EFFECT OF OXYGEN ON THE RADICAL-POLYMERIZATION OF ACRYLONITRILE AND VINYLIDENE CHLORIDE

A thesis submitted for the Degree of
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by

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ABSTRACT

The role of oxygen in the bulk polymerization of acrylonitrile and the solution polymerization of vinylidene chloride has been investigated.

The study of the effect of oxygen on the bulk polymerization of acrylonitrile was carried out dilatometrically at 50°C, using 2, 2′-azobisisobutyronitrile, AIBN, as the initiator. It was found that the induction period caused by the presence of oxygen in the above system was approximately inversely proportional to the square root of the initiator concentration. The induction period was proportional to the initial oxygen concentration to the power 0.66 - 0.78 indicating the existence of two types of termination reaction, the mutual termination of peroxy radicals ($RO_2\cdot + RO_2\cdot$) and the cross termination of peroxy radicals and alkyl radicals ($R\cdot + RO_2\cdot$). During the induction period a polymeric peroxide of relatively low molecular weight was formed. This polymeric peroxide was capable of free radical initiation but only slightly increased the polymerization rate at the end of induction periods. Apart from the polymeric peroxide, some other products such as CO_2, HCN, HCHO and possibly CO were identified using a recently developed organic analyser, the microwave plasma detector (MPD 850). The effect of oxygen on the thermal stability of polyacrylonitriles isolated after the end of induction periods was determined using a thermobalance.

The influence of oxygen on vinylidene chloride polymerization was examined in chlorobenzene solution at 40°C using AIBN as initiator. Approximately 40% of the oxygen consumed was converted to the polymeric peroxide of vinylidene chloride. Among the other compounds formed by the reaction between oxygen and vinylidene chloride, HCHO and CO_2 were identified using the MPD 850. The oxygen consumption was found to be auto-accelerating. This phenomenon was considered to be due to the formation of polymeric peroxide which was later demonstrated to be a relatively efficient initiator. The rate of the oxygen consumption under the above conditions was found to be approximately proportional to the monomer concentration and to the square root of the initiator concentration. The reaction rate depended on the initial pressure of oxygen to the power 0.14. In the vinylidene chloride-oxygen-initiator system, termination occurs predominantly between peroxy radicals ($RO_2\cdot + RO_2\cdot$).

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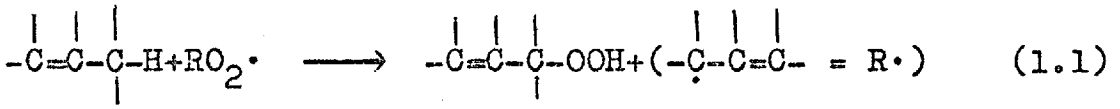
CHAPTER I

INTRODUCTION

1.1 Effect of oxygen on unsaturated monomers

The reaction of oxygen with unsaturated monomers can be classified in three different ways, depending on the type of substituent group.

I. With unsubstituted olefins hydrogen abstraction generally takes place which leads to the formation of a hydroperoxide[1,2]:

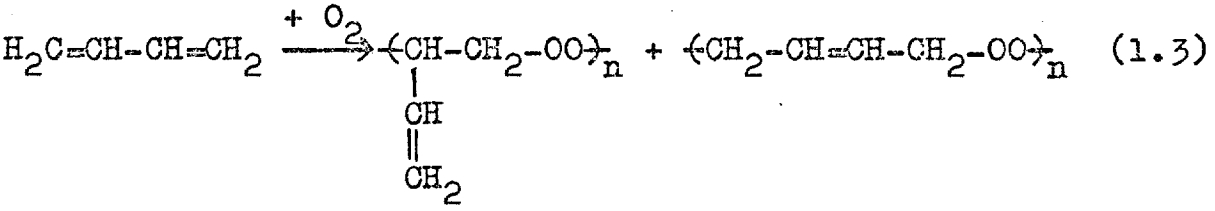


(1.1)



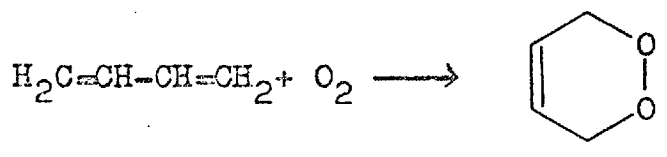
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II. 1,3 dienes and related aromatic compounds undergo two types of reaction with oxygen which vary with the experimental conditions[1,2]. In the presence of a free radical initiator a copolymer of the monomer and oxygen, may be formed by both 1,2 and 1,4 addition,



(1.3)

In the presence of light and a photo-sensitizer, 1,4 addition to oxygen takes place which results in the formation of an α 1,4-epi peroxide:



(1.4)

III. Finally, the substituted olefinic compounds (vinyl and vinylidene monomers) react with oxygen to

form a polymeric peroxide, with a generally accepted structure[1,2]:

$$nH_2C{=}CHR + nO_2 \longrightarrow \left(CH_2{-}\underset{\displaystyle R}{\underset{|}{CH}}{-}OO\right)_n \qquad (1.5)$$

The reaction is normally accompanied by the formation of various cleavage products, depending on the type of the monomer. The important characteristic of this reaction is the formation of either no homopolymer or only very small amounts. This reaction continues until all the oxygen in the system is consumed. In the later sections of this chapter various aspects of reaction 1.5 will be thoroughly reviewed.

1.2 Structure of peroxidic compounds

Formation of a polymeric peroxide was reported as early as 1925 and since then various hypotheses have been developed concerning the structure of polymeric peroxides[3]. Price[4] postulated a monomeric hydroperoxide structure (A) for the peroxide formed from methyl methacrylate. Heuck[5] assumed the concurrent formation of a cyclic alkylene peroxide (B) and a polyperoxide (C) :

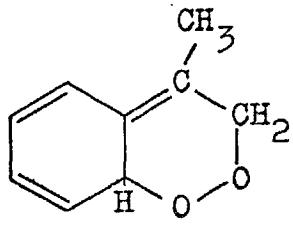
$$H_2C{=}\underset{\displaystyle CH_2OOH}{\underset{|}{C}}{-}C(O)OCH_3 \qquad (A)$$

$$R{-}\underset{\displaystyle O-O}{\underset{|\quad|}{CH}}{-}CH_2 \qquad (B)$$

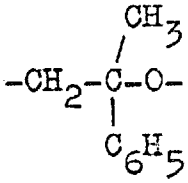
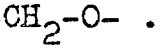
$$\left(CHR{-}CH_2{-}OO\right)_n \qquad (C)$$

However, the hydroperoxide structure for methyl methacrylate has been rejected by demonstrating the lack of active hydrogen and other predicted properties[6].

The cyclic peroxide has been suggested as one of the intermediates in the course of oxidation of chlorotrifluoroethylene in an aqueous system[7]. Hock and Siebert[8] identified a monomeric moloxide formed during the oxidation of α-methylstyrene in the absence of an added initiator,



However, most vinyl monomers form polymeric peroxides in the presence of oxygen rather than non-polymeric peroxides. The structure and the rate of formation of the polyperoxides depend on the pressure of oxygen[9,10,11]. At high oxygen pressure almost alternating copolymers of oxygen and some vinyl monomers have been reported[9,10,12]. As the pressure of oxygen decreases, there is an increasing possibility that a radical ending in a monomer unit reacts with more monomer. Mayo and Miller[9] reported that a significant change appeared in the infrared absorption of the α-methylstyrene polymeric peroxide prepared under oxygen at a pressure lower than 150mm Hg. Accordingly, the oxygen content of the α-methylstyrene-oxygen copolymer, prepared at low pressure was determined and the consistently low results were attributed to the presence of non-peroxide units such as

 and  . The structure of the polymeric peroxide has been determined by various analytical methods

such as micro-analysis, reduction by HI, polarography[6,13], IR spectroscopy and N.M.R. The N.M.R. studies have confirmed the previously proposed chain structure for styrene polymeric peroxide but provided no information about the end groups[14]. Indeed the only data available concerning the end groups are the infrared absorptions of the polymeric peroxides. On the basis of this data Mayo[10] suggested a series of chain transfer reactions which resulted in the formation of various end groups including unsaturation:

$$\sim OOCH_2\dot{C}HC_6H_5 + O_2 \longrightarrow \sim OO\text{-}CH = CHC_6H_5 + HO_2\cdot \qquad (1.6)$$

$$HO_2\cdot + CH_2 = CHC_6H_5 \longrightarrow HOOCH_2 - \dot{C}HC_6H_5 \qquad (1.7)$$

$$HO_2\cdot + CH_2 = CHC_6H_5 \longrightarrow H_2O + HC(=O) - \dot{C}HC_6H_5 \qquad (1.8)$$

According to Miller and Mayo[15] hydrogen abstraction from the monomer molecule is also possible but formation of the epoxy (A) and cyclic (B) end groups is not probable.

(A) $\sim OO\text{-}CH(O)\text{-}CHC_6H_5$ (B) $\sim OOCH\text{-}CH(O\text{-}O)\text{-}C_6H_5$

1.3 Properties and handling of polyperoxides

Polymeric peroxides have generally been described as either colourless oils or crystalline solids, but coloured polyperoxides have also been observed[16,17]. Most of the polyperoxides are soluble in the parent monomer. A polyperoxide dissolved in a solvent is less susceptible to heat and mechanical shock than an isolated polyperoxide which may be explosive. Indeed some isolated polyperoxides such as the polybutadiene peroxide has been

reported to be more sensitive to explosion than trinitroglycerine[18]. Thus, extensive care should be taken in the handling of these compounds. Thermal decomposition of polymeric peroxides yields mainly carbonyl compounds[19, 20]. The commercial preparation of carbonyl compounds from some vinyl polymeric peroxides has even been suggested[19]. Initiation by polymeric peroxides has been known for a long time and is due to the cleavage of a peroxide bond into two alkoxy radicals[20,21].

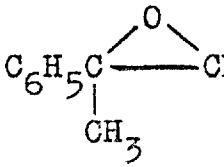
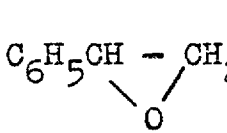
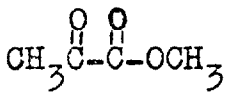
1.4 Cleavage products

Cleavage products are formed during vinyl copolymerization with oxygen. Most of the side products are formed by depolymerization of the growing radicals as well as by decomposition of the corresponding polymeric peroxide. Since the stability of the polymeric peroxides varies from one monomer to another, it is difficult to predict the amounts of the side products formed by depolymerization of the growing chains and by decomposition of the resulting polyperoxide. The dependence of the rate of formation of cleavage products on the pressure of oxygen has well been established[9,10,11]. For example, in the oxidation of α-methylstyrene the rate of acetophenone and epoxide formation increases up to about 80 and 20 mm Hg of oxygen pressure, respectively, and then both rates gradually decrease as the oxygen pressure increases[9]. The exact nature of the cleavage products depends on the particular polymerization system examined but formaldehyde is a common product of almost all systems. Formation of epoxides has also been reported in several

cases[9,10,22,23]. For ease of comparison, important data available for the oxidation of some vinyl monomers are presented in table 1.

