a paper published in 1970 that diphenyl ethers could be prepared by the base catalysed condensation of diphenyl carbonates (110);



where R1,R2 = $SO_2C_6H_5$ R3,R4 = H

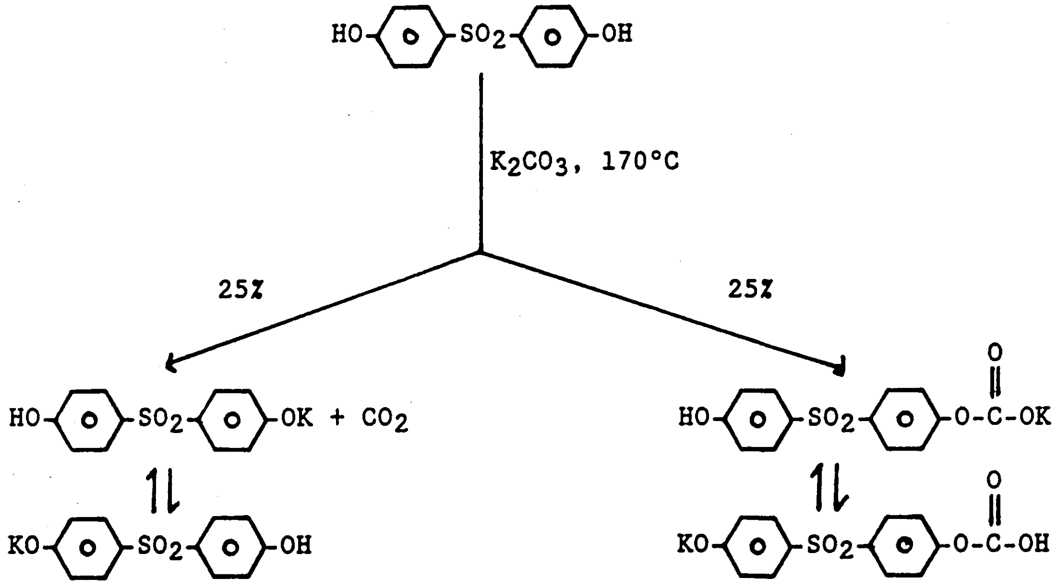
(NO_2, CN NO_2, Cl)

A prerequisite of the reaction was that at least one of the groups R1-R4 was a second order substituent (eg $-NO_2$, $-CN$, $-Cl$, $-SO_2C_6H_5$, $-COOCH_3$). Useful yields were only attainable from symmetrically substituted, particularly p,p'-disubstituted diphenyl carbonates. One system studied was where R1 and R2 were $-SO_2C_6H_5$ using one mole wt% K_2CO_3 catalyst with respect to the diphenyl carbonate;

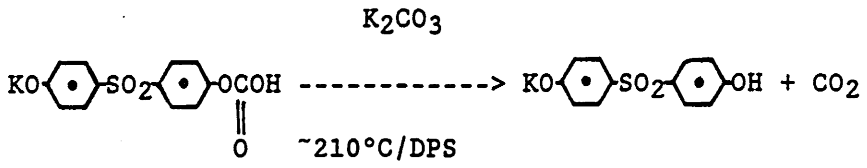


The 66% yield was without optimisation, and although the temperatures indicated are higher than postulated here, the effect of the DPS solvent may reduce the final temperature required.

In the system under investigation, if indeed 50% of the potassium carbonate does react almost immediately, 20-25% of the CO_2 may be evolved and detected as has been observed, whilst the other 30-25% may be incorporated as a phenyl carbonate:



Both products would be subject to an equilibrium involving the exchange of the potassium ion. The aryl carbonate would then be subject to base catalysed condensation as the temperature was increased to ~210°C;



Although the above system was not studied by Will et al (110), nor during a brief study of this chemistry undertaken within ICI (111), and although it is not symmetrical or p,p'-disubstituted, yields of ~25% are feasible. Also, it provides a theory which satisfies both the CO_2 evolution phenomenon and the studies by solution NMR.

Infra-red (IR) studies on three samples from the same laboratory polymerisation were also undertaken, primarily to verify the presence of the aryl carbonate group. The study was inconclusive, although it was evident that aryl carbonates were not present in concentrations expected from the hypothesis.

Three other resonances, at ~7.75 ppm, ~7.20 ppm and ~6.40 ppm are also affected by the polymerisation (Graph 63), but as yet the groups associated with these resonances have not been characterised. It can be seen, however, that all show an initial increase during the first two samples, remain relatively constant until Sample 26 (275°C), whereupon all three rapidly reduce to approximately zero.

9.1.2 Solid State NMR Study

Solid State ^{13}C Cross Polarisation (CP) Magic Angle Spinning (MAS) NMR was also used to study the laboratory polymerisation of PES. Samples from the same sequence as before were analysed, together with a number of standards. These standards were partial and full potassium salts of Bis-S and clearly demonstrated that the C4, C4' carbon was sensitive to the formation of the phenoxide ion. Resonances arising from carbons in DCDPS were masked by the presence of DPS and thus the polymerisation was followed by studying the effects of the reactions on the resonances of the carbons in Bis-S.

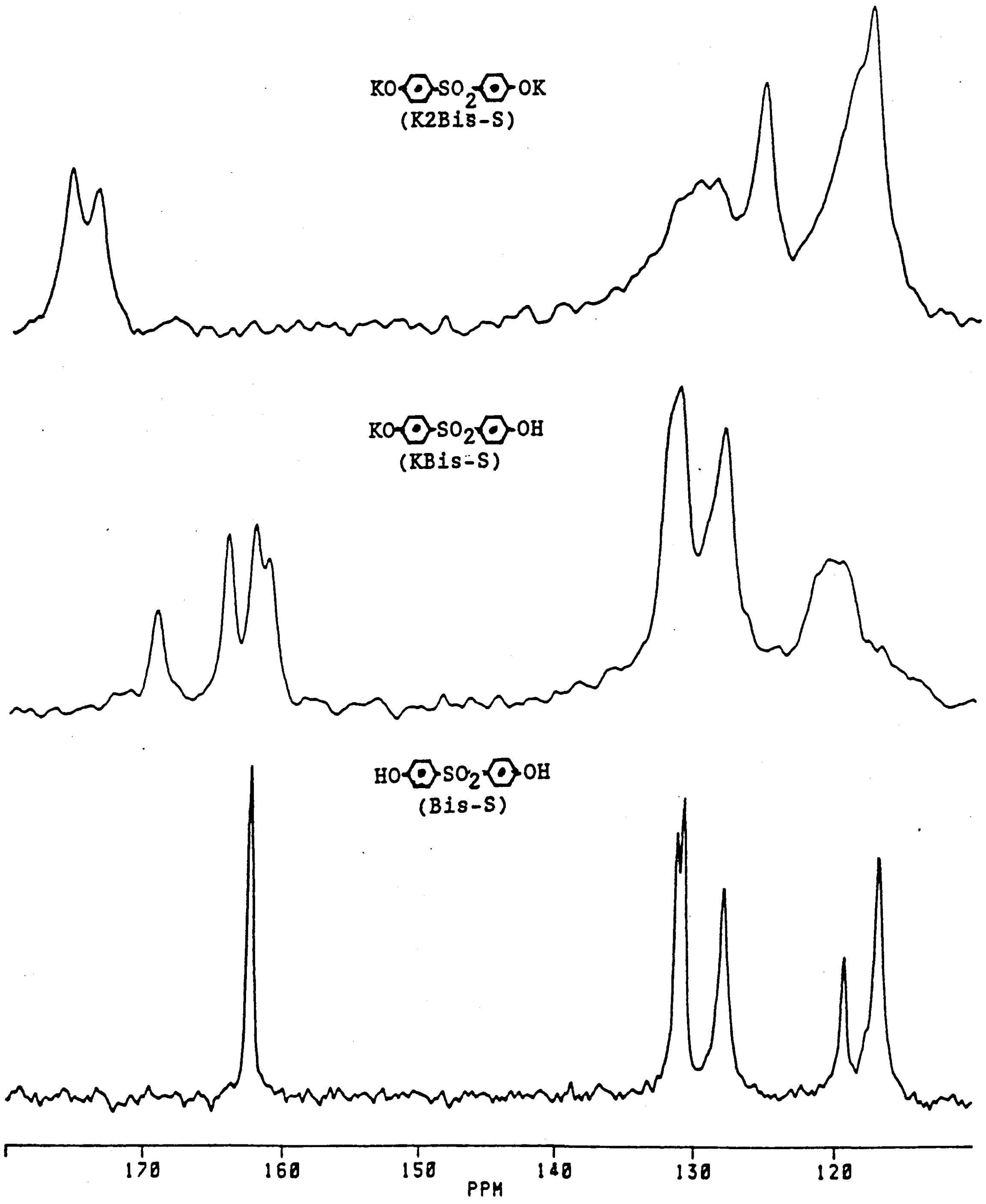
9.1.2.1 METHOD

The standards that were analysed were Bis-S and the corresponding mono (KBis-S) and dipotassium (K_2Bis-S) salts. Samples were taken from a normal laboratory polymerisation. Standard high resolution ^{13}C CP MAS NMR experiments were used throughout the study. A long cycle delay of thirty seconds was used to ensure that there were no saturation effects. In each analysis a contact time of 1ms was used in the cross-polarisation pulse sequence and a similar spinning rate was used.

9.1.2.2 RESULTS

The resonance shift of the C4, C4' carbon in Bis-S due to the formation of mono or di potassium salts can be seen in Spectrum 4. A sample of K_2CO_3 in DPS was also analysed and this gave a strong carbonate resonance at 169ppm.

Spectrum 4: NMR Spectra For Potassium Salts Of Bis-S



No major changes in the spectra of the polymerisation samples was observed until the temperature reached 263°C, which was 3 hours 45 minutes into the reaction. A set of typical spectra are shown in Spectra 5-9. These are due to the following samples;

Table 22: Identity of Spectra 5-9

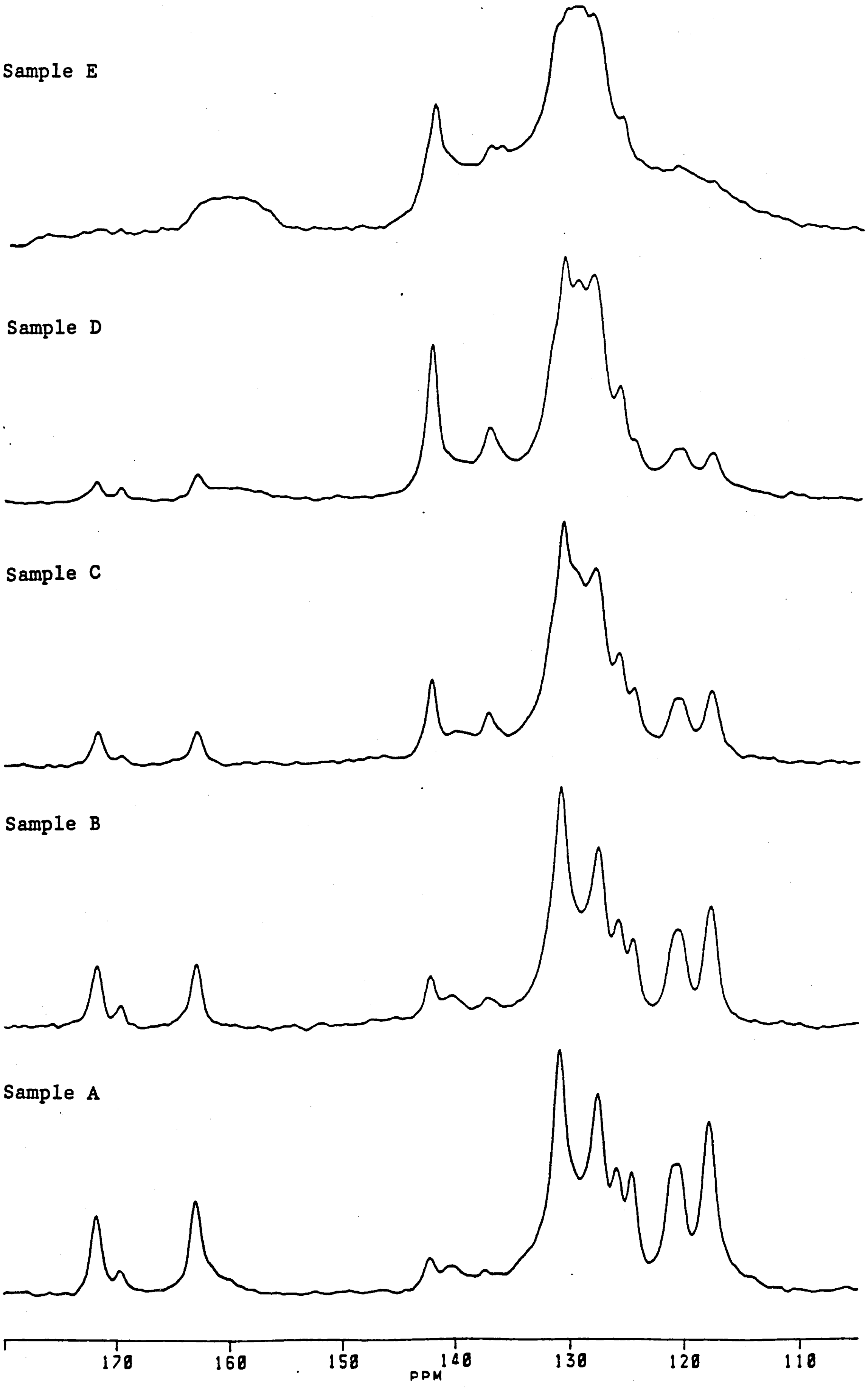
Spectrum	Time Hr.Min	Temp. °C
A	0.15	144
B	1.45	218
C	3.15	255
D	3.55	271
E	4.25	267

9.1.2.3 DISCUSSION

The resonance of the C4, C4' carbon in Bis-S occurs at 162.3ppm and those of the C4, C4' carbon in the dipotassium salt (K2Bis-S) occur at 175.8 and 173.7ppm. The chemical shift difference of ~12ppm is consistent with literature values of the ionisation shift (112). The presence of two resonances for K2Bis-S could be due to the loss of a crystallographic symmetry element relating to the two benzene rings.

The spectrum of the mono potassium salt (KBis-S) is more complex in the C4, C4' region and implies that a pure half salt has not been prepared. However, one possible interpretation of the four resonances is that the resonance at 169.4ppm is due to K2Bis-S (with a 4ppm shift of the resonance), the one at 164.3ppm is from the phenoxide C4 in KBis-S, and the two resonances at ~162ppm would then be the protonated C4(OH) and the other, at 161.3ppm, would be from Bis-S.

Spectra 5-9: NMR Spectra Of Samples From Normal PES Polymerisation



This would therefore indicate that the C4 resonances for KBis-S appear midway between the corresponding resonances arising from the free acid and the dipotassium salt.

The spectra of the samples from the polymerisation show a complex and rather uninformative aromatic region from 125 to 135ppm due to the presence of DCDPS, Bis-S and DPS (Spectra 5-9). However, outside of this region there are several resonances which are of value, namely the carbons ortho to the hydroxyl group at 120ppm, the ipso carbon in diphenyl sulphone at 142ppm and, of most value, the ipso carbon of the phenoxide at 170ppm and the ipso carbon next to the hydroxyl at 163ppm. There is a major change in the spectra as the sample number, and hence the temperature of the reaction, increases, with the apparent increase in the intensity of the DPS resonances such as the one at 142ppm. This is almost certainly due to the saturation of the DPS resonances at the lower temperatures, despite the long cycle delay. This phenomena is generally due to poor mixing of the medium, and to see such a difference in the ^1H T_1 implies a domain size of >200Å. This suggests that the Bis-S moiety is insoluble in DPS, due to reaction with K_2CO_3. Because of the broadening of the surrounding resonances, the effect of increased intensity is emphasised by the sharpness of the DPS resonance.

The major finding from this work confirms the earlier solution NMR study, in that little difference is observed in the early samples until the temperature reaches ~263°C. However, the presence of resonances at ~170ppm, typical of a phenoxide and carbonate ion, in even the earliest sample again demonstrate that the reaction between Bis-S and K_2CO_3 is rapid and occurs as soon as the polymerisation solvent DPS melts at ~129°C, allowing efficient mixing.

The spectra indicate that ~50% reaction between the carbonate and Bis-S occurs within ~5 minutes of the commencement of the temperature profile at ~144°C.

There is a small change between the first two samples (0mins @ 140°C and 25mins @ 144°C), but after that no reactions seem to occur which would affect the NMR spectrum. During this time the spectra are characterised by two main resonances, at 171.2 and 162.0ppm respectively, which are of similar intensity. There is also a minor resonance at 169.6ppm due to the carbonate.

Due to the relative intensities of the two main peaks it seems possible that a half salt has been formed, but with a 4ppm shift on the C4 phenoxide carbon. However, due to the complex nature of the half salt standard, it is not possible to verify the formation of the half salt. Thus the exact nature of the partial salt is unclear, but it is evident that the stoichiometric reaction between Bis-S and carbonate has not occurred. It is also evident from the saturation of the DPS resonance discussed earlier, that the two resonances at 171.2 and 162.0ppm are not due to a bis potassium salt and unreacted Bis-S. As the Bis-S is soluble in DPS, the domain effect described earlier would not be so apparent. Therefore, this study suggests that all the Bis-S reacts almost immediately with the K_2CO_3 to form partial potassium salts of Bis-S which are insoluble in DPS. This contradicts both the earlier oligomer study and the CO_2 evolution study, in that the former indicated oligomer formation as low as ~205°C and the latter was characterised by ~30% of the CO_2 being evolved at ~210-215°C. The NMR study would suggest that both of these phenomena must involve reactions which are either undetectable in the phenate region being analysed, or they involve changes to which the NMR spectrum is not sensitive.

A large change is observed in the NMR spectra at ~263°C, where a broad resonance is formed at ~159ppm with a consequent decrease in the resonance at ~170ppm. The broad resonance is due to aryl ether formation and its broadness is a function of the amorphous nature of the polymer;

Discrete resonances have been observed for oligomers containing six benzene rings or less, and thus the broadness of the aryl ether peak suggests that oligomer formation is not taking place through the phenoxide ion without immediate further reaction to higher molecular weight polymer. This indicates that the rate determining step is the formation of the phenoxide, and once this occurs polymerisation is rapid. The concentration of oligomers at any time would therefore be expected to be <5-10% of the mixture.

9.2 Use Of Solution NMR To Study Phenate-Ended Polymerisation

Due to the irregularities identified in the reaction of the Bis-S monomer, a polymerisation was undertaken using a 2.0% molar excess of Bis-S to control the molecular weight. This is normally achieved by the addition of a slight molar excess of DCDPS resulting in a polymer with chlorine end groups. With the addition of a small molar excess of Bis-S this would prolong the presence of hydroxyl-based end groups and thus could yield further information about the polymerisation process.

9.2.1 Method

Samples were taken once the temperature profile had reached 260°C, and spanned a 3.5 hour period as the polymerisation proceeded. A graph of the RV and temperatures against time was plotted (Graph 64), as well as the pertinent end group concentrations against time (Graph 65). It can be seen that the contents temperature was maintained at ~265°C for 1.25 hours before being raised to ~280°C for the final polymerisation temperature.

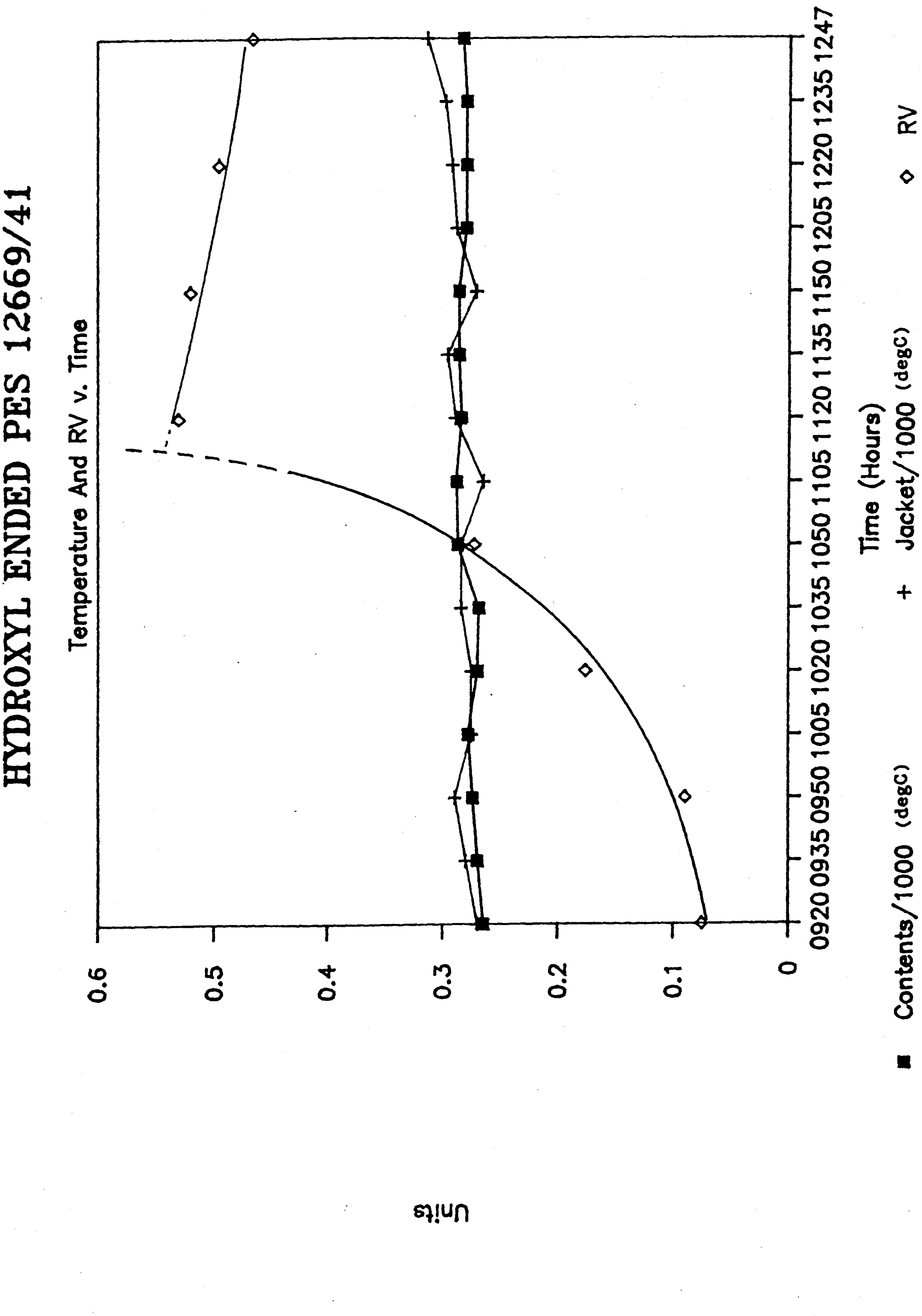
The sample taken at 0935 hrs does not appear to be representative as the end group concentrations of successive samples follow some sort of trend apart from this sample.

9.2.2 Results

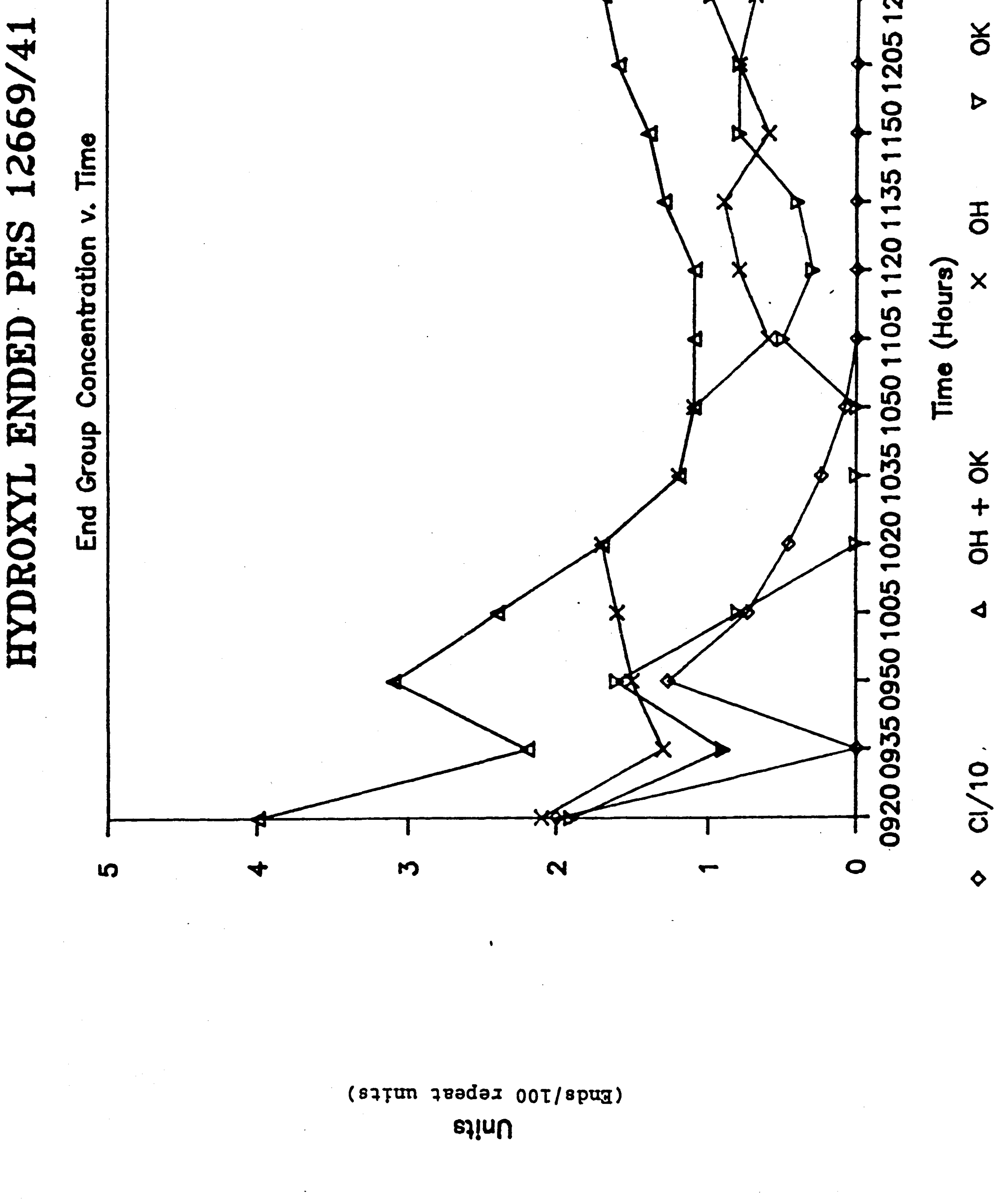
Table 23: Results for Phenate-Ended Polymerisation Studied by Solution NMR

Time	Jacket Temp°C	Contents Temp°C	RV	-Cl	OH+OK	%OK	OH	OK
0920	270	265	0.074	20.0	4.0	48	2.1	1.9
0935	280	270		?	2.2	41	1.3	0.9
0950	289	274	0.089	12.7	3.1	53	1.5	1.6
1005	275	278		7.4	2.4	34	1.6	0.8
1020	275	270	0.176	4.6	1.7	0	1.7	0.8
1035	284	269		2.4	1.2	0	1.2	0
1050	284	287	0.272	<0.8	1.1	0	1.1	0
1105	265	288		-	1.1	48	0.6	0.5
1120	289	284	0.527	-	1.1	24	0.8	0.3
1135	296	286		-	1.3	29	0.9	0.4
1150	271	286	0.517	-	1.4	58	0.6	0.8
1205	288	280		-	1.6	50	0.8	0.8
1220	292	280	0.492	-	1.7	58	0.7	1.0
1235	298	280		-	1.6	65	0.6	1.0
1247	314	283	0.463	-	1.7	62	0.7	1.0

Graph 64: RV And Temperature v. Time For Phenate-Ended Polymerisation



Graph 65: Graph Of End Groups v. Time For Phenate Ended Polymerisation

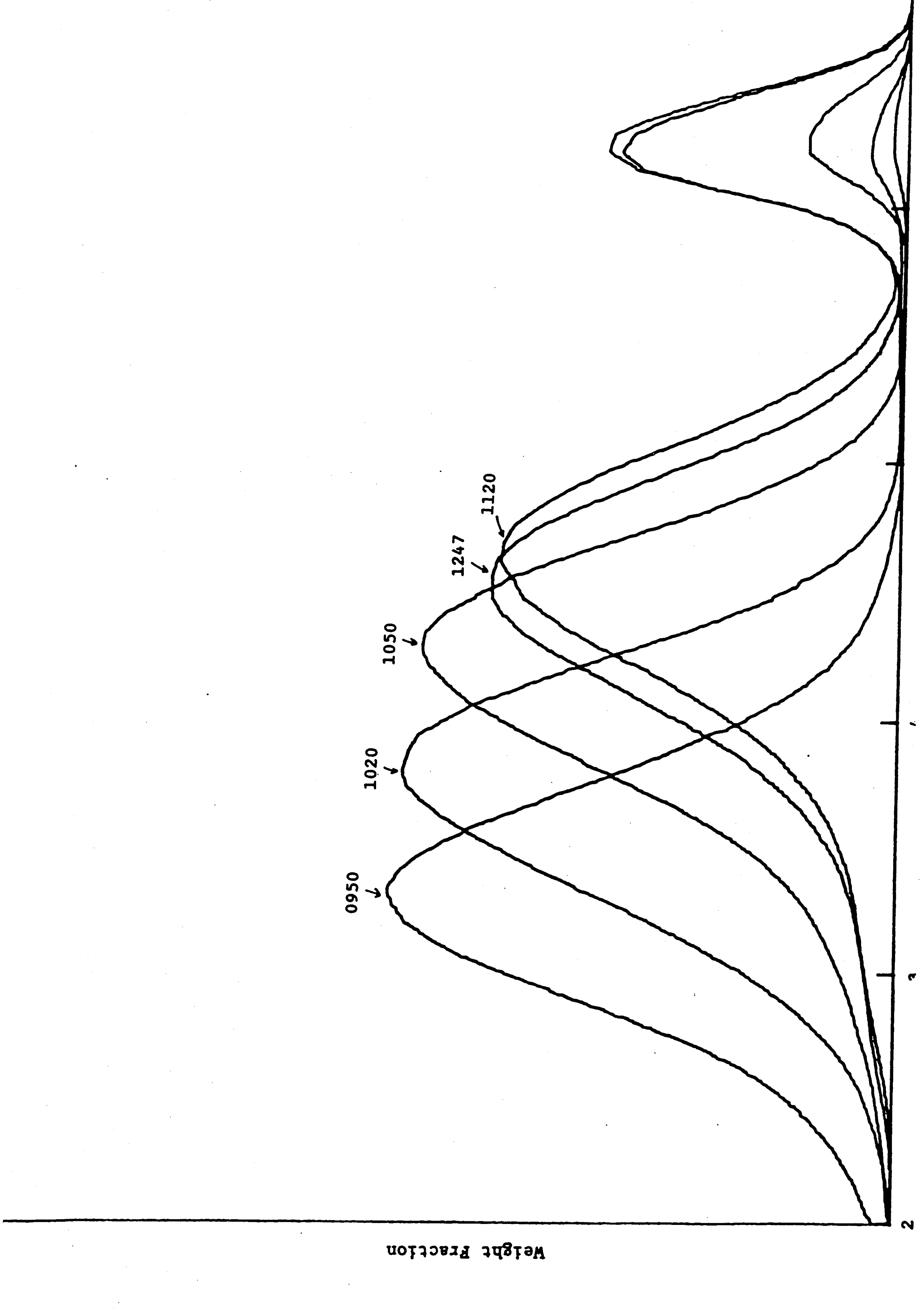


9.2.3 Discussion

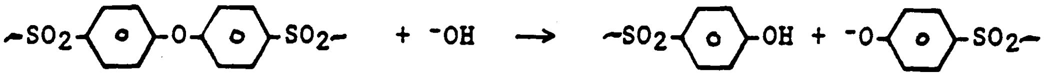
The Cl- group concentration can be seen to gradually decrease from 20-0 ends per 100 repeat units over the first 1.75 hours of sampling. This coincides with the change in RV against time (Graph 64), where the maximum RV was also determined to be after 1.75 hours. The combined -OH and -OK concentrations were again shown to decrease over the same time period from 4.0-1.1 ends per 100 repeat units.

However, the combined concentrations then drifted slowly upwards, reaching a final value of 1.7 ends per 100 repeats. On analysing the individual -OH and -OK components, it can be seen that the -OH concentration slowly reduced over the 3.5 hours from 2.1-0.7, whereas the -OK concentration initially reduced from 1.9-0.0 over the first hour, but then gradually increased over the subsequent 2.5 hours back to 1.0 ends per 100 repeat units. It therefore indicates that the final stages of polymerisation are due to the consumption of all -OK ends, with a consequent loss of -Cl ends as would be expected. However, from the data the -Cl ends are still being consumed when there are no detectable -OK ends, and therefore some of the remaining -OH ends are converted to -OK, which immediately polymerise. -OH ends can still be present at the end of the polymerisation process due to the agglomeration of K_2CO_3 preventing full reaction, despite the addition of a slight molar excess of the base. Further conversion of -OH ends to -OK ends results in a gradual build up of -OK ends due to the absence of any further -Cl ends.

GPC Chromatographs For Phenate-Ended Polymerisation



The gradual reduction in RV over the final 1.5 hours is due to cleavage of the aryl ether. This is thought to be by some form of inorganic base, eg KOH which is present in K_2CO_3;



The rise and subsequent fall in RV is also confirmed by GPC studies, which clearly show a substantial shift of the main peak to high molecular weight before slightly decreasing due to the above reaction scheme.

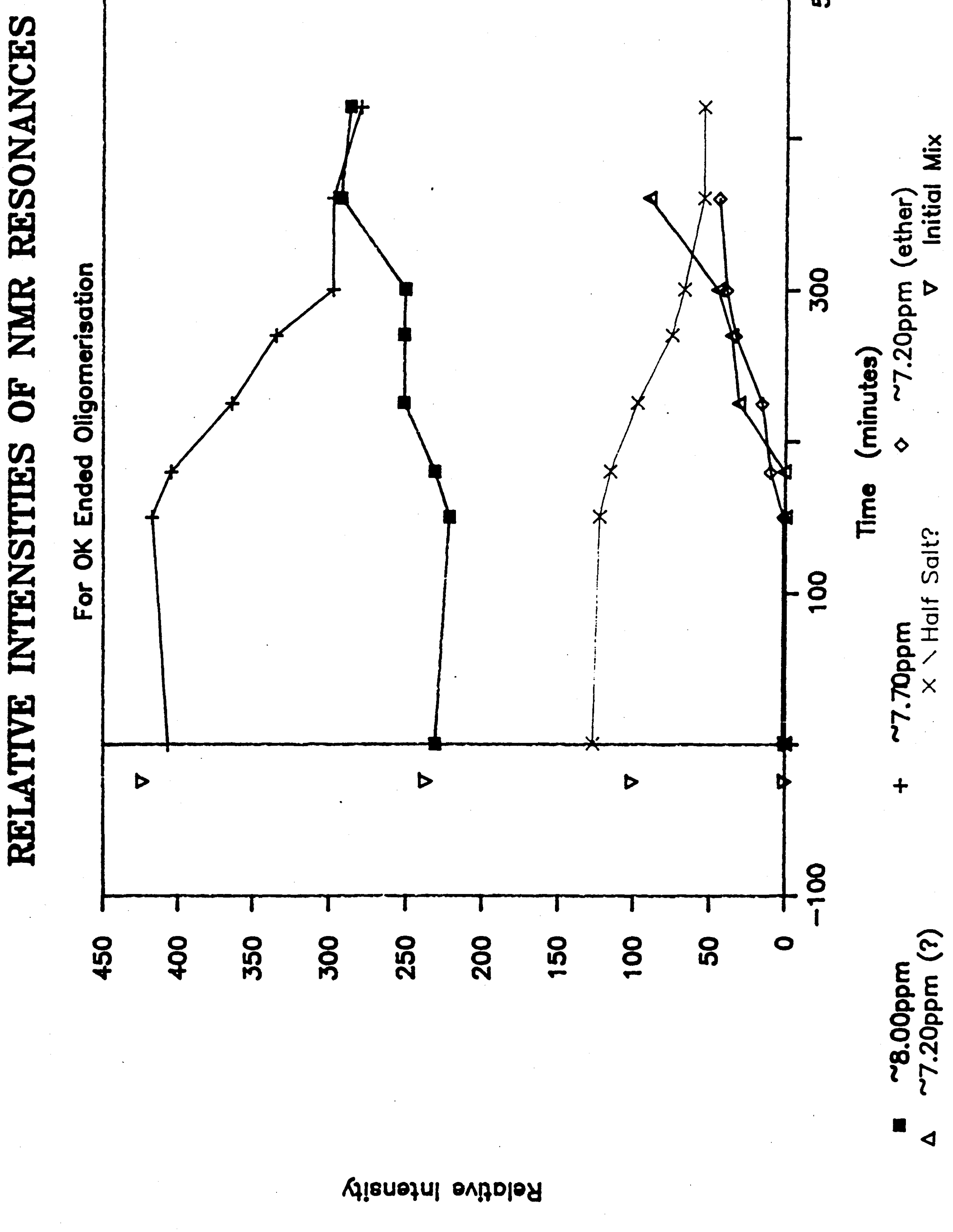
9.3 Use Of Solution NMR To Study Phenate-Ended Oligomerisation

As a final method of elucidating the mechanism of the polymerisation by NMR analysis a reaction was undertaken with a large molar excess of Bis-S, such that the final chain length of an average molecule would be 3-4 repeat units. Thus, Bis-S and like molecules would be present throughout the oligomerisation in relatively large proportions, which could highlight certain areas of interest.

9.3.1 Method

A 66.67% molar excess of Bis-S was used with 2% molar excess K_2CO_3 in a 0.2 molar scale polymerisation. Samples were taken after each temperature hold and a further five samples were taken from the beginning of the 260°C hold.

Graph 66: Graph Of End Groups v. Time For Phenate Ended Oligomerisation



9.3.2 Results

Table 24: Results for Phenate Ended Oligomerisation Studied by Solution NMR

Sample	Intensity @ 8.00ppm	Intensity @ 7.70ppm	Intensity @ 7.20ppm (ether) (?)		Intensity @~6.50ppm
Mix	237	424		0	101
A	231	407	1.5	0	127
B	222	418	1.2	0	123
C	232	405	10	1	116
D	252	364	16	32	98
E	252	335	34	37	76
F	251	298	40	46	68
G	293	298	45	91	55
H	287	280	145		55

9.3.3 Discussion

As can be seen from Graph 66, the rise or decline of the relative intensity of various resonances is similar to that observed in the chlorine-ended polymerisation by solution NMR. However, the presence of a large excess of Bis-S does seem to hinder the rise in the aryl ether formation and the consequent decline in the C-Cl group concentration. The majority of the change occurs during a ~70 minute interval during the -Cl ended polymerisation, whilst the corresponding change in the -OK ended oligomerisation takes ~150 minutes. This indicates that the poor solubility of low molecular weight OK or partially -OK ended oligomers reduces the initial formation of polymer. This is to be expected from previous work, as the solubility in DPS of an -OK ended oligomer of 4 repeat units would still be limited, thus reducing the rate of chain extension.

CONCLUSIONS

Earlier studies on the polymerisation of PES by the 'carbonate' route had led to the theory of the formation of the 'quarter salt' of Bis-S, involving the association of a Bis-S molecule with a monopotassium Bis-S salt as described in Chapter 7 Section 5 (104). This theory accounted for the staggered CO_2 evolution seen in PES manufacture and also indictated that oligomer formation could not occur before the temperature had reached ~265°C.

This work has shown that the kinetics and mechanisms of the 'carbonate' route are far more complex and involve essentially heterogeneous conditions. The energy of activation of the chain extending reaction involving the phenate and the activated halide was found to be ~110kJmol^{-1} by melt polymerisation studies using FTIR, by monitoring the extent of reaction by viscometry as well as by the use of a model compound. The viscometric study confirmed earlier work (102) indicating that M_c for PES is at an RV ~0.35. The chain extending reaction was found to be second order by the use of a model compound. This was expected, although pseudo first order kinetics are found under normal operating conditions due to the heterogeneity of the system. This effect was also seen in the study of the melt polymerisation by FTIR. The formation of aryl carbonates was postulated to explain the staggered evolution of CO_2. This could not be confirmed by Infra-Red studies, but would more readily account for the evolution of the initial 50% of the total theoretical CO_2 in the two stages at 170-180°C and 208-225°C.

From the study of chlorine ended oligomers by HPLC it is evident that chain extension occurs as low as ~200°C, although not to any great extent. In fact, due to the rapid formation and subsequent consumption of chlorine ended oligomers at ~260°C it indicates the rate determining step of the whole process is the reaction of the monopotassium salt of Bis-S with DCDPS to form the soluble chlorohydroxy dimer, which can then rapidly react with similar oligomers to form PES.

CHAPTER 10: EXPERIMENTAL

10.1 Preparation Of Diphenyl Ether-4,4'-Disulphonic Acid (Sodium Salt)

Diphenyl ether (317ml; 2.00 moles) was charged to a one litre, three necked round bottomed flask, fitted with nitrogen inlet/outlet, stirrer and condenser. Concentrated sulphuric acid (360ml; excess) was added via a dropping funnel, the resulting exotherm causing the temperature to rise to 50-60°C, where it was maintained by controlling the rate of addition of acid. A slow colour change from colourless to deep red was observed. When the addition was complete the reaction mixture was heated for a further 2 hours at 50-60°C. It was then cooled and poured into 1.5 litres of cold distilled water. 30% w/v sodium hydroxide solution was added until no further precipitation occurred, and the whole was alkaline to litmus. The disodium salt of the disulphonic acid was filtered and dried at 80°C in vacuo for 72 hours. The crude yield was 605g (81%), and the product was used in this form in the preparation of diphenyl ether-4,4'-disulphonyl chloride.

10.2 Preparation Of Diphenyl Ether-4,4'-Disulphonyl Chloride

Finely powdered, dry diphenyl ether-4,4'-disulphonic acid (sodium salt) (131g; 0.35 moles) was charged to one litre, three necked round bottomed flask, fitted with thermometer, nitrogen inlet/outlet, stirrer and condenser. Thionyl chloride (250ml; 3.43 moles) was carefully added and the mixture heated to reflux (85°C). Dimethylformamide (12ml; 0.15 moles) was added dropwise over a two hour period, during which time the consistency of the mixture went from a liquid to a paste. The reaction was maintained at 85°C until the SO_2 evolution had ceased.