TABLE 1

Side product identification and kinetic data for the oxidation of some vinyl monomers

Monomer	Side Product identified	Polymerization System	Rate of Reaction	Reference
$CH_2=C(CH_3)C_6H_5$	 , $HCHO$, $C_6H_5COCH_3$	Bulk, 50°C	$-d[O_2]/dt \propto [AIBN]^{0.5}$	9
$CH_2=CHC_6H_5$	 , $HCHO$, C_6H_5CHO	Bulk, 50°C and 35-80°C	$-d[O_2]/dt \propto [AIBN]^{0.5}[M]$ Oxygen pressure > 20mm H_g	10, 15
$CH_2=CHCN$	CO_2, CO, $HCHO$, HCN, $HOCH_2COOH$, $HOCH_2CH(CN)OH$	Aqueous solution, 50°C	$-d[O_2]/dt \propto [M]^{1.5}[K_2S_2O_8]$	16
$CH_2=C(CH_3)C(O)OCH_3$	$HCHO$, 	Bulk and in benzene, 50°C	$-d[O_2]/dt \propto [AIBN]^{0.5}[M]$ Oxygen pressure > 200mm Hg	24

(Continued)

TABLE 1 (Continued - p. 2)

Monomer	Side Product identified	Polymerization System	Rate of Reaction	Reference
$CH_2=CHCl$	-	Emulsion, 50°C	$IP \propto [K_2S_2O_8]^{-0.5}[O_2^0]^{0.5}$	25, 26
$CH_2=CHCl$	-	Bulk	$-d[O_2]/dt \propto [I]^{0.5}$	27
$CH_2=CHCl$	CO,HCHO	Bulk (dilatometrically), 55°C	$IP \propto [I]^{-0.46}[O_2^0]^{0.5}$	28, 29
$CH_2=CHCN$	$HOCH_2COOH$,HCN,CO, CO_2,HCHO,HCOOH, $HOCH_2CH(CN)OH$	Aqueous solution, 50°C	$-d[O_2]/dt \propto [K_2S_2O_8]^{0.69}[M]^{0.65}$	30
$CH_2=CHC(=O)CH_3$	CO,CO_2,HCOOH	Aqueous solution, 50°C	$-d[O_2]/dt \propto [K_2S_2O_8]^{0.4}[M]^{0.7}$	30
$CH_2=C(CH_3)CN$	CH_3COOH,HCN,HCHO, CH_3COCHO, $CH_3C(OH)(CN)CH_2OH$	Aqueous solution, 50°C	$-d[O_2]/dt \propto [K_2S_2O_8]^{0.6}$	30

(Continued)

TABLE 1 (Continued - p. 3)

Monomer	Side Product identified	Polymerization System	Rate of Reaction	Reference
$CH_2=CHC_6H_5$	-	In benzene (dilatometrically), 50°C	$IP \propto [AIBN]^{-0.5}[M]^{-1}[O_2^0]$	31
$CH_2=CHCN$	-	Solution (benzene, toluene, butanone and n-heptane), 50°C	$-d[O_2]/dt \propto [AIBN]^{0.5}[M]$	32
$CH_2=C(CH_3)CN$	-	In bromobenzene, 50°C	$-d[O_2]/dt \propto [AIBN]^{0.5}[M]$	33
$CH_2=CHCN$	-	In bromobenzene, 50°C	$-d[O_2]/dt \propto [I]^{0.6}[M]^{1.6}$	33
$CH_2=CHCN$	-	In chlorobenzene, 50°C	$-d[O_2]/dt \propto [AIBN]^{0.5}[M]$	33
$CH_2=C(CH_3)CN$	$CO, CO_2, HCHO, CH_3\overset{O}{\overset{\|}{C}}CN$	Bulk, 45-50°C	-	34
$CH_2=C(CH_3)C(O)OCH_3$	-	In benzene (dilatometrically), 50°C	$IP \propto [AIBN]^{-0.5}[M]^{-1}[O_2^0]$	35

(Continued)

TABLE 1 (Continued - p. 4)

Monomer	Side Product identified	Polymerization System	Rate of Reaction	Reference
$CH_2=CHC_6H_5$	-	Emulsion, 50°C	$IP \propto [K_2S_2O_8]^{-1} [O_2^o]$	36
$CH_2=CHOC(O)CH_3$	-	Bulk, 60°C	IP measurements made	37

In the above table, [M] and [I] represent concentrations of monomer and initiator, respectively. IP represents the induction period caused by added oxygen and $[O_2^o]$ represents the initial concentration of oxygen.

1.5 Effect of oxygen on the oxidation of vinyl monomers in the absence of added initiator

Molecular oxygen has been reported to have a considerable direct effect on some vinyl monomers[8,9,16,34,38,39]. This effect is apparently due to its reaction with the double bond of a vinyl monomer which opens to produce free radicals. A secondary effect is the formation of a peroxidic material which decomposes to form radicals capable of adding to vinyl monomers. These effects have been studied for the thermal oxidation of styrene by Abere et al[40]. Two types of initiation mechanism were suggested for the reaction in the absence of added initiator but with added oxygen.

The first initiation reaction, 1.9, is based on the formation of a biradical proposed by Flory[41]:

$$2CH_2{=}CHC_6H_5 \longrightarrow C_6H_5\dot{C}HCH_2{-}CH_2\dot{C}HC_6H_5 \qquad (1.9)$$

Oxygen then attacks the biradical to form a biperoxy radical:

$$C_6H_5\dot{C}HCH_2CH_2\dot{C}HC_6H_5+2O_2 \longrightarrow \cdot OO(C_6H_5)CHCH_2{-}CH_2CH(C_6H_5)OO\cdot \qquad (1.10)$$

Also there can be direct attack of an oxygen molecule on the monomer,

$$O_2+CH_2{=}CHC_6H_5 \longrightarrow \cdot OOCH_2{-}\dot{C}HC_6H_5 \qquad (1.11)$$

The above biradical, 1.11, can either form carbonyl compounds, 1.12, or it can react with a styrene molecule, 1.13.

$$\cdot OOCH_2\text{-}\dot{C}HC_6H_5 \longrightarrow HCHO + C_6H_5CHO \quad (1.12)$$

$$\cdot OOCH_2\text{-}\dot{C}HC_6H_5 + CH_2 = CHC_6H_5 \longrightarrow C_6H_5\dot{C}H\text{-}CH_2OOCH_2\text{-}\dot{C}HC_6H_5 \quad (1.13)$$

1.6 Kinetic mechanism for the oxidation of vinyl monomers in the presence of added initiator.

The reaction mechanism given in equations 1.14 - 1.22 has been suggested for the copolymerization of oxygen with methyl methacrylate[35], styrene[10,31], and vinyl chloride[25]. In these equations M is a monomer molecule, RM• and RO_2• are copolymer radicals ending in monomer and oxygen units, respectively, and I• is a radical formed in an initiation reaction.

$$\text{Initiator} \xrightarrow{k_d} 2I\cdot \quad (1.14)$$

$$I\cdot + M \xrightarrow{k_2} IM\cdot \quad \text{Chain initiation} \quad (1.15)$$

$$I\cdot + O_2 \xrightarrow{k_3} IO_2\cdot \quad (1.16)$$

$$RM\cdot + M \xrightarrow{k_4} RMM\cdot \quad (1.17)$$

$$RO_2\cdot + M \xrightarrow{k_5} RO_2M\cdot \quad \text{Propagation} \quad (1.18)$$

$$RM\cdot + O_2 \xrightarrow{k_6} RMO_2\cdot \quad (1.19)$$

$$RM\cdot + RM\cdot \xrightarrow{k_{t1}} P_1 \quad (1.20)$$

$$RM\cdot + RO_2\cdot \xrightarrow{k_{t2}} P_2 \quad \text{Termination} \quad (1.21)$$

$$RO_2\cdot + RO_2\cdot \xrightarrow{k_{t3}} P_3 \quad (1.22)$$

Under stationary state conditions a kinetic expression can be derived from the above scheme assuming: (I) that the reactions of RM• and RO_2• depend only on the nature of the end groups, (II) that reactions 1.16 and 1.17 can be neglected in establishing expressions for the overall rate of oxygen consumption, (III) that

reactions 1.20-1.22 account for all the chain terminations, and (IV) that reactions 1.18 and 1.19 essentially account for all the oxygen consumption as long as the kinetic chain length is $\gg 1$. The last assumption implies that the rate of reaction 1.18 can be set equal to the rate of reaction 1.19

$$k_5[RO_2\cdot][M] = k_6[RM\cdot][O_2] = -\frac{d[O_2]}{dt} \qquad (1.23)$$

Setting the rate of termination equal to the rate of production of effective radicals from the initiator one obtains:

$$R_i = 2k_d f[I] = 2k_{t1}[RM\cdot]^2 + 2k_{t2}[RM\cdot][RO_2\cdot] + 2k_{t3}[RO_2\cdot]^2 \qquad (1.24)$$

where k_d is the decomposition constant of the initiator, f is the initiator efficiency and $[I]$ is the initiator concentration. From equations 1.23 and 1.24,

$$[RM\cdot] = \left\{ \frac{k_d f[I]}{k_{t1} + k_{t2}\left(k_6[O_2]/k_5[M]\right) + k_{t3}\left(k_6[O_2]/k_5[M]\right)^2} \right\}^{\frac{1}{2}} \qquad (1.25)$$

If the mutual termination of the peroxy radicals is predominant, then from equations 1.23 and 1.25

$$-\frac{d[O_2]}{dt} = k_5\,[M] \left\{ \frac{k_d f[I]}{k_{t3}} \right\}^{\frac{1}{2}} \qquad (1.26)$$

The rate of oxygen uptake is proportional to the concentration of the monomer and to the square root of the initiator concentration.

If the cross termination of the peroxy radical and the alkyl radical is dominant, the rate of oxygen

uptake becomes:

$$-\frac{d[O_2]}{dt} = \left\{\frac{k_5 k_6 [M][O_2] k_d f[I]}{k_{t2}}\right\}^{\frac{1}{2}} \qquad (1.27)$$

The rate of oxygen consumption is proportional to the square root of the monomer, oxygen and initiator concentrations.

If the mutual termination of alkyl radicals is dominant, the rate of oxygen uptake becomes:

$$-\frac{d[O_2]}{dt} = k_6[O_2]\left\{\frac{k_d f[I]}{k_{t1}}\right\}^{\frac{1}{2}} \qquad (1.28)$$

The rate of oxygen absorption is now proportional to the concentration of oxygen and to the square root of the initiator concentration. Since many free radical polymerizations are inhibited by oxygen and often alternating copolymers are obtained, mutual termination of alkyl radicals is unlikely[25,35]. Other reactions leading to the formation of cleavage products are as follows:[10]

$$ROOCH_2\dot{C}XX_1 \longrightarrow RO\cdot + H_2C\overset{O}{\diagup\diagdown}CXX_1 \quad \text{Epoxidation} \qquad (1.29)$$

$$RO(OCH_2CXX_1O)_n^{\cdot} \longrightarrow RO\cdot + nHCHO + nXCOX_1 \qquad (1.30)$$

$$ROCH_2CXX_1O\cdot \longrightarrow RO\dot{C}H_2 + XCOX_1 \qquad (1.31)$$

$$RMO\dot{C}H_2 \longrightarrow RM\cdot + HCHO \qquad (1.32)$$

Cleavage by unzipping reaction

$$RO\cdot + M \longrightarrow ROM\cdot \quad \text{Addition of alkoxy radical} \qquad (1.33)$$

$$RMOO\cdot + H_2C = CXX_1 \longrightarrow RM\cdot + HCHO + XCOX_1 \qquad (1.34)$$

$$ROOCH_2\dot{C}XX_1 + O_2 \longrightarrow ROO\cdot + HCHO + XCOX_1 \qquad (1.35)$$

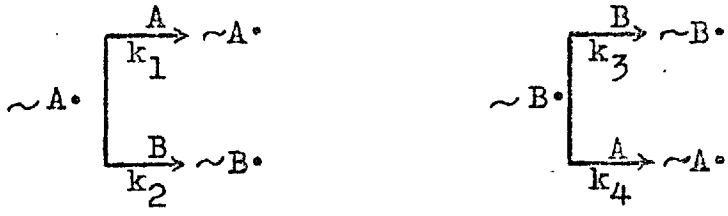
$$ROOCH_2CXX_1OO\cdot \longrightarrow ROO\cdot + HCHO + XCOX_1 \qquad (1.36)$$

$$2\ ROO\cdot \longrightarrow 2\ RO\cdot + O_2 \qquad (1.37)$$

High pressure cleavage

1.7 Correlation of the structure of vinyl monomers and their oxidizability

Oxygen has been regarded as a monomer which does not polymerize itself, but copolymerizes readily with vinyl monomers to form alternating copolymers[6]. Hence, the four chain propagation steps for copolymerization of two vinyl monomers are applicable to this type of reaction:



(1.38)

where A and B are vinyl monomers, and A• and B• are the corresponding radicals.

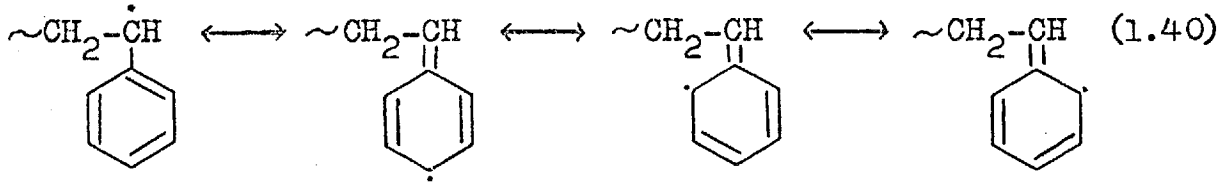
Since oxygen inhibits the radical homopolymerization of most vinyl monomers and because the reaction of a peroxy radical with oxygen leads to an unlikely structure[42], $\sim CH_2\text{-}CH(X)OO\text{-}OO\cdot$, two of these reactions can be neglected. The propagation step involving the polymeric radical with a terminal monomer unit and molecular oxygen is fast. Thus oxygen may be considered as a biradical and hence the reaction is a fast radical coupling[43]. Therefore the rate determining step is the addition of the polymeric peroxy radical to the vinyl monomer. The influence of the monomer structure on the rate of oxidation of vinyl monomers can be studied in the same manner as for ordinary copolymerizations. The attachment of a substituent to a carbon carbon double bond produces three major effects[4]: 1. Change of electron density inductively. 2. Stabilization of the resulting radical through resonance. 3. Steric hindrance.

Electron donating substituents such as $-CH_3$, $-OR$, $-C_6H_5$, $-CH=CH_2$ and $-O-C(O)R$ all increase the electron density of the double bond relative to ethylene, whereas electron withdrawing substituents such as $-F$, $-C(O)NH_2$, $-CN$, $-C(O)OR$ and $-C(O)R$ all decrease the electron density:



(1.39)

If one assumes an analogous influence on the corresponding radicals, then the lone electron will be on a relatively positive or negative carbon atom, depending on the nature of the substituent. However, the reactivity of a vinyl radical and to a lesser extent the corresponding vinyl monomer partly depends on the ability of a substituent to delocalize the lone electron of the free radical by resonance. For example the benzene ring repels electron charge inductively but resonance stabilizes the resulting polystyryl radical[44]:



(1.40)

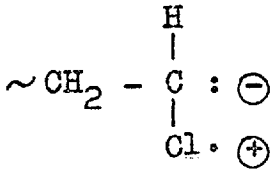
Acrylonitrile and methyl vinyl ketone have strong electron withdrawing groups which stabilize the resulting radicals but the resonance energies are smaller relative to the styrene radical[44]:



(1.41)

This phenomenon occurs in almost all vinyl monomers, even when there is no unsaturated group conjugated with the

ethylenic double bond, such as in vinyl chloride[44]:



(1.42)

The order of the reactivity of some vinyl monomer is[45]:

$$RCH_2- \langle RO- \langle -C \langle RO(O)C- \langle -CN \langle R(O)C- \langle CH_2=CH- \langle -C_6H_5 \quad (1.43)$$

$\longleftarrow$ decreasing reactivity

If the reaction of a peroxy radical with a vinyl monomer is the rate determining step, then the rate of oxidation of various vinyl monomers, carried out under identical conditions, should vary systematically with the monomer reactivities. The rates of oxygen uptake of some vinyl monomers have been measured in various media.

For water soluble vinyl monomers the oxidation rates and consequently their reactivities towards oxygen have been determined and decrease in the following order[30]:

$$CH_2=C(CH_3)CN \rangle CH_2=C(CH_3)C(O)CH_3 \rangle CH_2=CHC(O)CH_3 \rangle$$

$$CH_2=CHCN \rangle CH_2=CHC(O)NH_2 \rangle CH_2=CHC(O)OCH_3 \quad (1.44)$$

The rates of reaction of a number of undiluted vinyl monomers with oxygen initiated by AIBN gave the following order, in accordance with decreasing monomer reactivity[33].

$$CH_2=C(CH_3)CN \rangle CH_2=C(C_2H_5)CN \rangle CH_2=C(CH_3)C(O)CH_3 \rangle$$

$$CH_2=CHCN \rangle CH_2=CHC(O)CH_3 \quad (1.45)$$

A different method for determining the reactivities was employed by Mayo et al[46] who allowed oxygen to react with a mixture of two vinyl monomers and subsequently analysed the resulting terpolymer. Assuming that neither of the monomers reacts with a radical ending with a monomeric unit, the reactivity ratios can be defined as:

$$r_1 = \frac{\text{Rate constant for } M_1O_2\cdot + M_1}{\text{Rate constant for } M_1O_2\cdot + M_2} \qquad (1.46)$$

and,

$$r_2 = \frac{\text{Rate constant for } M_2O_2\cdot + M_2}{\text{Rate constant for } M_2O_2\cdot + M_1} \qquad (1.47)$$

The relative reactivitities of $CH_2=C(CH_3)C_6H_5$, $CH_2=CHC_6H_5$ and $CH_2=C(CH_3)C(O)OCH_3$, obtained from the above ratios, were 15:7:1 towards the α-methylstyrene peroxy radical, 17:8:1 towards the styrene peroxy radical and 24:13:1 towards the methyl methacrylate peroxy radical. The order of these monomer reactivities is in good agreement with that obtained from studies of the oxidation of some undiluted monomers under one atmosphere pressure of oxygen and with a constant concentration of AIBN (0.01 mol dm^{-3}) [46,47]. The reactivity of the monomers towards oxygen under such conditions decreases in the following order:

$$CH_2=C(CH_3)C_6H_5 > CH_2=CHC_6H_5 > C_6H_5CH=CHCH_3 > H_2C=C(C_6H_5)_2 > CH_2=CHCN > CH_2=C(CH_3)C(O)OCH_3 > CH_2=C(CH_3)C(O)OC_4H_9 > CH_2=CHOC(O)CH_3 > CH_2=CHC(O)OC_4H_9 \qquad (1.48)$$

The common assumption in all the studies described previously is that the reactivity of peroxy radicals is independent of the penultimate monomeric group. The

validity of this assumption was examined by Howard[48] who measured the absolute rate constants at 30°C for the following reactions using the rotating sector method:

$$-CH_2-\underset{R}{C}(X)OO\cdot + CH_2=\underset{R}{C}X \xrightarrow{k_p} -CH_2-\underset{R}{C}(X)OO\underset{R}{\overset{\cdot}{C}}X \qquad (1.49)$$

$$t\text{-}BuOO\cdot + CH_2=\underset{R}{C}X \xrightarrow{k_{t\text{-}BuOO\cdot}} t\text{-}BuOOCH_2\overset{\cdot}{\underset{R}{C}}X \qquad (1.50)$$

The propagation and termination rate constants were calculated from the kinetic expression for autoxidation assuming that only mutual termination by $RO_2\cdot$ radicals occurs:

$$-d[O_2]/dt = \frac{k_p[RH][R_i]^{0.5}}{[2k_t]^{0.5}} \qquad (1.51)$$

where R_i is the rate of initiation, k_p and k_t are the propagation and termination rate constants, respectively, and [RH] is the monomer concentration. Some of the results are given in table 2.

TABLE 2

Values of k_p and $2k_t$, kinetic rate constants defined in equations 1.49-1.51 at 30°C

Vinyl Compound	k_p / mol dm^{-3} s^{-1}	$2k_t \times 10^{-7}$ / mol dm^{-3} s^{-1}	$k_{t\text{-BuOO}}$ / mol dm^{-3} s^{-1}	$k_p/k_{t\text{-BuOO}}$
Vinyl acetate	-	-	0.002	1258
Isopropenyl acetate	0.2	0.16	0.01	20
Acrylonitrile	3.3	6	0.01	325
Methyl acrylate	0.6	1.7	0.02	30
Ethyl vinyl ether	2.74	2.7	0.04	68.5
Methyl methacrylate	1	0.8	0.08	12.5
Methacrylonitrile	4.5	0.9	0.094	4.8
Styrene	41	4.2	1.3	31
α-methylstyrene	10	0.06	2.5	20

From table 2, the reactivity of alkylperoxy radicals varies considerably with the nature of the penultimate unit. α-substituted secondary alkylperoxy radicals such as $\sim CH_2\text{-}CH(C_6H_5)OO\cdot$, when compared with the t-butyl peroxy radical, are more reactive towards addition to the same monomer, $CH_2{=}CHC_6H_5$. The reactivity of α-substituted tertiary alkylperoxy radicals such as $\sim CH_2\text{-}C(CH_3)(CN)OO\cdot$, although greater than that of the t-butyl peroxy radical, is less than the corresponding secondary peroxy radical, $\sim CH_2\text{-}CH(CN)OO\cdot$. However, the overall reactivity of the

secondary and tertiary radicals increases in the following order:

$$\sim CH\left(OC(O)CH_3\right)OO\cdot \rangle \sim CH(CN)OO\cdot \rangle \sim CH(OC_2H_5)OO\cdot \rangle$$

$$CH_3C_s(CN)OO\cdot \rangle \sim CH\left(C(O)OCH_3\right)OO\cdot \sim \backsim CH(C_6H_5)OO\cdot \rangle$$

$$CH_3C_s\left(OC(O)CH_3\right)OO\cdot \rangle CH_3C_t\left(C(O)OCH_3\right)OO\cdot \qquad (1.52)$$

CHAPTER 2

EFFECT OF OXYGEN ON THE BULK POLYMERIZATION OF ACRYLONITRILE

2.1. Experimental

2.1.A. Materials

(I) Acrylonitrile

Acrylonitrile (B.D.H.) was washed successively with dilute aqueous sulphuric acid (2% w/v), aqueous sodium carbonate (15% w/v) and distilled water. After drying first over anhydrous calcium chloride and then calcium hydride, it was distilled under vacuum into a flask fitted with a break seal. The flask was later sealed off after its contents had been frozen in liquid nitrogen and the monomer was stored in a refrigerator at -20°C until required.

(II) 2,2'-Azobisisobutironitrile (AIBN)

6 grams of AIBN (B.D.H.) was placed in a 500 cm^3 round bottomed flask and anhydrous diethyl ether (400 cm^3) was gradually added with continual shaking until a clear solution was formed. The flask was connected to a water pump and about half of the ether was pumped off and then was closed by a stopper, wrapped in aluminium foil and kept in a refrigerator overnight. After separating the precipitated AIBN by filtration, the above procedure was repeated and the AIBN was finally stored in a stoppered flask at -20°C until required. The purity of AIBN was

examined by determining its melting point (102°C).