The excess thionyl chloride (~200ml) was distilled off, the final traces being removed by vacuum distillation. The resulting green/yellow slurry was poured onto iced water (700ml) with vigorous stirring. The pale yellow product was filtered, washed with distilled water 2*25ml) and dried in vacuo at 65°C for 24 hours. The crude yield was 106g (83%) and the melting range was 132-133°C. Toluene is an appropriate recrystallisation solvent, but the product was used in the crude form in either of the following Friedel-Crafts reactions:

10.3 Preparation Of 'Dichlorodimer'

Diphenyl ether-4,4'-disulphonyl chloride (31g; 0.084 moles) was charged to a 500ml three necked round bottomed flask fitted with thermometer, nitrogen inlet/outlet, stirrer and condenser. As a precaution, the flask was surrounded with ice to prevent the subsequent reaction proceeding uncontrollably. Chlorobenzene (130ml; 1.28 moles) was added and the mixture set stirring. Aluminium chloride (25g; 0.19 moles) was carefully added via a solids dispenser, ensuring hydrogen chloride evolution was maintained at a reasonable rate. The ice bath was replaced by a heating mantle and the mixture was very slowly taken up to reflux at about 140°C. All the solids eventually dissolved and the mixture turned black. The flask was heated for one hour at the maximum temperature at which point hydrogen chloride evolution had ceased. The mixture was cooled and poured into iced water (200ml) and acidified with concentrated hydrochloric acid (5ml). The whole mixture was heated until no solids remained. The hot organic layer was separated, yielding a pale yellow product on cooling.

This was filtered, washed twice with chlorobenzene (2*25ml) and dried at 75°C in vacuo. The crude product (34g; 78%) was recrystallised from 50ml chlorobenzene to yield the pure product (31g; 71%). The melting range was 206-208°C at 0.2°C/min and micro analysis gave: Calculated; C = 55.50%, H = 3.10%. Found; C = 56.06%, H = 3.25%.

10.4 Preparation Of 'Difluorodimer'

Diphenyl ether-4,4'-disulphonyl chloride (182g; 0.49 moles) was charged to a one litre, three necked round bottomed flask fitted with thermometer, nitrogen inlet/outlet, stirrer and condenser. As a precaution, the flask was surrounded with ice to prevent the subsequent reaction proceeding uncontrollably. Fluorobenzene (284ml; 3.03 moles) was added and the mixture set stirring. Aluminium chloride (152g; 1.16 moles) was carefully added via a solids dispenser, ensuring hydrogen chloride evolution was maintained at a reasonable rate. The ice bath was replaced with a heating mantle and the mixture was slowly taken up to reflux at 90°C, with a consequent colour change from colourless to black. When hydrogen chloride evolution had ceased, the mixture was cooled and poured into water (500ml) and acidified with concentrated hydrochloric acid (10ml). Fluorobenzene (150ml) was added and the mixture was heated to reflux. After all the solids had dissolved, the hot organic layer was separated and on cooling, a faint yellow precipitate was formed. The product was filtered, washed with fluorobenzene and dried in vacuo at 65°C. The crude product (150g; 63%) was recrystallised from fluorobenzene (450ml) which yielded 144g of pure product. The melting range was 160-161°C at 1°C/min and micro analysis gave: Calculated; C = 59.25%, H = 3.32%. Found; C = 59.49%, H = 3.43%

10.5 Preparation Of 'Dihydroxydimer'

Potassium hydroxide (2.68g; 0.0492 moles) was dissolved in deionised water (5.0 ml) and dimethylsulphoxide (40 ml) in a 100 ml round bottomed flask fitted with thermometer, nitrogen inlet/outlet, stirrer and condenser. Difluorodimer (6.00g; 0.0123 moles) was added and the solution heated to 50°C (+/-10°C) for 40 hours, with a gradual colour change from yellow/green to dark green. The solution was then cooled, poured onto iced water (500ml) and filtered. The filtrate was made acidic by adding concentrated hydrochloric acid dropwise until the solution turned litmus paper red. This caused the bisphenol to precipitate out of solution. The off-white precipitate was filtered, washed with deionised water (50ml) and dried at 40°C in vacuo. The crude product (5.66g; 96%) was dissolved in the minimum amount of IMS (30ml), which was removed by rotary evaporation after precipitation had failed to occur on cooling. Melting range was 78-80°C and micro analysis gave: Calculated; C = 57.59%, H = 4.02%. Found; C = 57.47%, H = 4.36%, allowing for one water of crystallisation.

10.6 Preparation Of The Bisphenate Of 'Dihydroxydimer'

19.575ml of previously standardised 0.317M KOH solution ($6.2053*10^{-3}$ moles) was added to a solution of dihydroxydimer (1.4974g, $3.1033*10^{-3}$ moles) in methanol (20ml). The solvent was removed by rotary evaporation and the product was further dried at 110°C in vacuo for 36 hours. The crude yield was 1.5658g (90%).

10.7 Preparation Of Diphenyl Carbonate-4,4'-Disulphonyl Chloride

Chlorosulphonic acid (79.2ml; 1.2 moles) was dripped onto stirred diphenyl carbonate (42.8g; 0.2 moles) under a constant stream of nitrogen. Although the exhaust gases were bubbled into a phenol phthalein solution to detect the hydrogen chloride evolution, some chlorosulphonic acid vapour was also carried over, leading to seemingly high extents of reaction. When the hydrogen chloride evolution had apparently ceased, the resulting solution was heated to 80°C for two and a half hours and then allowed to cool. The reaction mixture was poured into ice/water (200ml) and the resulting suspension was extracted with dichloromethane (300ml). The dichloromethane solution was removed by rotary evaporation to yield a crude product (49.3g) which was recrystallised from 1,2-dichloroethane/petrol to yield a white crystalline compound (44.8g) which had a melting range of 146-148°C.
Empirical formula of the product was $C_{13}H_8O_7Cl_2S_2$:
Calculated: C = 37.97%, H = 1.96%, Found: C = 38.01%, H = 2.00%
The yield was 61%, which was higher than the quoted literature yield.

10.8 Preparation Of 4-(p-chlorobenzenesulphonyl)diphenyl Ether

Diphenyl ether (170g: 1.0 mole) and p-chlorobenzene sulphonylchloride (211g: 1.0 mole) were heated under nitrogen to 70°C. Anhydrous ferric chloride catalyst (5g) was added and the mixture heated to 110-120°C for approximately 2 hours.

If the evolution of hydrogen chloride was slow, a further portion of catalyst was added. Between 80-95% of the theoretical volume of hydrogen chloride should have been detected. The reaction was vacuum distilled, with the excess diphenyl ether distilling over at 80-86°C and the product distilling over between 200-220°C. The vacuum had to be better than 0.5mmHg. A yellow viscous product was obtained which was recrystallised twice from IMS. The crude product was further recrystallised from benzene and petroleum ether (B.Pt.80-100°C), yielding a white crystalline compound with melting range 92-94°C. The empirical formula of the crystals was $C_{18}H_{13}O_3ClS$: Calculated; C = 62.70%, H = 3.80%. Found; C = 62.57%, H = 3.89%. The yield was 73%.

10.9 Preparation Of 4-(p-chlorobenzenesulphonyl)-4'-(p-hydroxybenzenesulphonyl)diphenyl Ether

4-(p-chlorobenzenesulphonyl)-4'-(p-hydroxybenzenesulphonyl) diphenyl ether was prepared by heating a mixture of 4-(p-chlorobenzenesulphonyl) diphenyl ether (34.5g: 0.1 moles), diphenyl carbonate-4,4'-disulphonyl chloride (20.6g: 0.05 moles), nitrobenzene (100ml) and anhydrous ferric chloride (0.4g) at 110°C for 14-15 hours. Cold methanol (200ml) was added and the resulting suspension was stirred and then decanted. A further 200ml methanol was added, stirred and again decanted. To remove the remaining nitrobenzene, the resultant oil was steam distilled for 5 hours. The remaining solid was stirred in methanol (400ml) and 50% potassium hydroxide (56g) was added to hydrolyse the carbonate. The temperature was kept below 20°C, in order to produce a clear solution. Ice was added and the mixture was neutralised with concentrated hydrochloric acid to pH = 4.

The suspension was stirred for one hour and then filtered. The product was recrystallised from a triple mixture of isopropanol, benzene and 60-80 petroleum ether in the ratio 1:5:2. The melting range was 242-245°. The empirical formula of the product was $C_{24}H_{17}O_6S_2Cl$: Calculated; C = 57.54%, H = 3.42%. Found; C = 57.39%, H = 3.20%.

The potassium salt of the above compound was prepared by slurrying the phenol in methanol and titrating the required amount of 3.125M KOH(aq). The salt obtained on rotary evaporation was dried under vacuum at 70°C.

LABORATORY POLYMERISATION OF PES

A typical laboratory polymerisation of PES by the 'carbonate' route was based on 0.25 moles of Bis-S. It involved charging 72.507g DCDPS (0.2525 moles - 1% molar excess to control the molecular weight), 62.568g Bis-S (0.25 moles), 35.238g K_2CO_3 (0.255 moles - 2% molar excess to ensure complete reaction) and 143.815g DPS (0.6589 moles - to yield 43% w/v polymer) to a 500ml round bottomed flask. The whole was manually mixed before being fitted with nitrogen inlet/outlet and stirrer. The flask was purged overnight with nitrogen before being heated to 180°C by the use of an oil bath controlled by a thermocouple accurate to +/-2°C. After 30 minutes at equilibrium temperature the oil bath was raised to 225°C and held above 217°C for 90 minutes. Further temperature holds of 60 minutes at 265°C and 90 minutes at 285°C were incorporated to ensure full polymerisation. At the end of the final hold the contents was poured into a 5l beaker containing water, which quenched any further reaction. The solid mass was milled to produce particles between 250-850 micrometers. The polymer was then isolated by placing the powder in a leaching column and refluxing with water/methanol (200ml/700ml) for a minimum of 8 hours, followed by water (700ml) for 16 hours, followed finally by methanol/acetone (600ml/300ml) for a minimum of 3 hours. The isolated polymer was then dried @ 120°C overnight.

Appendix 1

Computer Program For Generation Of Model Compound Kinetic Data

```
5 INPUT "ENTER TEMP. ";TE
10 INPUT "ENTER DPS MASS";D
20 INPUT "ENTER CHLOROPHENATE MASS";CL
30 INPUT "ENTER CHLOROPHENATE CONC.";C
31 INPUT "ENTER NUMBER OF SAMPLES";S
35 FOR Z = 1 TO S
40 INPUT "ENTER SAMPLE MASS - 999 TO QUIT";M(Z)
45 IF M(Z) = 999 THEN 999
50 INPUT "ENTER SAMPLE TIME";T(Z)
60 INPUT "ENTER SAMPLE ABSORBANCE";A(Z)
70 CA = C/100
80 TM(Z) = CA*M(Z)
90 CO(Z) = TM(Z)*0.01060072
100 TA(Z) = CO(Z)*15858.7
110 PD(Z) = A(Z)/15858.7
120 MP(Z) = PD(Z)*94.33319
130 B(Z) = (D+CL)/M(Z)
140 MPT(Z) = MP(Z)*B(Z)
150 MO(Z) = MPT(Z)/539.0468
160 MOI(Z) = 1/MO(Z)
170 NEXT Z
180 PRINT #8, TAB(1)"TEMP. = ";TE;" deg C"; TAB(30)"DPS MASS = ";D;" grams"
181 PRINT #8,
182 PRINT #8, TAB(1)"CHLOROPHENATE MASS = ";CL;" grams"; TAB(30)"CHLOROPHENATE C
ONC. = ";C;" %w/w"
183 PRINT #8,
184 PRINT #8, TAB(1)"NUMBER OF SAMPLES = ";S
185 PRINT #8,
200 PRINT #8, TAB(1)"TIME"; TAB(15)"MASS"; TAB(30)"THEO MASS P"; TAB(45)"CONC. P
"
205 PRINT#8, TAB(1)"(secs)"; TAB(15)"(grams)"; TAB(30)"(grams)"; TAB(45)"(moll-1
)"
210 PRINT #8,
215 FOR Z = 1 TO S
220 PRINT #8, TAB(1)T(Z);
230 PRINT #8, TAB(15)M(Z);
240 PRINT #8, TAB(30)TM(Z);
250 PRINT #8, TAB(45)CO(Z)
255 NEXT Z
260 PRINT #8,
265 PRINT #8,
270 PRINT #8, TAB(1)"THEO ABS."; TAB(15)"ACTUAL ABS."; TAB(30)"P DETECTED"; TAB(
45)"MASS P"
275 PRINT#8, TAB(1)"(320nm)"; TAB(15)"(320nm)"; TAB(30)"(moll-1)"; TAB(45)"(gram
s)"
280 PRINT #8,
285 FOR Z = 1 TO S
290 PRINT #8, TAB(1)TA(Z);
300 PRINT #8, TAB(15)A(Z);
310 PRINT #8, TAB(30)PD(Z);
320 PRINT #8, TAB(45)MP(Z)
325 NEXT Z
330 PRINT #8,
335 PRINT #8,
340 PRINT #8, TAB(1)"MASS P TOTAL"; TAB(15)"MOLES P"; TAB(30)"1/(a-x)"
345 PRINT #8, TAB(1)"(grams)"; TAB(15)"(moles)"; TAB(30)"(moles-1)"
350 PRINT #8,
355 FOR Z = 1 TO S
360 PRINT #8, TAB(1)MPT(Z);
370 PRINT #8, TAB(15)MO(Z);
380 PRINT #8, TAB(30)MOI(Z)
385 NEXT Z
390 PRINT #8,
395 PRINT #8,
999 END
```

The following four pages are representatives of other spectra and data found in Appendices 2, 3 and 4. Supplementary data can be obtained from the author or from his colleagues in Victrex R&T, ICI Advanced Materials Group, Wilton.

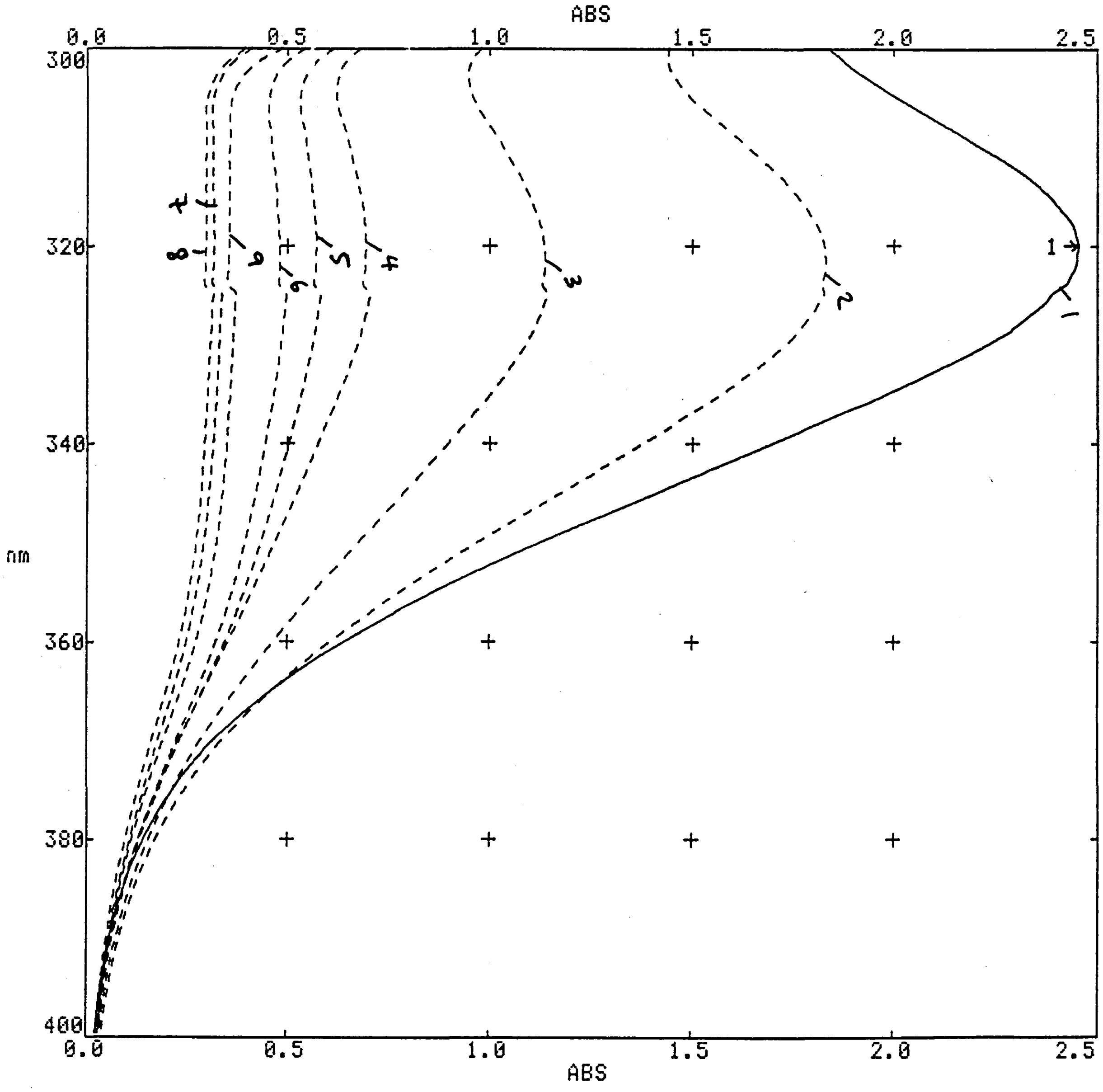
KINETIC DATA FOR RUN 16 (CHAPTER 6 SECTION 5)

```
                          KINETIC RUN No.  16

TEMP. =  213.75  deg C           DPS MASS =  7.98  grams

CHLOROPHENATE MASS =  1.3979  grams
                                 CHLOROPHENATE CONC. =  14.906  % w/w

NUMBER OF SAMPLES =  9

TIME             MASS             THEO MASS P      CONC. P
(secs)           (grams)          (grams)          (moll-1)

 900              0.1929           0.028753674      2.13367E-04
 2700             0.2403           0.035819118      2.65796E-04
 5400             0.2335           0.03480551       2.58274E-04
 9600             0.2151           0.032062806      2.37922E-04
 13320            0.2317           0.034537202      2.56284E-04
 15300            0.2213           0.032986978      2.44780E-04
 22320            0.1941           0.028932546      2.14694E-04
 25020            0.1917           0.028574802      2.12039E-04
 26880            0.2389           0.035610434      2.64247E-04

THEO ABS.        ACTUAL ABS.      P DETECTED       MASS P
(320nm)          (320nm)          (moll-1)         (grams)

 3.38372024       2.455            1.54805E-04      2.08617E-02
 4.21517871       1.833            1.15583E-04      1.55762E-02
 4.09589774       1.137            7.16957E-05      9.66183E-03
 3.77313749       0.695            4.38245E-05      5.90587E-03
 4.06432337       0.572            3.60685E-05      4.86066E-03
 3.88189367       0.481            3.03304E-05      4.08737E-03
 3.40476982       0.318            2.00521E-05      2.70225E-03
 3.36267065       0.296            1.86648E-05      2.51530E-03
 4.19062086       0.354            2.23221E-05      3.00817E-03

MASS P TOTAL     MOLES P          1/(a-x)
(grams)          (moles)          (moles-1)

 1.01420037       1.88147E-03      531.499315
 0.607873469      1.12768E-03      886.774679
 0.388041411      7.19866E-04      1389.14762
 0.257483195      4.77664E-04      2093.52226
 0.196731766      3.64962E-04      2740.00896
 0.173208084      3.21323E-04      3112.13419
 0.130558779      2.42203E-04      4128.76717
 0.123047868      2.28269E-04      4380.78944
 0.11808415       2.19061E-04      4564.93781
```

```
[illegible] Series UV/VIS Spectrophotometer      V 1.20  Date 9 .7 .87 Time 17.2 .4

I.D. 2    1   AST KINETIC RUN No. 16 SAMPLE 1
Mode ABSORBANCE                        High AUTO      ABS
Start λ 300.0                          Low AUTO      ABS
Stop λ 400.0                           Display SEQUENTIAL
Bandwidth 2.0 nm                       No of Cycles 1
Scan Speed 500  nm/min                 Cycle Time CONTINUOUS
Smoothing NONE                         Autosave ON
Peak Table ON
```

UV SPECTRUM FOR KINETIC RUN 16 (CHAPTER 8 SECTION 3.2)

```
2  1 AST KINETIC RUN No. 16 SAMPLE 1
9  1 AST KINETIC RUN No. 16 SAMPLE 9
```



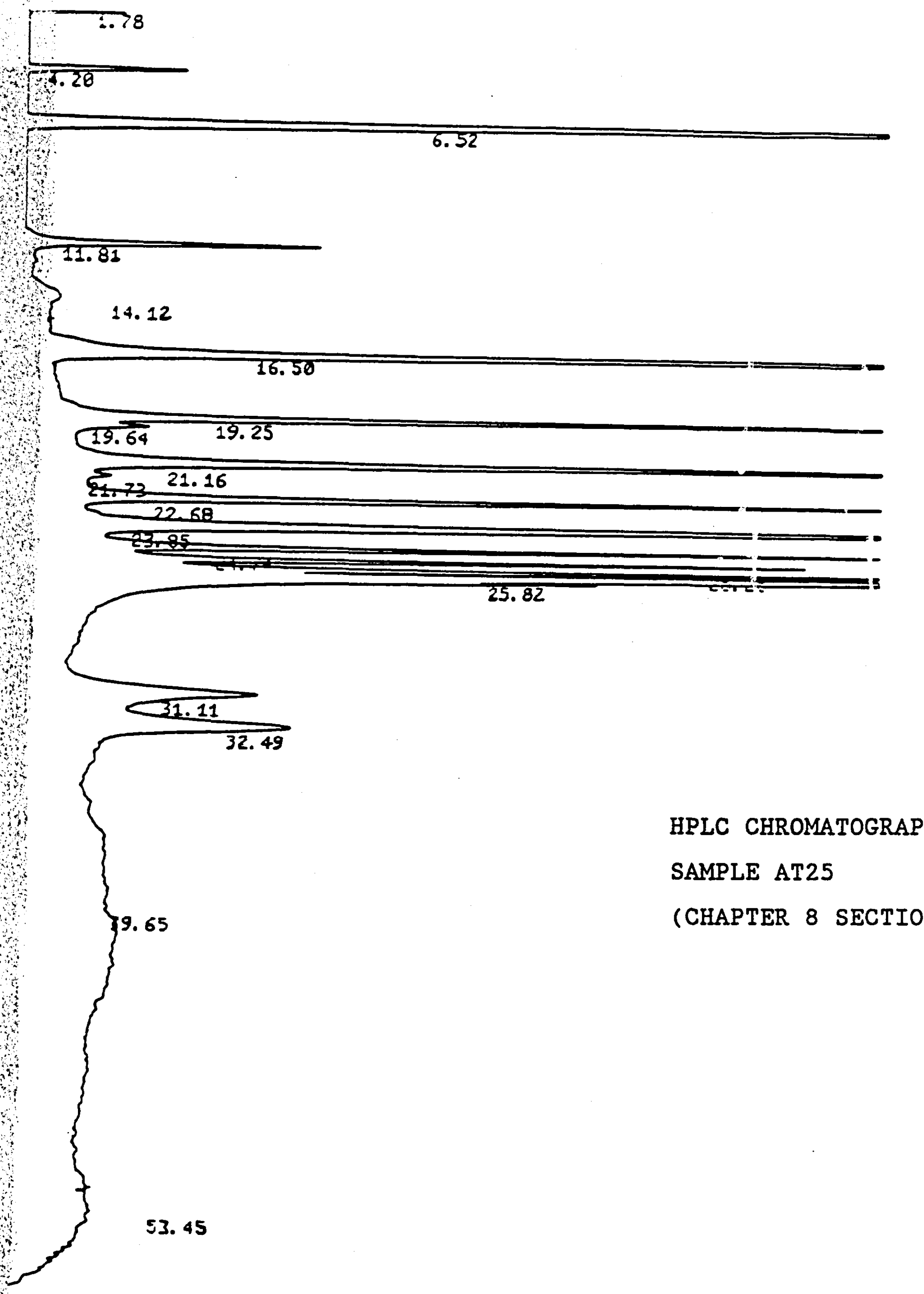
SAMPLE KINETIC RUN No. 16

REFERENCE THF + QAS

CELL PATH 1cm.

OPERATOR AST

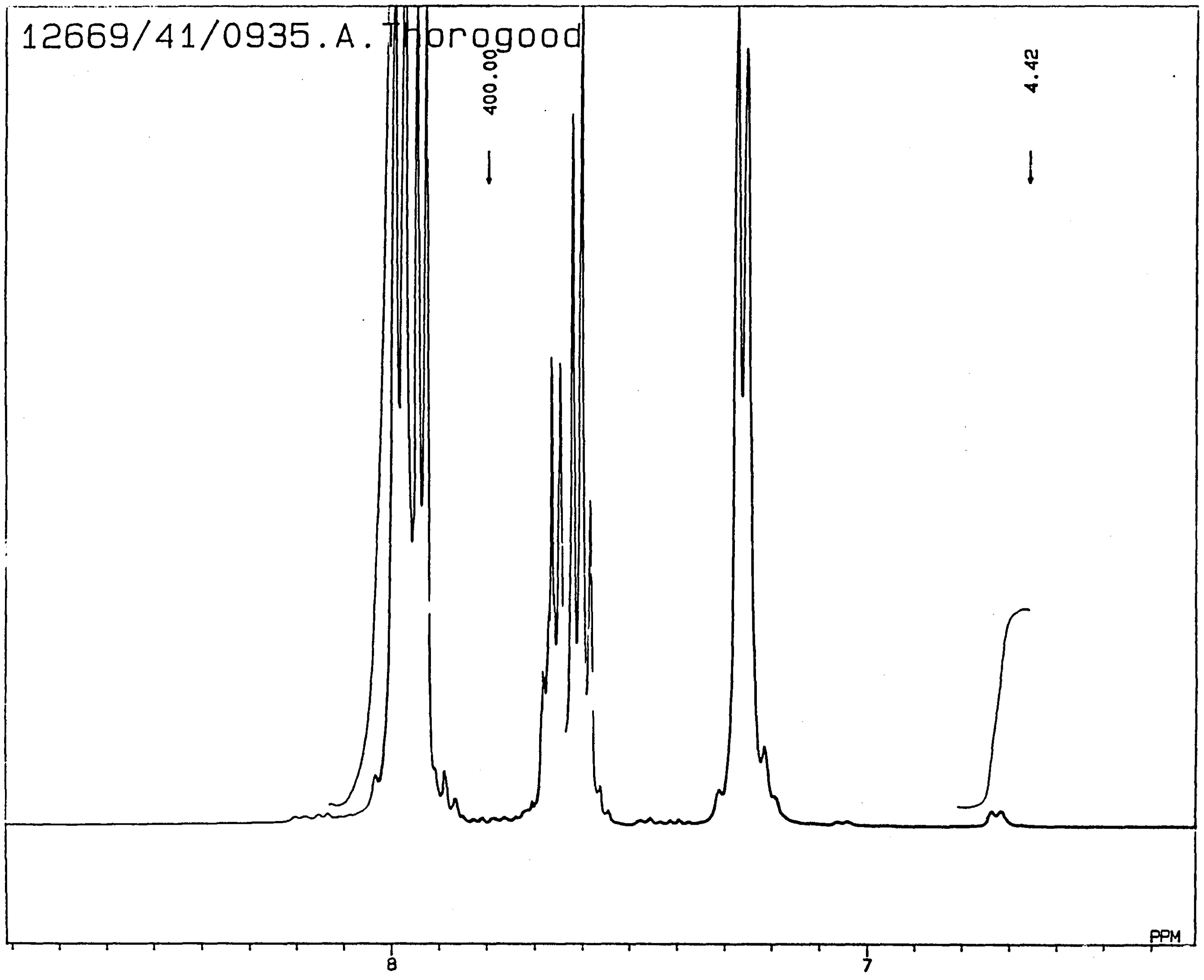
```
2    1  AST KINETIC RUN No. 16 SAMPLE 1
               1         2         3         4         5         6         7         8
   λ       320.0
  ABS      2.455
```



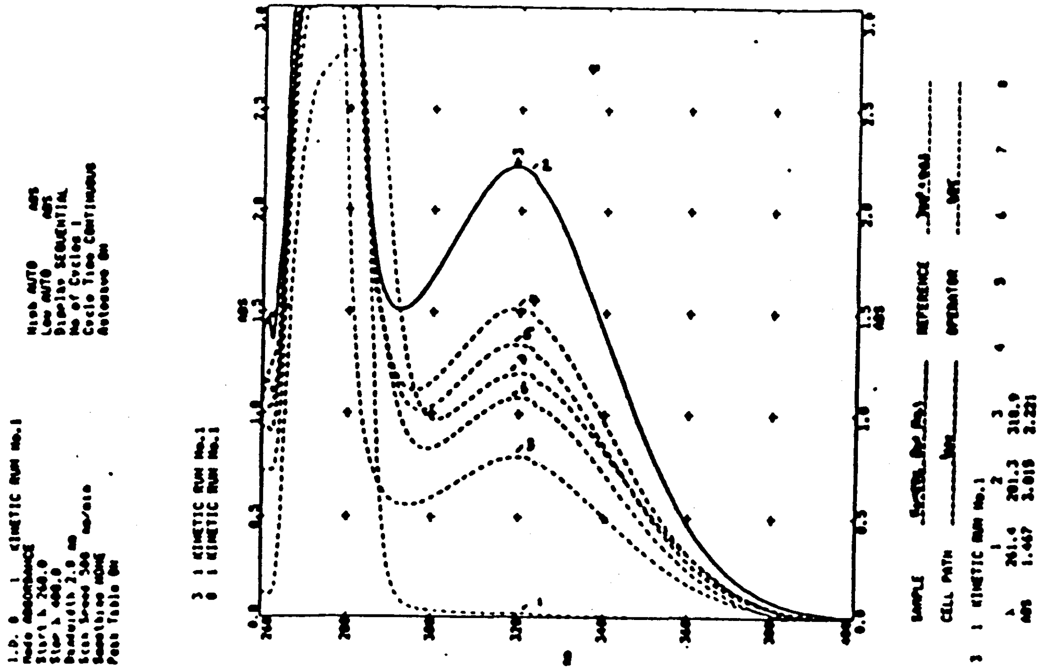
HPLC CHROMATOGRAPH OF
SAMPLE AT25
(CHAPTER 8 SECTION 3.2)

```
NAME              CONC       RT       AREA BC      RF

  1                0.       1.78       4687 01
  2                0.       4.2       42341 01
  3                0.       6.52     330418 01
  4                0.      11.81      60902 01
  5                0.      14.12      18262 01
  6                0.      16.5      366396 01
  7                0.      19.25     182296 02
  8                0.      19.64      17957 03
  9                0.      21.16     255654 02
 10                0.      21.73       8997 02
 11                0.      22.69     171213 02
 12                0.      23.85     291882 02
 13                0.      24.74     142050 02
 14                0.      25.25     119449 02
 15                0.      25.83    1433537 03
 16                0.      31.11     133968 02
 17                0.      32.49     154747 03
 18                0.      39.65     219838 02
 19                0.      53.45      33602 03

TOTALS             0.               3988196
```

SOLUTION NMR SPECTRA OF SAMPLE 0935 (CHAPTER 9 SECTION 2)



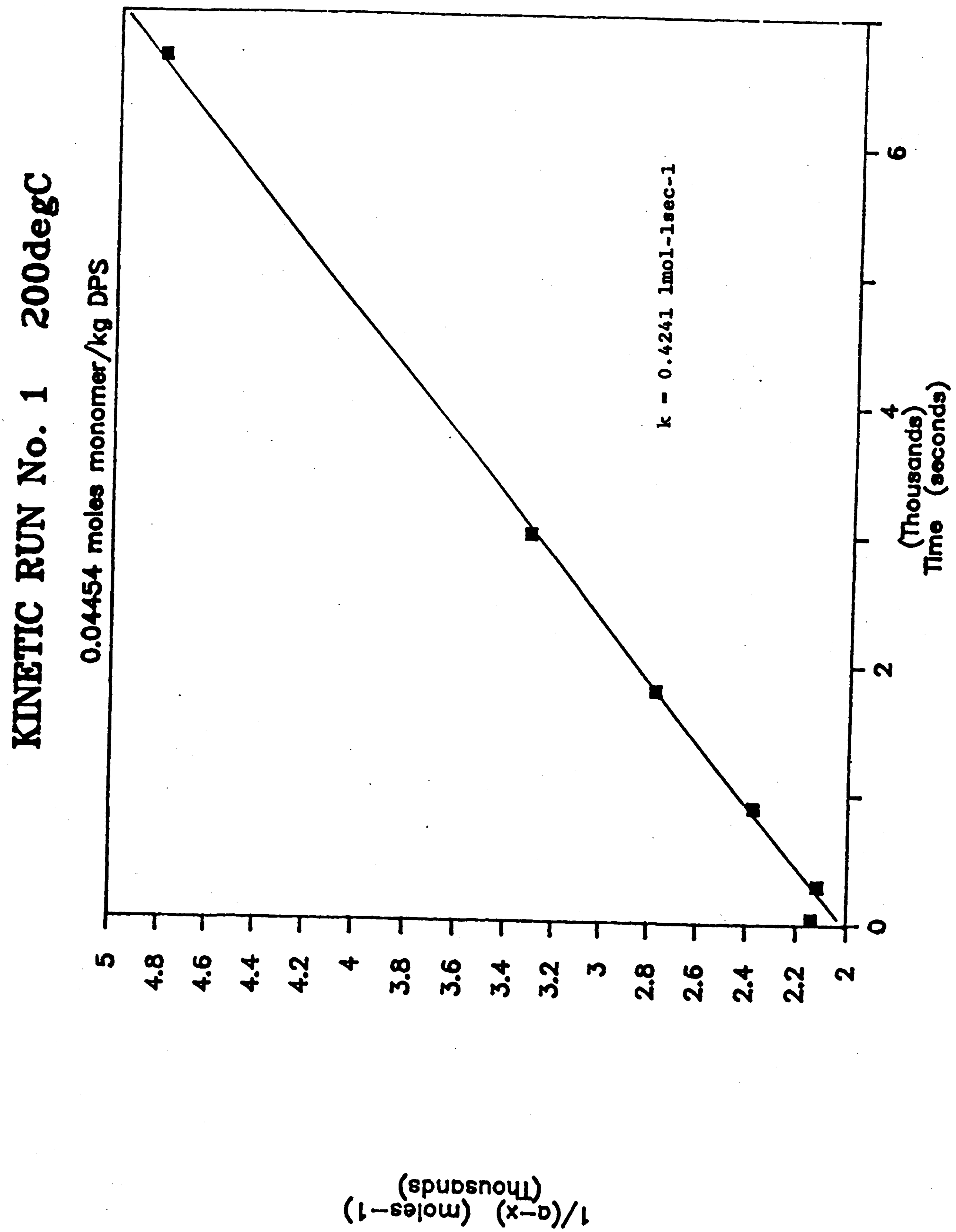
```
17-MAR-88 11:02:07

DFILE Z53907

--------------------
ICI WILTON MATERIALS
CENTRE NMR TEAM
--------------------
EXMOD NON
OBNUC 1H
POINT       32768
FREQU      6002.4 Hz
SCANS         500
ACQTM       2.730 sec
PD          0.100 sec
PW1           4.5 us
ADBIT    16
IRRPW          30 us
IRATN           0
TEMP.  80.0 c
SPEED          15 Hz
SLVNT DMSO
EXREF        2.49 ppm
BF           0.00 Hz
RGAIN    14
WNDMD           0

PROBE           0
YG           3.00
XE     1000.0000 Hz
XS    -1359.3750 Hz
```

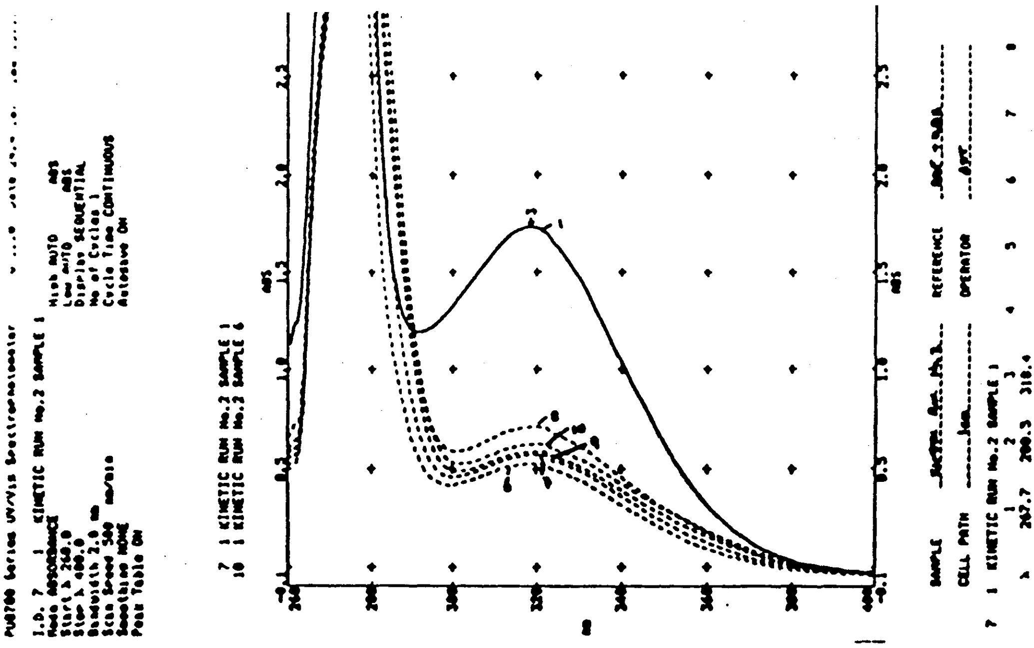


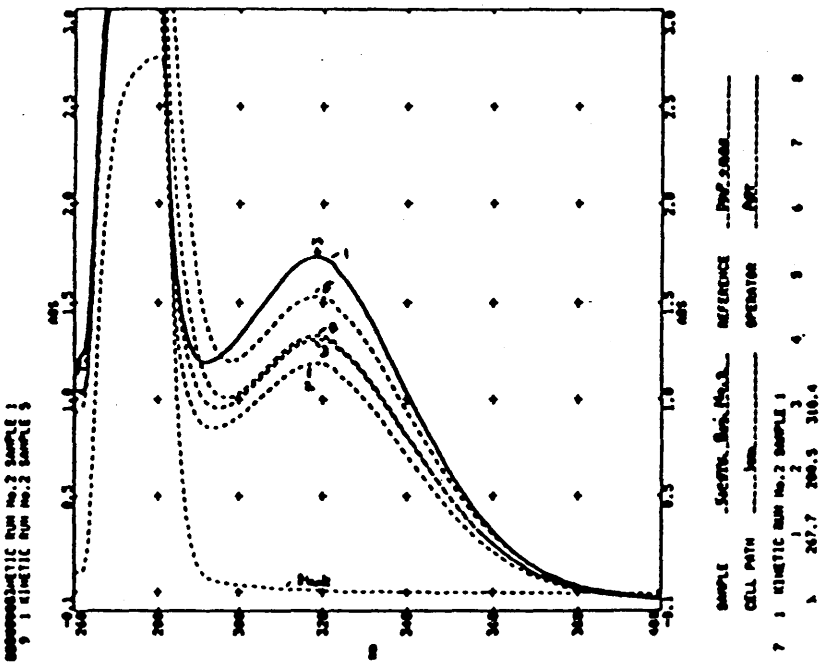
```
KINETIC RUN No. 1
*****************

     TEMP = 200degC        DPE MASS =    10.63g
     CHLOROPHENATE MASS = 0.2552g
     CHLOROPHENATE CONC. =2.34%
     NUMBER OF SAMPLES =  7

    TIME          MASS       THEO MASS P    CONC. P
   (secs)        (grams)       (grams)      (moll-1)

        45        0.3662       0.01339   1.44096E-04
       300        0.1962       0.00471   4.99327E-05
       900        0.4206       0.01029   1.09082E-04
      1800        0.4412       0.01059   1.12783E-04
      3600        0.4217       0.01012   1.07322E-04
      6600        0.6830       0.01640   1.73870E-04

  THEO ABS     ACTUAL ABS    P DETECTED      MASS P
  (320nm)       (320nm)       (moll-1)       (grams)

     2.205         2.221   1.38851E-04   1.30902E-02
     0.792         0.790   4.86160E-05   4.58617E-03
     1.730         1.520   9.46484E-05   8.92047E-03
     1.781         1.340   8.32981E-05   7.85776E-03
     1.792         1.079   6.68403E-05   6.30523E-03
     2.757         1.199   7.44071E-05   7.01904E-03

MASS P TOTAL    MOLES P        1/(a-x)
  (grams)       (moles)       (moles-1)

    0.2510   4.67120E-04          2141
    0.2544   4.71943E-04          2119
    0.2268   4.20742E-04          2377
    0.1939   3.59700E-04          2780
    0.1628   3.02014E-04          3311
    0.1119   2.07580E-04          4817
```