(III) Propionitrile

Propionitrile (B.D.H.) was washed with dilute aqueous sulphuric acid and dilute sodium carbonate solutions, respectively. After drying over calcium hydride, it was distilled in vacuo into a flask which was subsequently sealed off after its contents had been frozen in liquid nitrogen.

(IV) Other reagents

All other reagents such as methanol 'AnalaR' (James Burrough Ltd.), glacial acetic acid 'AnalaR' (B.D.H.), potassium iodide 'AnalaR' (B.D.H.) and sodium thiosulphate 'AnalaR' (B.D.H.) were used as received without further purification.

2.2 Apparatus

2.2.A. Dilatometers

The dilatometers consisted of a thick walled (1.5 mm) pyrex tube joined to a length (about 20 cm) of capillary. Some of the dilatometers were equipped with 2 mm i.d. precision bore capillary for the polymerization rate measurements, while others were made with ordinary 3 mm bore capillary. All the dilatometers were cleaned scrupulously by chromic acid and then were washed several times with distilled water. In order to calibrate the dilatometers, the total volume, v, of a given dilatometer with a meniscus height about half way up the capillary was measured, using distilled water. If this volume, v,

is regarded as the final volume of the monomer at 50°C ($d=0.773$ g cm^{-3}) [49], the volume of the monomer at -76°C, V, ($d=0.911$ g cm^{-3}) can be calculated. Distilled water with a volume equal to the calculated volume, V, was transferred into the dilatometers and its height in the dilatometer bulb was carefully marked using a diamond pencil. Finally, all the dilatometers were dried in an oven at 120°C before further use.

2.2.B. Constant temperature water bath

This was a 30 cm pyrex bath efficiently stirred by a stirrer (Griffin and George KQPS). Constant temperature was maintained by a mercury thermometer (Gallenkamp JUNO), connected to an electric control relay. The temperature of this thermostat at 50°C varied by ± 0.02°C as measured by a previously calibrated thermometer (Sugden, Powell Ltd.).

2.2.C. Vacuum line

A glass vacuum line was constructed and combined with an oil vacuum pump (Edwards 'Speedivac', Model 2S C30) and a mercury diffusion pump. This arrangement proved to be capable of achieving an ultimate pressure of 10^{-6} torr or below as measured by a McLeod gauge. The diffusion pump was connected to an electrical cut-out (Laycock 'Truflo') which was triggered by any failure in the cooling system. High vacuum stopcocks (Springham Ltd.) were used and lubricated by either Apiezon N or silicone grease depending on whether or not the stopcock was in contact with volatile material.

2.2.D. Apparatus for monitoring oxygen

An apparatus, A, similar to that used by Boardman and Selwood[50] was prepared and its volume, V_1, enclosed by the stopcocks T_2, T_3, T_4 and T_5 was carefully determined several times, gravimetrically, using distilled water. The mean value of V_1 used in this study was 19.00(5) cm^3. The lower part of the apparatus was joined to a B10 cone, to connect to the dilatometers, and the upper part was attached to the vacuum line through taps T_2, T_4 and T_5 as shown in figure 1. A mercury manometer (2 mm i.d.) was joined to the apparatus A by means of tap T_4.

2.3 Method of adding oxygen to the monomer-initiator mixtures.

An appropriate amount of AIBN was transferred to the dilatometers as a solution in chloroform. The solvent was subsequently removed in vacuo at room temperature and the dilatometers, after being closed by greased B10 stoppers were wrapped in aluminium foil and stored in a refrigerator at -20°C until required. A 5 dm^3 pyrex bulb was connected to the vacuum line for storing oxygen at less than one atmosphere pressure.

The dilatometer containing AIBN was connected to the vacuum line and after complete evacuation (10^{-5} torr) the purified monomer from a flask fitted with a break seal was distilled in vacuo into the dilatometer cooled by a mixture of solid CO_2 and methylated spirits (-76°C). Monomer was added until the solution in the

dilatometer bulb at -76°C reached the calibration mark. The dilatometer contents were maintained at -76°C for five minutes to ensure that the monomer was at true thermal equilibrium. A final adjustment of the monomer volume at -76°C was made by distillation from or distillation to the dilatometer bulb. Eventually, with the stopcocks T_2, T_3 and T_7 closed and T_4, T_5 and T_6 open, the apparatus was evacuated through T_8. The height of the mercury meniscus in the manometer was recorded using a cathetometer (h_1). Stopcocks T_2, T_3, T_4 and T_8 were closed and T_5 and T_6 were opened and oxygen was admitted through T_7 into the calibrated apparatus A and its pressure was recorded by means of the manometer (h_2). After closing stopcock T_5, oxygen was allowed to come in contact with acrylonitrile at -76°C by opening T_3. Finally, the dilatometer was immersed in liquid nitrogen and sealed off while stopcock T_3 was closed. Each dilatometer was stored in liquid nitrogen until required. It was found possible to control the initial concentrations of oxygen in the monomer, approximately, by varying the immersion times of dilatometers in liquid nitrogen. After sealing off the dilatometer, the part of apparatus A below tap T_3 was allowed to cool to room temperature. With T_2, T_3, T_4, T_5 and T_7 closed and T_6 and T_8 open, the apparatus was evacuated and the meniscus height was recorded (h_3). Stopcock T_6 was then closed and T_4 and T_3 were opened. The remaining oxygen was expanded into a final volume, V_2, and the height of the mercury meniscus was measured (h_4). The volume of oxygen and consequently

its initial concentration in the dilatometer contents can be determined once the final volume V_2 is known. Assuming that oxygen is an ideal gas and the ideal gas equation, $PV = nRT$, is applicable, V_2 can be determined by allowing a known volume of oxygen (P'_1, V_1) in the calibrated bulb A to expand into the unknown volume (P'_2, V_2), where P'_1 and P'_2 are the appropriate pressures measured using the mercury manometer.

The calculation involving the initial oxygen concentration measurement for dilatometer 3, batch 1, is given as an example.

$$P'_1 = h'_1 - h'_2 = 45.239 - 2.140 = 43.099 \text{ cm Hg}$$

$$P'_2 = h'_3 - h'_4 = 45.230 - 12.937 = 32.293 \text{ cm Hg}$$

where h'_1, h'_2, h'_3 and h'_4 are the respective meniscus heights. Therefore,

$$V_2 = P'V_1/P'_2 = (43.099 \times 19.005)/32.293 = 25.364 \text{ cm}^3$$

Since the mercury meniscus height in the calibration experiment is lower than that of the original experiment, the difference in volume should be substracted from the value obtained for V_2. Thus,

$$V_2 = 25.364 - (h_4 - h'_4)\pi r^2 = 25.364 - (29.539 - 12.937)3.14 \times 0.01$$

$$= 24.842 \text{ cm}^3$$

where r is the radius of the manometer (0.1 cm). The same calculation was once more repeated ($V'_2 = 24.846 \text{ cm}^3$) and a mean value of $V_2 = 24.844 \text{ cm}^3$ was obtained. To calculate the number of moles of oxygen, n, one can write

$P_1 = h_1 - h_2/76 = (45.234 - 20.315)/76 = 0.328$ atm.

and

$P_2 = h_3 - h_4/76 = (45.231 - 29.539)76 = 0.206$ atm.

where P_1 and P_2 are pressures of oxygen in the actual experiment. Hence,

$n = P_2V_2/RT_2 - P_1V_1/RT_1 = 4.56 \ 10^{-5}$ moles of oxygen.

Since the monomer weight in the dilatometer is 3.76 g, the initial concentration of oxygen, assuming that all the oxygen is dissolved in the monomer is 387.6 ppm w/w.

The contents of each sealed-off dilatometer were allowed to melt and oxygen remaining in the capillary was introduced into the bulb by inverting and shaking the dilatometer until acrylonitrile filled the capillary. The dilatometer was then immersed in the thermostat at $50 \pm 0.02^{\circ}C$.

Because of the lack of stirring, it was found necessary to rotate the dilatometer at an angle of about 45° with respect to the water surface[28]. Rotation throughout the induction period was maintained at an approximate speed of 30 rpm. The main difficulty in this technique is that oxygen in the bulb does not penetrate far enough into the capillary tube. Consequently, due to the depletion of oxygen, the monomer in the capillary starts to polymerize. The precipitated polymer in the capillary tube then enters the dilatometer bulb and the end of the induction period cannot be measured accurately. This difficulty was overcome by taking the dilatometer out of the water bath at intervals of 15-20

minutes and reintroducing the oxygen bubble into the capillary. This procedure added another source of error, so that except for the polymerization rate measurements, dilatometers were equipped with wider (3 mm) bore capillaries. In the latter case, an oxygen bubble was introduced into the capillary by temporarily stopping rotation of the dilatometer when it was approximately in a vertical position and tapping the clamp holding the dilatometer.

At the end of the induction period the dilatometers used for rate measurements were first quenched in liquid nitrogen in an upright position and subsequently they were immersed in the thermostat, at 50 ± 0.02°C, in a fixed vertical position. The decrease in the meniscus height in the capillary was measured using a cathetometer. The % conversion was calculated from the following equation:

$$\frac{(\ell_o - \ell_t)v \times 100}{V_m(1 - d_m/d_p)} \qquad (2.1)$$

where, ℓ_o is the height of the monomer meniscus after attaining thermal equilibrium (cm), ℓ_t is the height (cm) at time t (min), v is volume of unit length of the capillary (0.0314 cm^3), V_m is the initial volume of the monomer (cm^3), d_m is the density of the monomer at 50°C (0.773 g cm^{-3}) and d_p is the density of polyacrylonitrile at 50°C (1.176 g cm^{-3}).

2.4 Preparation of the polymeric peroxide of acrylonitrile

About 300 cm^3 acrylonitrile was purified as described earlier and then transferred into a double-necked round bottomed flask. Medical grade oxygen was bubbled through the solution for about five minutes using a long

condenser on the other neck (figure 2). An appropriate amount of AIBN was quickly added to give a final concentration of about 0.05 mol dm^{-3}. The flask was immersed in a water bath at 50°C for a period of five hours during which time stirring was maintained by means of a magnetic follower. No polymerization occurred throughout the reaction and the solution gradually turned yellow. At the end of the reaction time approximately 300 cm^3 petroleum ether (b.p. 80-100°C) was added to the solution. The polyperoxide slowly precipitated as a highly viscous yellowish oil which was separated by decanting the supernatant liquid. After two more washings with petroleum ether followed by decantation, the petroleum ether remaining in the flask was completely removed by vacuum distillation at room temperature. A solubility test on the polyperoxide prepared under the conditions described above was carried out by examining several solvents such as chloroform, dioxan, tetrahydrofuran, dimethylformamide propionitrile, acetonitrile and acetone. The polyperoxide was found to be soluble only in dimethylformamide, propionitrile and acetonitrile. This result is not in complete agreement with the finding of Smeltz and Dyer[16], who reported acetone, dioxan and dimethylformamide as solvents for a polyperoxide sample obtained from an aqueous system. The insolubility of the sample prepared in bulk, in acetone and dioxan, could be due to its relatively higher molecular weight ($\bar{M}_n$ = 595) compared with that prepared in an aqueous system ($\bar{M}_n$ = 177). Another possible explanation for the insolubility of the bulk sample is the insufficient

number of polar end groups such as -OH and -OOH. Owing to the hazardous nature of the side products, HCN and HCHO, all gases evolved from the reaction flask were passed through an aqueous NaOH solution. Furthermore, the whole experiment was carried out in a fume cupboard. In further experiments it was observed that the polymeric peroxide initiated the free radical polymerization of acrylonitrile.

2.5 Estimation of 'available' oxygen of acrylonitrile polymeric peroxide.

In order to estimate the number of peroxide bonds, ~~(~~O–O~~)~~, and consequently the 'available' oxygen two methods, I and II, were examined[51].