UV Spectrum And Data For Kinetic Run 1

Graph 10 : 1/(a-x) v. Time For Kinetic Run No.1



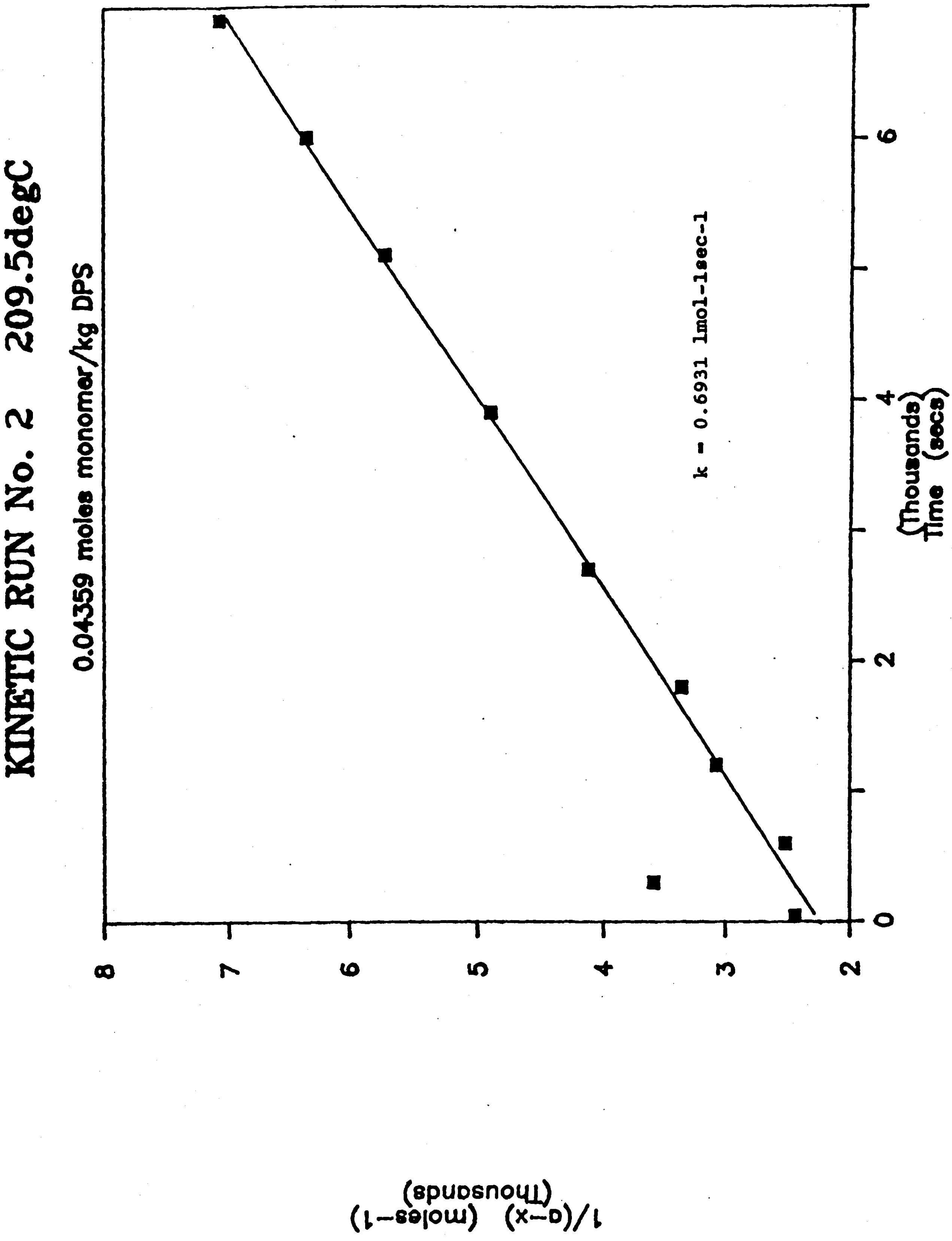


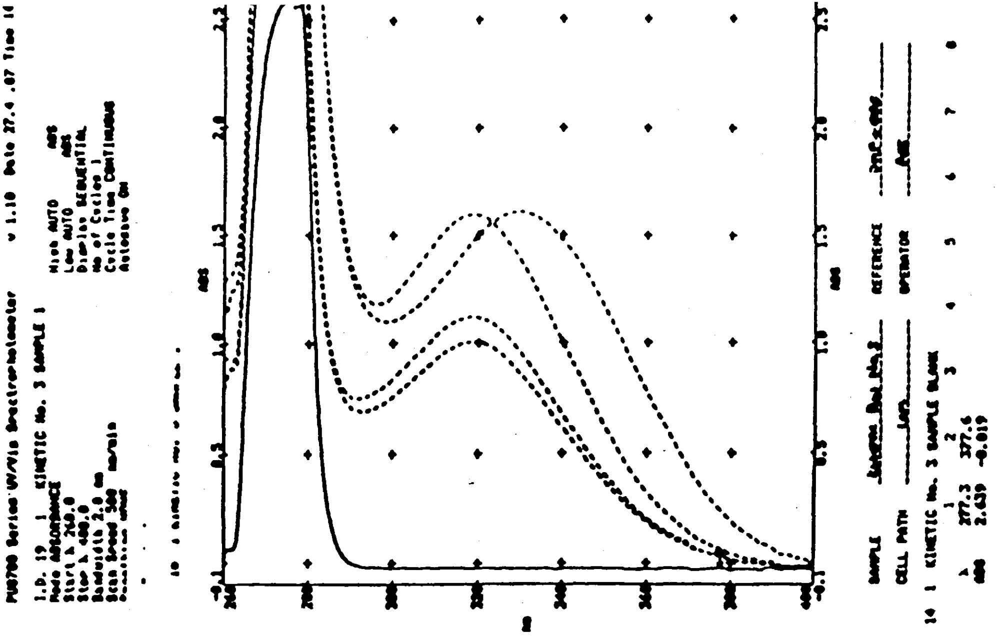


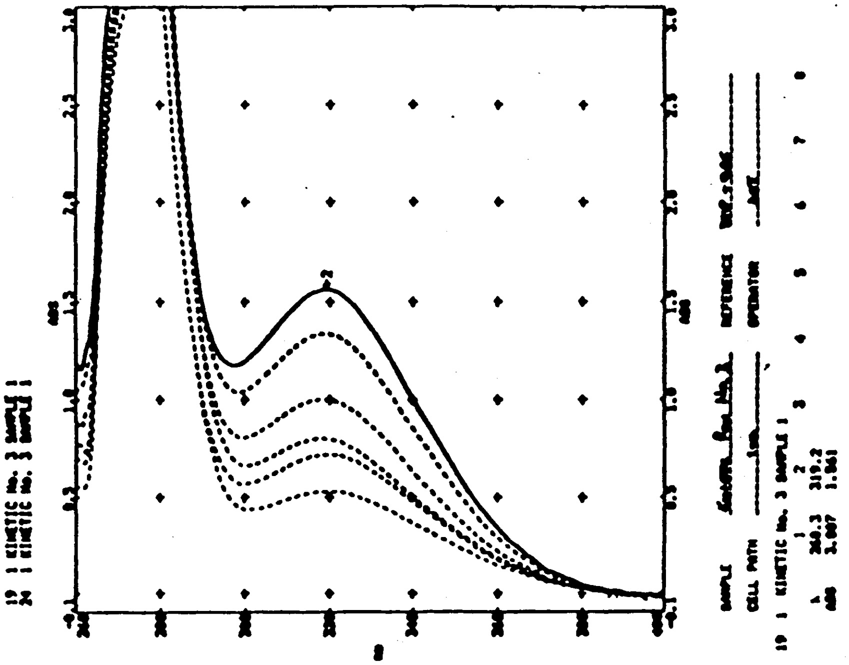
```
KINETIC RUN No. 2
*****************

    TEMP :  209.5degC     DPS MASS :   10.30g
    CHLOROPHENATE MASS : 0.2480g
    CHLOROPHENATE CONC. =2.296%
    NUMBER OF SAMPLES :  10

      TIME          MASS       THEO MASS P     CONC. P
     (secs)        (grams)       (grams)       (moll-1)

         45         0.4998       0.01147    1.21633E-04
        300         0.5038       0.01161    1.23096E-04
        600         0.3898       0.00893    9.40632E-05
       1200         0.4863       0.01116    1.18347E-04
       1800         0.6120       0.01405    1.48940E-04
       2700         0.2554       0.00586    6.21364E-05
       3900         0.3296       0.00757    8.02144E-05
       5100         0.4777       0.01097    1.16258E-04
       6000         0.4381       0.01006    1.06472E-04
       6900         0.5190       0.01192    1.26308E-04


   THEO ABS     ACTUAL ABS    P DETECTED      MASS P
   (320nm)       (320nm)       (moll-1)       (grams)

      1.929         1.733   1.08710E-04   1.02349E-02
      1.952         1.187   7.42810E-05   7.00715E-03
      1.504         1.311   8.21000E-05   7.74474E-03
      1.877         1.330   8.32901E-05   7.85776E-03
      2.362         1.531   9.59726E-05   9.05330E-03
      0.986         0.527   3.26435E-05   3.08125E-03
      1.272         0.571   3.54380E-05   3.34297E-03
      1.844         0.707   4.40137E-05   4.15194E-03
      1.691         0.586   3.63838E-05   3.43219E-03
      2.003         0.623   3.87169E-05   3.65228E-03


  MASS P TOTAL    MOLES P        1/(a-x)
    (grams)       (moles)      (moles-1)

      0.2222   4.12208E-04          2426
      0.1500   2.78269E-04          3594
      0.2151   3.99037E-04          2506
      0.1750   3.24647E-04          3080
      0.1602   2.97191E-04          3365
      0.1306   2.42279E-04          4127
      0.1098   2.03693E-04          4909
      0.0941   1.74567E-04          5728
      0.0848   1.57314E-04          6357
      0.0762   1.41360E-04          7074
```

UV Spectra And Data For Kinetic Run 2

Graph 11 : 1/(a-x) v. Time For Kinetic Run No.2



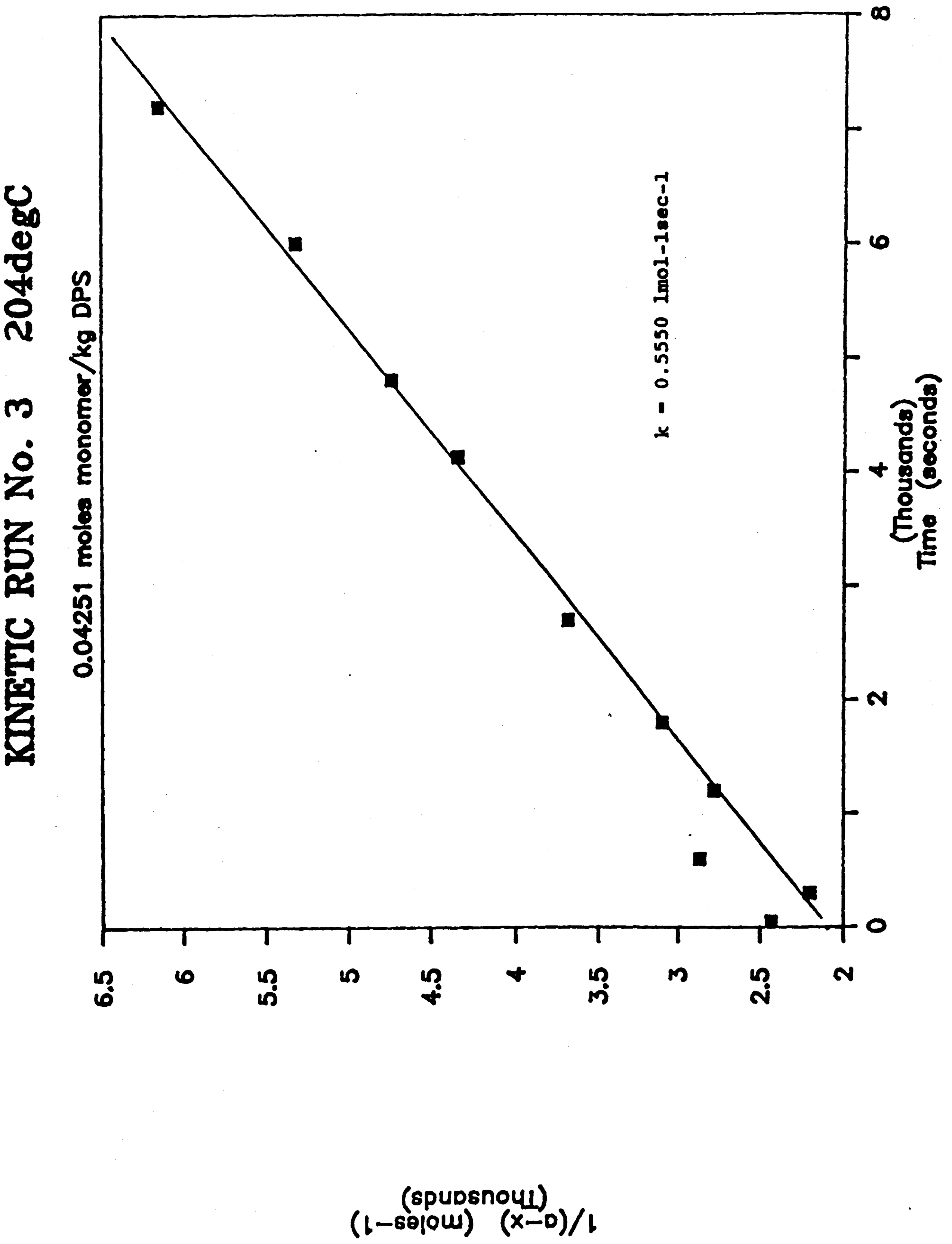


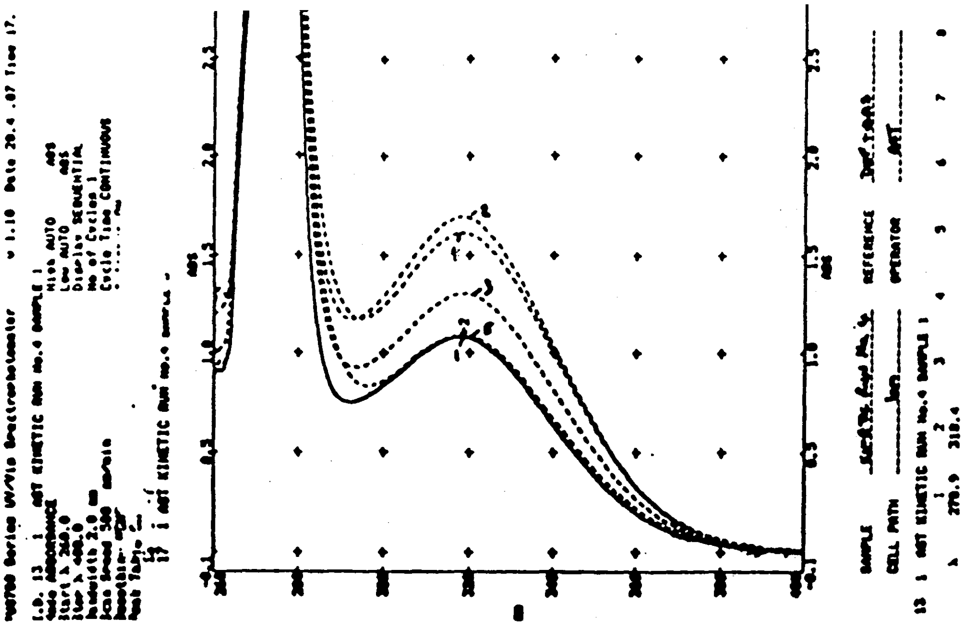


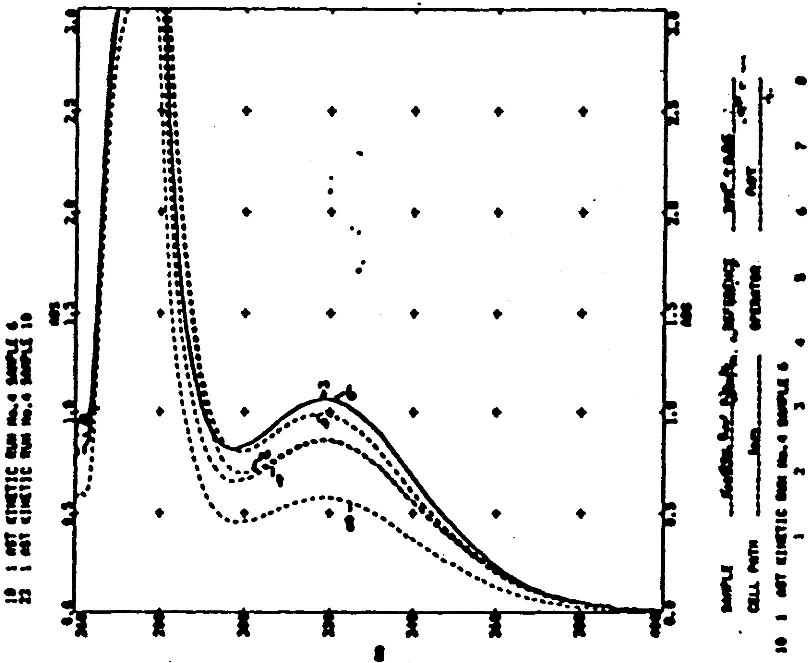
```
KINETIC RUN No. 3
*****************

     TEMP :  204degC        DPE MASS :   10.87g
     CHLOROPHENATE MASS : 0.2491g
     CHLOROPHENATE CONC. :2.240%
     NUMBER OF SAMPLES :  10

   TIME          MASS        THEO MASS P    CONC. P
  (secs)        (grams)        (grams)     (moll-1)

       45        0.3344        0.00749   7.94137E-05
      300        0.2717        0.00609   6.45253E-05
      600        0.3634        0.01267   1.34280E-04
     1200        0.3450        0.01221   1.29435E-04
     1800        0.3939        0.01331   1.41096E-04
     2700        0.6052        0.01356   1.43725E-04
     4130        0.5341        0.01197   1.26838E-04
     4800        0.4163        0.00933   9.88639E-05
     6000        0.5217        0.01169   1.23901E-04
     7200        0.4008        0.00879   9.31849E-05

  THEO ABS     ACTUAL ABS   P DETECTED      MASS P
  (320nm)       (320nm)      (moll-1)       (grams)

     1.239         1.120   7.06237E-05   6.66214E-03
     1.023         1.006   6.34352E-05   5.98403E-03
     2.129         1.606   1.01269E-04   9.55301E-03
     2.053         1.597   1.00702E-04   9.49932E-03
     2.238         1.561   9.84310E-05   9.28537E-03
     2.279         1.337   8.43070E-05   7.95293E-03
     2.011         1.001   6.31199E-05   5.95429E-03
     1.568         0.713   4.50057E-05   4.25307E-03
     1.965         0.798   5.03194E-05   4.74670E-03
     1.310         0.531   3.34832E-05   3.15857E-03

MASS P TOTAL    MOLES P       1/(a-x)
  (grams)       (moles)     (moles-1)

    0.2215   4.10910E-04         2434
    0.2449   4.54320E-04         2201
    0.1879   3.48578E-04         2869
    0.1938   3.59523E-04         2781
    0.1738   3.22420E-04         3102
    0.1461   2.71034E-04         3690
    0.1240   2.30035E-04         4347
    0.1136   2.10742E-04         4745
    0.1012   1.87739E-04         5327
    0.0876   1.62509E-04         6154
```

UV Spectra And Data For Kinetic Run 3

Graph 12 : 1/(a-x) v. Time For Kinetic Run No.3



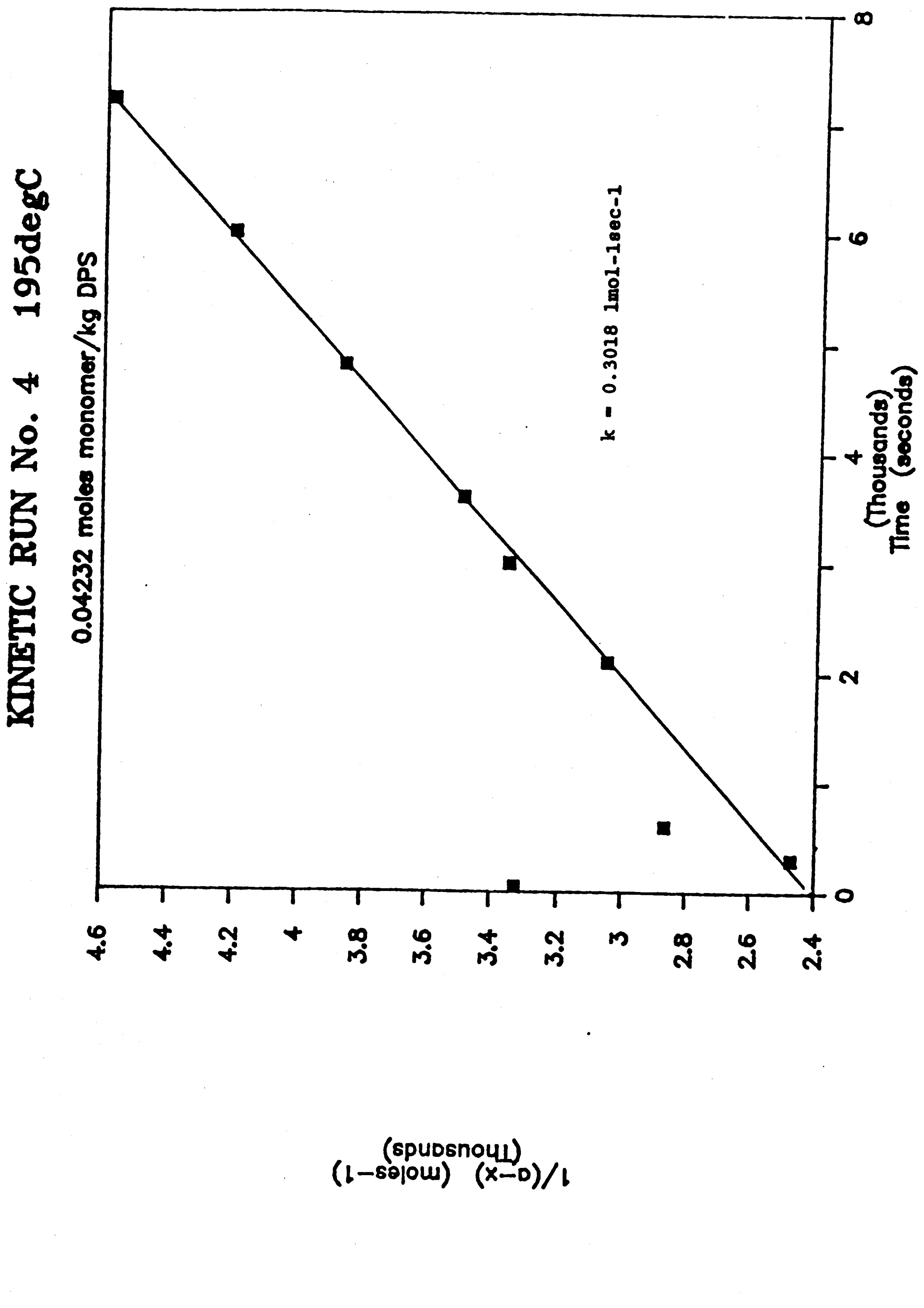


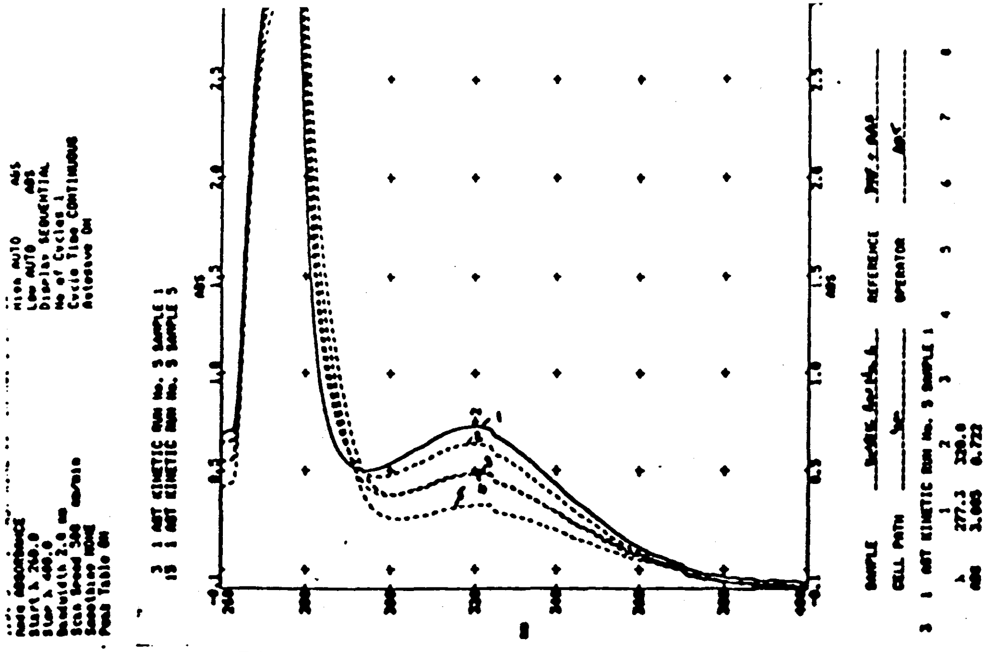


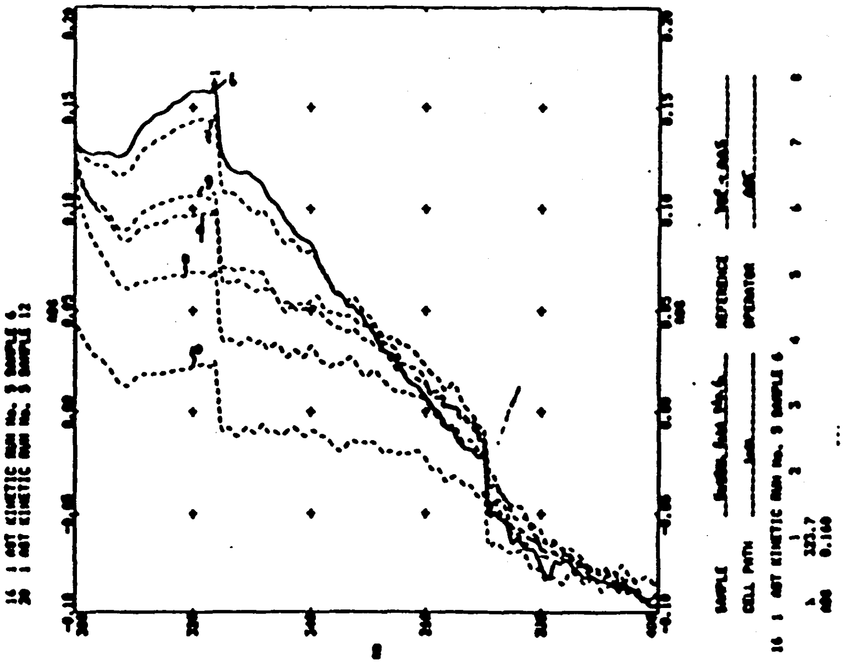
```
KINETIC RUN No. 4
*****************

     TEMP =  195degC        DPS MASS =   10.89g
     CHLOROPHENATE MASS = 0.2484g
     CHLOROPHENATE CONC. =2.230%
     NUMBER OF SAMPLES =  10

    TIME          MASS       THEO MASS P    CONC. P
   (secs)       (grams)       (grams)     (moll-1)

        45        0.4417       0.00985   1.04416E-04
       300        0.5152       0.01149   1.21792E-04
       600        0.4592       0.01024   1.08552E-04
      1200        0.4565       0.01018   1.07916E-04
      2100        0.4096       0.00913   9.68280E-05
      3000        0.4395       0.00980   1.03896E-04
      3600        0.3683       0.00821   8.70640E-05
      4800        0.2745       0.00612   6.48765E-05
      6000        0.5122       0.01142   1.21082E-04
      7200        0.4840       0.01081   1.14605E-04


   THEO ABS     ACTUAL ABS   P DETECTED      MASS P
   (320nm)       (320nm)     (moll-1)       (grams)

      1.656         1.000  6.81014E-05   6.42421E-03
      1.933         1.696  1.06944E-04   1.00883E-02
      1.721         1.304  8.22261E-05   7.75663E-03
      1.711         1.612  1.01647E-04   9.58867E-03
      1.536         1.092  6.88581E-05   6.49559E-03
      1.648         1.065  6.71555E-05   6.33490E-03
      1.381         0.858  5.41027E-05   5.10367E-03
      1.029         0.570  3.64468E-05   3.43814E-03
      1.920         0.991  6.24893E-05   5.89480E-03
      1.817         0.862  5.43550E-05   5.12747E-03


 MASS P TOTAL    MOLES P       1/(a-x)
   (grams)       (moles)     (moles-1)

     0.1620   3.00530E-04        3327
     0.2181   4.04602E-04        2472
     0.1881   3.48949E-04        2866
     0.2340   4.34099E-04        2304
     0.1766   3.27615E-04        3052
     0.1606   2.97933E-04        3356
     0.1543   2.86246E-04        3494
     0.1395   2.58790E-04        3864
     0.1282   2.37827E-04        4205
     0.1178   2.18534E-04        4576
```

UV Spectra And Data For Kinetic Run 4

Graph 13: 1/(a-x) v. Time For Kinetic Run No.4



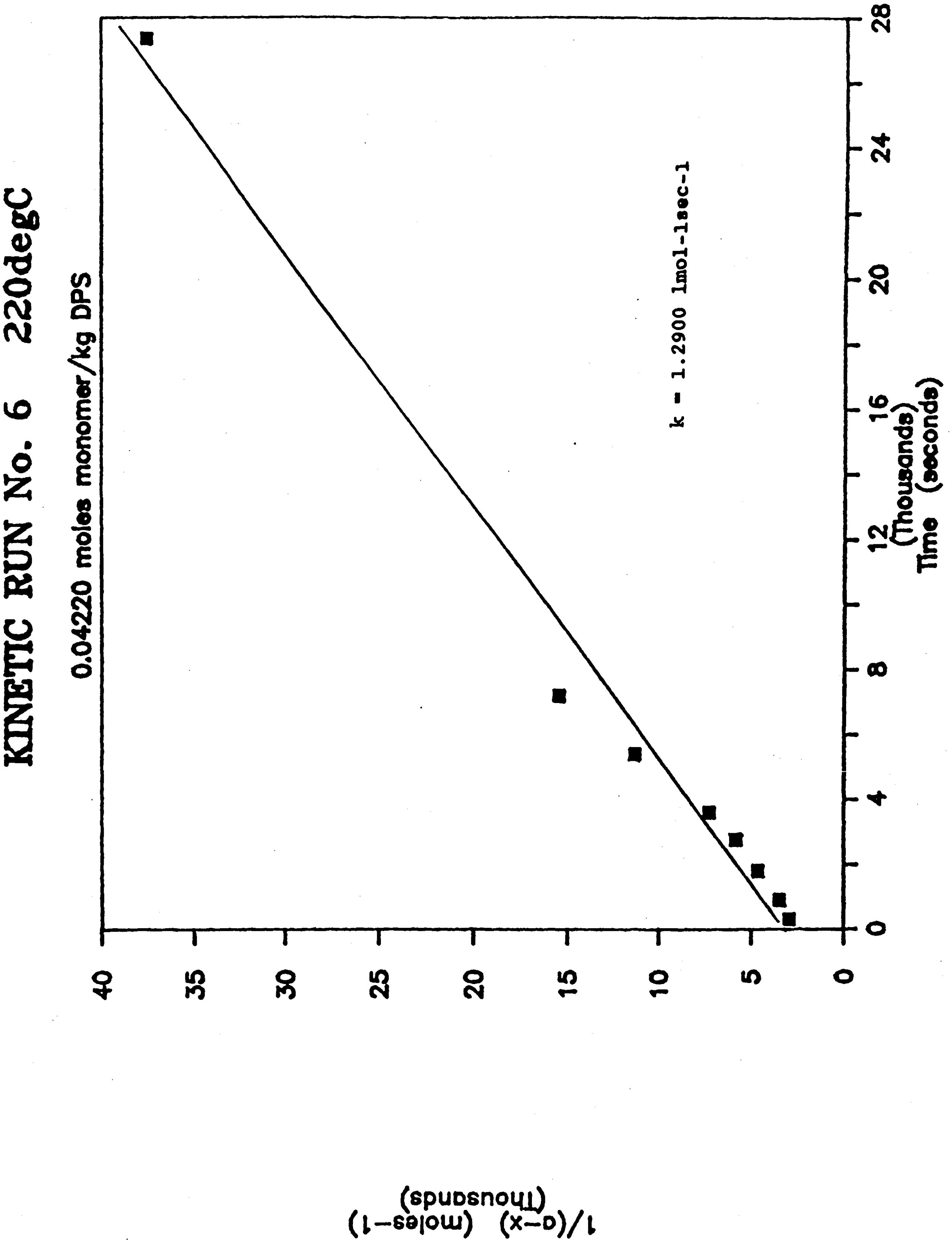


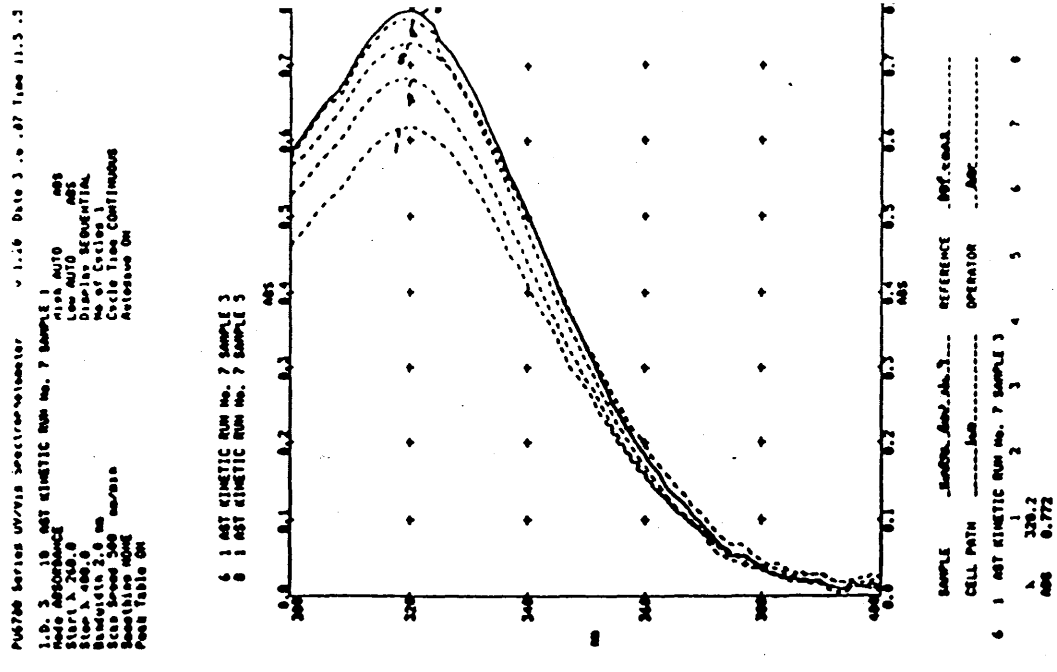


```
KINETIC RUN NO. 6
*****************

    TEMP : 220degC           DPS MASS :   11.270
    CHLOROPHENATE MASS : 0.2552g
    CHLOROPHENATE CONC. :2.226%
    NUMBER OF SAMPLES :  12

TIME           MASS          THEO MASS P  CONC. P
(secs)         (grams)       (grams)      (moll-1)

        300       0.2676        0.00595  6.30744E-05
        900       0.2768        0.00616  6.53009E-05
       1800       0.2803        0.00641  6.79507E-05
       2760       0.3530        0.00791  8.38518E-05
       3600       0.2975        0.00662  7.01769E-05
       5400       0.2256        0.00502  5.32137E-05
       7200       0.2808        0.00624  6.61486E-05
      10800       0.3732        0.00830  8.79861E-05
      14400       0.3847        0.00856  9.07401E-05
      23220       0.2421        0.00538  5.70320E-05
      27360       0.4158        0.00925  9.80548E-05

  THEO ABS     ACTUAL ABS   P DETECTED    MASS P
  (320nm)      (320nm)      (moll-1)      (grams)

      1.000        0.722  4.55271E-05  4.29471E-03
      1.036        0.633  3.99150E-05  3.76530E-03
      1.078        0.491  3.09609E-05  2.92063E-03
      1.330        0.482  3.03934E-05  2.86710E-03
      1.113        0.324  2.04304E-05  1.92726E-03
      0.844        0.157  9.89993E-06  9.33890E-04
      1.049        0.143  9.01713E-06  8.50613E-04
      1.395        0.106  6.68403E-06  6.30525E-04
      0.935        0.097  6.11653E-06  5.76990E-04
      0.904        0.023  1.45031E-06  1.36812E-04
      1.555        0.069  4.35093E-06  4.10436E-04


MASS P TOTAL   MOLES P       1/(a-x)
  (grams)      (moles)       (moles-1)

     0.1842  3.41714E-04          2926
     0.1561  2.89585E-04          3453
     0.1163  2.15751E-04          4635
     0.0925  1.71599E-04          5828
     0.0743  1.37836E-04          7255
     0.0475  8.81184E-05         11348
     0.0340  6.45583E-05         15490
     0.0194  3.59894E-05         27786
     0.0172  3.19081E-05         31340
     0.0065  1.20583E-05         82930
     0.0113  2.10234E-05         47566
```

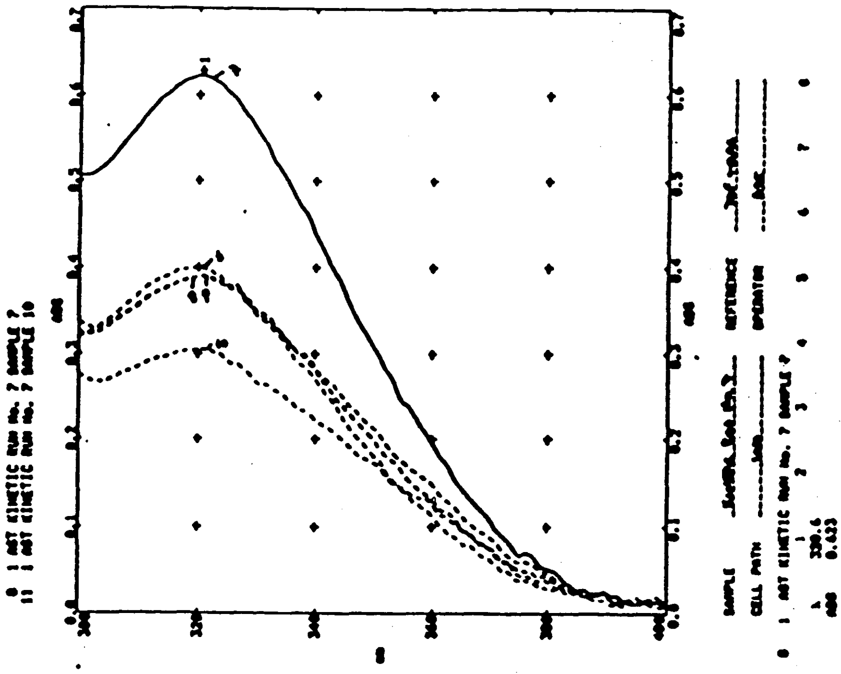
UV Spectra And Data For Kinetic Run 6

Graph 14: 1/(a-x) v. Time For Kinetic Run No.6





```
PU8700 Series UV/Vis Spectrophotometer     v 1.26  Date 3 .0 .87 Time 11.3 .3

I.D. 3     10  AST KINETIC RUN No. 7 SAMPLE 1
Mode ABSORBANCE                High AUTO      ABS
Start λ 260.0                  Low AUTO       ABS
Stop λ 400.0                   Display SEQUENTIAL
Bandwidth 2.0 nm               No of Cycles 1
Scan Speed 300  nm/min         Cycle Time CONTINUOUS
Smoothing NONE                 Autosave ON
Peak Table ON
```



TEMP. = 109 deg C   DPS MASS = 10.76 grams

CHLOROPHENATE MASS = 0.232 grams
CHLOROPHENATE CONC. = 2.111 %w/w

NUMBER OF SAMPLES = 10

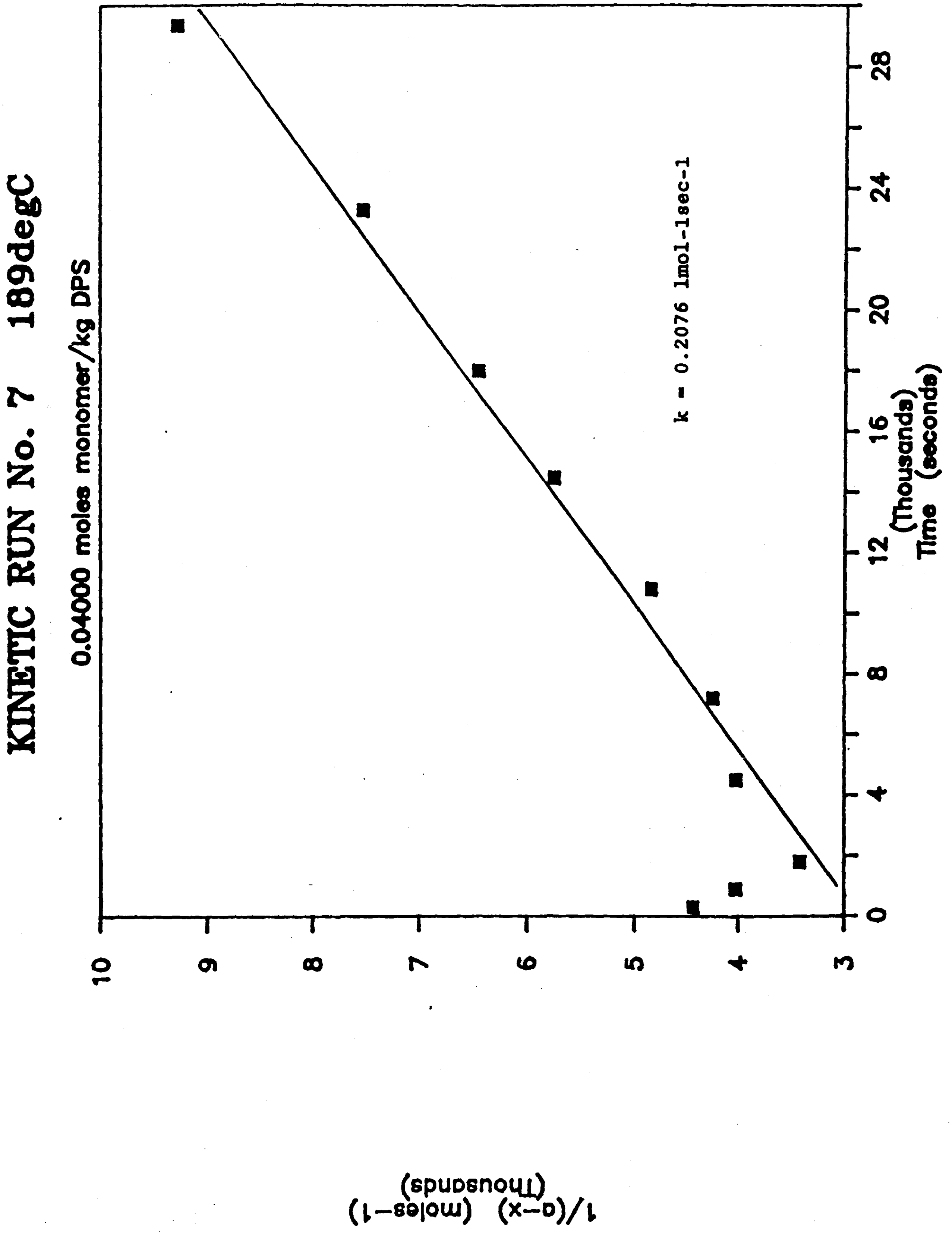
TIME (secs)	MASS (grams)	THEO MASS P (grams)	CONC. P (moll-1)
300	0.3326	0.007016964	7.43049E-05
900	0.3714	0.007846254	8.31122E-05
1800	0.32	0.0067582	7.16100E-05
4500	0.3331	0.007031741	7.45415E-05
7200	0.3736	0.007920916	8.40522E-05
10800	0.2981	0.006962961	6.26110E-05
14460	0.4331	0.009184961	9.73472E-05
18000	0.3052	0.006442772	6.82700E-05
23208	0.3566	0.007527826	7.90004E-05
29340	0.3432	0.007244952	7.68017E-05

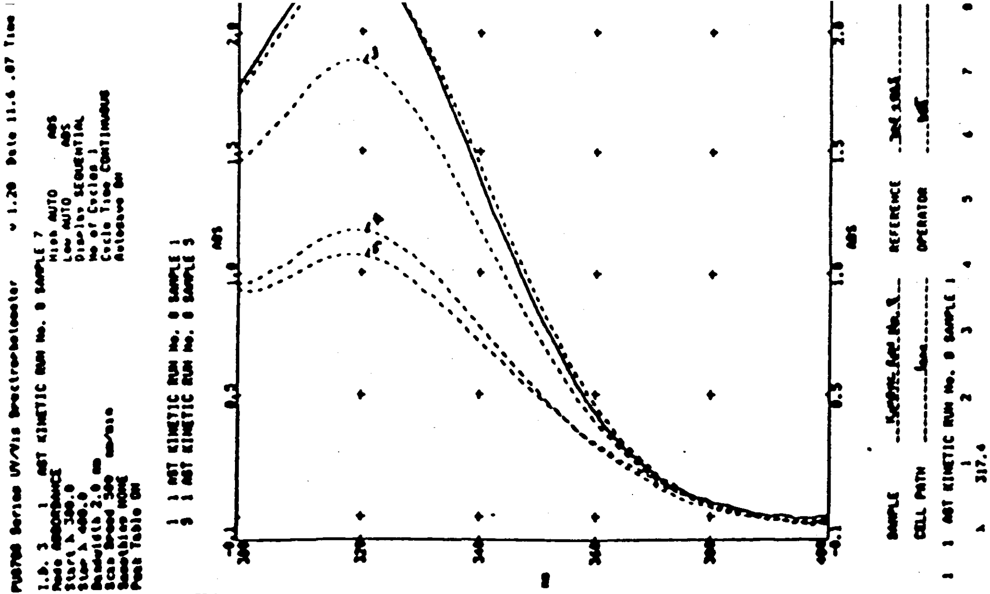
THEO ABS. (320nm)	ACTUAL ABS. (320nm)	P DETECTED (moll-1)	MASS P (grams)
1.17964735	0.610	3.89691E-05	3.67600E-03
1.31805362	0.761	4.79642E-05	4.52670E-03
1.17564125	0.772	4.86799E-05	4.59213E-03
1.10213156	0.682	4.30040E-05	4.05670E-03
1.33293092	0.729	4.59685E-05	4.33433E-03
0.83434143	0.4	2.52227E-05	2.37934E-03
1.54411721	0.623	3.92844E-05	3.70503E-03
1.08311704	0.39	2.45922E-05	2.31984E-03
1.26553022	0.39	2.45922E-05	2.31984E-03
1.21797524	0.308	1.97272E-05	1.81425E-03