I. This method has been applied to relatively unstable peroxides and involves treating a peroxidic sample with a solution of potassium iodide (0.5g) in methanol (10 cm^3) and glacial acetic acid (25 cm^3) followed by refluxing the solution for 10 minutes at the boiling point of the mixture.

II. This method has been developed for extremely stable peroxides such as dicumyl peroxide and involves adding a mixture of KI (3 g), glacial acetic acid (50 cm^3) and 2 cm^3 35% HCl solution to a peroxide sample and refluxing it for 30 minutes at 120°C. Except for very stable peroxides, both methods have proved to be effective for a great variety of peroxides.

2.5.A. Experimental

The polymeric peroxide was prepared in the manner described earlier using AIBN. At the end of the polyperoxide preparative reaction, the solution containing acrylonitrile polyperoxide was divided into some flasks and the polyperoxide in each flask was precipitated and carefully weighed. Some of the polyperoxide samples were analysed by applying method I and the rest were analysed by method II. Air in all the flasks were excluded by purging with nitrogen for two minutes prior to refluxing. The liberated iodine, after the solution had cooled and adequate volume of distilled water ($\sim 150\ cm^3$) had been added, was titrated against $Na_2S_2O_3$ using starch as an indicator. The % active oxygen (w/w) for a series of samples determined by method I and II are presented in table 3.

If the polyperoxide had the alternating structure, $\{CH_2-\underset{CN}{CH}-OO\}_n$, and was of such a high molecular weight ($\bar{M}_n \to \infty$) so that the end group could be neglected, then % oxygen expected would be: % O = 32/85 x 100 = 37.6 %.

Clearly the actual % oxygen values in table 3 are extremely low. However, the polyperoxide examined is of very low molecular weight ($\bar{M}_n$ = 595). Nevertheless, the existence of end groups can only play a very insignificant part in reducing the % active oxygen. For example, if the structure was $(CH_3)_2\underset{CN}{C}-O\{O-CH_2-\underset{CN}{CH}-O\}_n O-\underset{CN}{C}(CH_3)_2$ with n equal to 5 having a molecular weight of 593, the % active oxygen would be 32.4%.

The low oxygen content for acrylonitrile polyperoxide is mostly due to the heat liberated by the reaction which decomposes a large proportion of the polyperoxide. During the reaction, even when the flask containing polyperoxide was kept at 0°C and the reagents were added dropwise, a white gas was evolved from the reaction flask. The white gas, after being dissolved in ethanol, was analysed by the MPD instrument and found to be CO_2, HCN and HCHO.

2.6 % Conversion of oxygen to the acrylonitrile polymeric peroxide.

Dilatometers containing various concentrations of AIBN and initial oxygen were prepared and placed in a thermostat at 50°C. At the end of induction period, the dilatometer contents were transferred to a flask and acrylonitrile was removed in vacuo at room temperature. The polyperoxide was reduced by method I described earlier and the liberated iodine was titrated against $Na_2S_2O_3$ solution (table 4).

The amounts of gaseous oxygen added were very small and so were the maximum amounts of active oxygen in the polyperoxide. The % conversion of oxygen should therefore be approximately correct since the thermal effects would be negligible.

2.7 Determination of k_d for the decomposition of the polyperoxide of acrylonitrile at 50°C.

The polymeric peroxide (approximately 2 g) was dissolved in 100 cm^3 propionitrile. The solution was

then split into equal volumes and each was transferred into a dilatometer. After twice degassing, the contents of the dilatometers were frozen and dilatometers were sealed off. Eventually, the dilatometers were wrapped in aluminium foil, placed in a thermostat at 50 ± 0.02°C and the polyperoxide remaining in the solution was determined iodometrically at intervals of time using method I. k_d and half life values of $(2.49 \pm 0.69) \times 10^{-5}$ s^{-1} and 464 minutes respectively, were calculated from the logarithmic plot of the N/10 $Na_2S_2O_3$ volume vs. time.

2.8 IR spectrum of the polymeric peroxide of acrylonitrile.

The IR spectrum of the polyperoxide, after several washings with chloroform and removal of the residual chloroform in vacuum, was recorded using a Perkin-Elmer model 157 G grating spectrophotometer (figure 3). The absorption bands in the region 3450, 3000, 2250, 1710, 1620 and 890 cm^{-1} were assigned to the presence of $-OH$, $-CH$, $-C \equiv N$, $-\overset{O}{\overset{\|}{C}}-$, $-C=C-$ and $-O-O-$ groups, respectively.

2.9 Determination of the molecular weight of acrylonitrile polyperoxide by vapour pressure osmometry.

In the thermoelectric determination of molecular weights, a drop of a solution of concentration C and a drop of solvent are suspended in an atmosphere saturated with solvent vapour. The temperature difference between the two drops, caused by the lowering of vapour pressure of the solution, is measured in terms of a resistance

change, ΔR, and has the following relationship with the solution concentration,

$$\Delta R = a_1 C + a_2 C^2 + a_3 C^3 + \ldots \qquad (2.2)$$

where a_1, a_2 and a_3 are constants for a given solute-solvent system. ΔR is the change in the thermistor resistance in replacing solvent by solution and a_1 can be expressed as $k/\bar{M}_n$ where k is a calibration constant and $\bar{M}_n$ is the number average molecular weight. At low concentrations $a_3 C^2$ is negligible so that,

$$\Delta R/C = \frac{k}{\bar{M}_n} + a_2 C \qquad (2.3)$$

To determine the molecular weight of an unknown compound the apparatus should be calibrated by low molecular weight standards such as benzil, glucose and methyl stearate. The calibration constant k can be obtained by plotting $(\Delta R/C)$ against C and extrapolating to $C = 0$ to give an intercept of $(k/\bar{M}_n)$, where C is the solute concentration. Once the calibration constant was calculated at a certain temperature, the molecular weight of the unknown can be determined by calculating $(\Delta R/C)_{C=0}$ for the unknown at the same temperature. This technique is particularly suitable for the low molecular weight compounds with relative molecular weights of $50\text{-}25 \times 10^3$. The advantages of this method for molecular weight measurement are its speed and small sample requirement.

2.9.A. Experimental

The molecular weight of the polymeric peroxide was determined using a Dampfdruck Osmometer (Herbert Knaur and Co. GmbH.). The apparatus was calibrated using

benzil in propionitrile at 37°C (figure 5.A). AIBN may contaminate the polyperoxide sample during its preparation, because both are insoluble in petroleum ether. AIBN was therefore removed by several washings of the polyperoxide with chloroform. After evaporating residual chloroform under vacuum, the sample was dissolved in propionitrile and dilute solutions were prepared. The vapour pressure lowering of the solution, in terms of resistance, was measured by applying two droplets of the solvent and solution to the matched thermistors. The experimental constant for the polyperoxide was determined by extrapolating (Δ R/C) vs. C (figure 5.B). A molecular weight of 595 g mol^{-1} was obtained by this method. Assuming an alternating copolymer of acrylonitrile and oxygen, this molecular weight corresponds to about five units of $\left\{CH_2-\underset{CN}{CH}-O-O\right\}$. This molecular weight might be slightly high since some low molecular weight polymeric peroxide could have been lost during precipitation in petroleum ether.

2.10 Results

The induction period results obtained from the dilatometric work together with the polymerization rate measurements for some of the dilatometers are presented in table 5. Logarithmic plots of the induction periods against the initial oxygen concentrations are illustrated in figures 6-10. The slopes of the lines in all the graphs were calculated by the least mean squares method (table 6). In order to determine the dependence of the induction period on the concentration of the initiator, the induction periods at various constant initial oxygen concentrations were calculated from the logarithmic plots of induction period against initial oxygen concentration. These values were then plotted logarithmically against the concentration of the initiator (figures 11.A - 11.D) and the slopes were also determined by the least mean squares method (table 7). The rates of polymerization for some of the dilatometers, at a constant conversion of 0.5%, were measured and their dependence on the initial oxygen concentration is shown in figure 12.

There are relatively high experimental errors involved in the determination of both induction periods and polymerization rates. Dilatometers were filled with monomer at -76°C to a fixed mark on the dilatometer bulbs. The final true monomer volume at 50°C differed by ± 3% from the predicted volumes, after allowing for expansion due to temperature rise. Owing to this variation in monomer volume, constant initiator concentrations were reproducible with an error of about ± 3%. There are,

of course, other sources of error. For example, during the operation involving the introduction of the initiator dissolved in chloroform into a dilatometer, some AIBN particles were sometimes lost when the last traces of the solvent were being distilled off.

TABLE 3. Oxygen content of the acrylonitrile polymeric peroxide

Sample	Weight/g	Method	N/5 $Na_2S_2O_3/cm^3$	% O available
A	5.51	1	69.5	4.04
B	4.87	1	31.7	2.08
C	6.05	1	43.0	2.27
D	3.13	1	21.7	2.22
E	1.50	1	14.2	3.03
F	4.50	2	27.3	1.94
G	7.50	1	42.8	1.82
H	1.74	2	23.0	4.23

TABLE 4. % Conversion of oxygen to the acrylonitrile polyperoxide

Dilatometer	10^3 AIBN conc./ mol dm^{-3}	Gaseous oxygen added/mg	% Conversion
A_1	1	11.29	8.0
A_2	1	14.06	25.9
A_3	1	10.34	10.2
B_1	2	12.21	10.2
B_2	2	11.87	13.2
C_1	3	10.14	7.2
C_2	3	9.60	9.2
D_1	4	12.10	7.0
D_2	4	12.17	9.2

TABLE 5. Dilatometric data for the polymerization of acrylonitrile at 50°C in the presence of AIBN and oxygen.

Batch	Dilato-meter	10^3x[I]/ mol dm^{-3}	$[O_2^0]$/ppm w/w	IP/min	(R_p at 0.5% conv.)/% min^{-1}
I	1	1	194	57	-
I	2	1	222	70	-
I	3	1	388	93	-
I	4	1	283	82	-
I	5	1	139	62	-
I	6	1	792	160	-
I	7	1	95	43	-
I	8	1	609	123	-
I	9	1	459	91	-
I	10	1	407	120	-
I	11	1	633	163	-
I	12	1	751	183	-
I	13	1	847	234	-
II	1	2	199	69	0.082
II	2	2	283	80	0.080
II	3	2	287	71	0.077
II	4	2	482	107	0.071
II	5	2	435	84	-
II	6	2	160	45	0.079
II	7	2	104	25	0.084
II	8	2	147	52	0.072
II	9	2	94	32	0.073
II	10	2	442	89	0.072
II	11	2	0	2	0.080

Continued.

TABLE 5 (Page 2)

Batch	Dilato-meter	10^3x[I]/ mol dm^{-3}	$[O_2^o]$/ppm w/w	IP/min	(R_p at 0.5% conv.)/% min^{-1}
III	1	2	143	40	-
III	2	2	167	53	-
III	3	2	313	62	-
III	4	2	382	63	-
III	5	2	452	70	-
III	6	2	455	88	-
III	7	2	1127	159	-
IV	1	2	130	44	-
IV	2	2	200	57	0.074
IV	3	2	288	62	-
IV	4	2	422	72	0.068
IV	5	2	651	100	0.07
IV	6	2	1190	187	0.085
IV	7	2	1351	215	0.078
V	1	3	987	121	-
V	2	3	326	47	-
V	3	3	402	57	-
V	4	3	233	41	-
V	5	3	183	32	-
V	6	3	578	76	-
V	7	3	870	109	-
V	8	3	422	59	-
VI	1	4	475	72	0.119
VI	2	4	701	103	0.14

Continued

TABLE 5 (Page 3)

Batch	Dilato-meter	10^3x[I]/ mol dm^{-3}	$[O_2^o]$/ppm w/w	IP/min	(R_p at 0.5% conv.)/% min^{-1}
VI	3	4	306	57	0.108
VI	4	4	278	61	0.107
VI	5	4	518	76	0.122
VI	6	4	315	43	0.106
VI	7	4	293	40	0.111
VI	8	4	271	38	0.110
VI	9	4	134	27	0.117
VI	10	4	0	2	0.111
VII	1	4	264	39	-
VII	2	4	129	20	-
VII	3	4	254	34	-
VII	4	4	762	81	-
VII	5	4	330	40	-
VII	6	4	862	96	-
VII	7	4	410	46	-
VII	8	4	958	106	-

In the above table [I], $[O_2^o]$, IP and R_p represent the initiator concentration, the initial oxygen concentration, induction period and rate of polymerization, respectively.

TABLE 6. Dependence of induction period on initial oxygen concentration.

Batch	(10^3 x AIBN Conc.)/ mol dm^{-3}	Slope	95% Confidence limit
I	1	0.69	± 0.14
IV	2	0.67	± 0.17
II, III and IV	2	0.66	± 0.09
V	3	0.78	± 0.08
VI and VII	4	0.74	± 0.15

TABLE 7. Dependence of induction period on AIBN concentration.

(Initial oxygen conc.)/ ppm w/w	Slope	70% Confidence limit
126	-0.57	± 0.17
224	-0.54	± 0.13
447	-0.50	± 0.09
794	-0.47	± 0.05

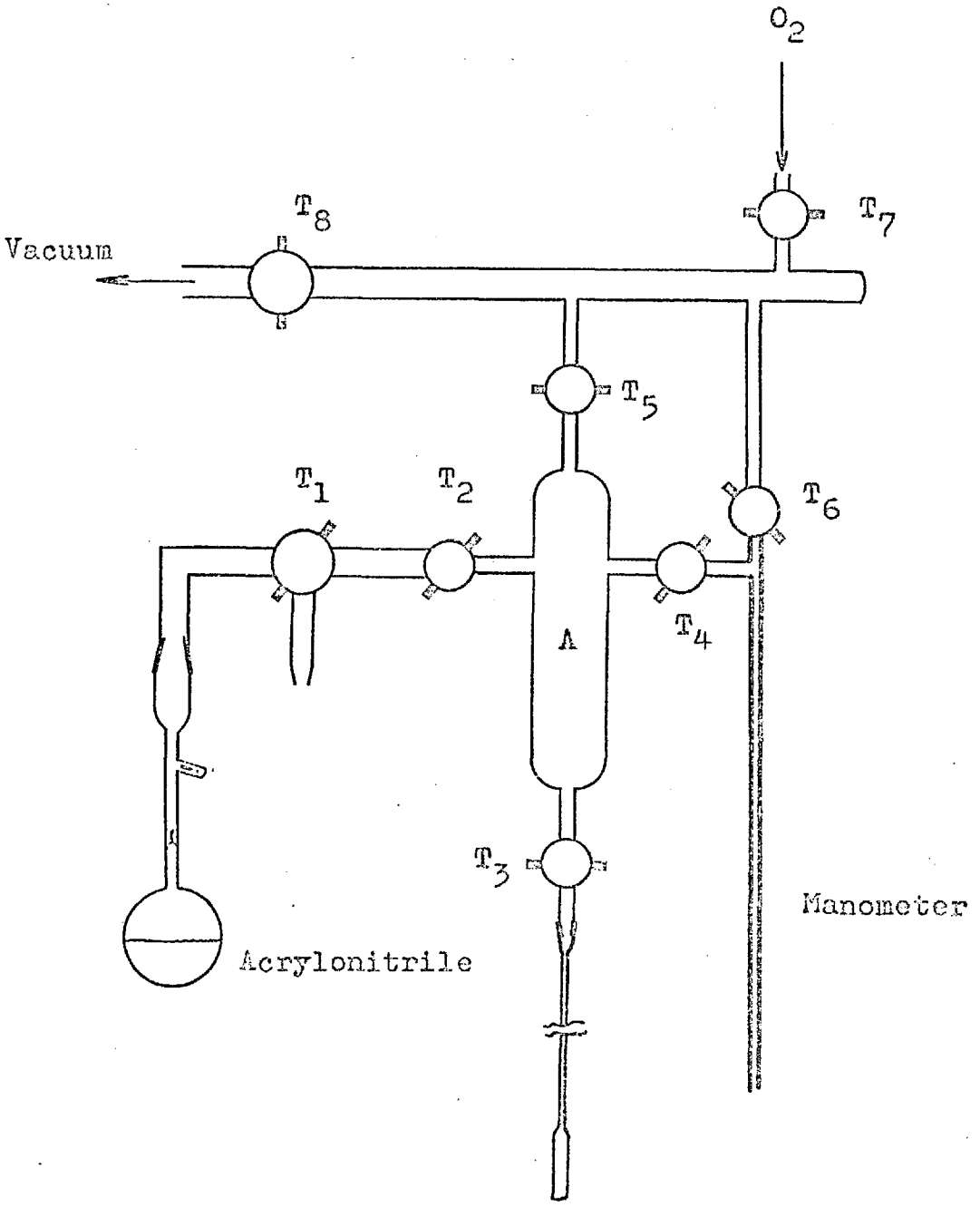


Fig. 1. Apparatus for monitoring oxygen.

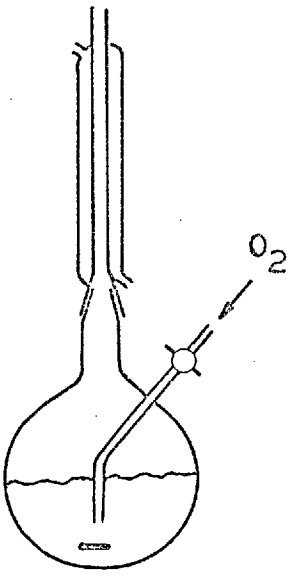


Fig. 2. Apparatus for preparation of the acrylonitrile polymeric peroxide.

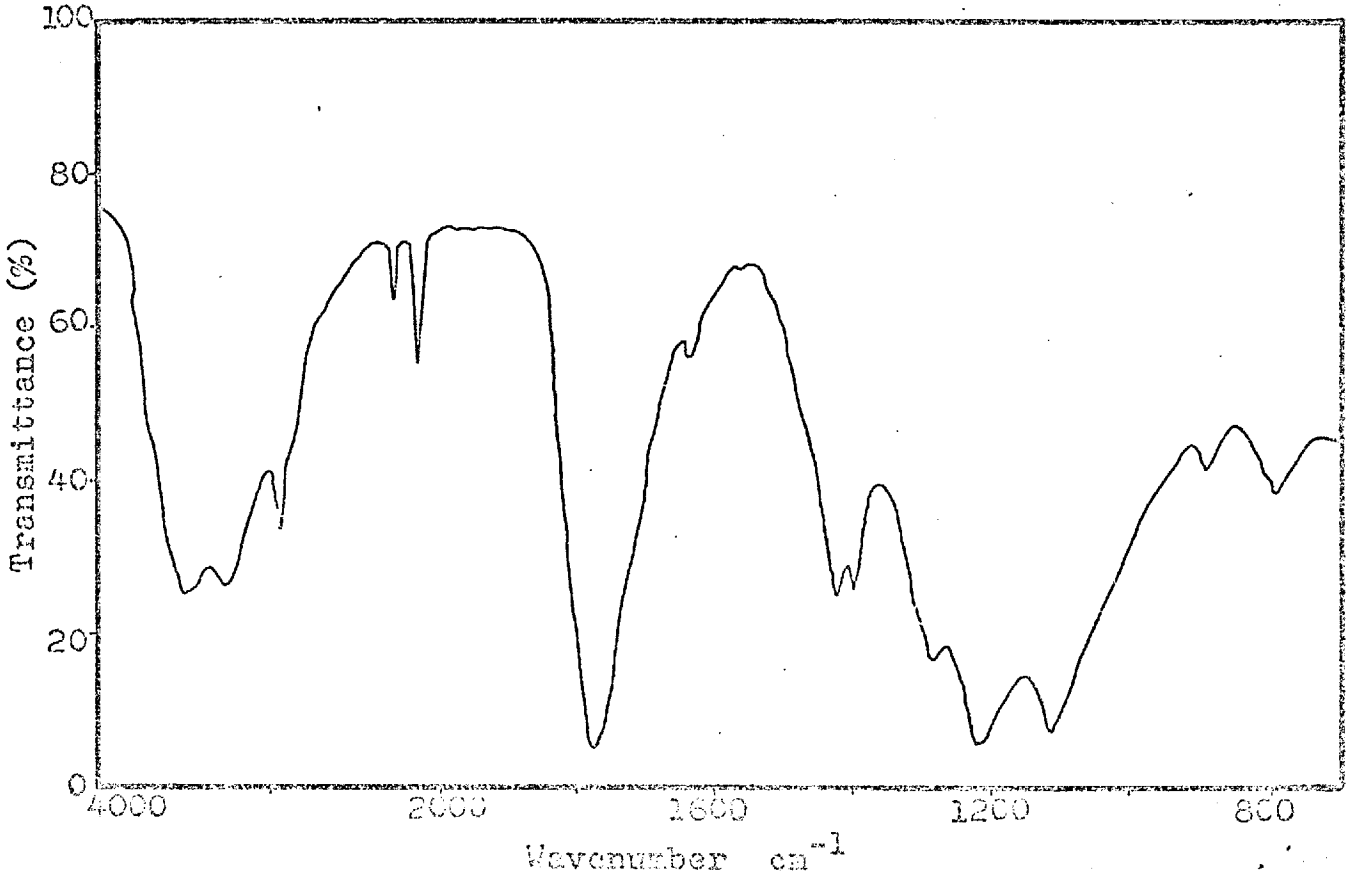


Fig. 3. IR spectrum of acrylonitrile polymeric peroxide.