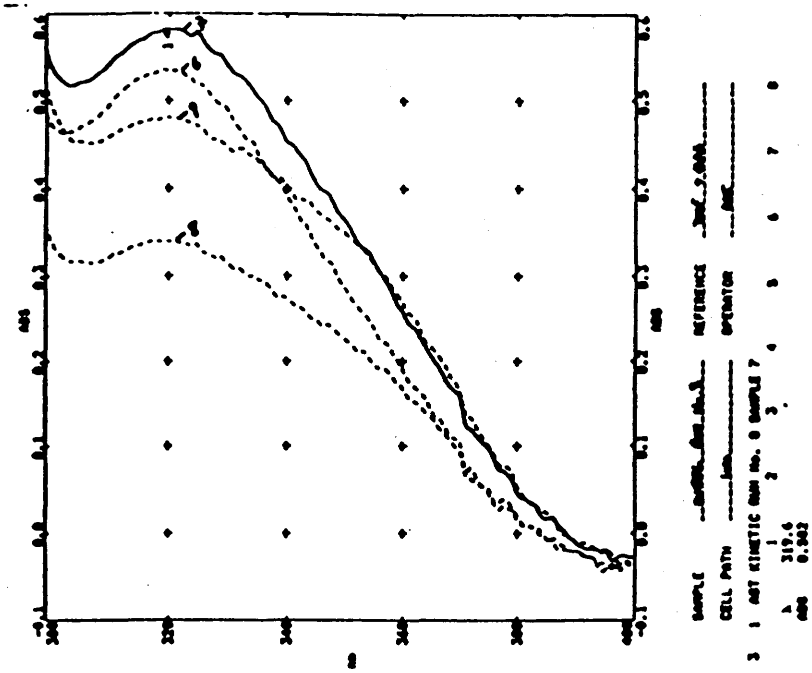
MASS P TOTAL (grams)	MOLES P (moles)	1/(a-x) (moles-1)
0.121562910	2.25513E-04	4434.30209
0.133972732	2.48534E-04	4023.55407
0.137739609	2.92627E-04	3417.31878
0.133670042	2.48344E-04	4026.6425
0.124904005	2.35423E-04	4247.67099
0.111245133	2.06374E-04	4845.57640
9.36209E-02	1.73679E-04	5757.7639
8.33314E-02	1.54990E-04	6451.6700
7.15004E-02	1.32657E-04	7538.23203
5.81047E-02	1.07795E-04	9276.04483

UV Spectra And Data For Kinetic Run 7

Graph 15 : 1/(a-x) v. Time For Kinetic Run No.7







TEMP. = [illegible] Run No. 8 [illegible] grams

[illegible] grams
[illegible]

[illegible]

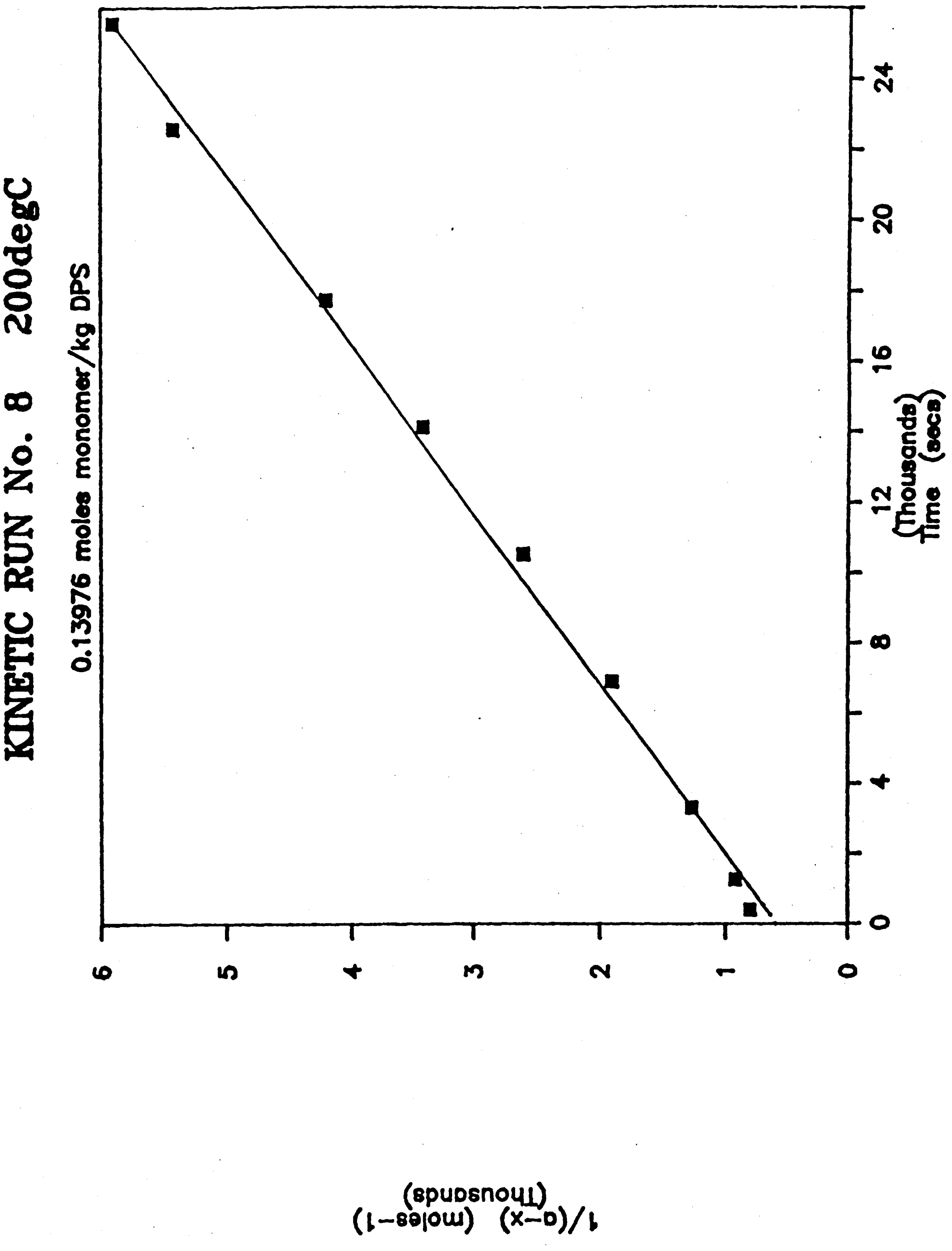
TIME (secs)	ABS	THEO MASS F (grams)	CONC. F (mol l-1)
360	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
3360	[illegible]	[illegible]	1.02724E-04
[illegible]	[illegible]	[illegible]	1.95024E-04
10560	0.325	[illegible]	1.44121E-04
14160	[illegible]	[illegible]	[illegible]
17760	[illegible]	[illegible]	1.13300E-04
[illegible]	[illegible]	[illegible]	1.07462E-04
25560	[illegible]	[illegible]	1.46164E-04

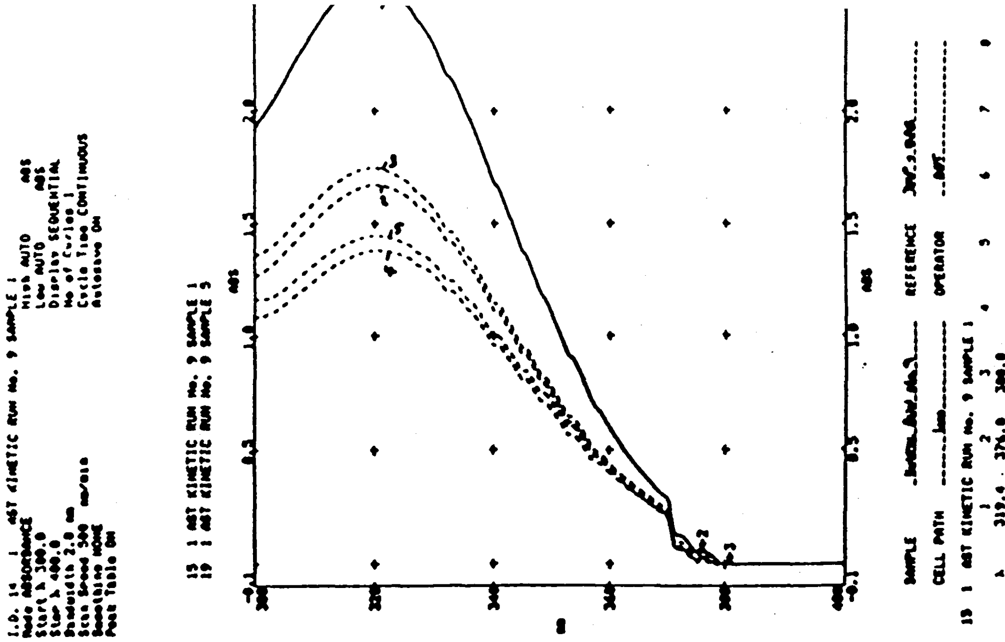
THEO ABS. (320nm)	ACTUAL ABS. (320nm)	F DETECTED (mol l-1)	MASS F (grams)
2.5723241	1.777	1.47235E-04	1.38194E-02
2.4379108.4	[illegible]	1.45401E-04	1.37169E-02
3.3077404	[illegible]	1.16673E-04	1.11943E-02
[illegible]	[illegible]	7.41944E-05	6.99527E-03
[illegible]	[illegible]	[illegible]	6.37448E-03
[illegible]	0.737	3.37734E-05	3.13237E-03
[illegible]	[illegible]	[illegible]	3.45194E-03
[illegible]	0.34	2.14353E-05	2.02244E-03
[illegible]	0.411	3.03304E-05	2.86116E-03

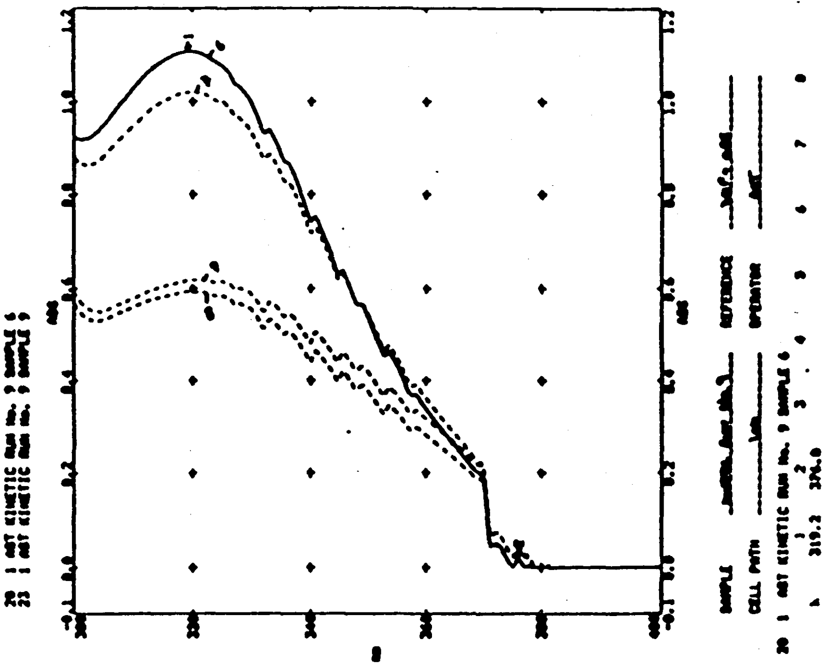
MASS F TOTAL (grams)	MOLES F (moles)	1 (a-x) (mo.dm-1)
[illegible]	[illegible]	[illegible]
0.564447127	1.06422E-03	922.314187
[illegible]	7.57114E-04	1272.56527
[illegible]	[illegible]	1906.57643
0.206479447	[illegible]	2610.70655
0.157633477	[illegible]	3415.25369
0.127937601	2.37340E-04	4213.35711
9.94226E-02	1.84442E-04	5421.76318
9.13574E-02	[illegible]	5900.41771

UV Spectra And Data For Kinetic Run 8

Graph 16: 1/(a-x) v. Time For Kinetic Run No. 8



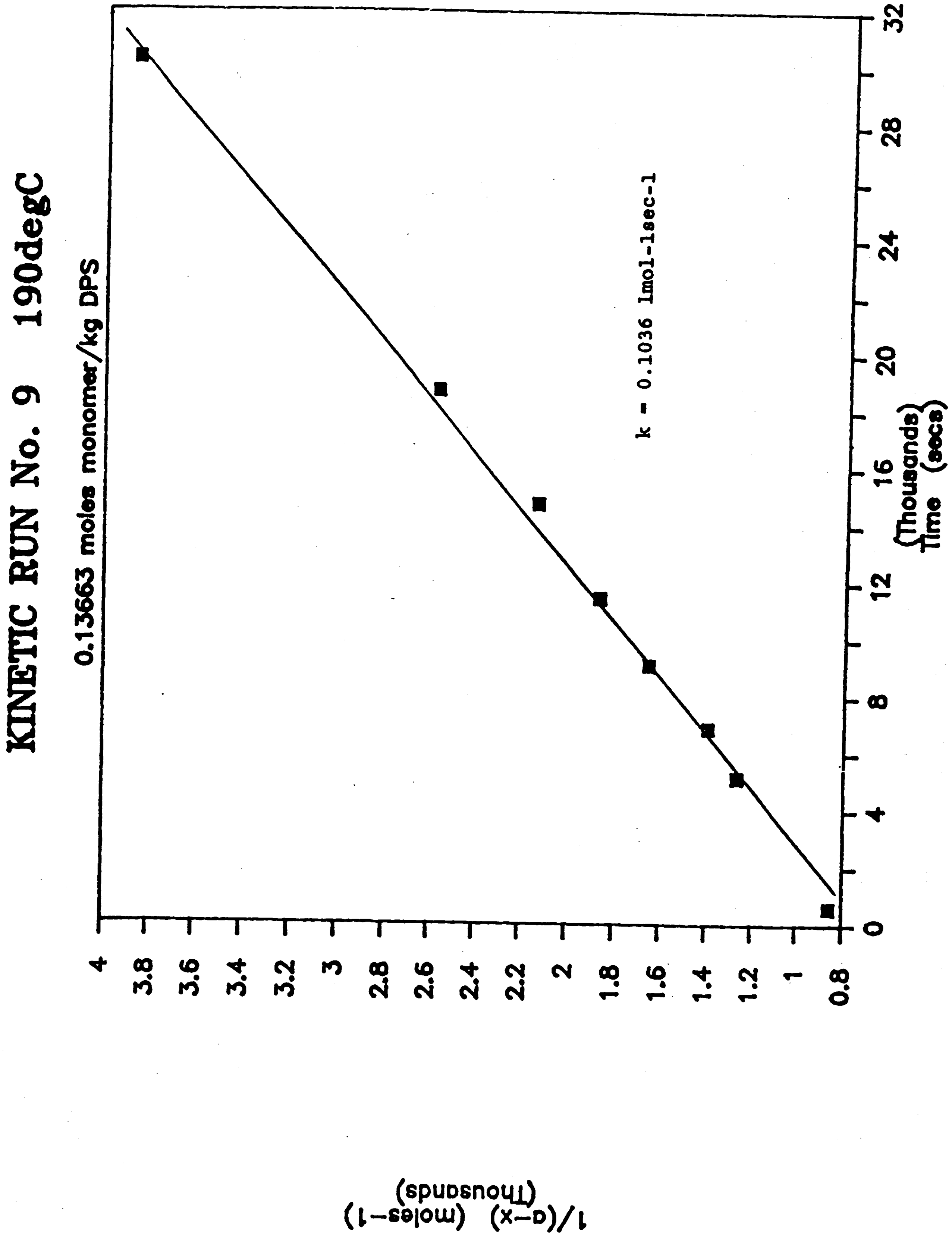


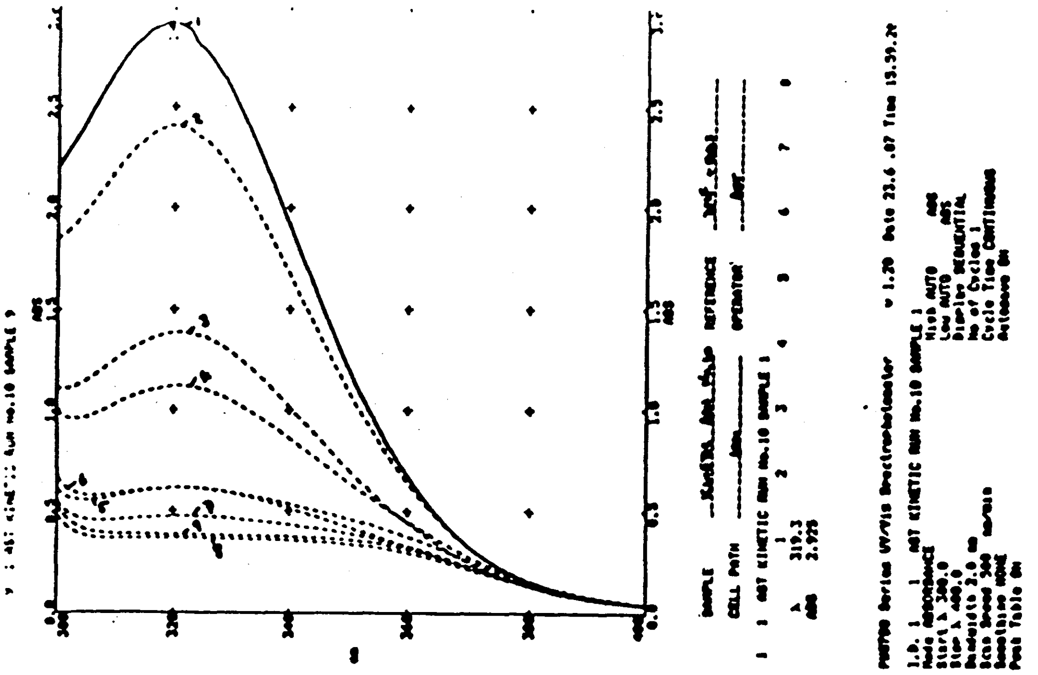


```
TEMP  =  [illegible] deg C          DPS MASS =  10.3? grams
CHLOROPHENATE MASS =  0.7387  grams
                              CHLOROPHENATE CONC. =  6.00  [illegible]

NUMBER OF SAMPLES =  9

TIME           MASS            THEO MASS P     CONC. P
(secs)         (grams)         (grams)         (moll-1)

 600            0.2643          0.01813098      1.82201E-04
 2100           0.251           0.0172186       1.82530E-04
 6900           0.2695          0.0198587       2.10827E-04
 9120           0.2719          0.01865234      1.97728E-04
 11460          0.32            0.0220206       2.33434E-04
 14760          0.2811          0.01928346      2.04419E-04
 18720          0.3125          0.0214375       2.27253E-04
 30300          0.2725          0.0186835       1.98185E-04
 31440          0.2964          0.02033304      2.15545E-04

THEO ABS       ACTUAL ABS.     P DETECTED      MASS P
(320nm)        (320nm)         (moll-1)        (grams)

 3.04806501     2.392           1.83443E-04     1.54181E-02
 2.89468145     1.888           1.02179E-04     9.92188E-03
 3.33868643     1.744           1.09871E-04     1.03739E-02
 3.13571274     1.381           8.70815E-05     8.21468E-03
 3.70196318     1.448           9.11802E-05     8.60132E-03
 3.24181291     1.108           6.98670E-05     6.59078E-03
 3.60393612     1.021           6.43811E-05     6.07327E-03
 3.1426323      0.393           3.73927E-05     3.52737E-03
 3.41826133     0.618           3.89691E-05     3.67606E-03

MASS P TOTAL   MOLES P         1/(a-x)
(grams)        (moles)         (moles-1)

 0.62820017     1.16539E-03     858.08127
 0.425679309    7.89689E-04     1266.32136
 0.385885205    7.15866E-04     1396.90974
 0.325345412    6.03557E-04     1656.84463
 0.288561593    5.35300E-04     1868.11237
 0.252487062    4.68395E-04     2134.9482
 0.209283856    3.88246E-04     2575.87188
 0.138395387    2.56596E-04     3887.0347
 0.13355818     2.47767E-04     4036.04482
```

UV Spectra And Data For Kinetic Run 9

Graph 17: 1/(a-x) v. Time For Kinetic Run No.9

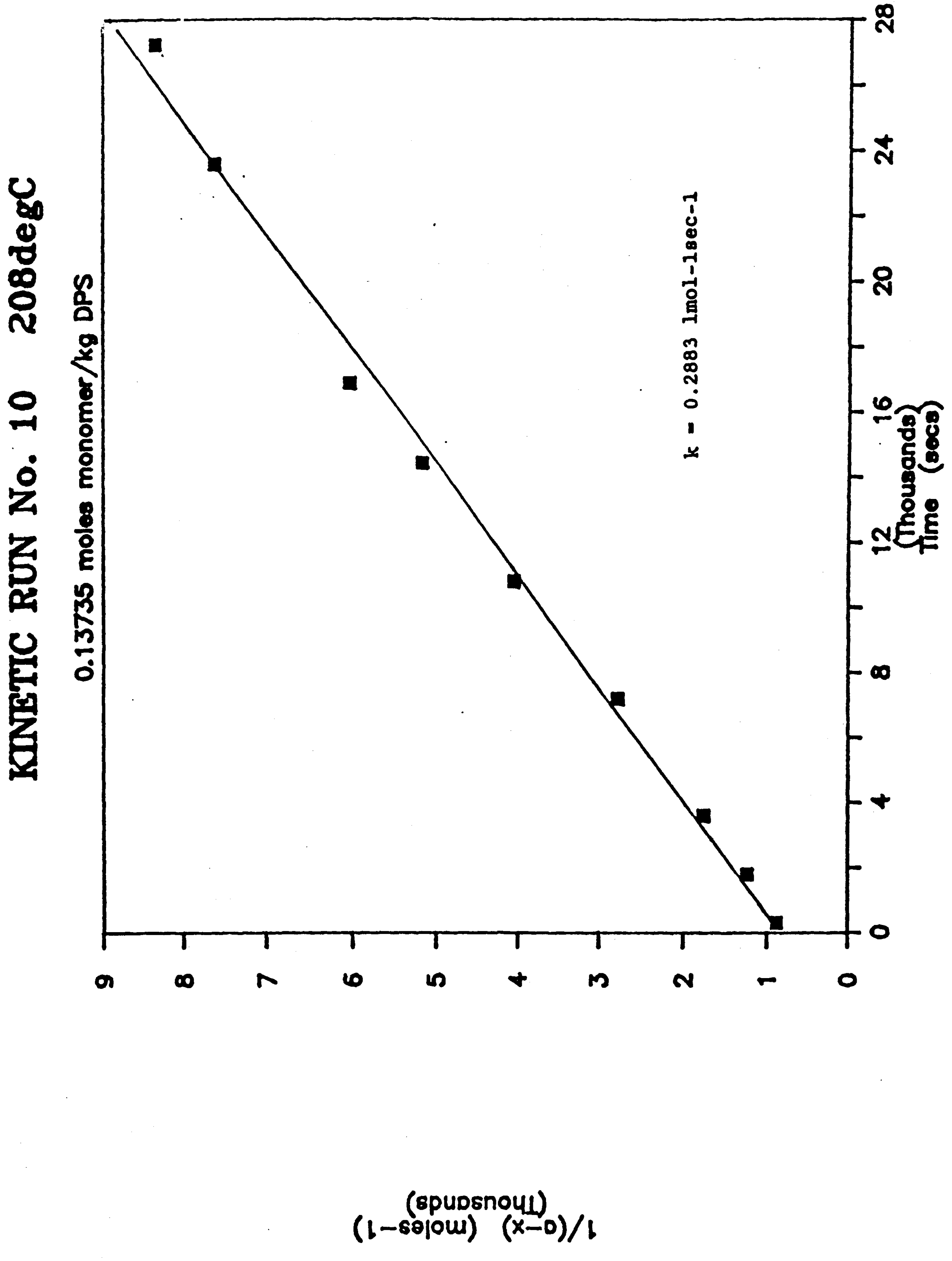


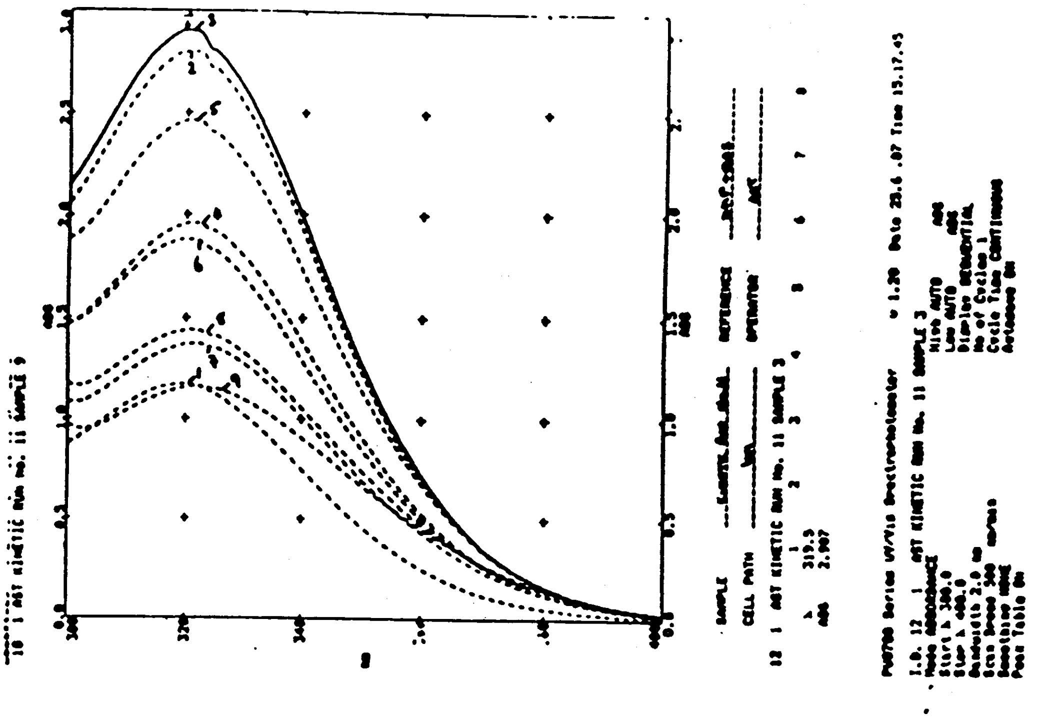


```
                         KINETIC RUN No.  10

TEMP. =  308  deg C               BPS MASS =  9.91  grams

CHLOROPHENATE MASS =  0.7337  grams
                                  CHLOROPHENATE CONC. =  6.893  %m/w

NUMBER OF SAMPLES =  9

TIME          MASS            THEO MASS P     CONC. P
(secs)        (grams)         (grams)         (moll-1)

 300           0.3027          0.0208645111    2.21185E-04
 1800          0.382           0.02426336      2.57209E-04
 3600          0.2848          0.019769124     2.09367E-04
 7200          0.366           0.025322838     2.67439E-04
 10800         0.2927          0.020175811     2.13678E-04
 14400         0.3741          0.025786713     2.73358E-04
 16860         0.3376          0.023270768     2.46487E-04
 23580         0.3304          0.022774472     2.41426E-04
 27240         0.3779          0.026048647     2.76134E-04

THEO ABS.     ACTUAL ABS.     P DETECTED      MASS P
(320nm)       (320nm)         (moll-1)        (grams)

 3.30770972    2.925           1.84441E-04     1.73989E-02
 4.07900173    2.409           1.51904E-04     1.43296E-02
 3.32349936    1.388           8.75229E-05     8.25633E-03
 4.24123478    1.121           7.06868E-05     6.66811E-03
 3.39182899    0.615           3.87800E-05     3.65824E-03
 4.33509814    0.615           3.87800E-05     3.65824E-03
 3.91213347    0.476           3.00151E-05     2.83142E-03
 3.82869938    0.369           2.32680E-05     2.19494E-03
 4.37913282    0.385           2.42769E-05     2.29012E-03

MASS P TOTAL  MOLES P         1/(a-x)
(grams)       (moles)         (moles-1)

 0.611790899   1.13495E-03     881.096468
 0.453295021   8.03817E-04     1244.06416
 0.306407846   5.68425E-04     1759.24607
 0.193916199   3.59739E-04     2779.79253
 0.133027661   2.46783E-04     4052.1407
 0.104082321   1.93084E-04     5179.04282
 8.92676E-02   1.65603E-04     6038.54622
 7.07092E-02   1.31175E-04     7623.43291
 6.45020E-02   1.19659E-04     8357.08138
```

UV Spectrum And Data For Kinetic Run 10

Graph 18: 1/(a-x) v. Time For Kinetic Run No.10



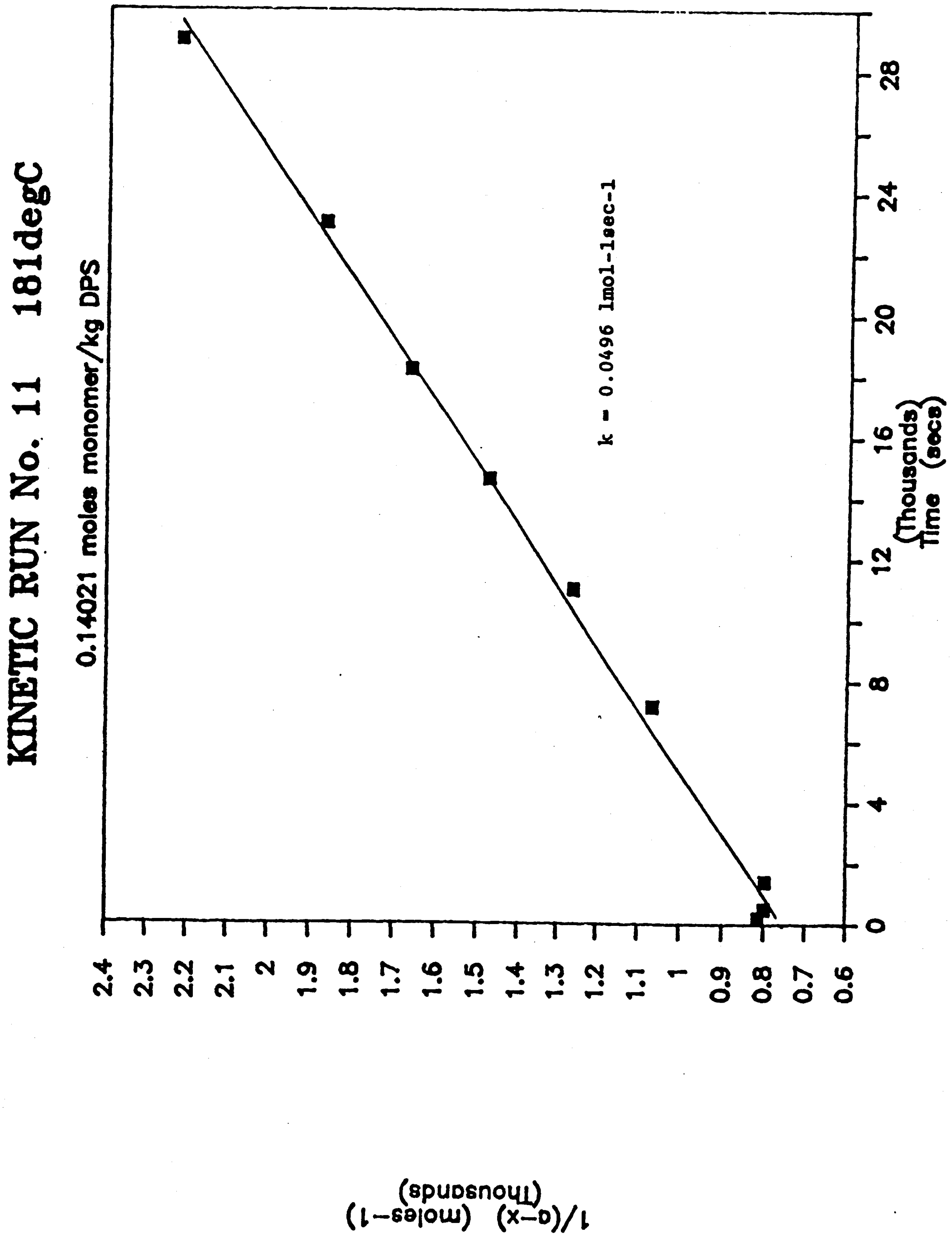


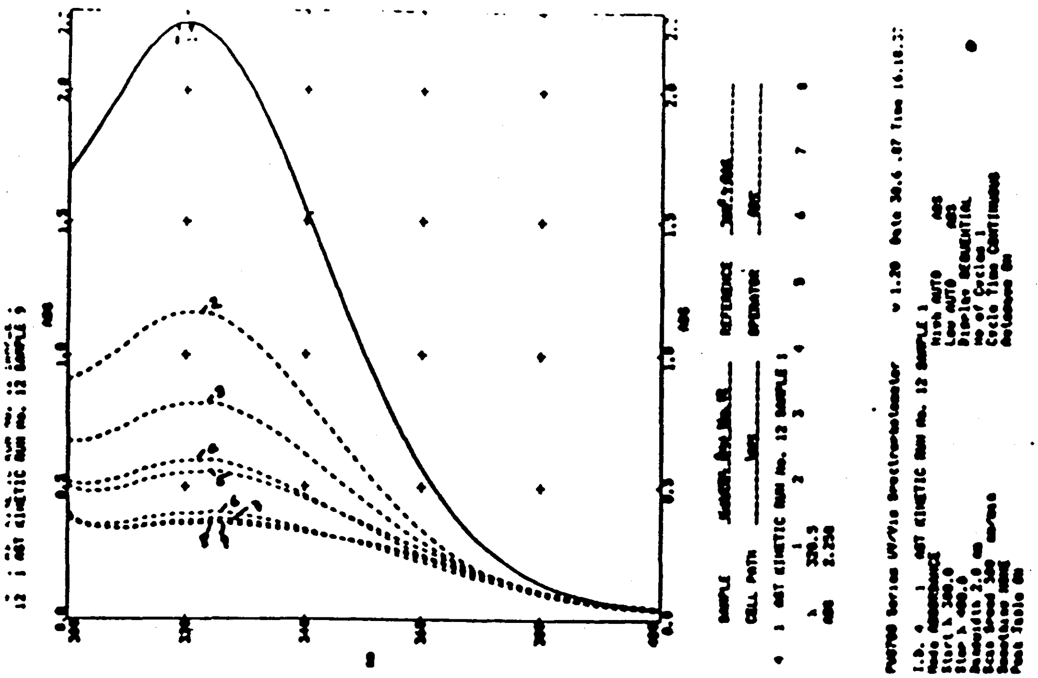
```
SAMPLE     ___Kinetic Run No.11___   REFERENCE  ___[illegible]___
CELL PATH  _______1cm__________      OPERATOR   ____AST________

12  1  AST KINETIC RUN No. 11 SAMPLE 3
            1       2       3       4       5       6       7       8
   λ      319.5
   ABS    2.907

PU8700 Series UV/Vis Spectrophotometer      v 1.20  Date 23.6 .87 Time 15.17.45

I.D. 12   1   AST KINETIC RUN No. 11 SAMPLE 3
Mode ABSORBANCE                              High AUTO      ABS
Start λ 300.0                                Low AUTO       ABS
Stop λ 400.0                                 Display SEQUENTIAL
Bandwidth 2.0 nm                             No of Cycles 1
Scan Speed 300  nm/min                       Cycle Time CONTINUOUS
Smoothing NONE                               Autozero On
Peak Table On
```

```
                         KINETIC RUN No.  11

TEMP. =  101  deg C              BPS MASS =  10.47  grams

CHLOROPHENATE MASS =  0.7913  grams
                                 CHLOROPHENATE CONC. =  7.027  %w/w

NUMBER OF SAMPLES =  9

TIME          MASS             THEO MASS P      CONC. P
(secs)        (grams)          (grams)          (moll-1)

 210           0.1189           0.008355103      8.85701E-05
 810           0.2788           0.019591276      2.07682E-04
 1410          0.2885           0.020272895      2.14907E-04
 7170          0.2608           0.018305335      1.94050E-04
 11010         0.3873           0.027219871      2.88500E-04
 14610         0.3472           0.024397744      2.58634E-04
 18210         0.2844           0.019904788      2.11853E-04
 23010         0.3358           0.023575385      2.49918E-04
 29010         0.3213           0.022577781      2.39340E-04

THEO ABS.     ACTUAL ABS.      P DETECTED       MASS P
(320nm)       (320nm)          (moll-1)         (grams)

 1.40460676    1.175            7.40910E-05      6.98932E-03
 3.29356069    2.804            1.76811E-04      1.66792E-02
 3.40819014    2.907            1.83304E-04      1.72919E-02
 3.07737647    1.96             1.23591E-04      1.16588E-02
 4.37530866    2.464            1.55372E-04      1.46567E-02
 4.10159351    1.891            1.19241E-04      1.12483E-02
 3.35471542    1.374            8.66401E-05      8.17304E-03
 3.96357737    1.442            9.09280E-05      8.57753E-03
 3.79562787    1.163            7.33351E-05      6.91794E-03

MASS P TOTAL  MOLES P          1/(a-x)
(grams)       (moles)          (moles-1)

 0.661974831   1.22800E-03      814.30105
 0.67370645    1.24981E-03      800.12118
 0.674970325   1.25216E-03      798.622962
 0.504003798   9.34991E-04      1069.52924
 0.426165876   7.90592E-04      1264.87556
 0.364835657   6.76816E-04      1477.5058
 0.323625404   6.00364E-04      1665.65045
 0.287910962   5.34111E-04      1872.26911
 0.242468014   4.49809E-04      2223.16664
```

UV Spectrum And Data For Kinetic Run 11

Graph 19: 1/(a-x) v. Time For Kinetic Run No.11



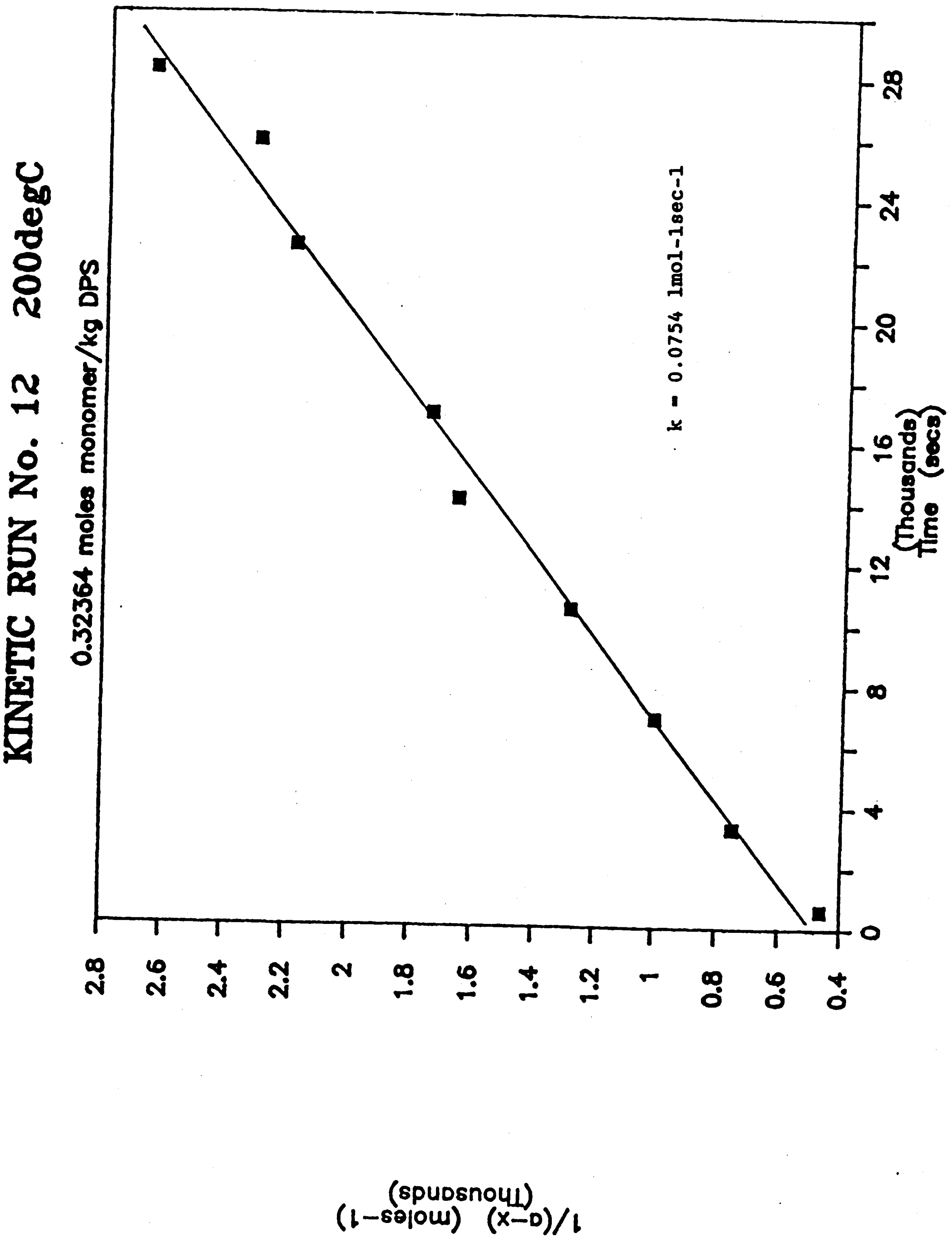


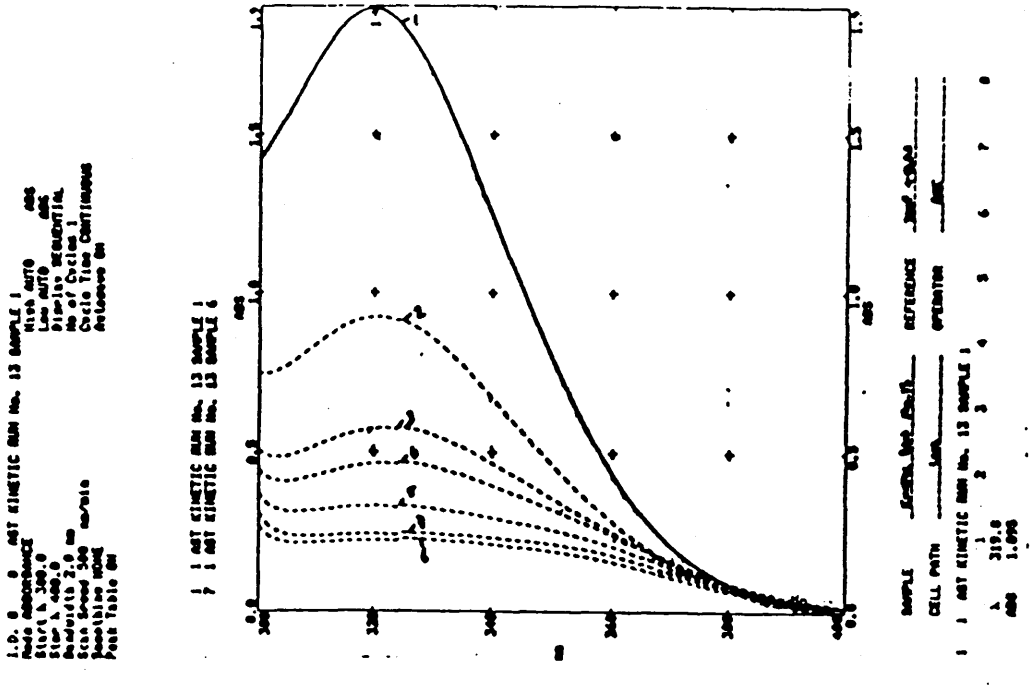
```
SAMPLE      [illegible]        REFERENCE  [illegible]
CELL PATH   [illegible]        OPERATOR   [illegible]
4   1  AGT KINETIC RUN No. 12 SAMPLE 1
          1        2        3        4        5        6        7        8
  λ      320.5
  ABS    2.258

PU8700 Series UV/Vis Spectrophotometer       v 1.20  Date 30.6 .87 Time 16.18.3:
I.D. 4    1   AGT KINETIC RUN No. 12 SAMPLE 1
Mode ABSORBANCE                                 High AUTO      ABS
Start λ 300.0                                   Low AUTO       ABS
Stop λ 400.0                                    Display SEQUENTIAL
Bandwidth 2.0 nm                                No of Cycles 1
Scan Speed 300  nm/min                          Cycle Time CONTINUOUS
Smoothing NONE                                  Autozero On
Peak Table On
```

```
                         KINETIC RUN No.  12

TEMP. =  200  deg C             BPS MASS =  0.17  grams

CHLOROPHENATE MASS =  1.4253  grams
                                CHLOROPHENATE CONC. =  14.854  %w/w

NUMBER OF SAMPLES =  9

TIME            MASS            THEO MASS P      CONC. P
(secs).         (grams)         (grams)          (moll-1)

 600             0.2785          0.0413386682     0.000175288
 3300            0.2309          0.034297886      1.45453E-04
 6900            0.2171          0.032248034      1.36741E-04
 10800           0.2051          0.030465354      1.29183E-04
 14100           0.2452          0.036422008      1.54440E-04
 16920           0.1885          0.02799979       1.18727E-04
 22380           0.2221          0.032990734      1.39890E-04
 25800           0.2274          0.033777996      1.43228E-04
 28140           0.257           0.03817478       1.61072E-04

THEO ABS.       ACTUAL ABS.     P DETECTED       MASS P
(320nm)         (320nm)         (moll-1)         (grams)

 2.7798398       2.258           1.42382E-04      3.35785E-02
 2.30637805      1.16            7.31460E-05      1.72502E-02
 2.16853475      0.819           5.16434E-05      1.21793E-02
 2.04867102      0.601           3.78972E-05      8.93740E-03
 2.44921567      0.559           3.52488E-05      8.31283E-03
 1.88285951      0.408           2.57272E-05      6.06732E-03
 2.21847798      0.383           2.41508E-05      5.69555E-03
 2.27141779      0.372           2.34572E-05      0.005531971
 2.56708167      0.366           2.30788E-05      5.44275E-03

MASS P TOTAL    MOLES P         1/(a-x)
(grams)         (moles)         (moles-1)

 1.15772722      2.14773E-03     465.60778
 0.716852112     1.32985E-03     751.963747
 0.538294065     9.98604E-04     1001.39837
 0.418123257     7.73672E-04     1289.20549
 0.325302091     6.03477E-04     1657.06528
 0.308847664     5.72951E-04     1745.34847
 0.246062648     4.56477E-04     2190.68908
 0.233425536     4.33034E-04     2309.29003
 0.203209231     3.76979E-04     2652.6686
```

UV Spectrum And Data For Kinetic Run 12

Graph 20: 1/(a-x) v. Time For Kinetic Run No.12

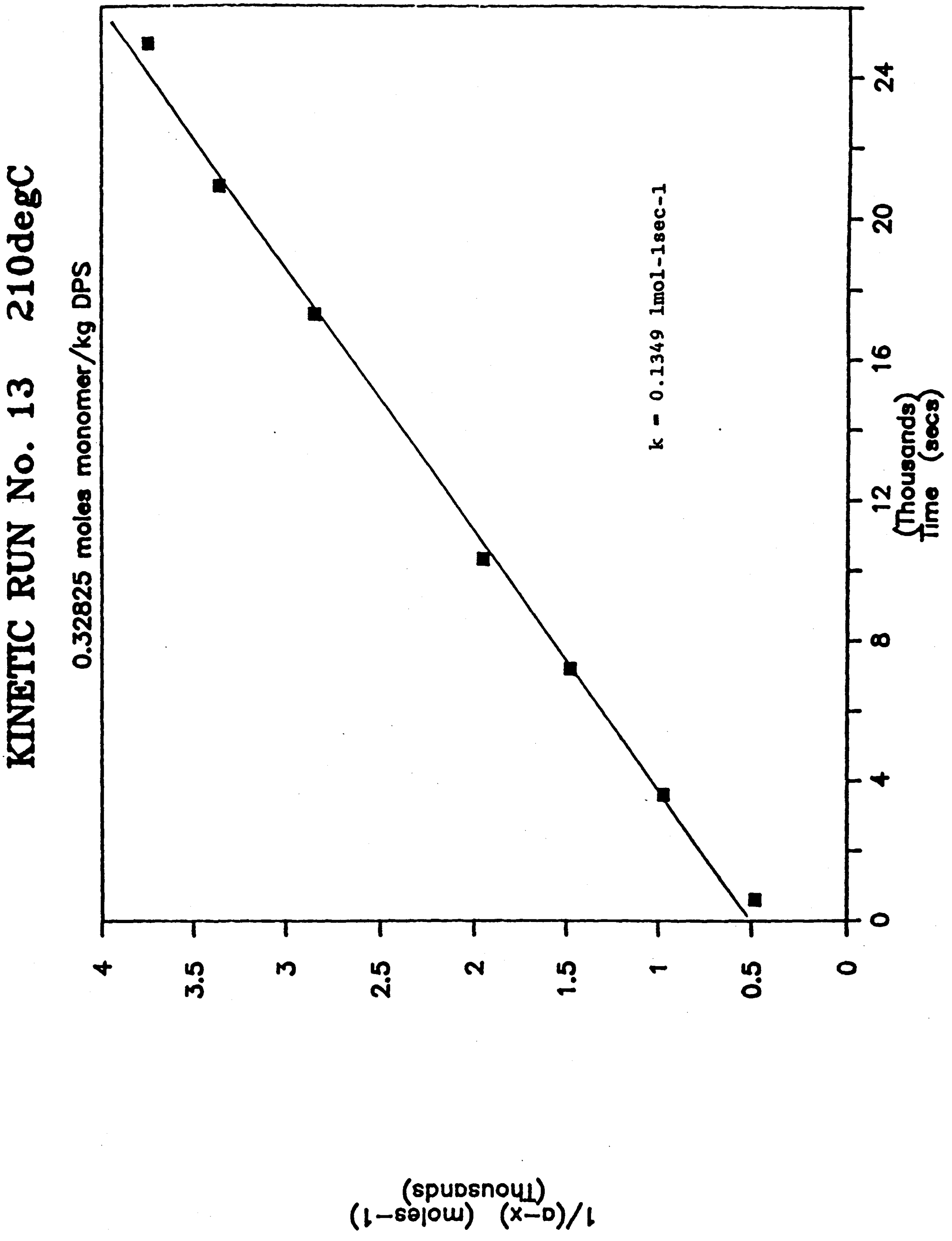


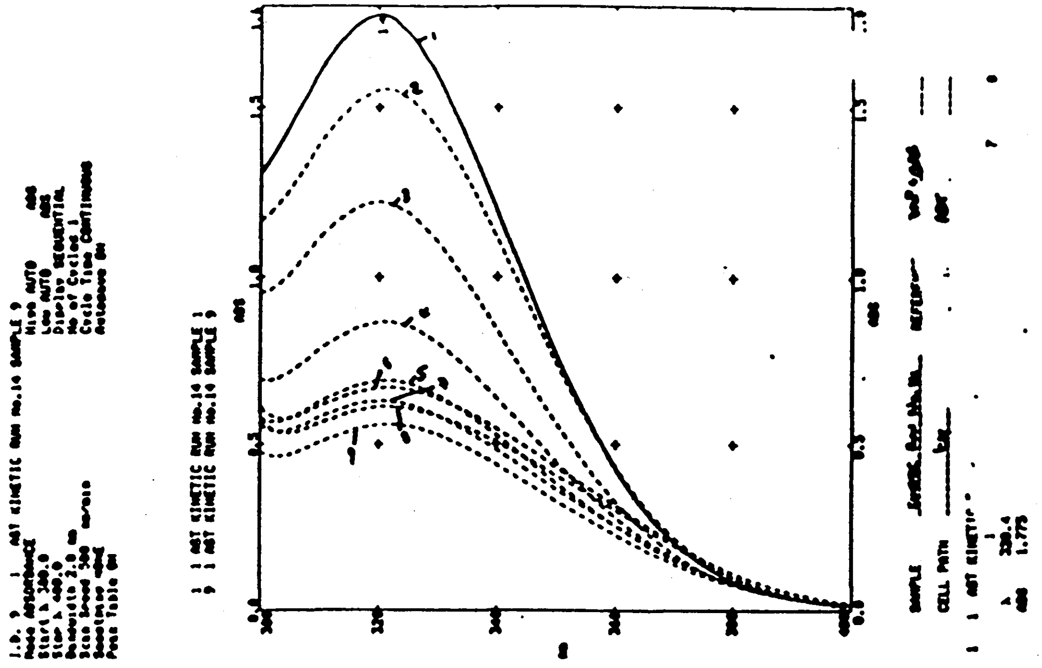


```
                    KINETIC RUN No.  13

TEMP. = 310  deg C              DPE MASS = 7.98  grams

CHLOROPHENATE MASS = 1.412  grams
                                CHLOROPHENATE CONC. = 15.034  %w/w

NUMBER OF SAMPLES = 7

TIME          MASS            THEO MASS P     CONC. P
(secs)        (grams)         (grams)         (mol l-1)

 600           0.2367          0.035585470     1.30093E-04
 3600          0.2327          0.034984118     1.48343E-04
 7200          0.2218          0.033345412     1.41394E-04
 10320         0.2379          0.035766086     1.51638E-04
 17280         0.2475          0.03720915      1.57778E-04
 20940         0.2012          0.030248608     1.28763E-04
 24960         0.2439          0.036681738     1.34845E-04

THEO ABS.     ACTUAL ABS.     P DETECTED      MASS P
(320nm)       (320nm)         (mol l-1)       (grams)

 2.3979638     1.098           1.19493E-04     7.81003E-02
 2.35252408    0.923           8.82013E-05     1.37236E-02
 2.34232847    0.578           3.64449E-05     8.99337E-03
 2.40309443    0.47            2.96367E-05     6.98973E-03
 2.30214741    0.338           2.11241E-05     4.98173E-03
 2.03404693    0.231           1.49461E-05     3.43318E-03
 2.45564286    0.28            1.57642E-05     3.71772E-03

MASS P TOTAL  MOLES P         1/(a-x)
(grams)       (moles)         (moles-1)

 1.11016326    0.002074338     482.081812
 0.553987999   1.02772E-03     973.029742
 0.363966436   6.75204E-04     1481.03437
 0.275927704   5.11885E-04     1953.56368
 0.189044739   3.50702E-04     2851.42419
 0.160333731   2.97474E-04     3361.6108
 0.143749894   2.66674E-04     3749.89338
```

UV Spectrum And Data For Kinetic Run 13

Graph 21: 1/(a-x) v. Time For Kinetic Run No.13

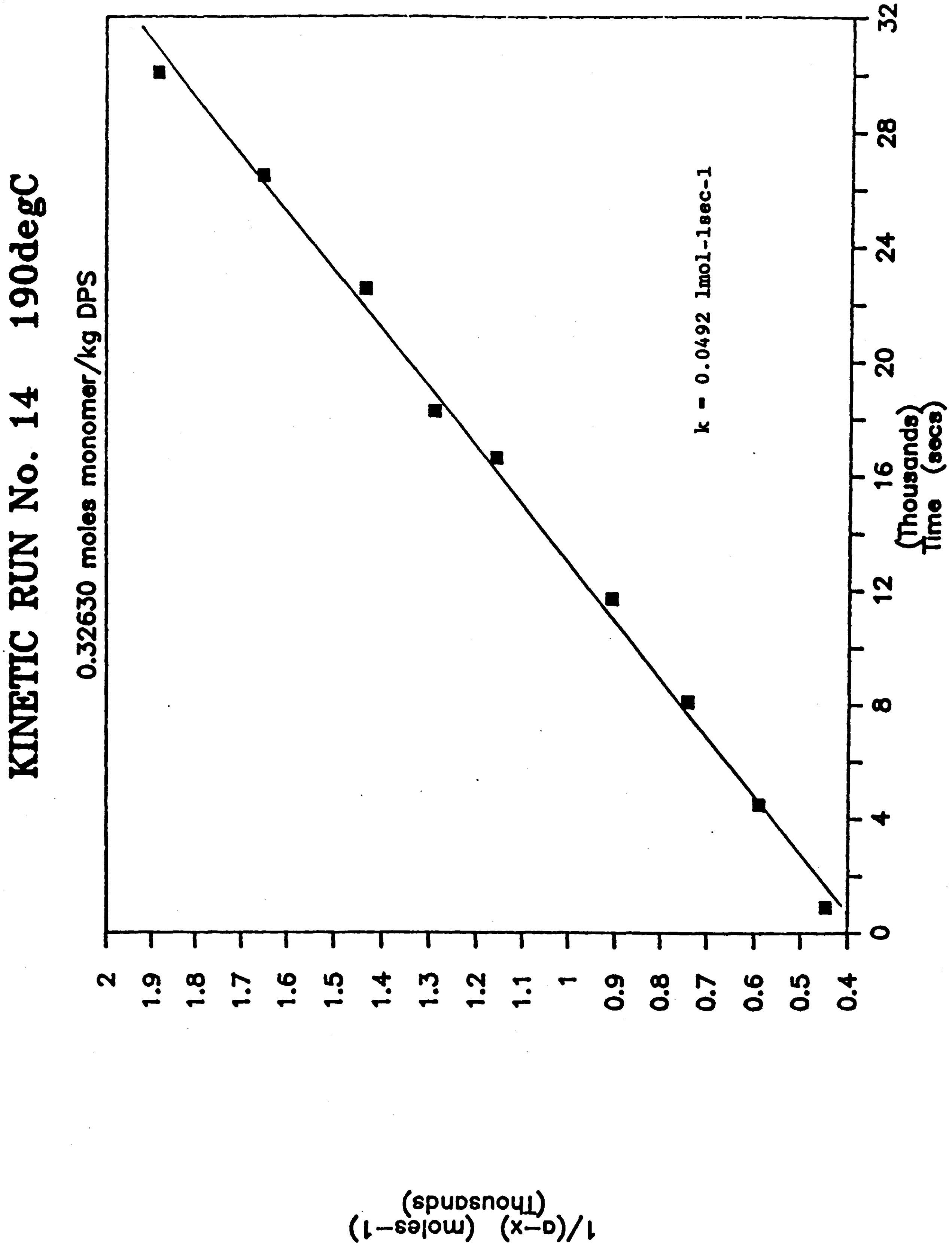


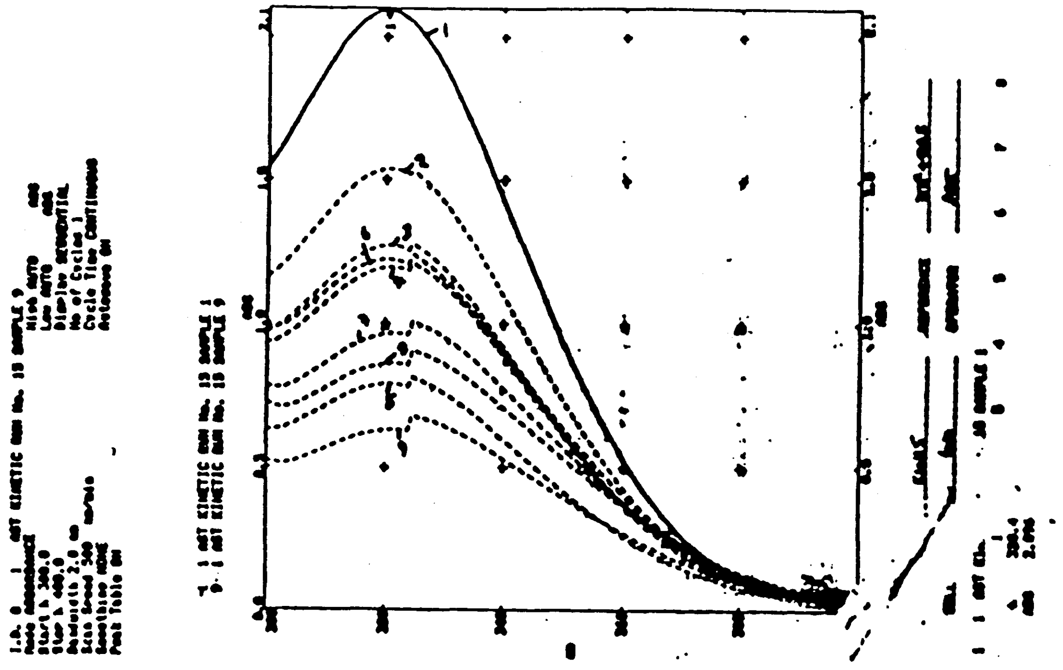


```
                          KINETIC RUN No.  14

TEMP. =  190  deg C              BPS MASS =  0.01  grams

CHLOROPHENIDATE MASS =  1.4000  grams
                                 CHLOROPHENIDATE CONC. =  14.000  %w/v

NUMBER OF SAMPLES =  9

TIME             MASS              THEO MASS P      CONC. P
(secs)           (grams)           (grams)          (moll-1)

 900              0.2062            0.030842306      1.30784E-04
 4800             0.2322            0.034734682      1.51528E-04
 8100             0.2352            0.035181218      1.49179E-04
 11700            0.2047            0.030619089      1.29834E-04
 14820            0.2079            0.031097882      1.31063E-04
 18240            0.1878            0.028091124      1.19115E-04
 22500            0.2352            0.035181218      1.49179E-04
 26400            0.288             0.04307904       1.82666E-04
 30000            0.2996            0.044818042      1.90215E-04

THEO ABS.        ACTUAL ABS.       P DETECTED       MASS P
(320nm)          (320nm)           (moll-1)         (grams)

 2.07407910       1.775             1.11926E-04      2.63856E-02
 2.40299475       1.554             9.79904E-05      2.31004E-02
 2.36577801       1.218             7.68033E-05      1.81127E-02
 2.06099132       0.867             5.46705E-05      1.29031E-02
 2.08117877       0.69              4.35087E-05      0.010290914
 1.88900131       0.558             3.52488E-05      8.31283E-03
 2.36577801       0.629             3.96628E-05      9.35379E-03
 2.89687103       0.67              4.22481E-05      9.96350E-03
 3.01886813       0.612             3.85906E-05      9.10096E-03

MASS P TOTAL     MOLES P           1/(a-x)
(grams)          (moles)           (moles-1)

 1.20672103       2.23677E-03       447.074227
 0.911112803      1.69023E-03       591.636020
 0.72534916       1.34561E-03       743.184828
 0.593280687      1.10056E-03       908.632102
 0.464470238      8.62393E-04       1159.56405
 0.418820807      7.73440E-04       1292.92434
 0.374588075      6.94903E-04       1439.06038
 0.325851289      6.04485E-04       1654.27237
 0.285632822      5.30246E-04       1885.86130
```

UV Spectrum And Data For Kinetic Run 14

Graph 22: 1/(a-x) v. Time For Kinetic Run No.14

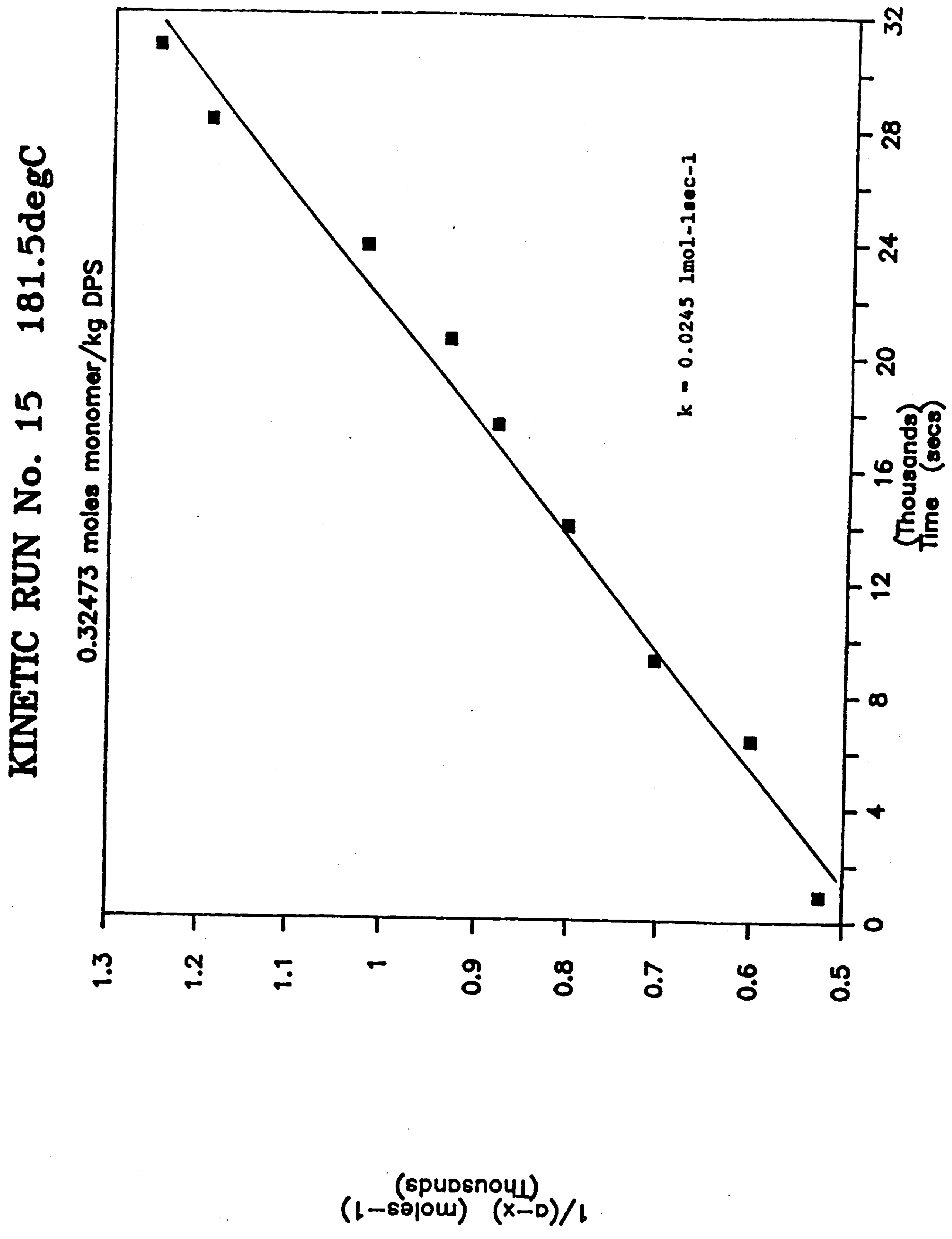


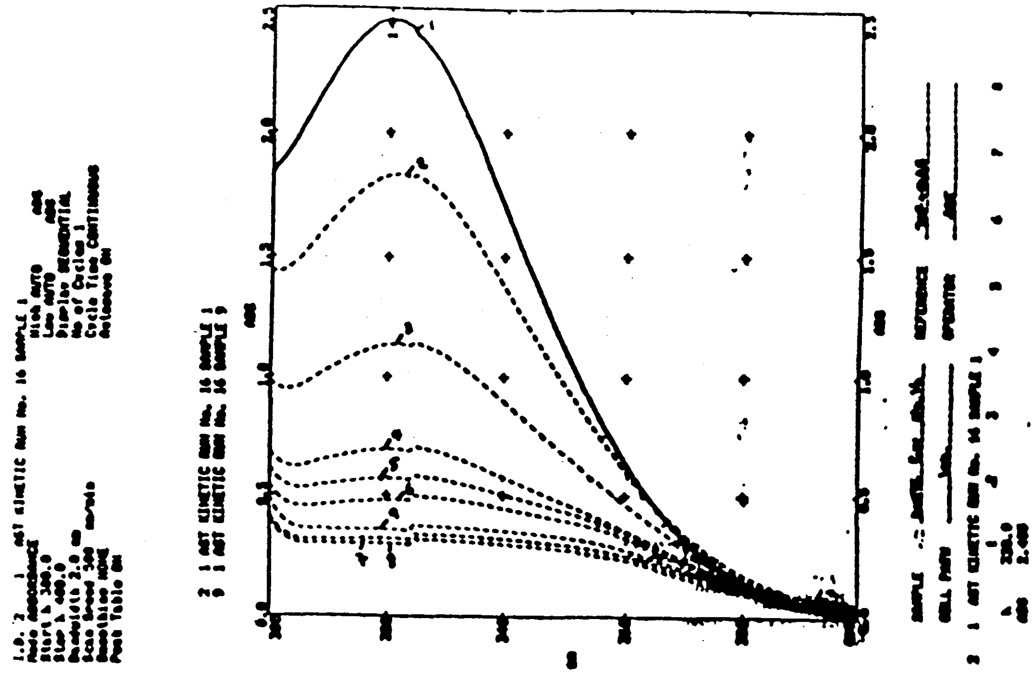


```
                         KINETIC RUN No.  15

TEMP. =  101.5  deg C          BPS MASS =  7.93  grams

CHLOROPHENATE MASS =  1.3881  grams
                               CHLOROPHENATE CONC. =  14.897  %w/w

NUMBER OF SAMPLES =  9

TIME            MASS            THEO MASS P     CONC. P
(secs)          (grams)         (grams)         (moll-1)

 900             0.283           0.04215881      1.78764E-04
 6420            0.2381          0.035469757     1.50402E-04
 9240            0.2306          0.034352482     1.45664E-04
 13980           0.2472          0.036825384     1.56150E-04
 17520           0.1797          0.026769909     1.13512E-04
 20820           0.294           0.04379718      1.85713E-04
 23820           0.2617          0.038985449     1.65310E-04
 30840           0.2777          0.041368969     1.75416E-04
 35380           0.1938          0.028870386     1.22419E-04

THEO ABS.       ACTUAL ABS.     P DETECTED      MASS P
(320nm)         (320nm)         (moll-1)        (grams)

 2.83496954      2.096           1.32167E-04     0.031169385
 2.38518108      1.539           9.70445E-05     2.28863E-02
 2.31004938      1.271           8.01453E-05     1.89009E-02
 2.47634088      1.196           7.54160E-05     1.77856E-02
 1.80015557      0.793           5.00041E-05     1.17926E-02
 2.9451627       1.224           7.71816E-05     1.82020E-02
 2.62189351      0.996           6.28044E-05     1.48114E-02
 2.78187647      0.863           5.44181E-05     1.28336E-02
 1.94160317      0.632           3.98519E-05     9.39840E-03

MASS P TOTAL   MOLES P          1/(a-x)
(grams)         (moles)         (moles-1)

 1.0262878       1.90389E-03     525.239413
 0.895660738     0.001661564     601.842601
 0.763748851     1.41685E-03     705.790653
 0.670420114     1.24371E-03     804.043299
 0.611490103     1.13439E-03     881.529885
 0.576897171     1.07022E-03     934.389744
 0.527373485     9.78348E-04     1022.13094
 0.430624999     7.98864E-04     1251.77777
 0.451884469     8.38303E-04     1192.88873
```

UV Spectrum And Data For Kinetic Run 15

Graph 23: 1/(a-x) v. Time For Kinetic Run No.15

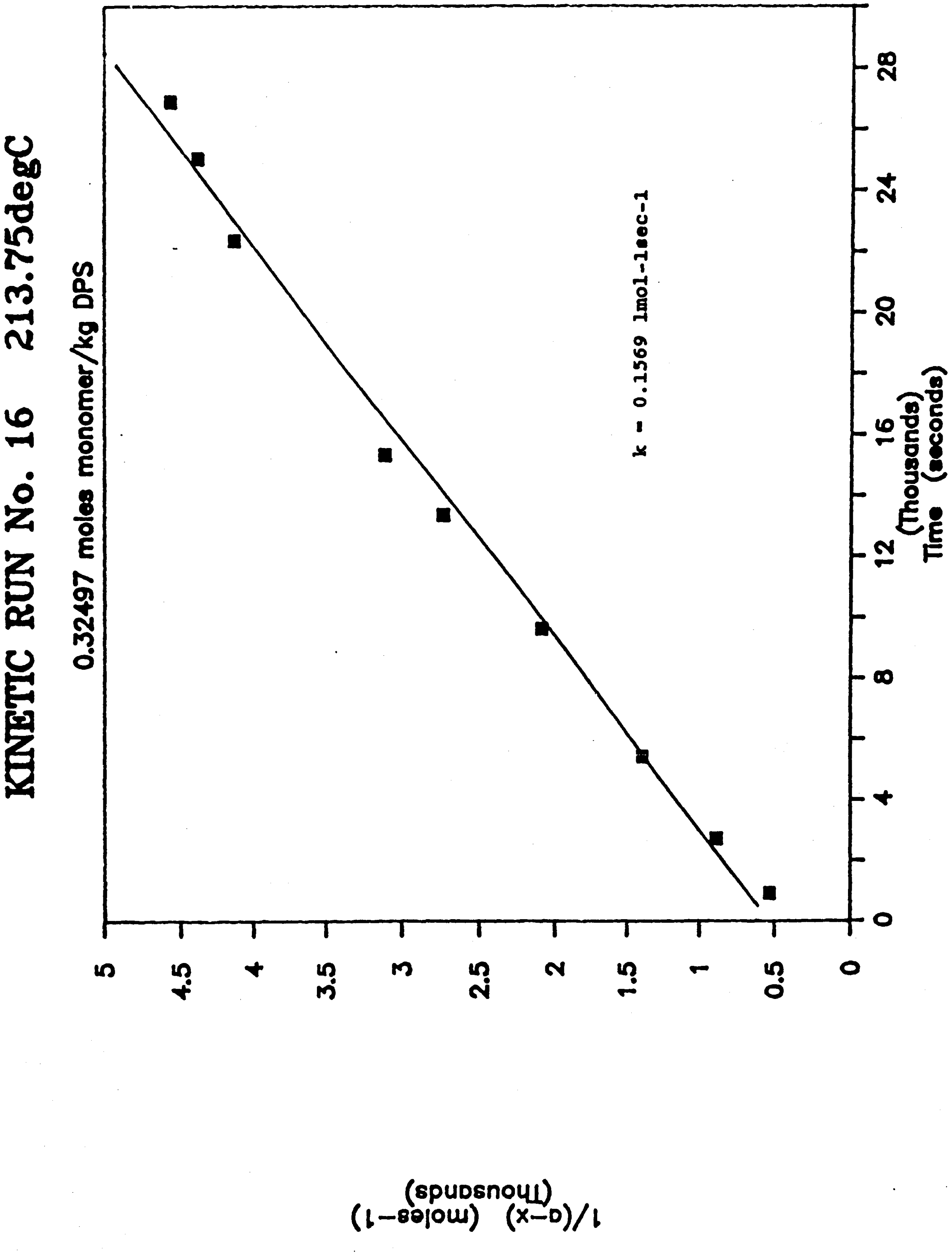


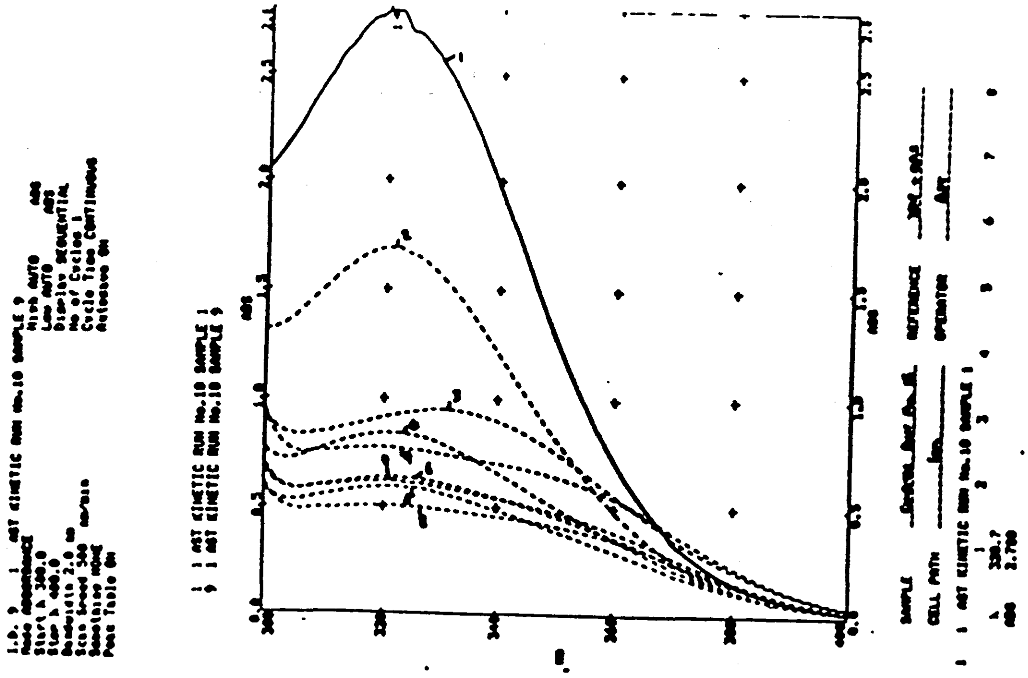


```
                      KINETIC RUN No.  16

TEMP. =  213.75  deg C        BPS MASS =  7.98  grams

CHLOROPHENATE MASS =  1.3979  grams
                              CHLOROPHENATE CONC. =  14.906  %w/w

NUMBER OF SAMPLES =  9

TIME           MASS             THEO MASS P      CONC. P
(secs)         (grams)          (grams)          (moll-1)

 900            0.1929           0.028753674      2.13367E-04
 2700           0.2403           0.035819118      2.65796E-04
 8400           0.2335           0.03480081       2.58274E-04
 9600           0.2151           0.032062806      2.37922E-04
 13320          0.2317           0.034537202      2.56284E-04
 15300          0.2213           0.032986978      2.44780E-04
 22320          0.1941           0.028932546      2.14694E-04
 25020          0.1917           0.028574802      2.12039E-04
 26880          0.2389           0.035610434      2.64247E-04

THEO ABS.      ACTUAL ABS.      P DETECTED       MASS P
(320nm)        (320nm)          (moll-1)         (grams)

 3.38372024     2.455            1.54805E-04      2.08617E-02
 4.21517871     1.833            1.15583E-04      1.55762E-02
 4.09509774     1.137            7.16957E-05      9.66183E-03
 3.77313749     0.695            4.38245E-05      5.90587E-03
 4.06432337     0.572            3.60685E-05      4.86066E-03
 3.88189367     0.481            3.03304E-05      4.08737E-03
 3.40476982     0.318            2.00521E-05      2.70225E-03
 3.36267065     0.296            1.86648E-05      2.51530E-03
 4.19062086     0.354            2.23221E-05      3.00817E-03

MASS P TOTAL   MOLES P          1/(a-x)
(grams)        (moles)          (moles-1)

 1.01420037     1.88147E-03      531.499315
 0.607873469    1.12768E-03      886.774679
 0.388041411    7.19864E-04      1389.14762
 0.257483195    4.77664E-04      2093.52226
 0.196731766    3.64962E-04      2740.00896
 0.173208084    3.21323E-04      3112.13419
 0.130558779    2.42203E-04      4128.76717
 0.123047848    2.28269E-04      4380.78944
 0.118008418    2.19061E-04      4564.93781
```

UV Spectrum And Data For Kinetic Run 16

Graph 24: 1/(a-x) v. Time For Kinetic Run No.16

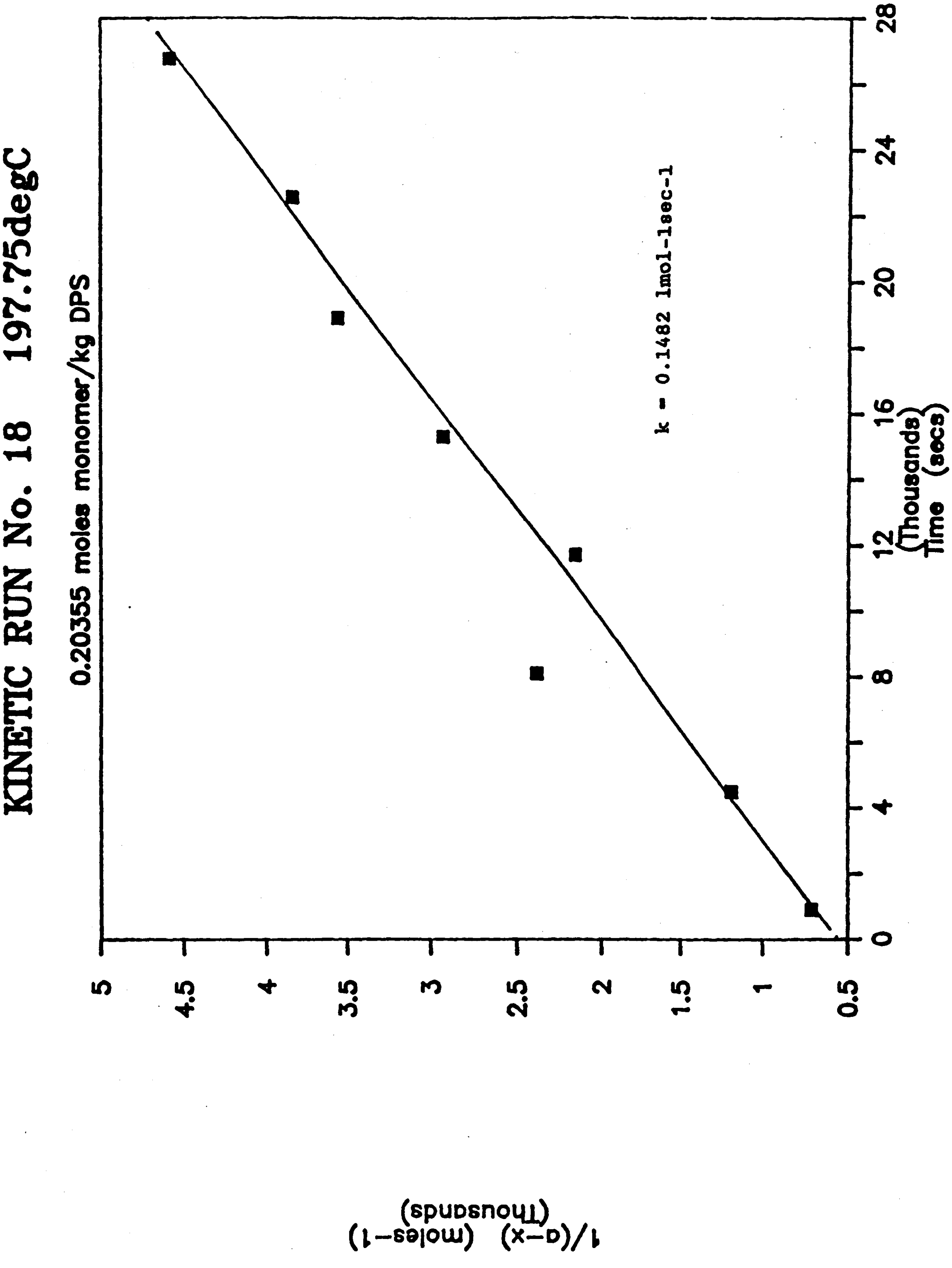


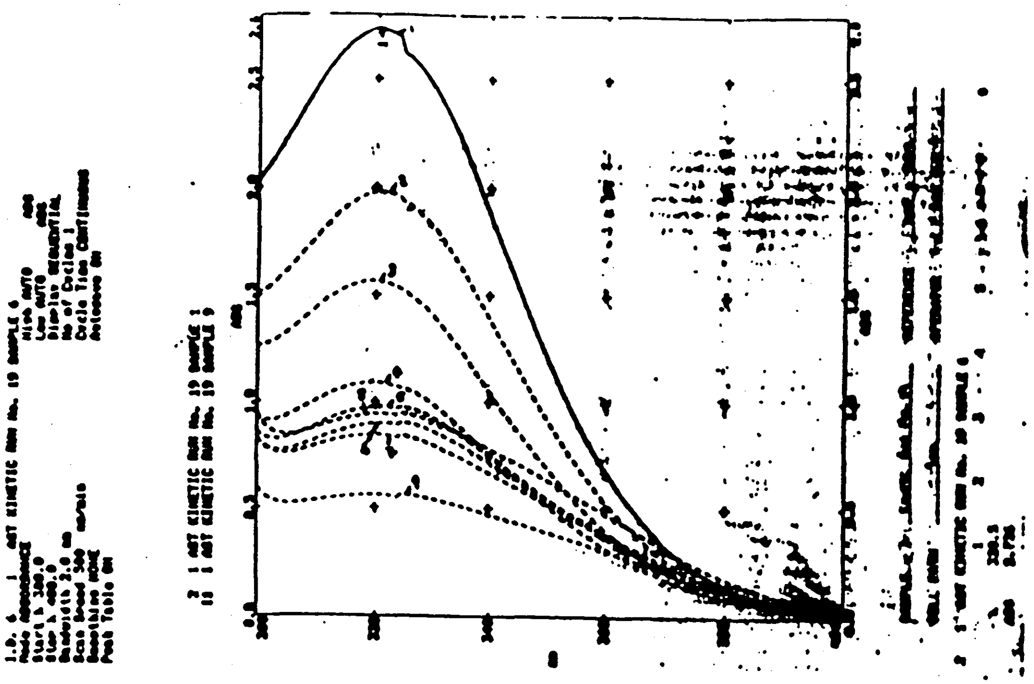


```
                        KINETIC RUN No.  18

TEMP. =  197.78  deg C          BPS MASS =  7.97  grams

CHLOROPHENATE MASS =  0.0745  grams
                                CHLOROPHENATE CONC. =  9.886  %w/w

NUMBER OF SAMPLES =  9

TIME           MASS             THEO MASS P      CONC. P
(secs)         (grams)          (grams)          (moll-1)

 900            0.2399           0.023716814      2.51412E-04
 4500           0.2438           0.02407241       2.55105E-04
 8100           0.2663           0.026326418      2.79079E-04
 11700          0.2208           0.021828288      2.31396E-04
 15300          0.3116           0.020918776      2.21734E-04
 18900          0.2738           0.027265388      2.89035E-04
 22560          0.2898           0.028649628      3.03707E-04
 26760          0.2816           0.027838976      2.95113E-04
 30000          0.4369           0.043191934      4.57864E-04

THEO ABS.      ACTUAL ABS.      P DETECTED       MASS P
(320nm)        (320nm)          (moll-1)         (grams)

 3.21584276     2.788            2.17962E-04      2.05611E-02
 3.26412081     1.689            1.32044E-04      1.24561E-02
 3.56975512     0.92             7.19244E-05      6.78484E-03
 2.95982701     0.843            6.59047E-05      6.21700E-03
 2.83650088     0.596            4.65945E-05      0.004395411
 3.69710278     0.64             5.00344E-05      4.71990E-03
 3.88477294     0.623            4.87054E-05      4.59453E-03
 3.77485183     0.507            3.96366E-05      3.73905E-03
 5.85663045     0.774            6.05104E-05      5.70813E-03

MASS P TOTAL   MOLES P          1/(a-x)
(grams)        (moles)          (moles-1)

 0.758034618    1.40625E-03      711.11106
 0.45243605     8.39326E-04      1191.43203
 0.225342537    4.18039E-04      2392.12183
 0.249031924    4.61984E-04      2164.56907
 0.183720286    3.40824E-04      2934.06248
 0.151360387    2.80793E-04      3561.3466
 0.140222008    2.60130E-04      3844.23819
 0.117436136    2.17859E-04      4590.12641
 0.11555412     2.14368E-04      4664.88604
```