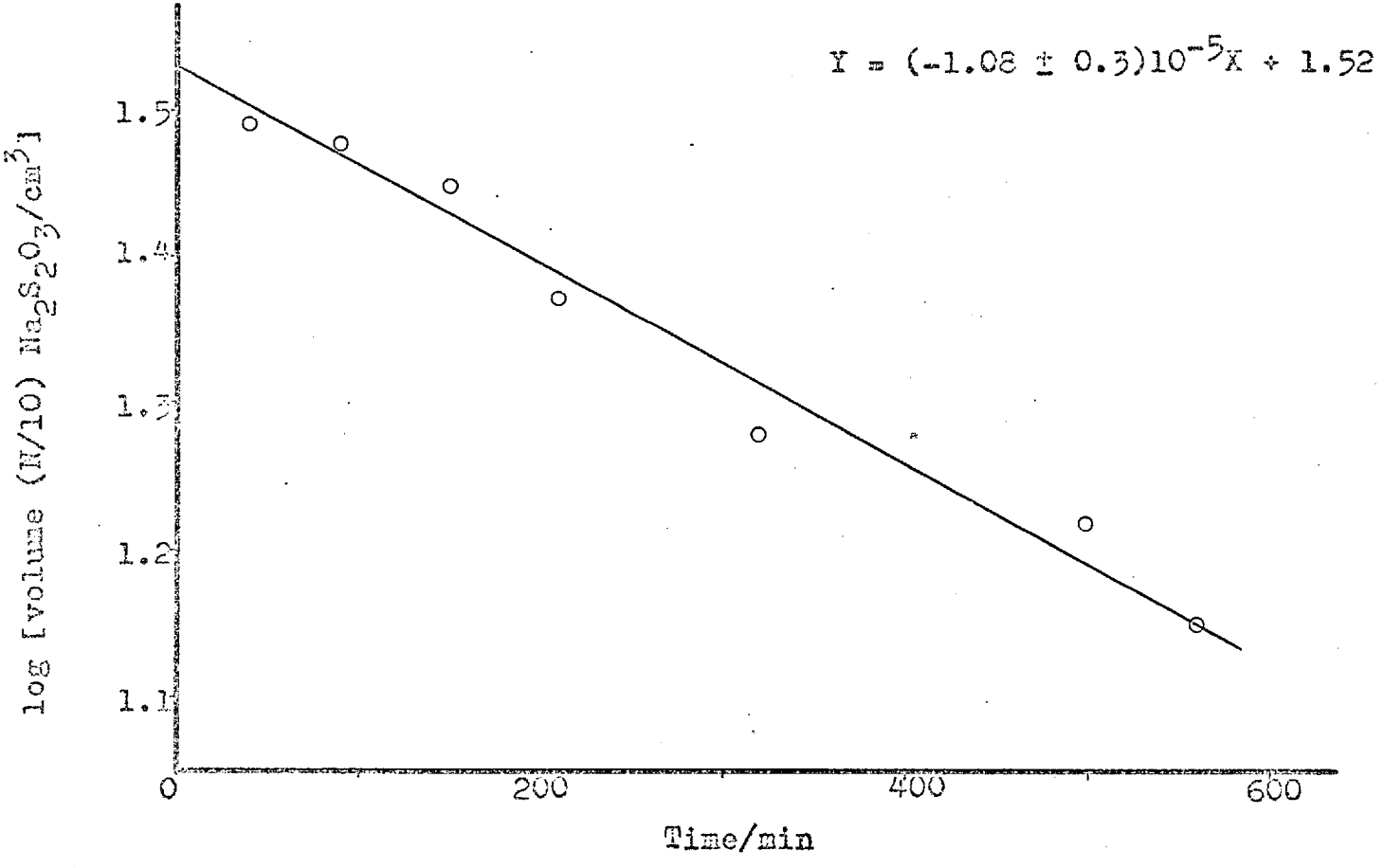


Fig. 4. Decomposition of acrylonitrile polymeric peroxide in propionitrile at 50°C.

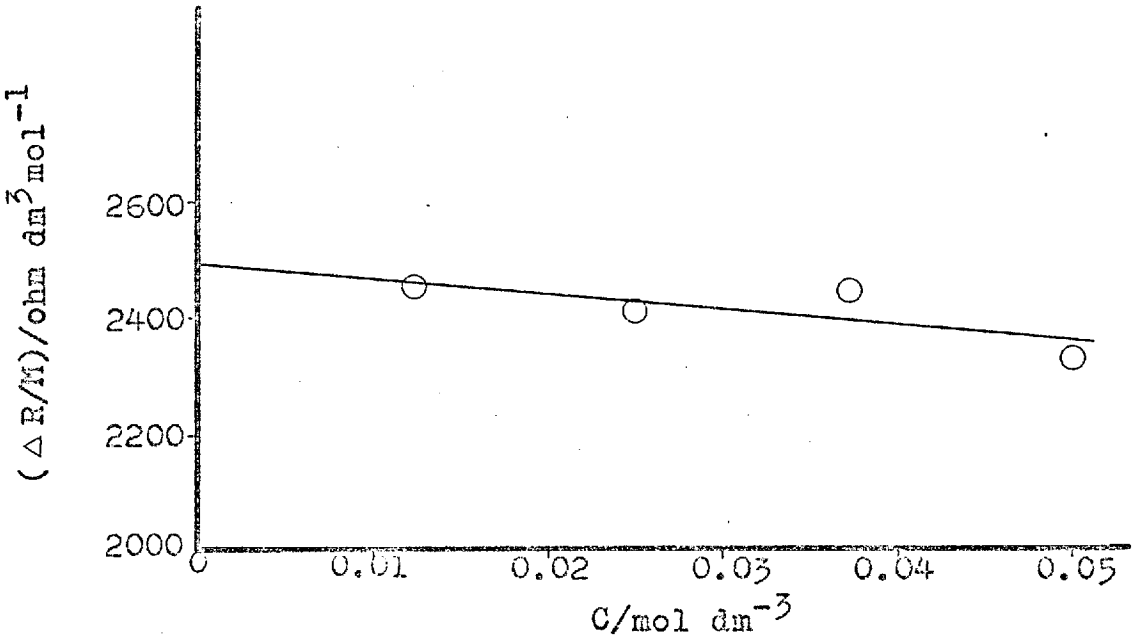


Fig. 5.A. Calibration of vapour pressure osmometer using propionitrile at 37°C.

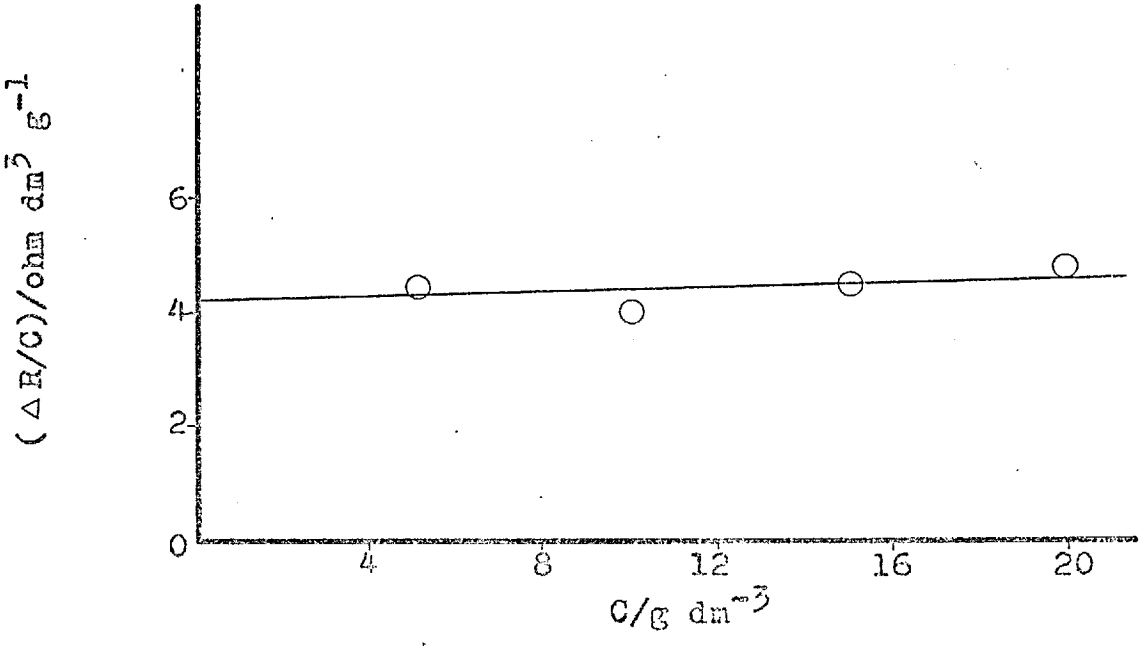


Fig. 5.B. Vapour pressure osmometry results for the polyperoxide in propionitrile at 37°C.

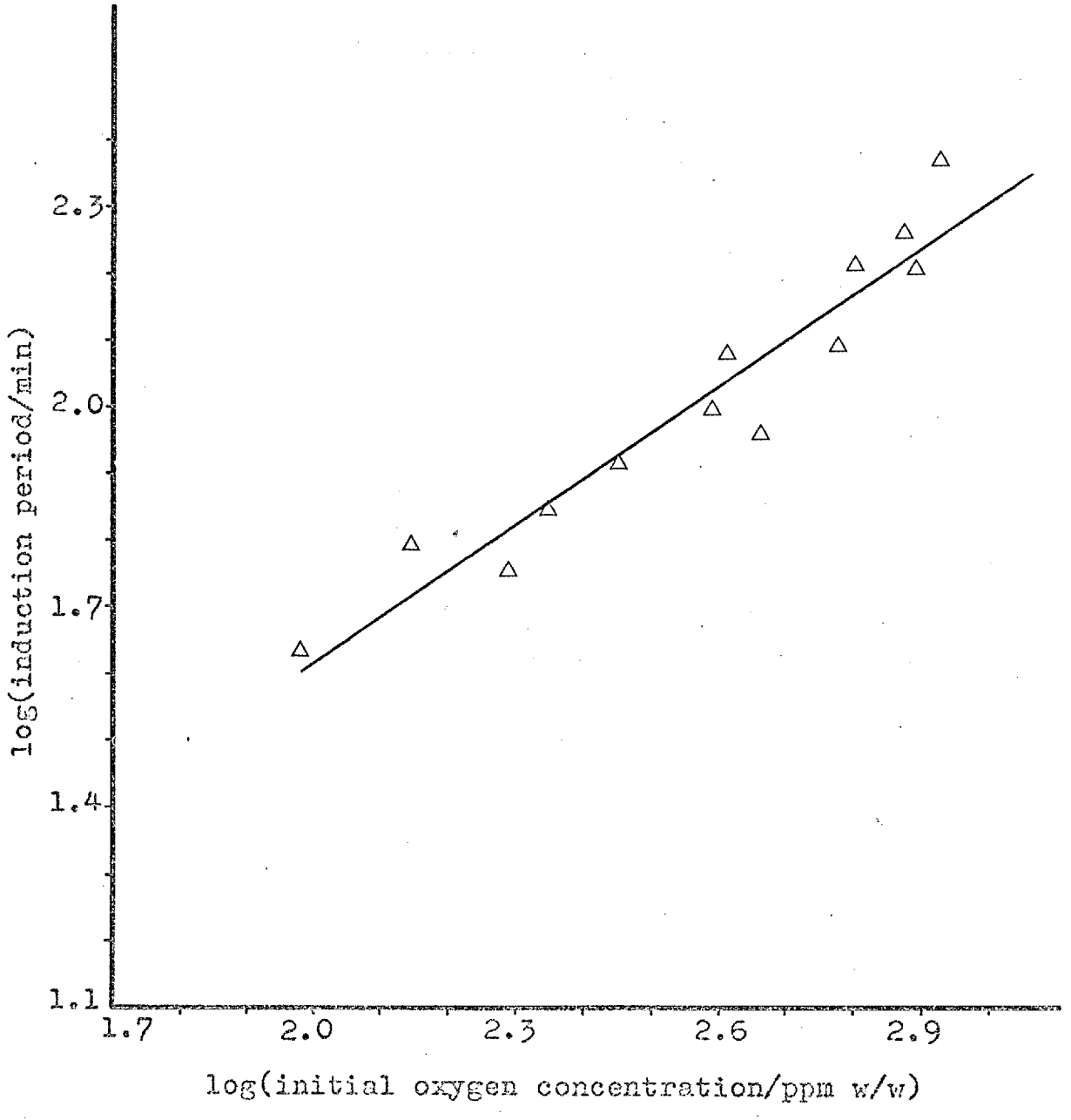


Fig. 6. log(induction period) vs. log(initial oxygen concentration) at 50°C at a constant AIBN concentration of 10^{-3} mol dm^{-3}, batch I.