UV Spectrum And Data For Kinetic Run 18

Graph 25: 1/(a-x) v. Time For Kinetic Run No.18

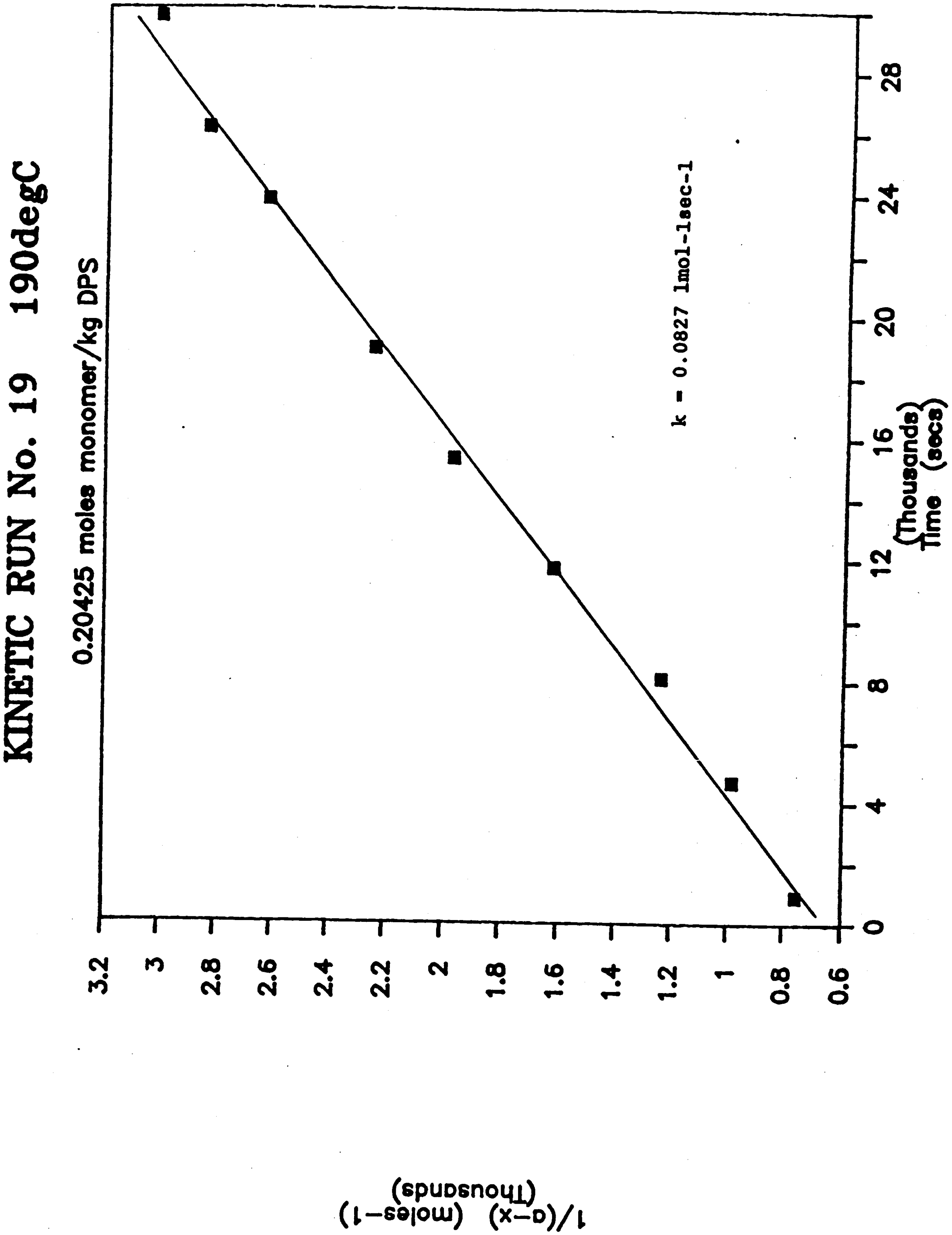


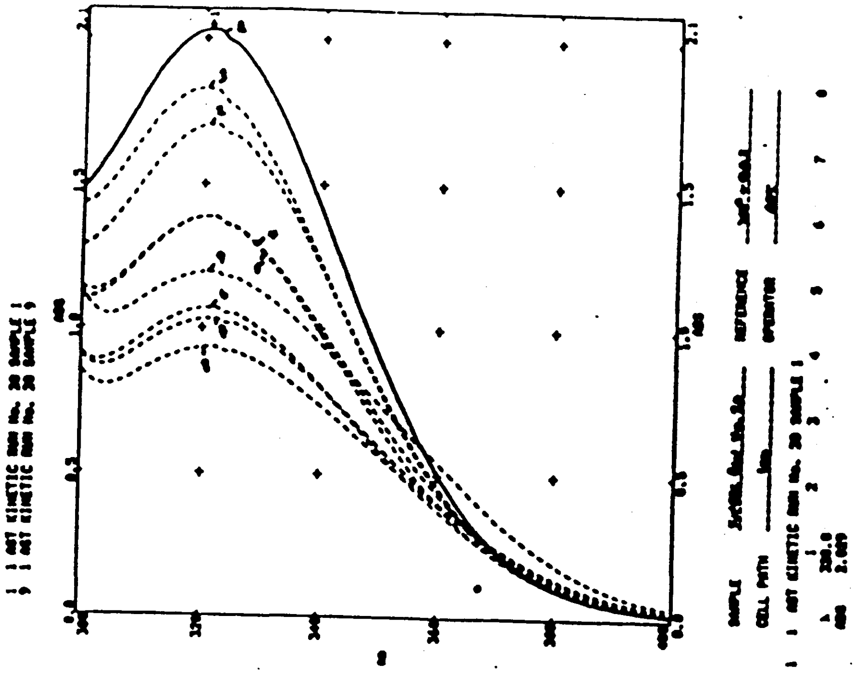


```
                         KINETIC RUN No.  19

TEMP. =  190  deg C              BPS MASS =  8.02  grams

CHLOROPHENATE MASS =  0.883  grams
                                 CHLOROPHENATE CONC. =  9.918  %w/w

NUMBER OF SAMPLES =  9

TIME            MASS            THEO MASS P      CONC. P
(secs)          (grams)         (grams)          (moll-1)

 900             0.2319          0.024983442      2.64842E-04
 4680            0.2383          0.023634994      2.50544E-04
 8100            0.2374          0.023549332      2.49597E-04
 11700           0.2166          0.021482388      2.27729E-04
 15300           0.2357          0.023376726      2.47810E-04
 18900           0.2471          0.024507378      2.59794E-04
 23760           0.2712          0.026897616      2.85134E-04
 26100           0.3277          0.032301286      3.44537E-04
 29700           0.2069          0.022320342      2.17530E-04

THEO ABS.       ACTUAL ABS.     P DETECTED       MASS P
(320nm)         (320nm)         (moll-1)         (grams)

 3.38765305      2.736           2.13897E-04      2.01776E-02
 3.20475475      1.982           1.54950E-04      0.014616954
 3.19265118      1.87            1.22741E-04      1.15785E-02
 2.91292437      1.095           8.56057E-05      8.07544E-03
 3.1697889       0.981           7.66934E-05      7.23473E-03
 3.3231007       0.902           7.05172E-05      6.65212E-03
 3.64720725      0.847           6.62174E-05      6.24630E-03
 4.40704209      0.946           7.39571E-05      6.97661E-03
 2.78247485      0.563           4.40144E-05      4.15204E-03

MASS P TOTAL    MOLES P          1/(a-x)
(grams)         (moles)          (moles-1)

 0.713144489     1.32297E-03      755.873191
 0.546096273     1.01308E-03      987.091154
 0.43421872      8.05531E-04      1241.41769
 0.331929057     6.15770E-04      1623.98196
 0.27327445      5.06959E-04      1972.54737
 0.239675365     4.44628E-04      2249.07053
 0.205061122     3.80414E-04      2628.71281
 0.189341494     3.51623E-04      2843.95141
 0.178664188     3.31445E-04      3017.09485
```

UV Spectrum And Data For Kinetic Run 19

Graph 26: 1/(a-x) v. Time For Kinetic Run No.19

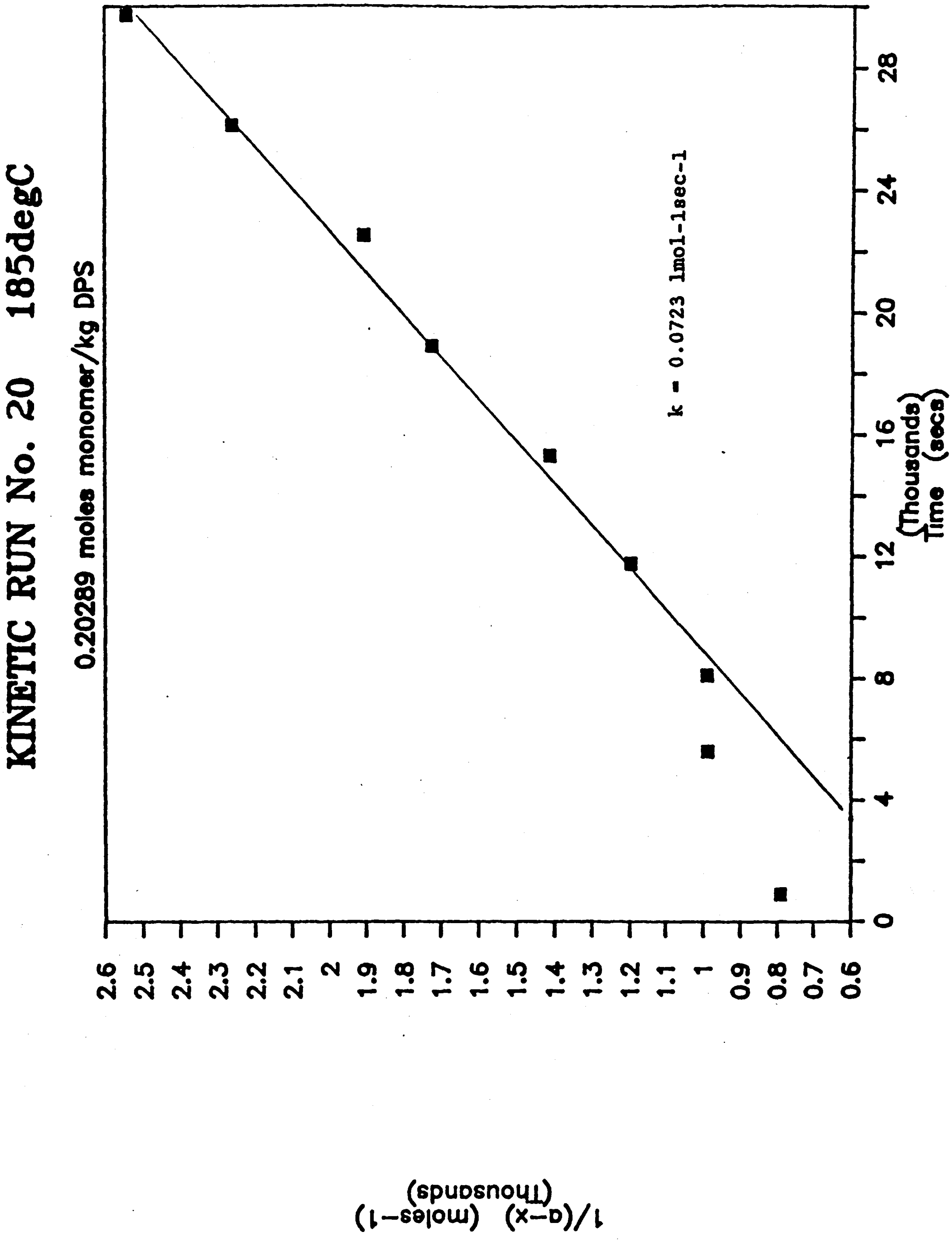


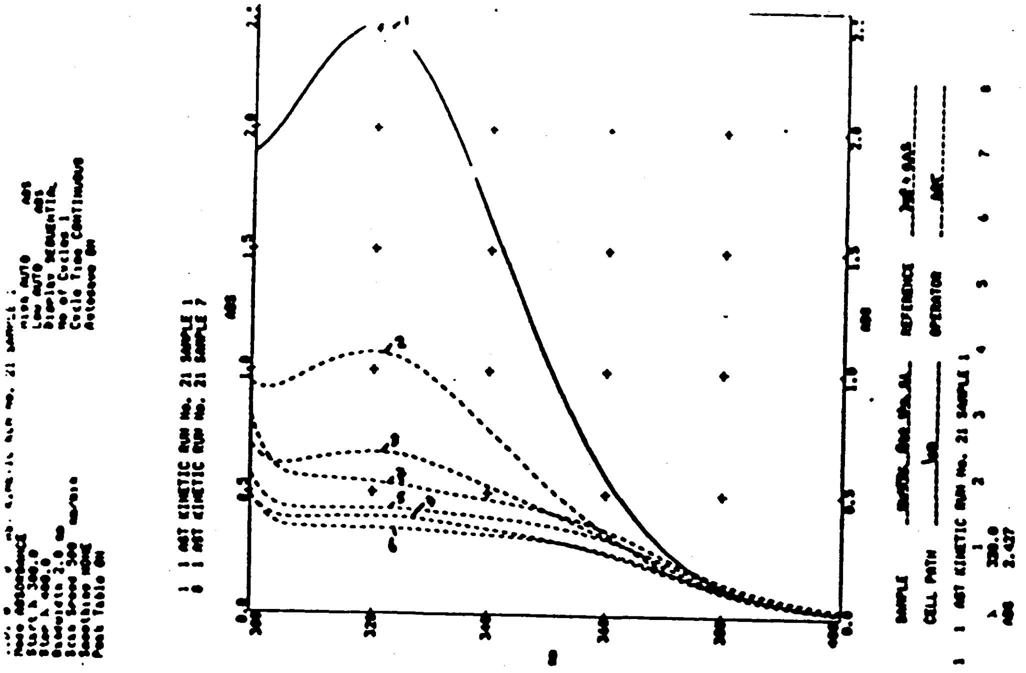


```
                    KINETIC RUN No.  20

TEMP. =  188  deg C              DPS MASS =  7.92  grams

CHLOROPHENATE MASS =  0.8662  grams
                                 CHLOROPHENATE CONC. =  9.859  %m/w

NUMBER OF SAMPLES =  9

TIME          MASS            THEO MASS P      CONC. P
(secs)        (grams)         (grams)          (moll-1)

 900           0.1931          0.019037729      2.01814E-04
 4500          0.2029          0.020003911      2.12056E-04
 8100          0.2179          0.021482761      2.27733E-04
 11700         0.2001          0.019727859      2.09130E-04
 15300         0.2362          0.023286938      2.46859E-04
 18900         0.2227          0.021955993      2.32749E-04
 22500         0.2373          0.023393407      2.48008E-04
 26100         0.2538          0.025022142      2.65253E-04
 29700         0.3662          0.036103658      3.82725E-04

THEO ABS.      ACTUAL ABS.    P DETECTED       MASS P
(320nm)        (320nm)        (moll-1)         (grams)

 2.38143856    2.029           1.58625E-04      0.014963572
 2.71244891    1.706           1.33373E-04      1.25815E-02
 2.91297495    1.829           1.42989E-04      1.34886E-02
 2.67301738    1.388           1.08512E-04      1.02363E-02
 3.15761672    1.388           1.08512E-04      1.02363E-02
 2.97714328    1.072           8.38074E-05      7.90584E-03
 3.17232196    1.034           8.08360E-05      7.62560E-03
 3.39290061    0.933           7.29408E-05      6.88074E-03
 4.89550907    1.198           9.36581E-05      8.83507E-03

MASS P TOTAL   MOLES P         1/(a-x)
(grams)        (moles)         (moles-1)

 0.680854151    1.26307E-03     791.721398
 0.54481781     1.01071E-03     989.40745
 0.543889647    1.00898E-03     991.095902
 0.449465843    8.33816E-04     1199.30537
 0.380771022    7.06378E-04     1415.67181
 0.311909703    5.78632E-04     1728.21427
 0.28234306     5.23782E-04     1909.1909
 0.238201418    4.41894E-04     2262.98737
 0.211978978    3.93248E-04     2542.92574
```

UV Spectrum And Data For Kinetic Run 20

Graph 27: 1/(a-x) v. Time For Kinetic Run No.20

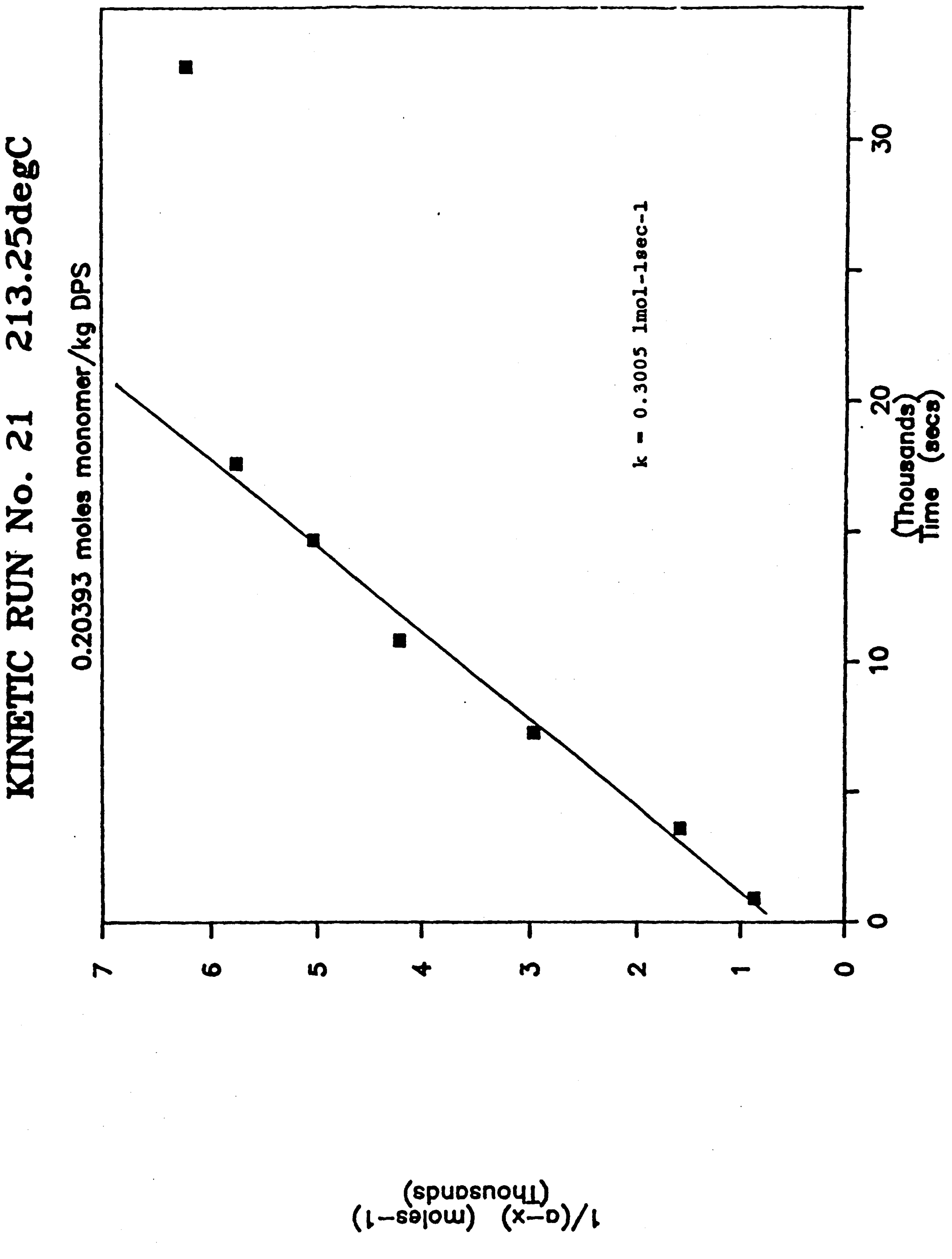


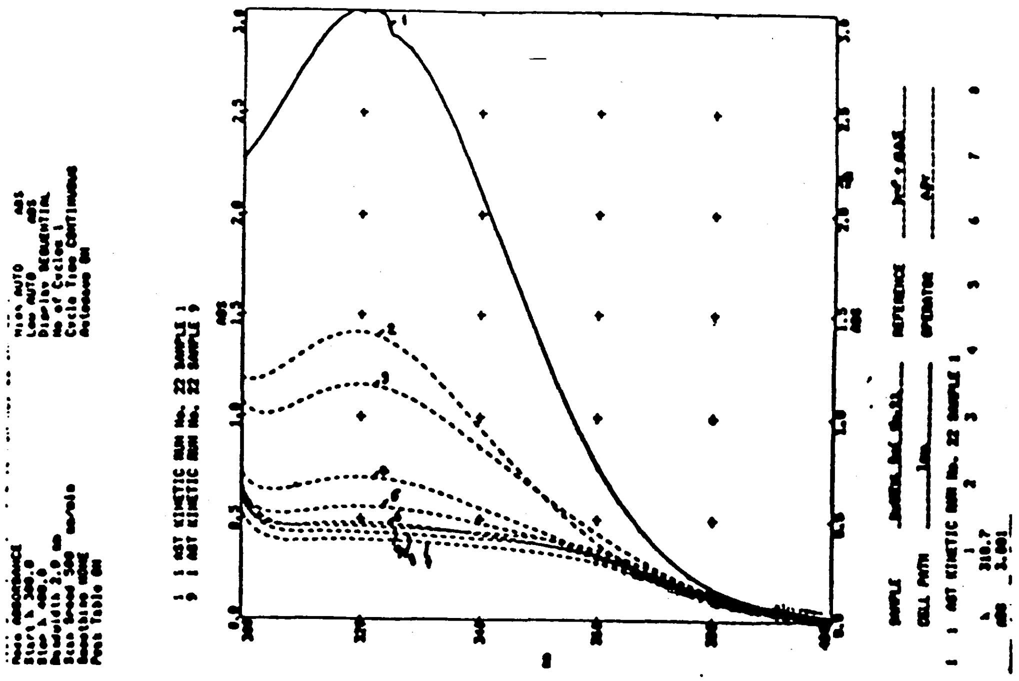


```
                         KINETIC RUN No.  21

TEMP. =  213.25  deg C          BPS MASS =  8.07  grams

CHLOROPHENATE MASS =  0.8871  grams
                                CHLOROPHENATE CONC. =  9.904  %w/w

NUMBER OF SAMPLES =  7

TIME            MASS            THEO MASS P       CONC. P
(secs)          (grams)         (grams)           (moll-1)

 900             0.2604          0.025790016       2.73393E-04
 3600            0.2082          0.020620128       2.18588E-04
 7260            0.2407          0.023838928       2.52710E-04
 10800           0.2064          0.020441856       2.16698E-04
 14640           0.2675          0.0264932         2.80847E-04
 17380           0.2473          0.024492592       2.59639E-04
 32760           0.4151          0.041111504       4.35812E-04

THEO ABS.       ACTUAL ABS.     P DETECTED        MASS P
(320nm)         (320nm)         (moll-1)          (grams)

 3.4970212       2.427           1.89740E-04       1.78988E-02
 2.79600543      1.074           8.39640E-05       7.92059E-03
 3.23246161      0.661           5.16762E-05       4.87478E-03
 2.77183247      0.4             3.12715E-05       2.94994E-03
 3.59237008      0.433           3.38514E-05       3.19331E-03
 3.32109578      0.35            2.73626E-05       2.58120E-03
 5.57455261      0.544           4.25292E-05       4.01192E-03

MASS P TOTAL    MOLES P         1/(a-x)
(grams)         (moles)         (moles-1)

 0.615672048     1.14215E-03     875.542076
 0.340756548     6.32147E-04     1581.91179
 0.181403651     3.36527E-04     2971.53226
 0.128017975     2.37490E-04     4210.71182
 0.106926355     1.98362E-04     5041.29031
 9.34899E-02     1.73436E-04     5765.83075
 0.086569881     1.60598E-04     6226.72451
```

UV Spectrum And Data For Kinetic Run 21

Graph 28: 1/(a-x) v. Time For Kinetic Run No.21

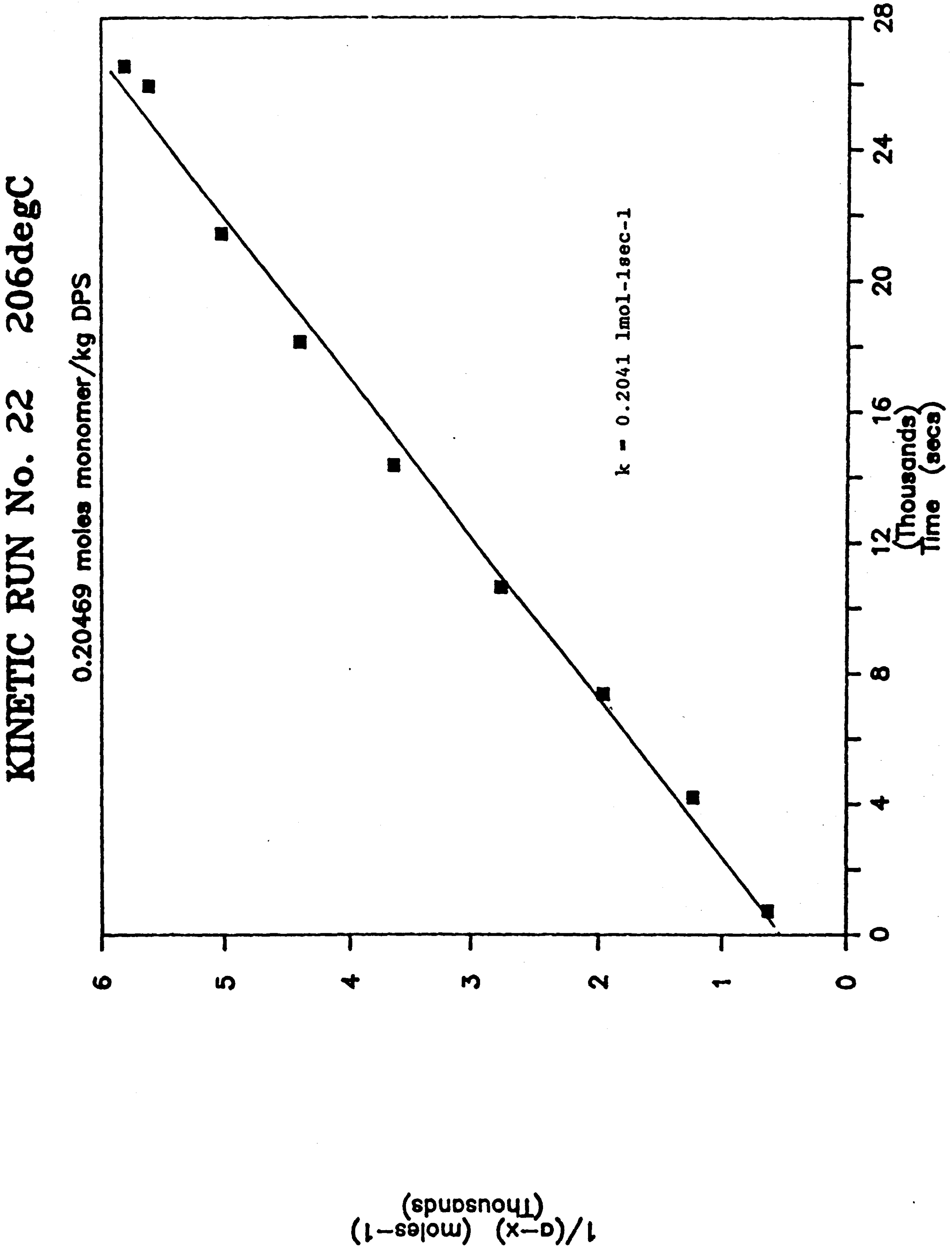




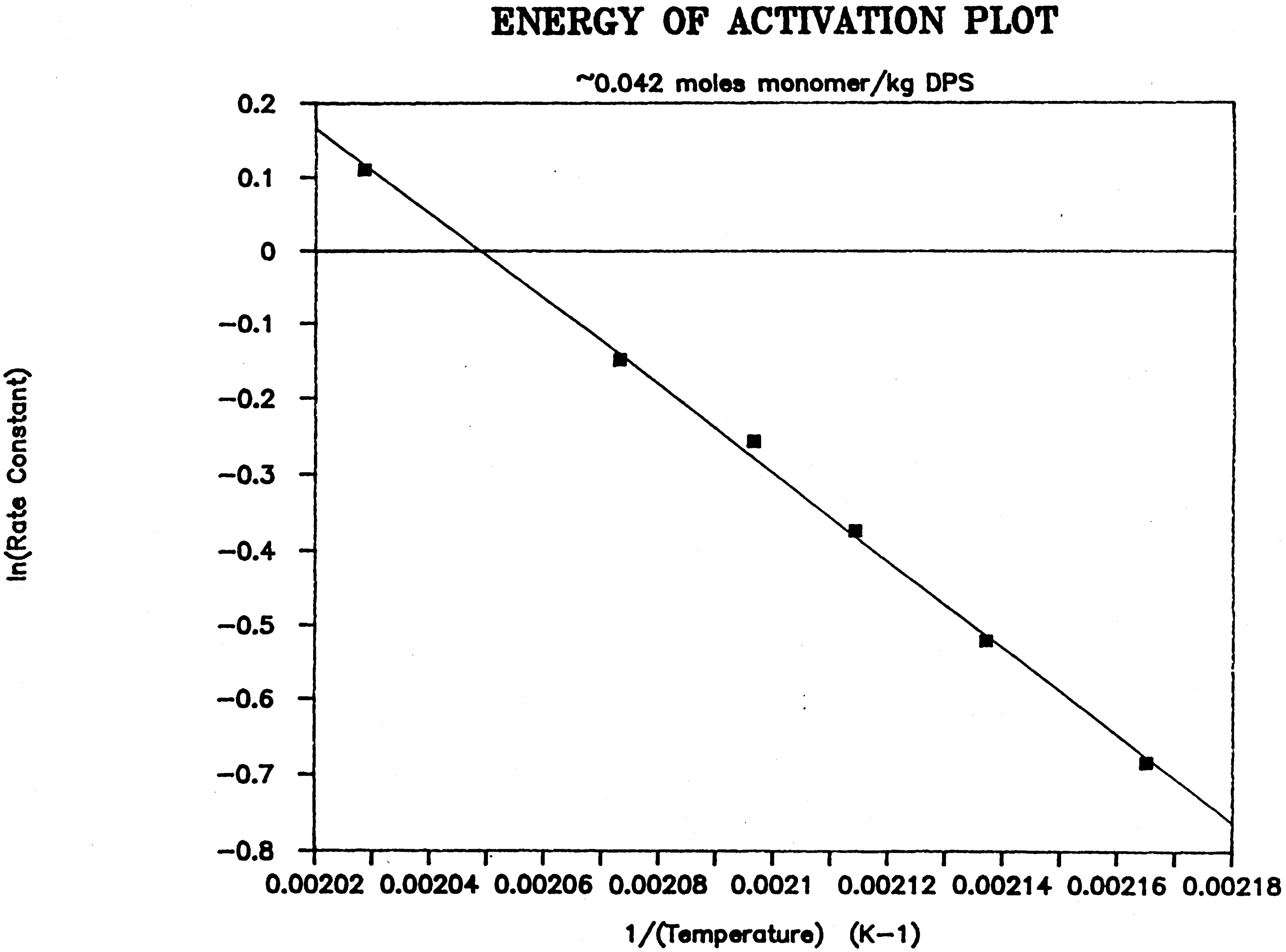
```
                    KINETIC RUN No.  22

TEMP. =  306  deg C            DPS MASS =  8.08  grams

CHLOROPHENATE MASS =  0.8882  grams
                               CHLOROPHENATE CONC. =  9.937  %w/w

NUMBER OF SAMPLES =  9

TIME          MASS              THEO MASS P     CONC. P
(secs)        (grams)           (grams)         (mol l-1)

 720           0.2348            0.023530816     2.49444E-04
 4200          0.214             0.02126318      2.25426E-04
 7380          0.2784            0.027664608     2.93265E-04
 10620         0.2374            0.023590438     2.50076E-04
 14340         0.2502            0.024862374     2.63559E-04
 18120         0.26              0.0258362       2.73882E-04
 21420         0.2451            0.024335387     2.58187E-04
 25920         0.2993            0.029741441     3.15281E-04
 26520         0.3303            0.032821911     3.47934E-04

THEO ABS.     ACTUAL ABS.       P DETECTED      MASS P
(320nm)       (320nm)           (mol l-1)       (grams)

 3.19068287    3.1               2.42354E-04     2.28620E-02
 2.88347188    1.416             1.10701E-04     1.04428E-02
 3.73120824    1.159             9.06092E-05     8.54745E-03
 3.19876737    0.703             5.49597E-05     5.18452E-03
 3.37123672    0.561             4.38583E-05     4.13729E-03
 3.50328356    0.483             3.77603E-05     3.56205E-03
 3.30251846    0.399             3.11933E-05     2.94257E-03
 4.03281834    0.436             3.40859E-05     3.21543E-03
 4.45081734    0.465             3.63531E-05     3.42931E-03

MASS P TOTAL  MOLES P           1/(a-x)
(grams)       (moles)           (moles-1)

 0.862945355   1.60087E-03       624.659252
 0.436166975   8.09145E-04       1235.87257
 0.274421103   5.09084E-04       1964.30521
 0.195199145   3.62119E-04       2761.52235
 0.147801508   2.74190E-04       3647.09954
 0.122455138   2.27170E-04       4401.99343
 0.107308194   1.99070E-04       5023.35173
 0.096024728   1.78138E-04       5613.62503
 9.27999E-02   1.72156E-04       5808.69795
```

UV Spectrum And Data For Kinetic Run 22

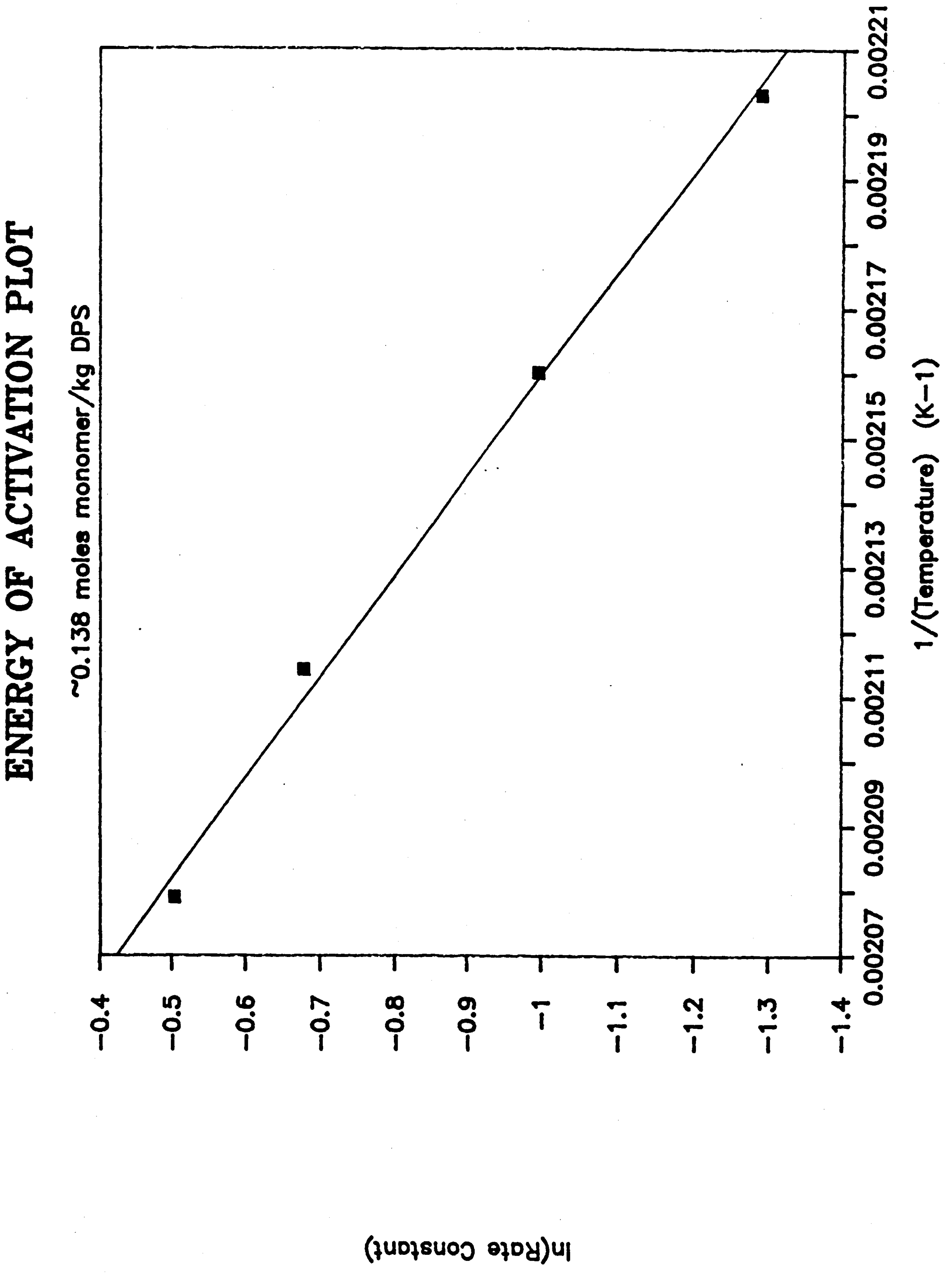
Graph 29: 1/(a-x) v. Time For Kinetic Run No.22



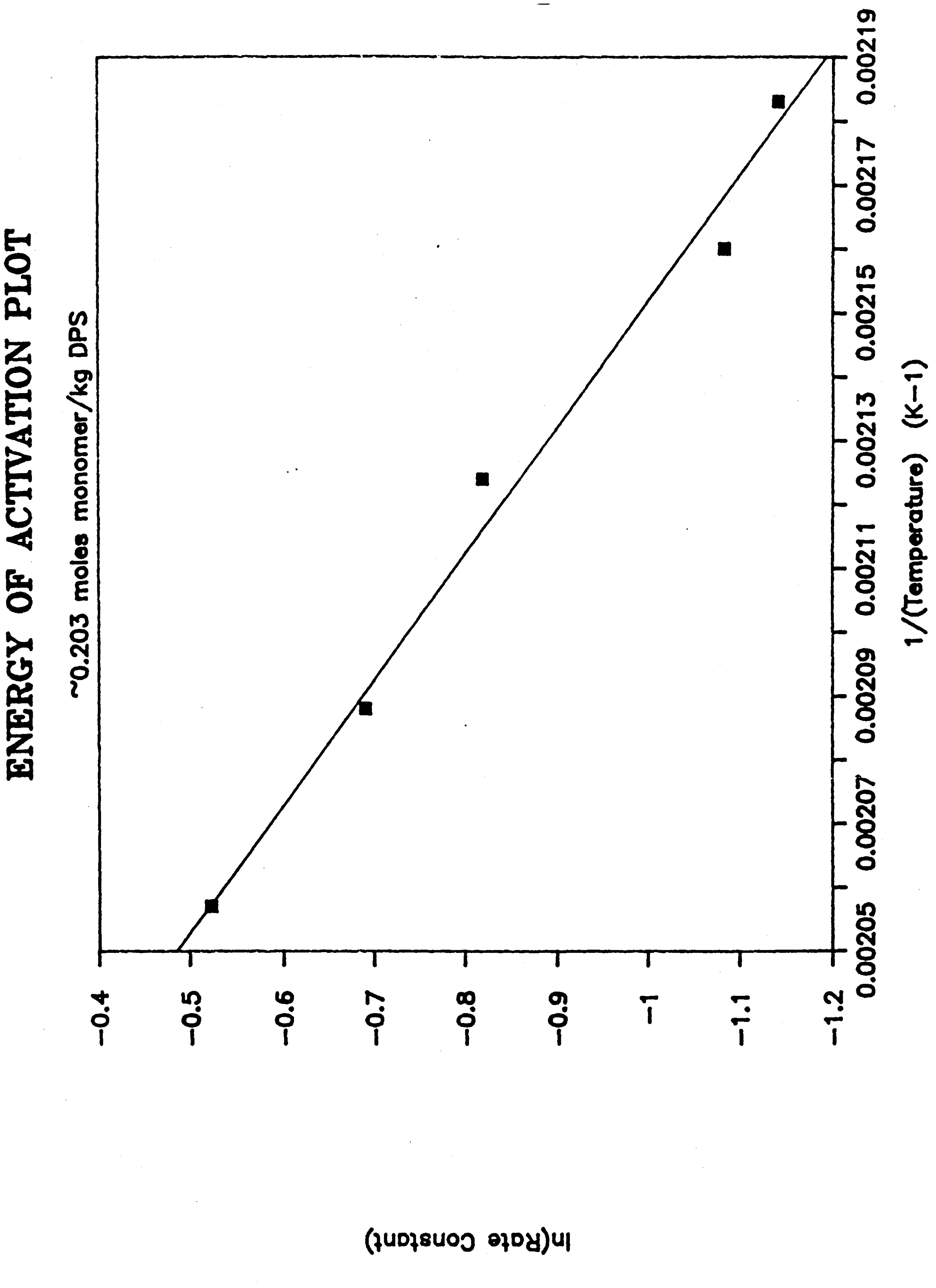
Graph 30: Energy Of Activation Plot For 0.042 moles mono./kg DPS



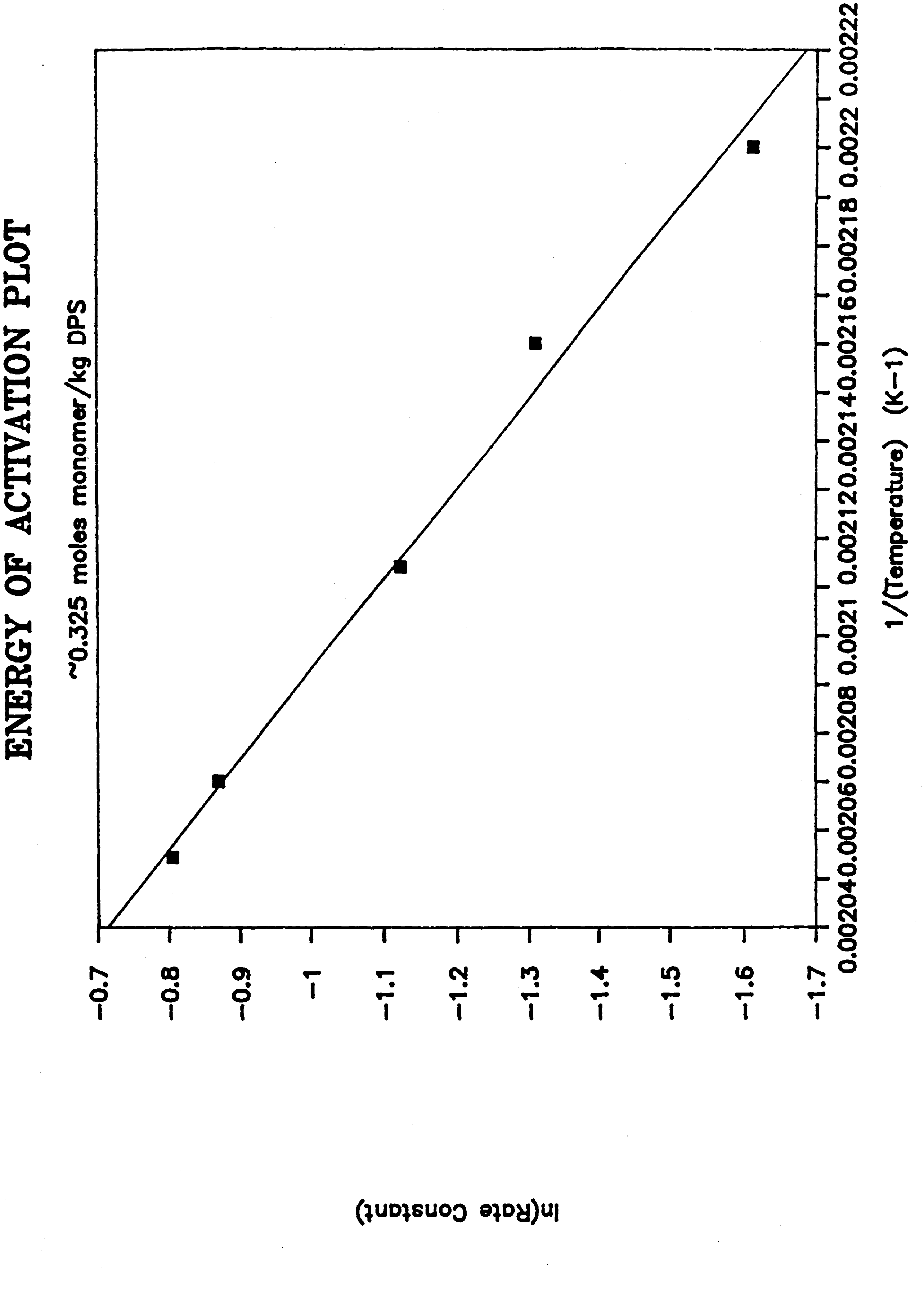
Graph 31: Energy Of Activation Plot For 0.138 moles mono./kg DPS



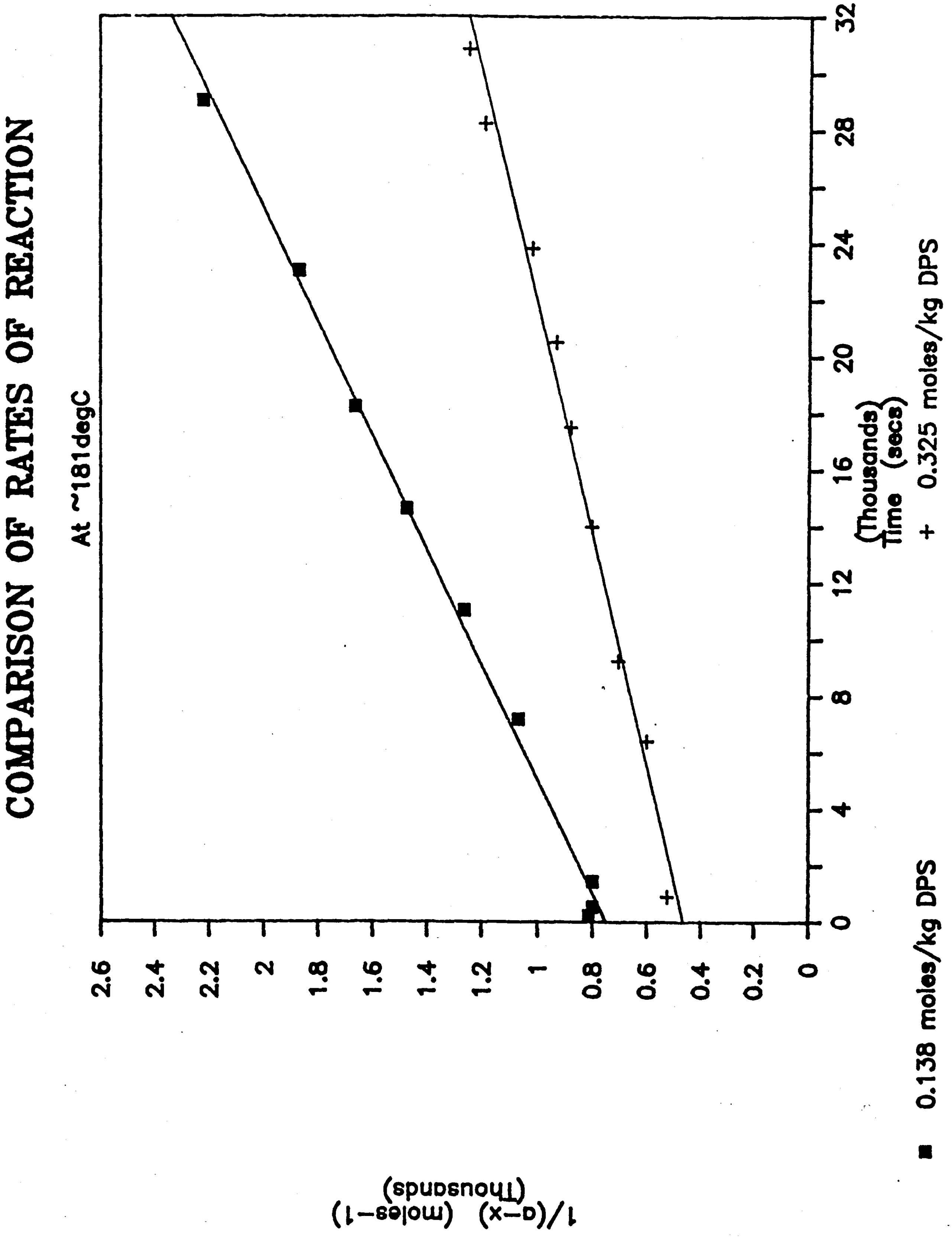
Graph 32: Energy Of Activation Plot For 0.203 moles mono./kg DPS



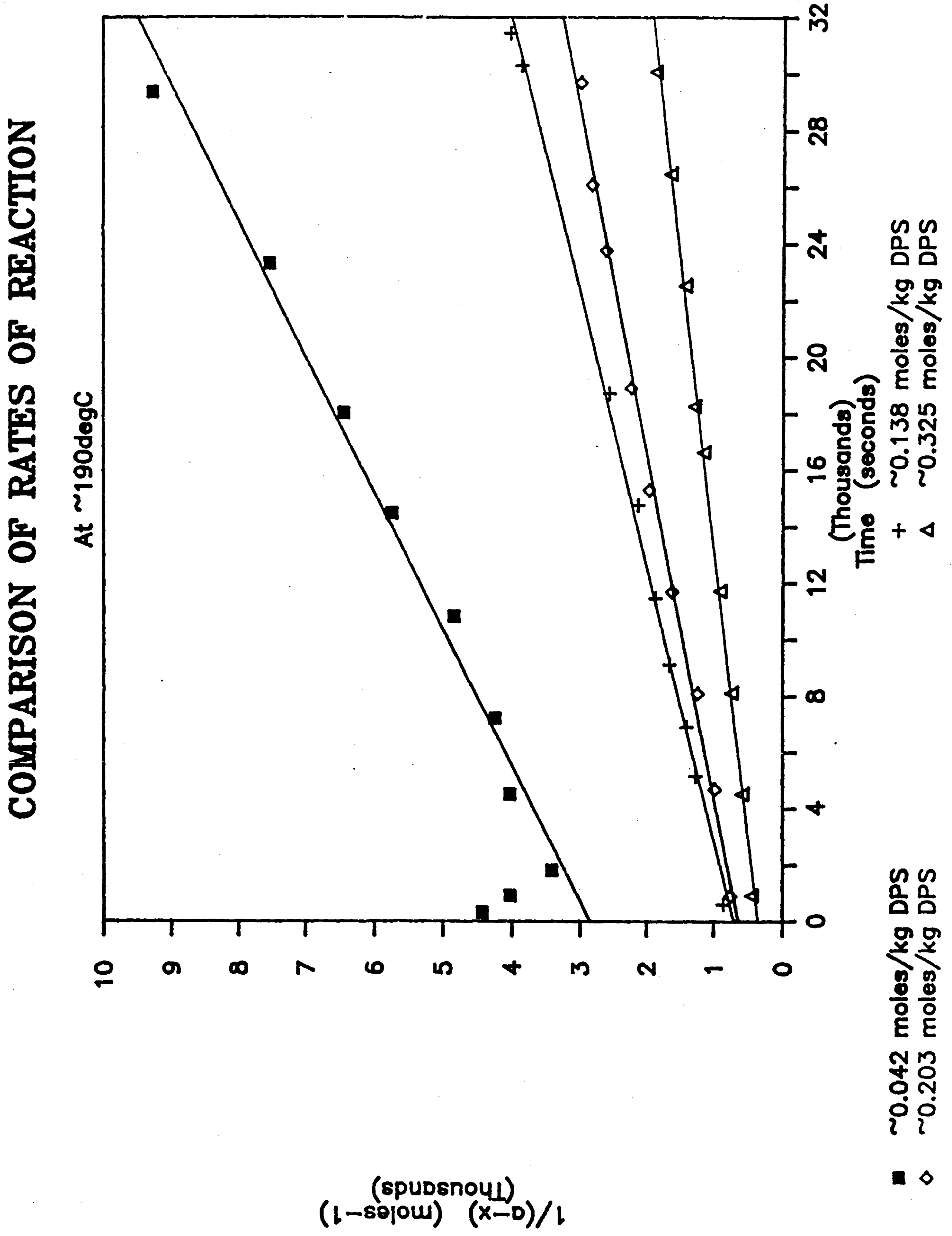
Graph 33: Energy Of Activation Plot For 0.325 moles mono./kg DPS



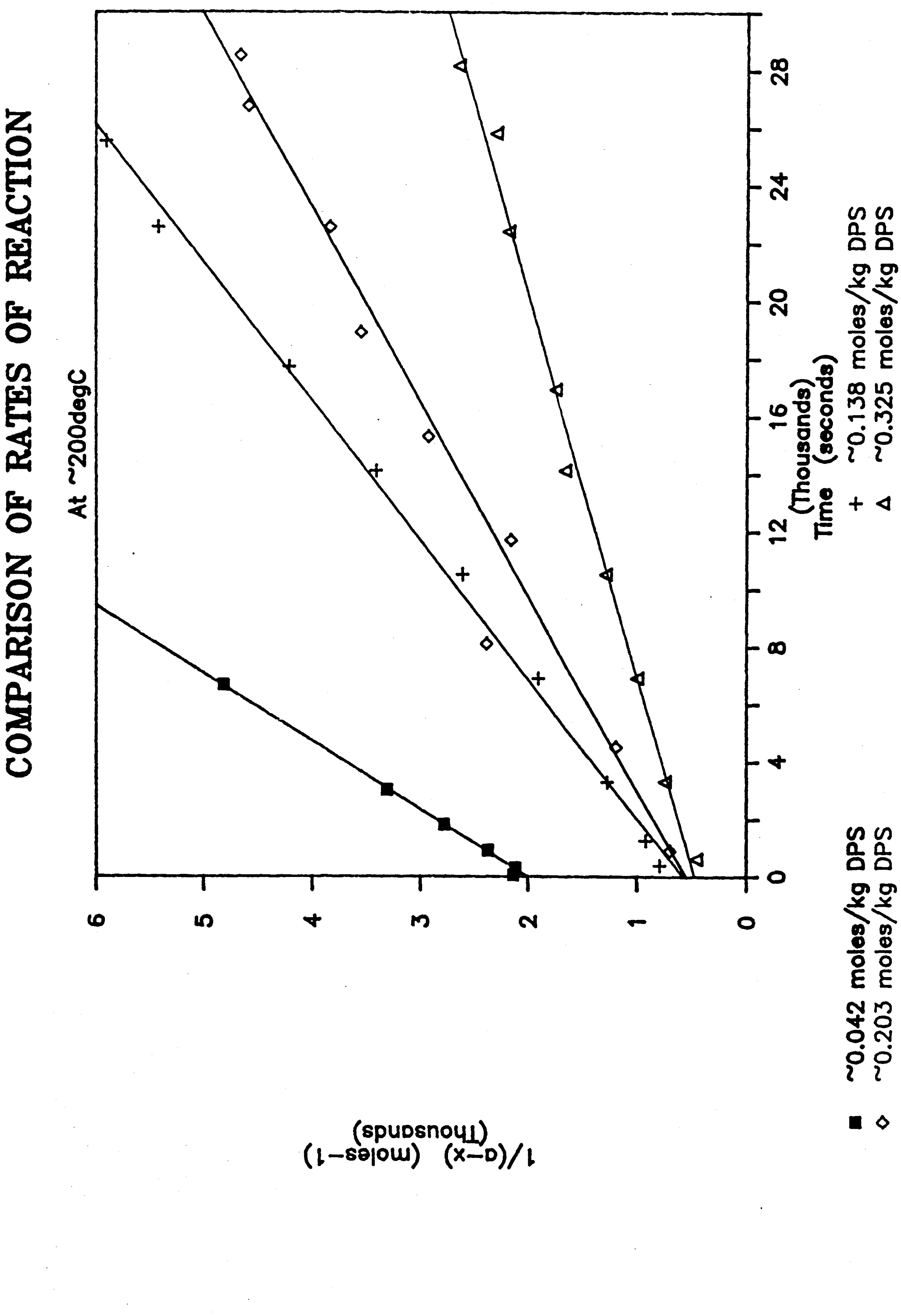
Graph 37 : Effect Of Varying Concentration At ~181°C



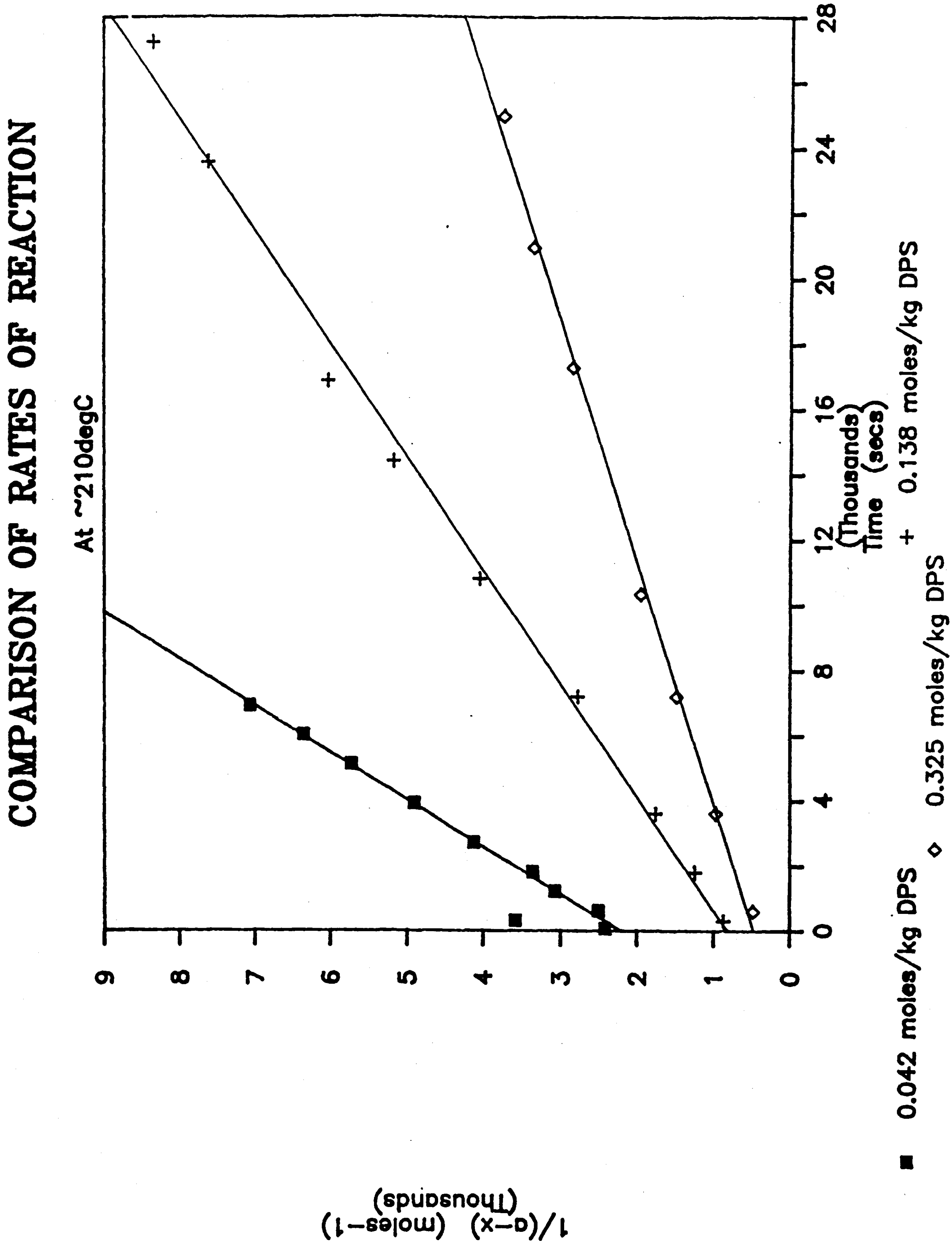
Graph 38 : Effect Of Varying Concentration At ~190°C



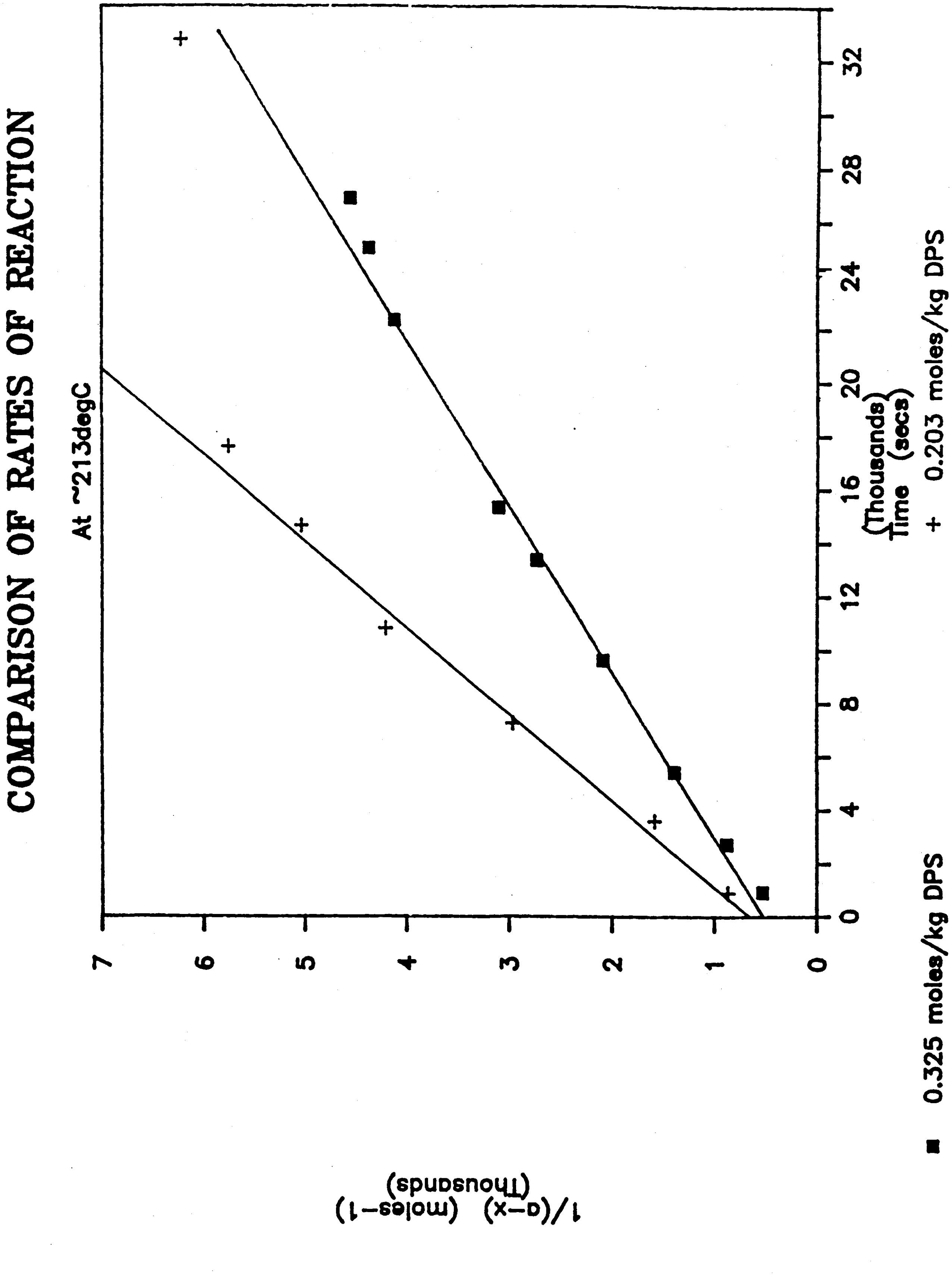
Graph 39 : Effect Of Varying Concentration At ~200°C



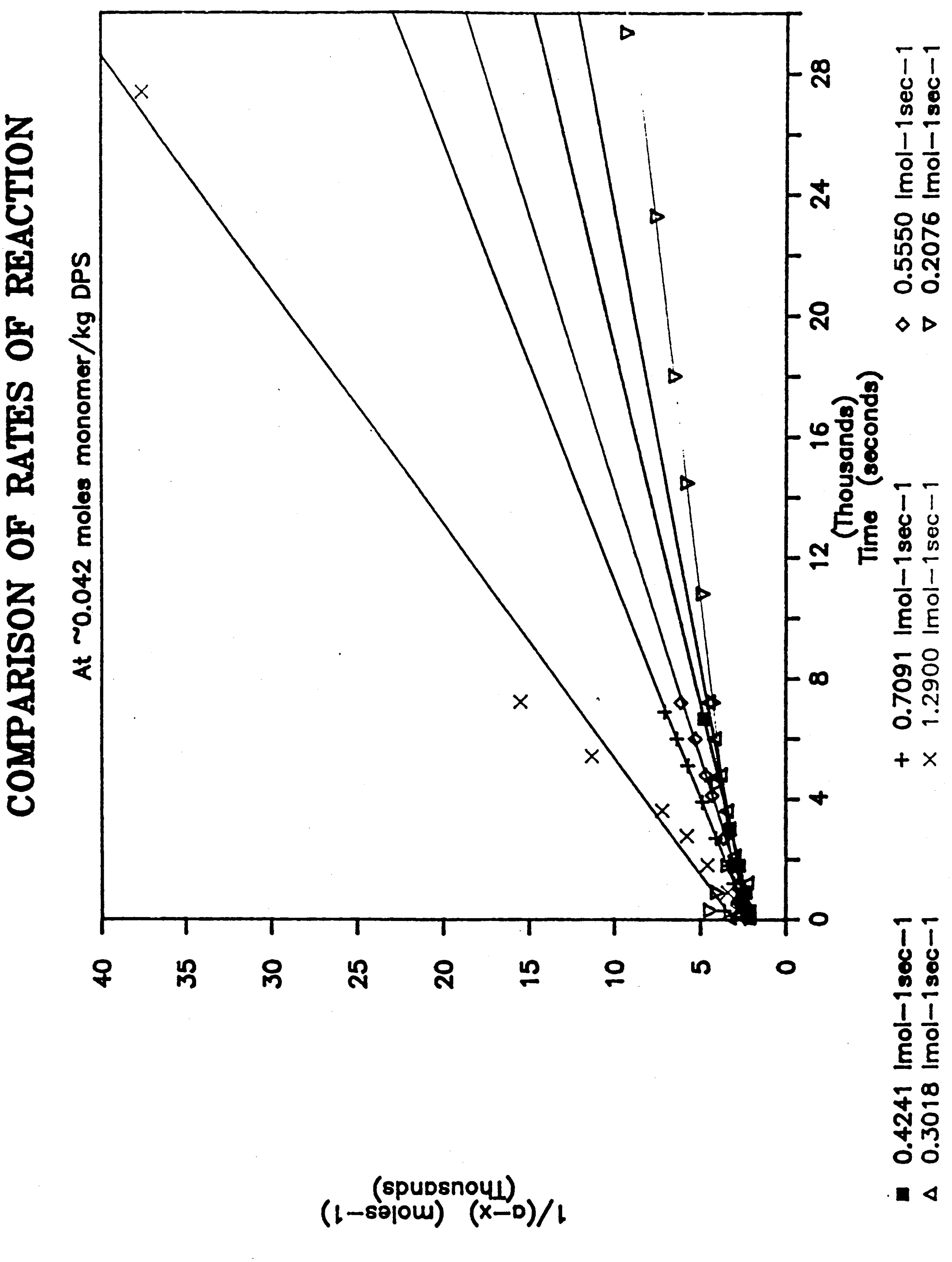
Graph 40 : Effect Of Varying Concentration At ~210°C



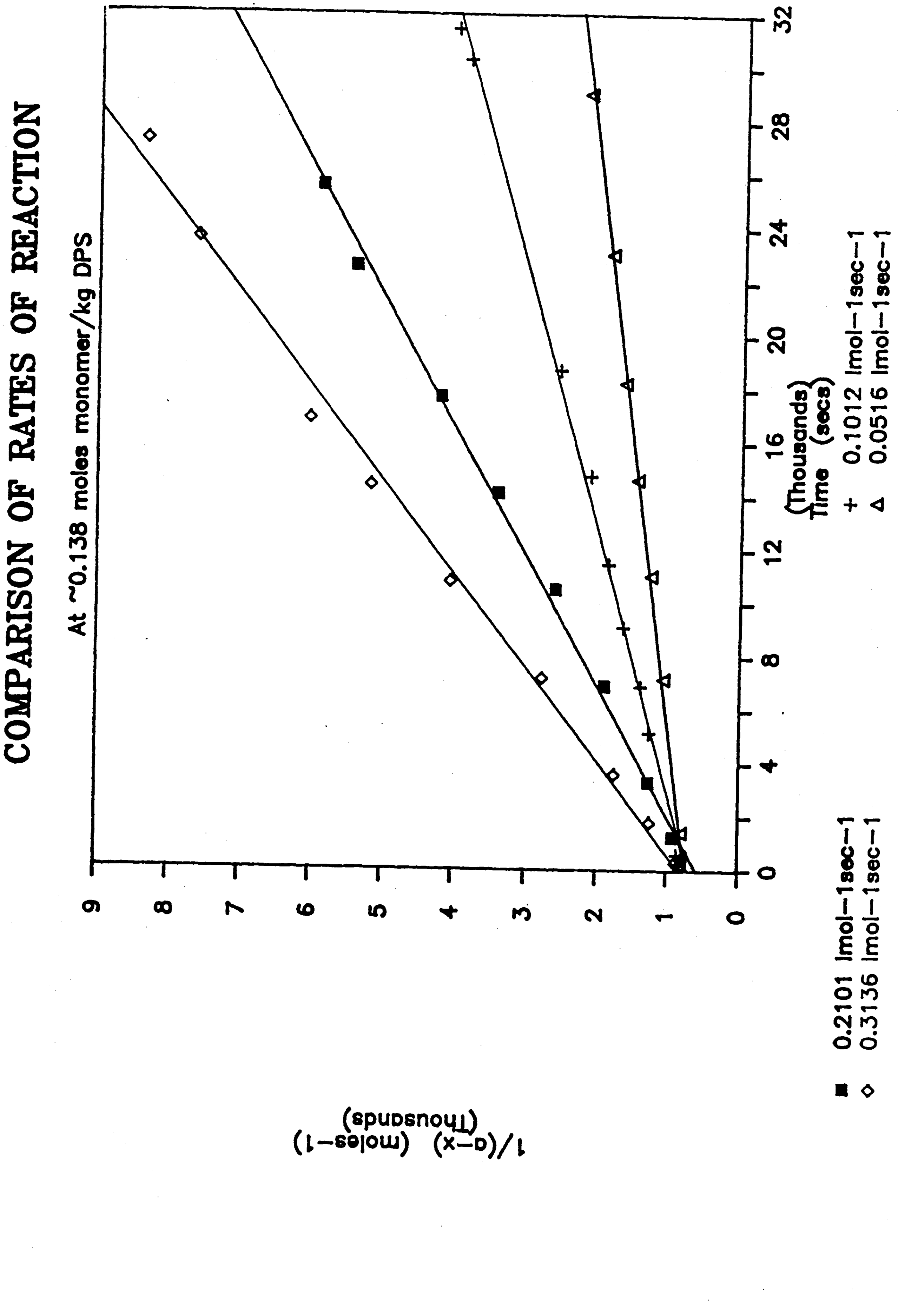
Graph 41 : Effect Of Varying Concentration At ~213°C



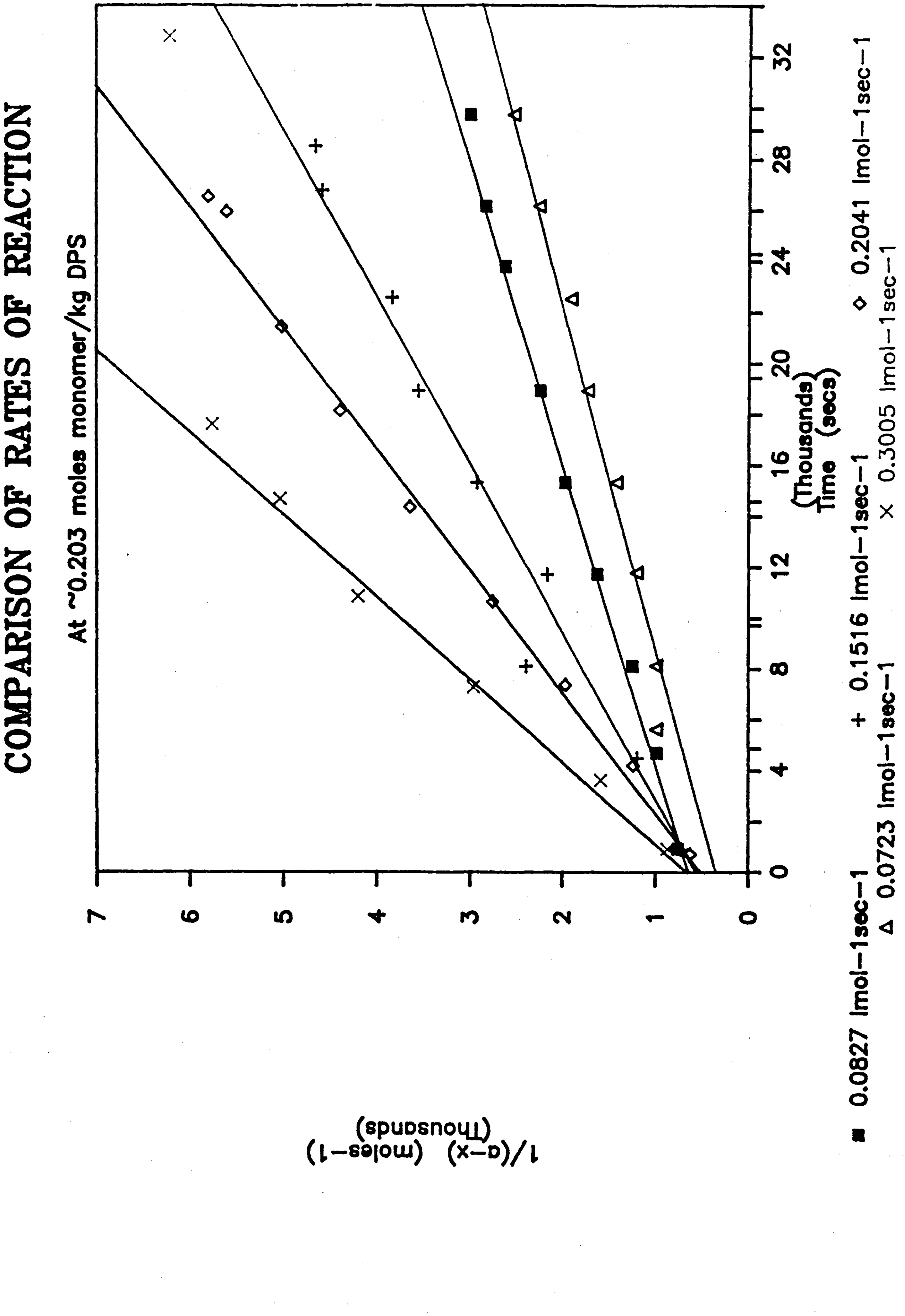
Graph 42 : Effect Of Varying Temperature At ~0.042 moles mono.kg/DPS



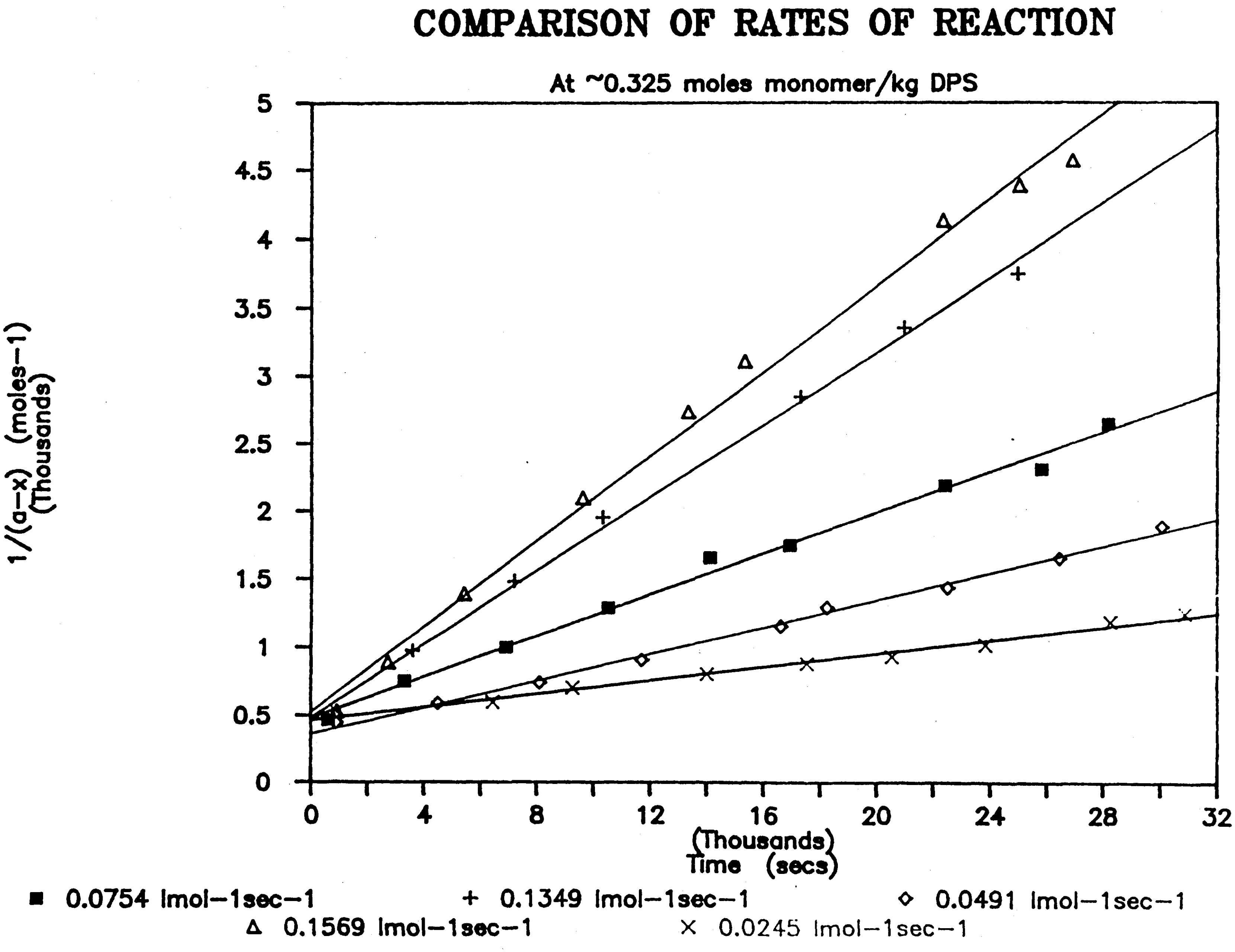
Graph 43 : Effect Of Varying Temperature At ~0.138 moles mono.kg/DPS



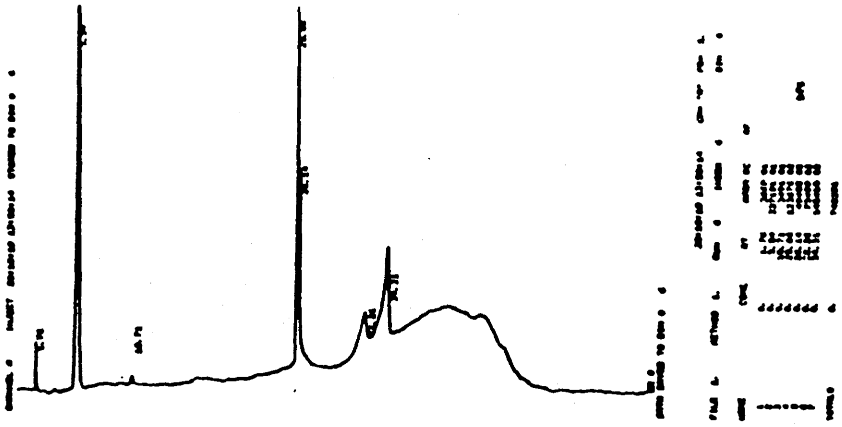
Graph 44 : Effect Of Varying Temperature At ~0.203 moles mono.kg/DPS



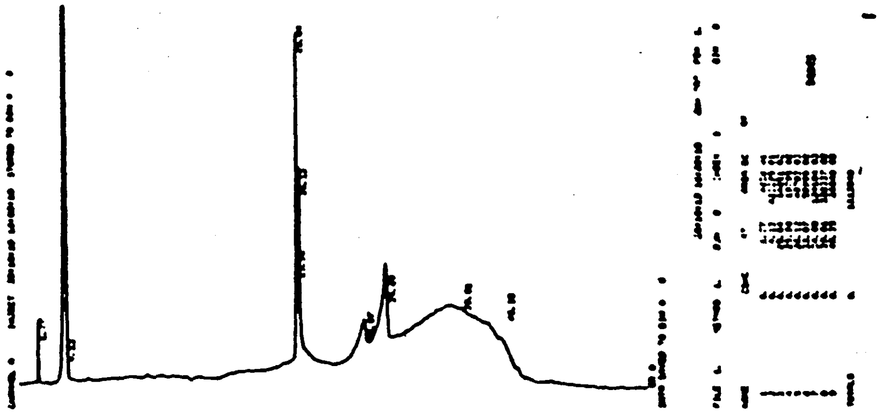
Graph 45 : Effect Of Varying Temperature At ~0.325 moles mono.kg/DPS



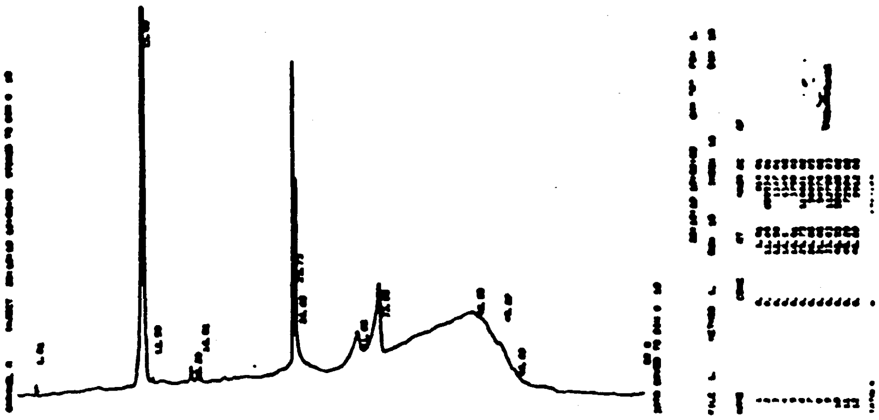
Appendix 3 HPLC Chromatographs For Chapter 8



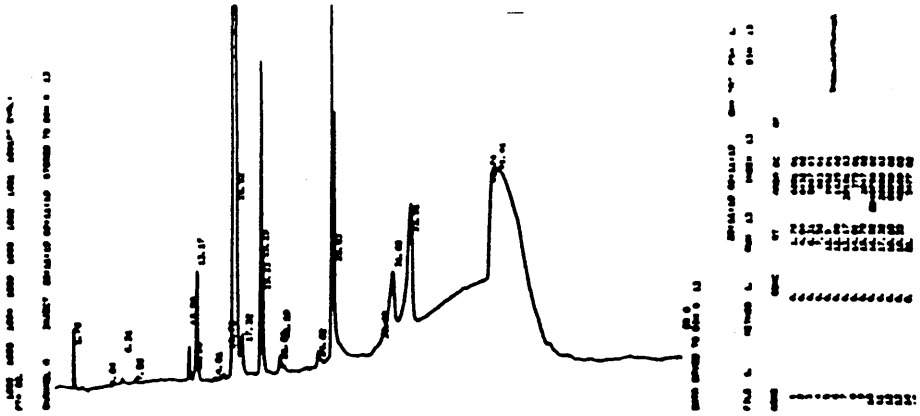
HPLC 1: DPS



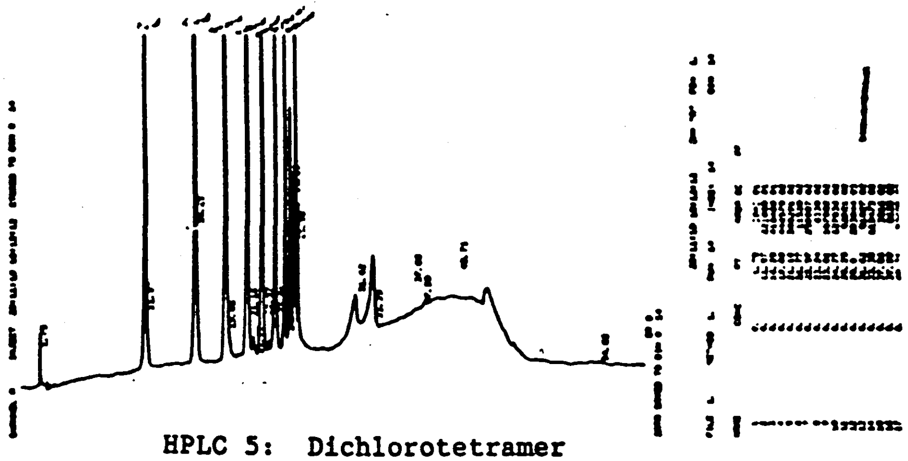
HPLC 2: DCDPS



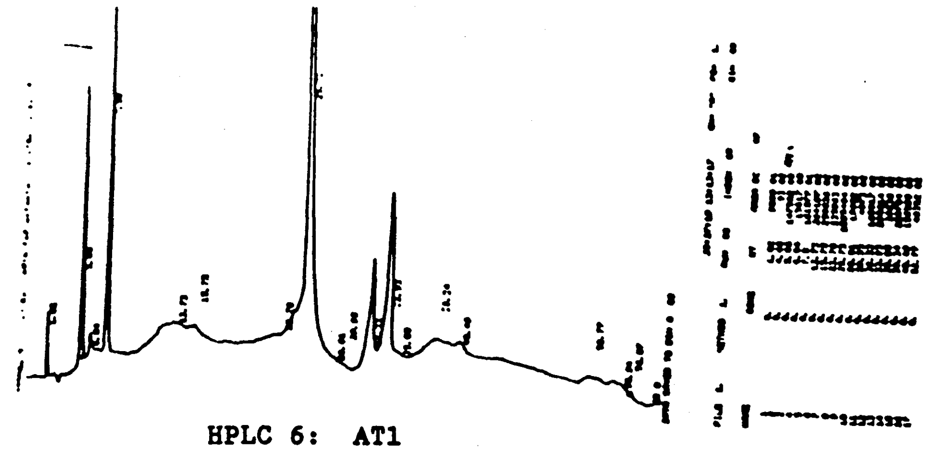
HPLC 3: Dichlorodimer



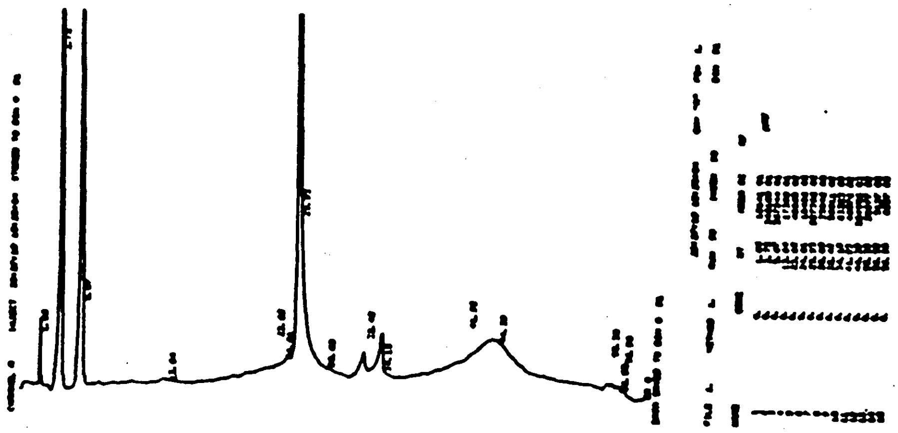
HPLC 4: Dichlorotrimer



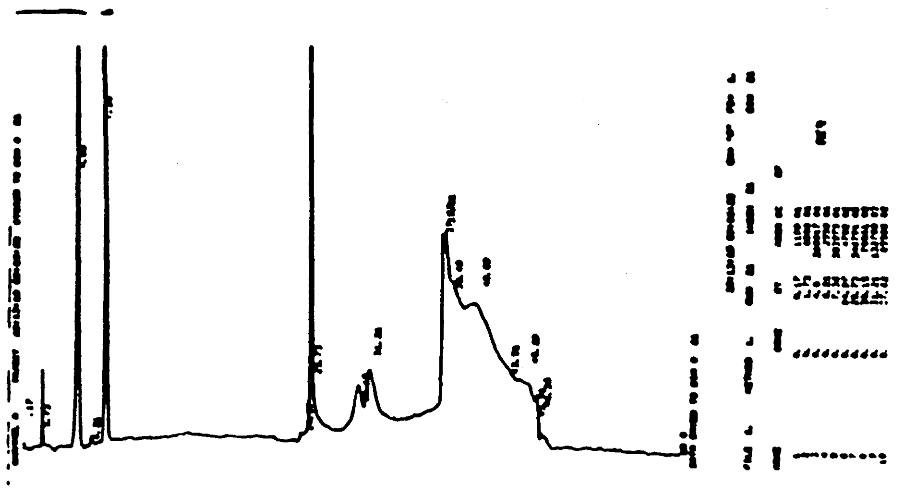
HPLC 5: Dichlorotetramer



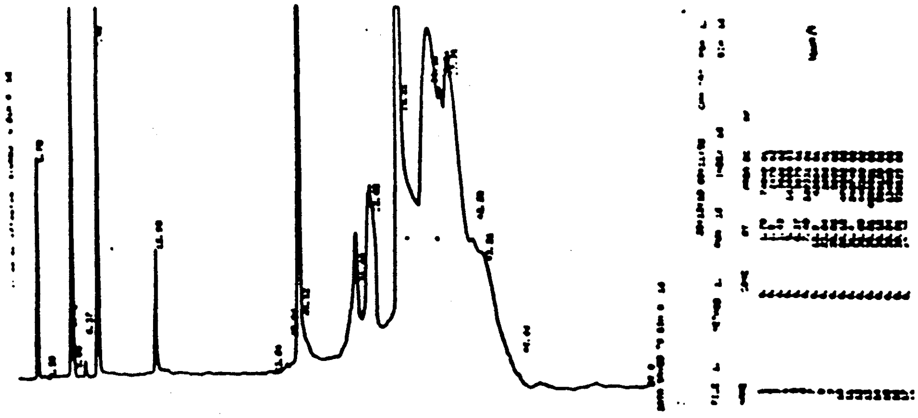
HPLC 6: AT1



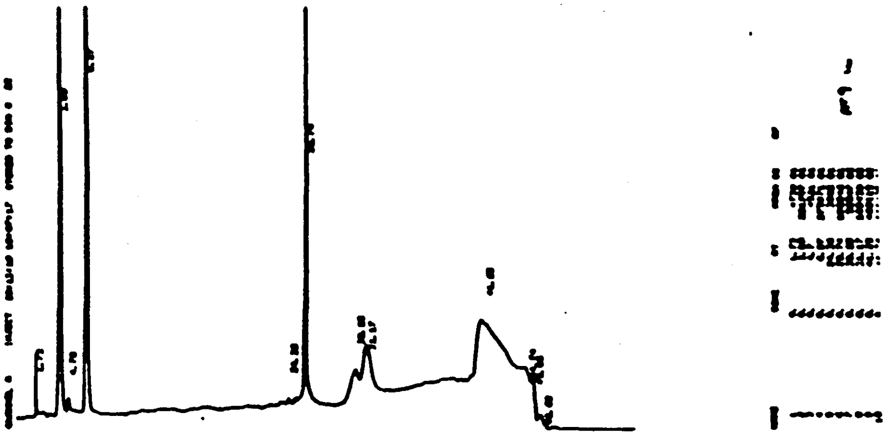
HPLC 7: AT5



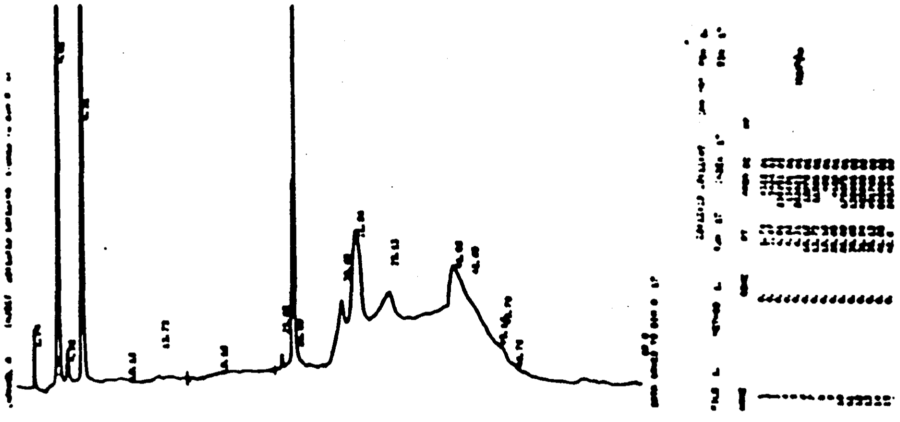
HPLC 8: AT7



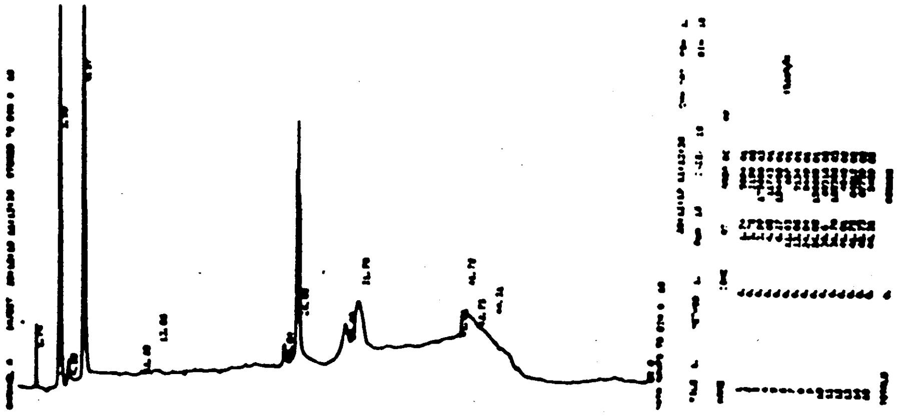
HPLC 9:   AT8



HPLC 10:   AT9

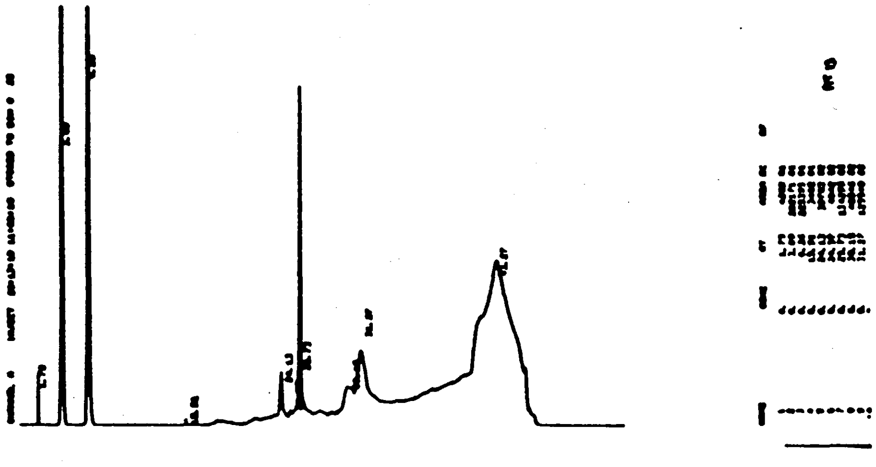


HPLC 11:   AT10

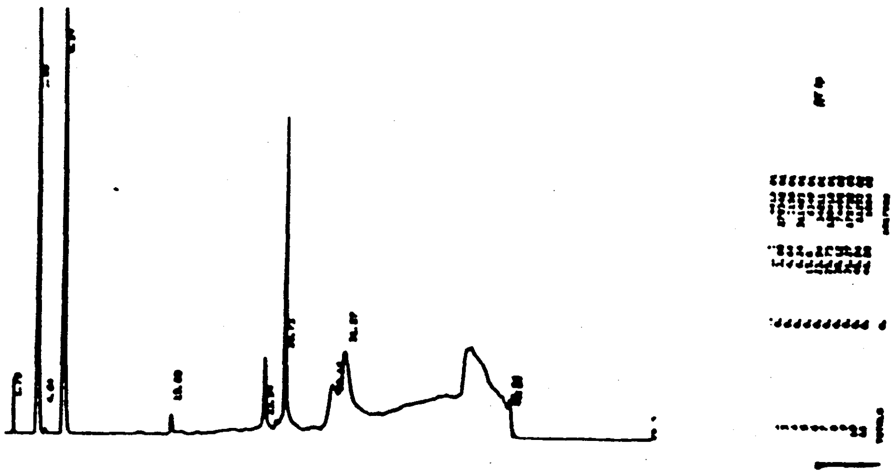


HPLC 12: AT11

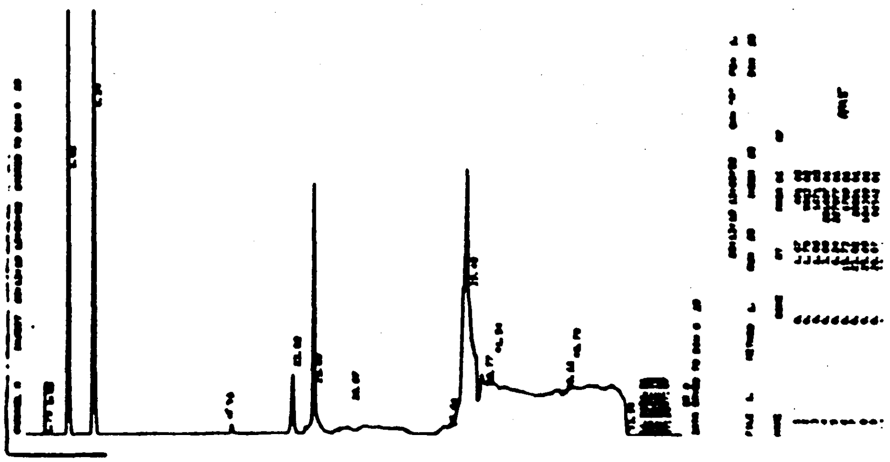
HPLC 13: AT12



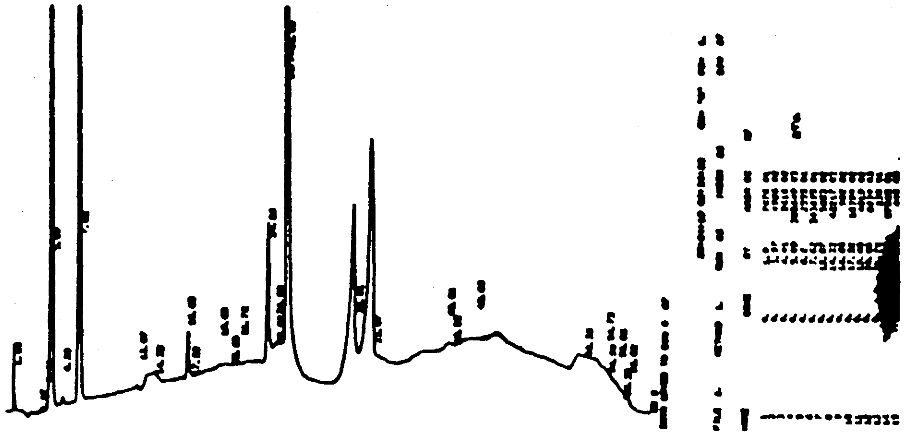
HPLC 14: AT13



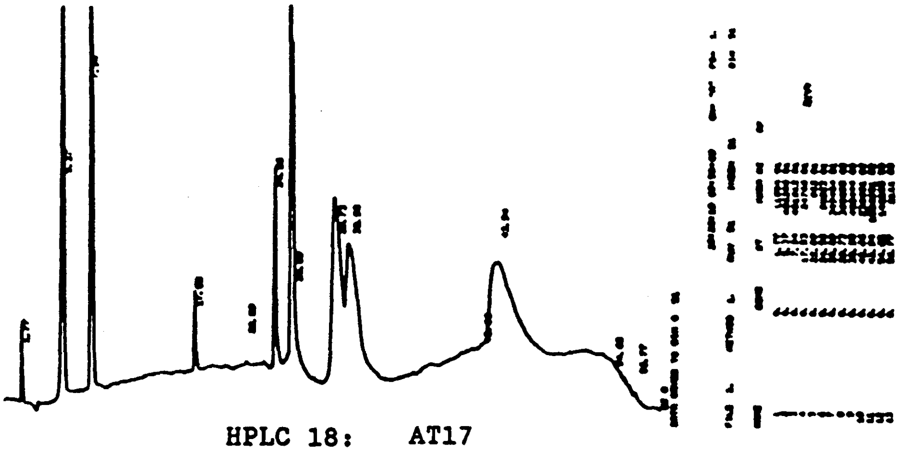
HPLC 15: AT14



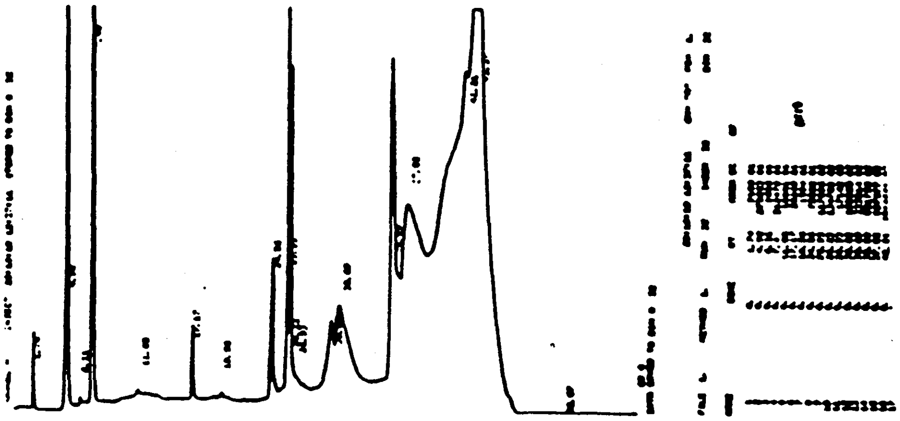
HPLC 16: AT15



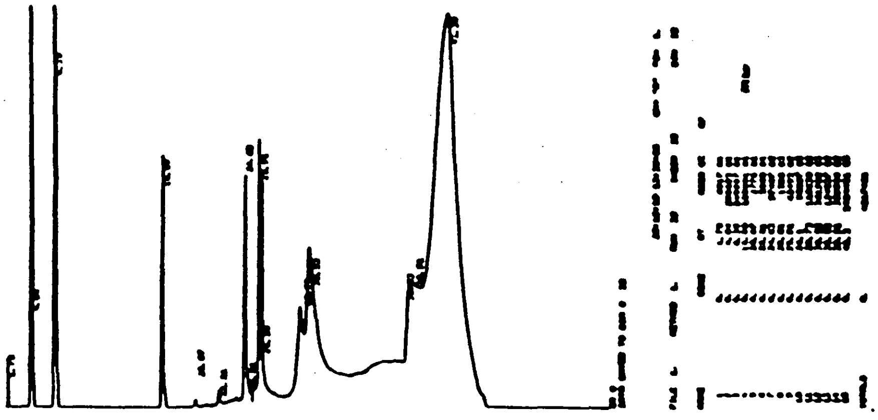
HPLC 17: AT16



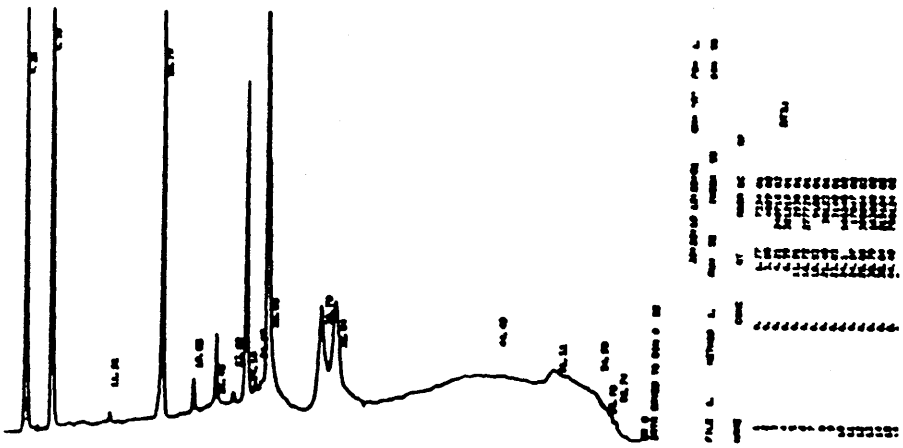
HPLC 18: AT17



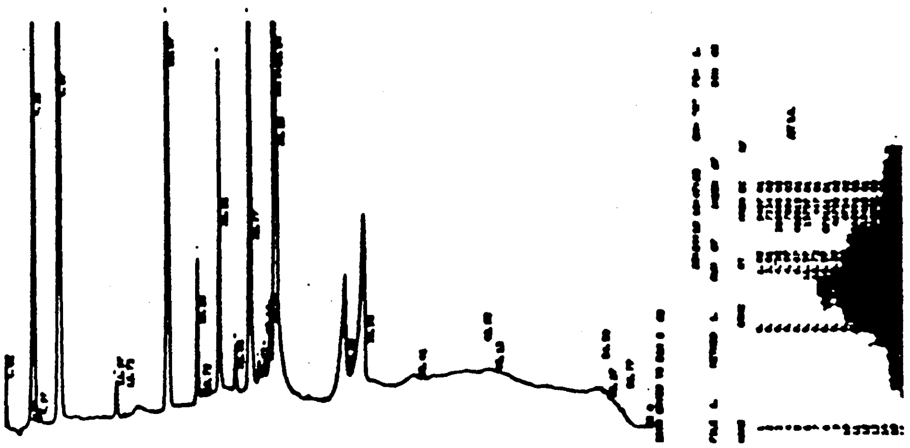
HPLC 19: AT18



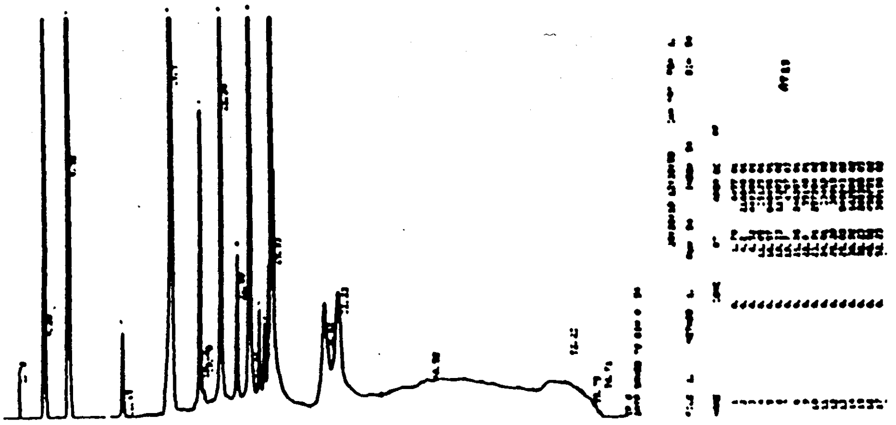
HPLC 20: AT20



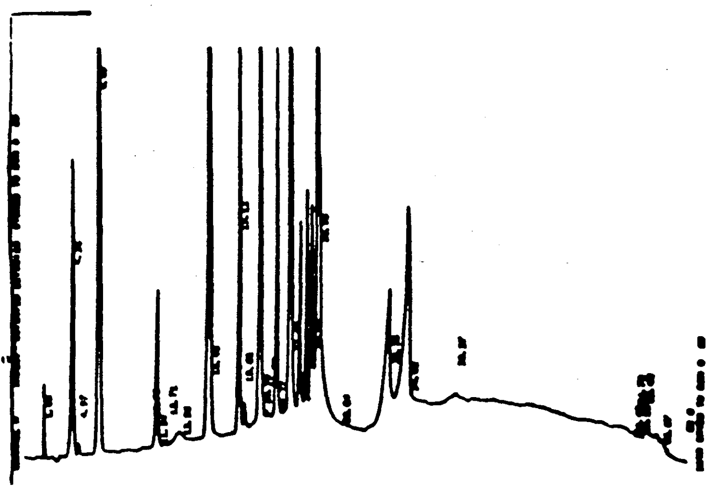
HPLC 21: AT21



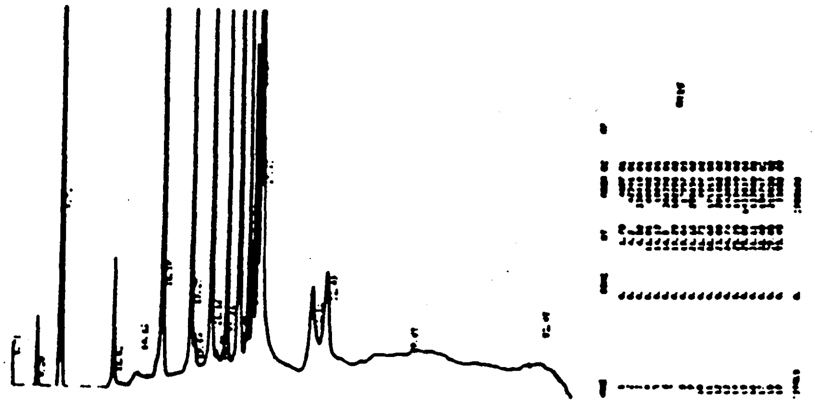
HPLC 22: AT22



HPLC 23: AT23



HPLC 24: AT24



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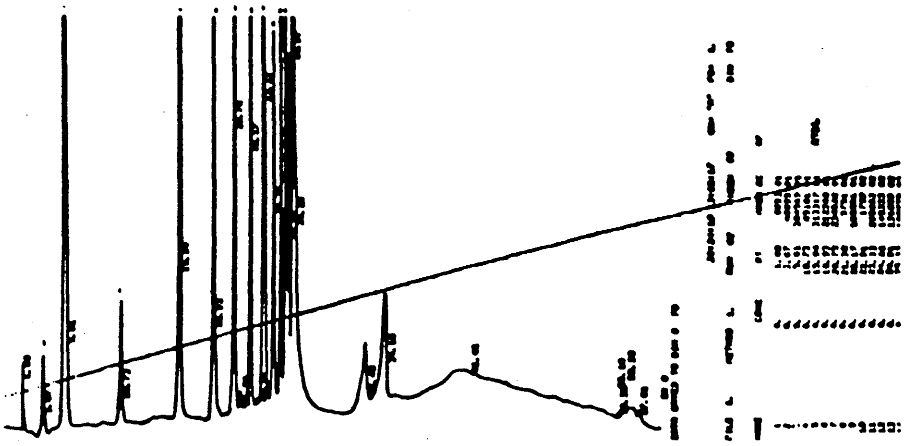
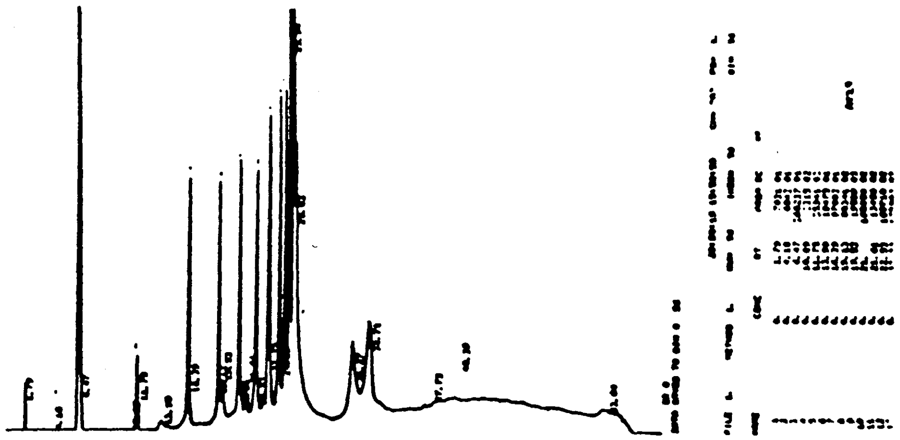
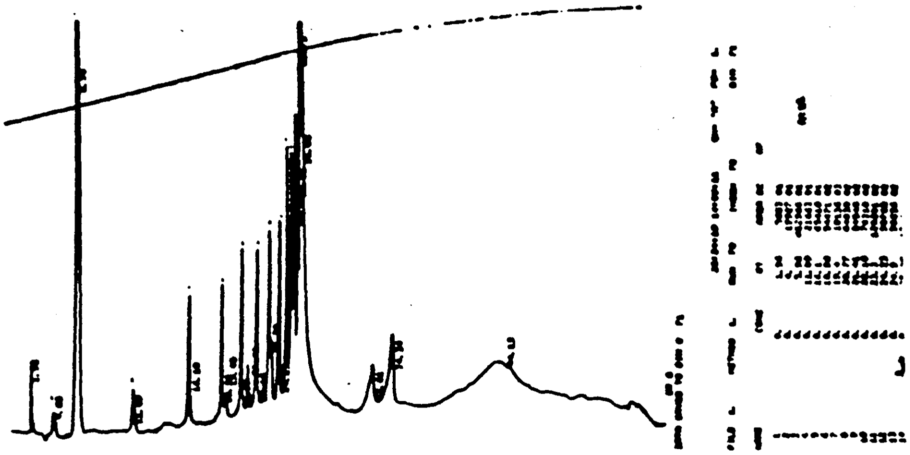


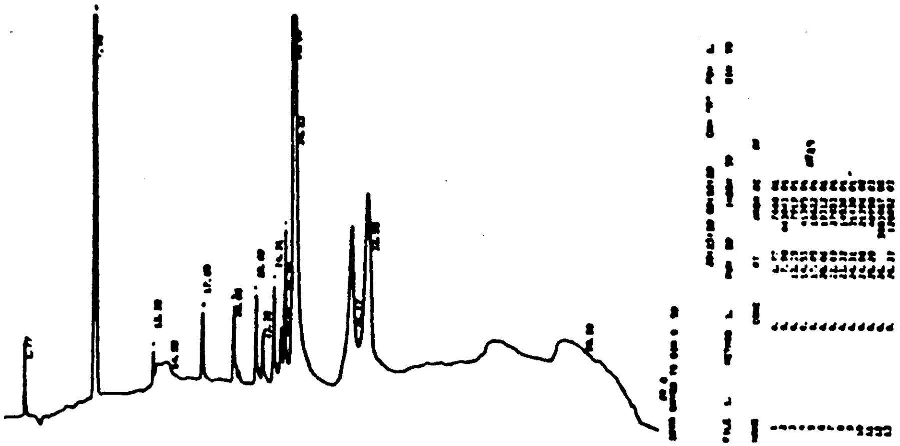
HPLC 26: AT26



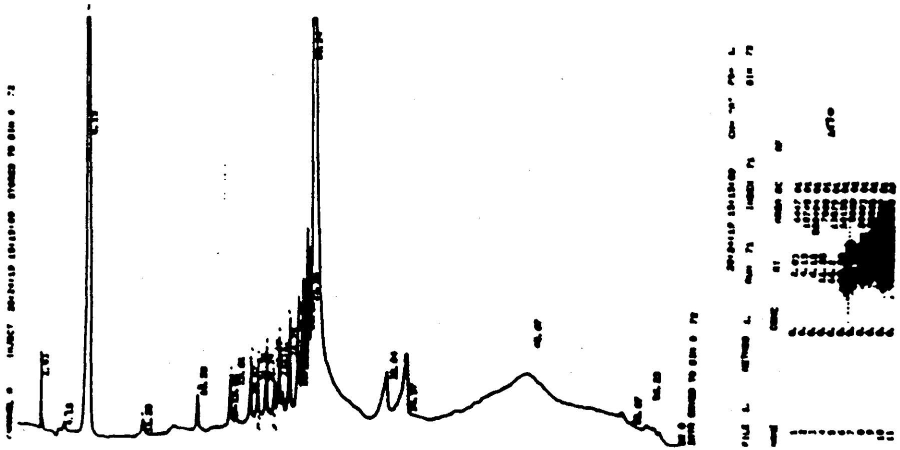
HPLC 27: **AT27**



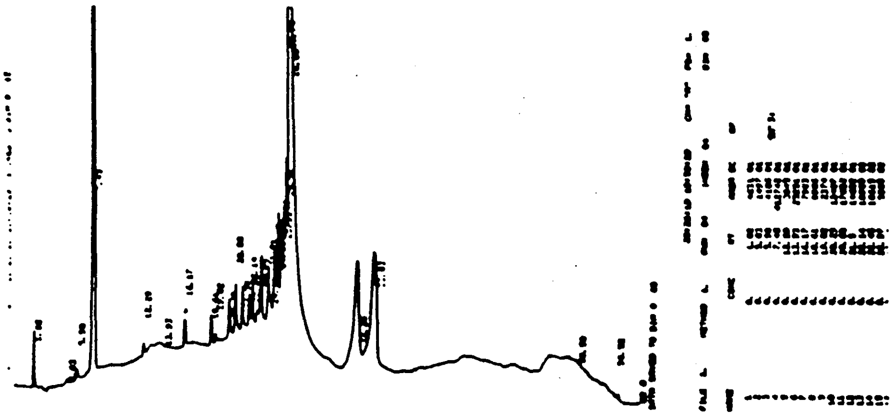
HPLC 28: **AT28**



HPLC 29: **AT29**



HPLC 30: AT30



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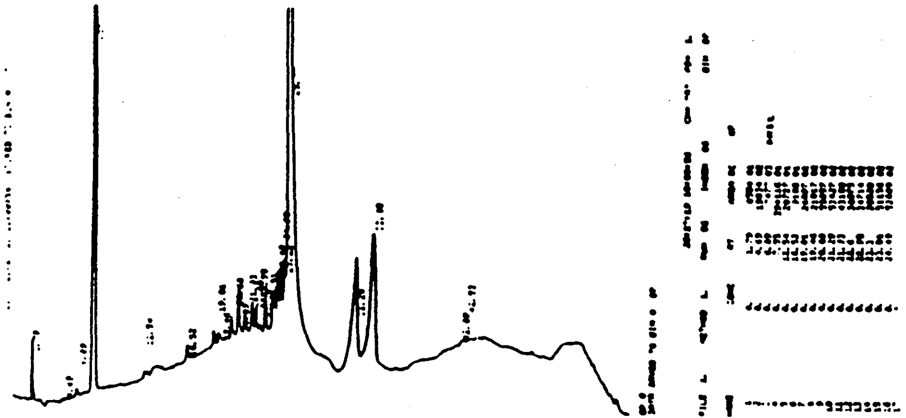
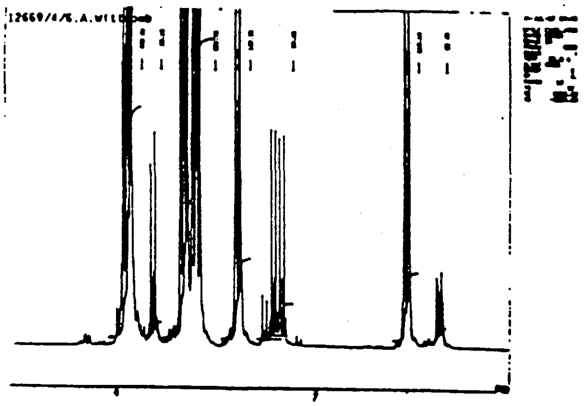


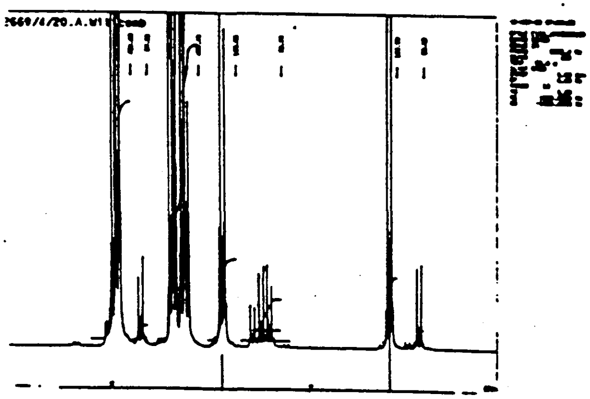
HPLC 32: AT32

Selected NMR Spectra For Chapter 9

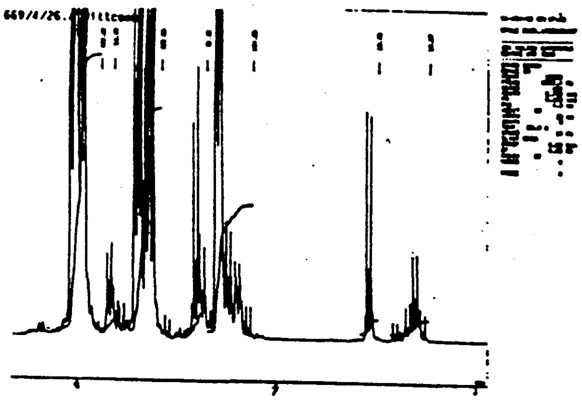
NMR Spectra For Normal PES Polymerisation



AT6



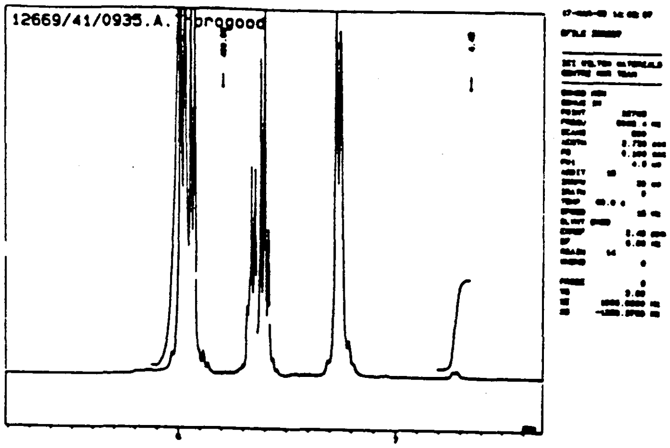
AT20



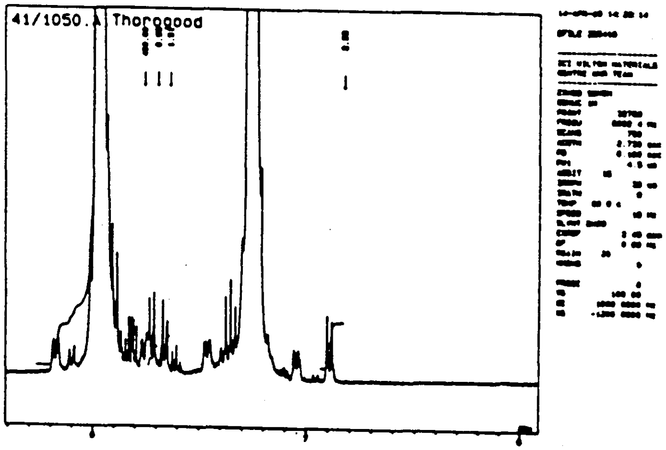
AT26

AT33

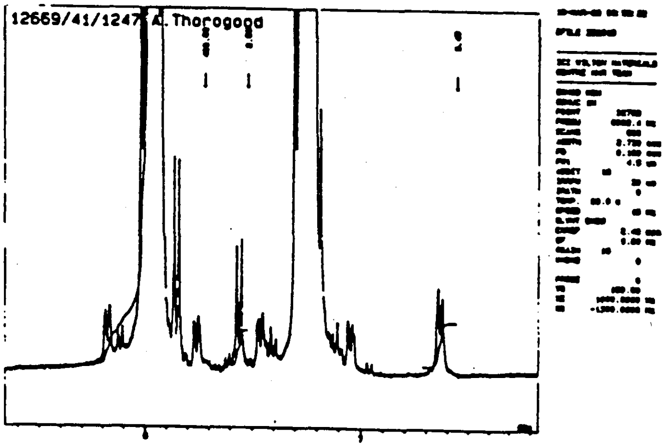
NMR Spectra For Phenate-Ended Polymerisation



0935

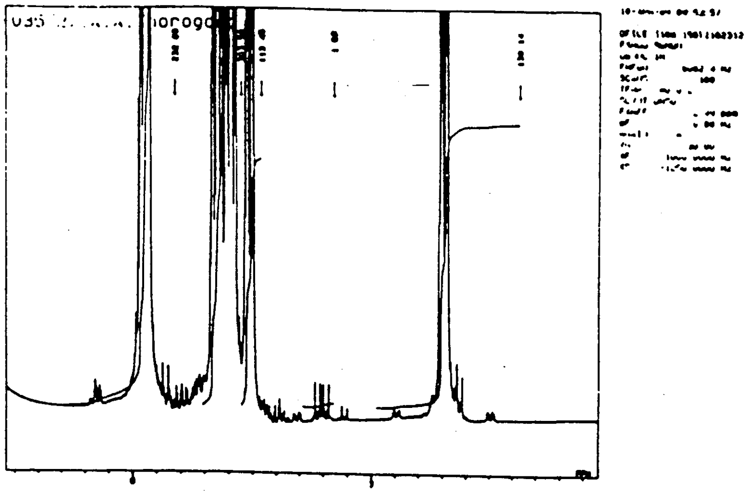


1050

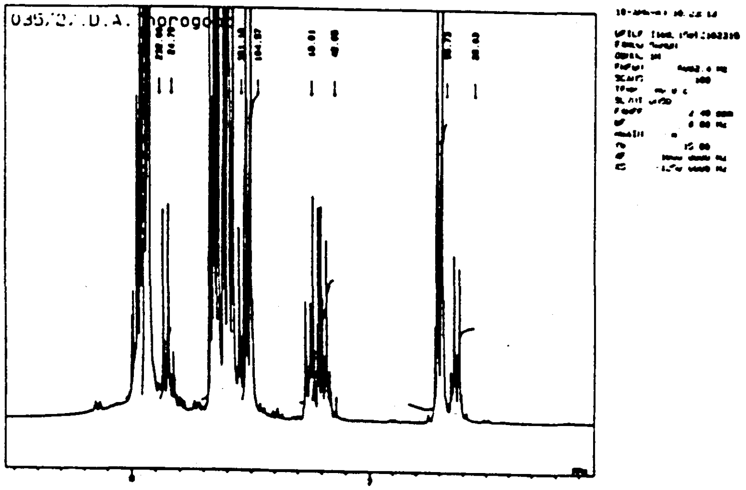


1247

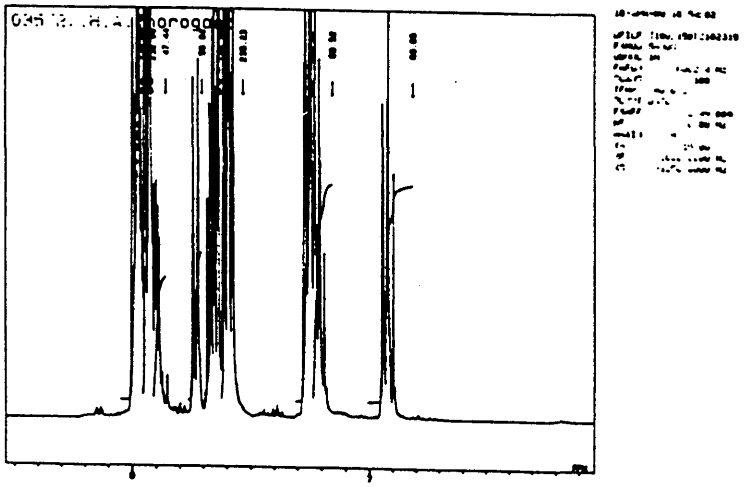
NMR Spectra For Phenate-Ended Oligomerisation



Sample A



Sample D



Sample H

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