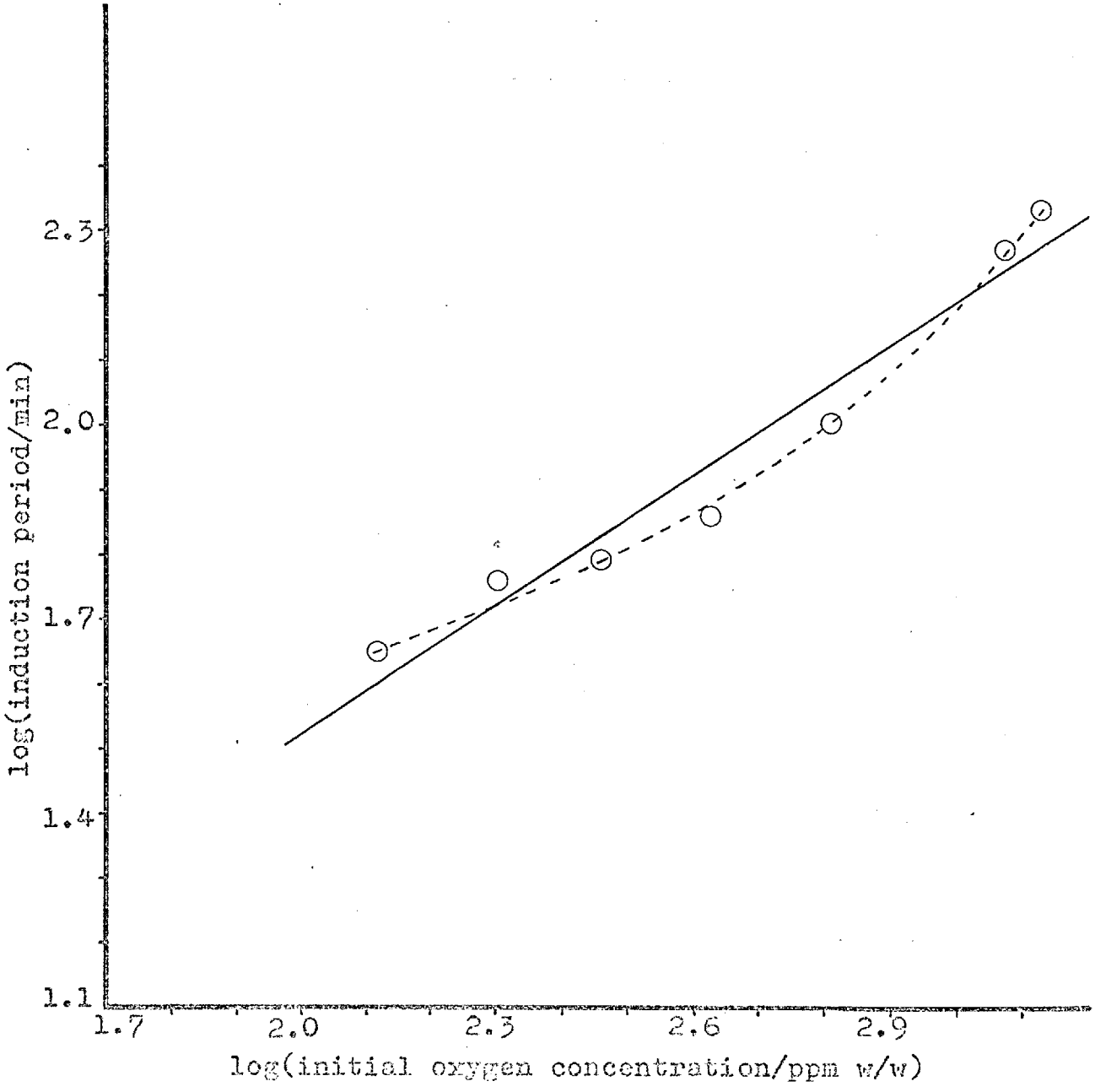


Fig. 7. log(induction period) vs. log (initial oxygen concentration) at 50°C at a constant AIBN concentration of 2×10^{-3} mol dm^{-3}, batch IV.

(—) The best line calculated by the least mean squares method.

(– –) Possible curve due to different termination reactions.

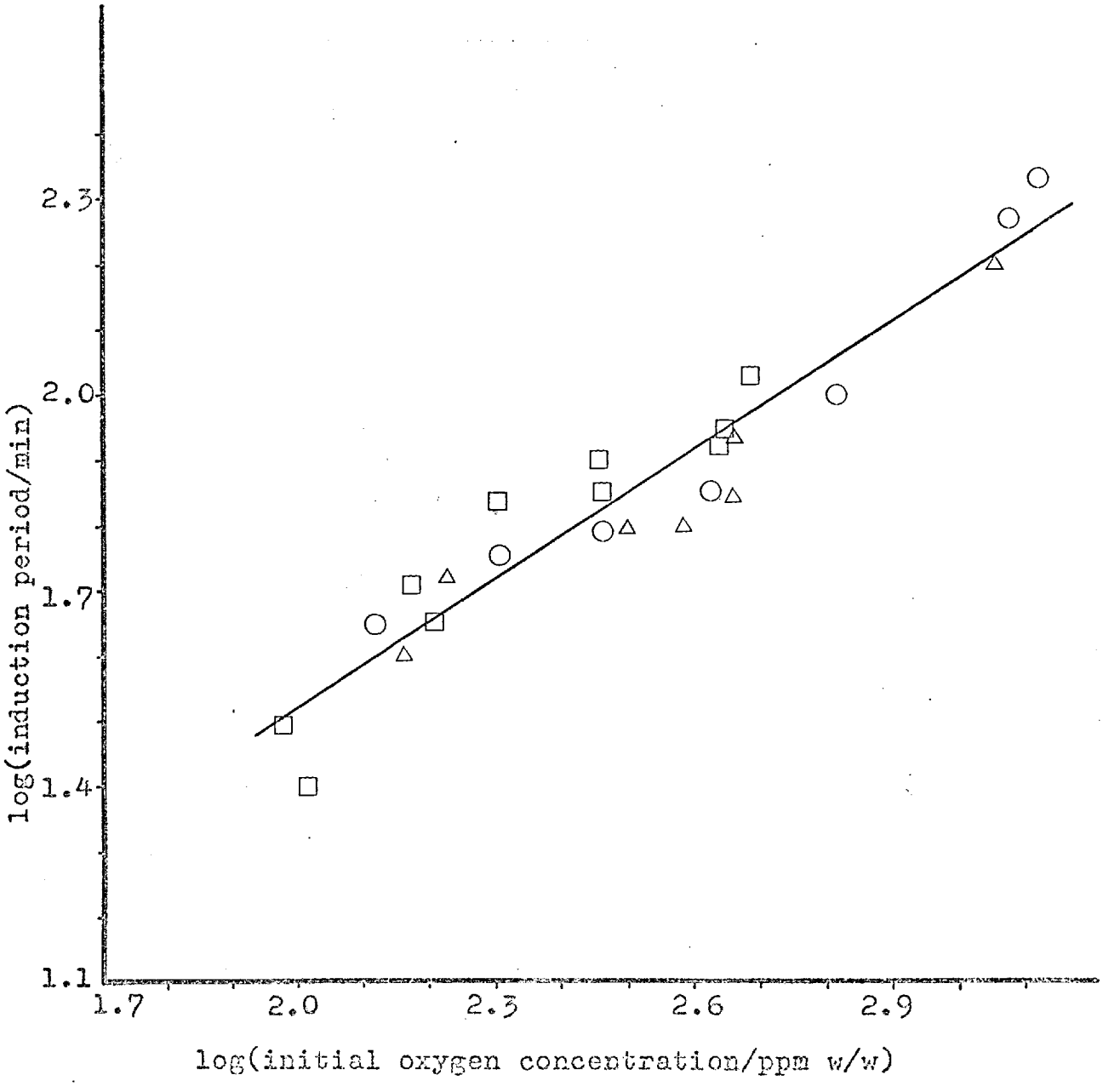


Fig. 8. log(induction period) vs. log(initial oxygen concentration) at 50°C at a constant AIBN concentration of 2×10^{-3} mol dm^{-3}, (□) batch II, (△) batch III and (○) batch IV.

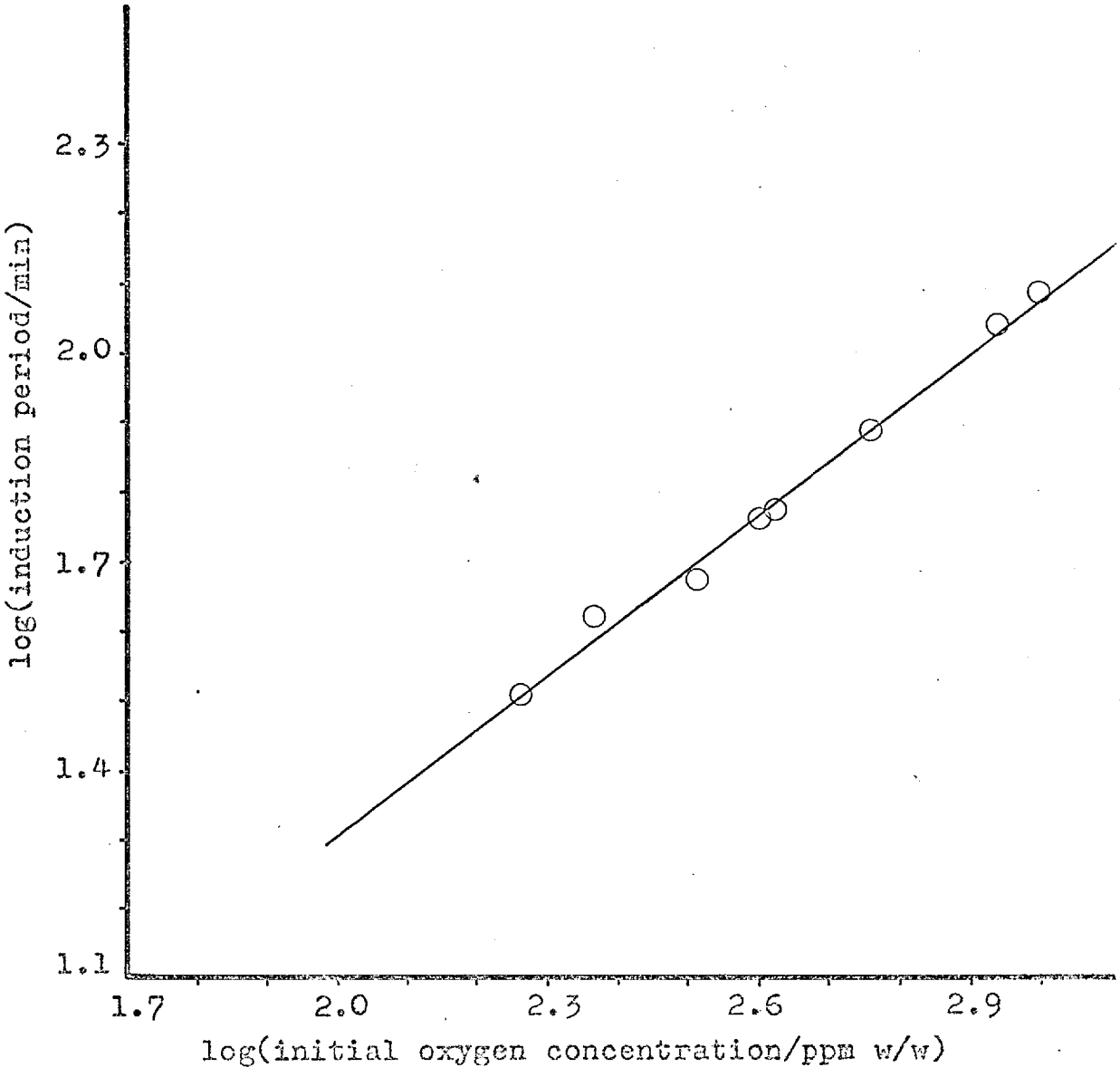


Fig. 9. log(induction period) vs. log (initial oxygen concentration) at 50°C at a constant AIBN concentration of 3×10^{-3} mol dm^{-3}, batch V.

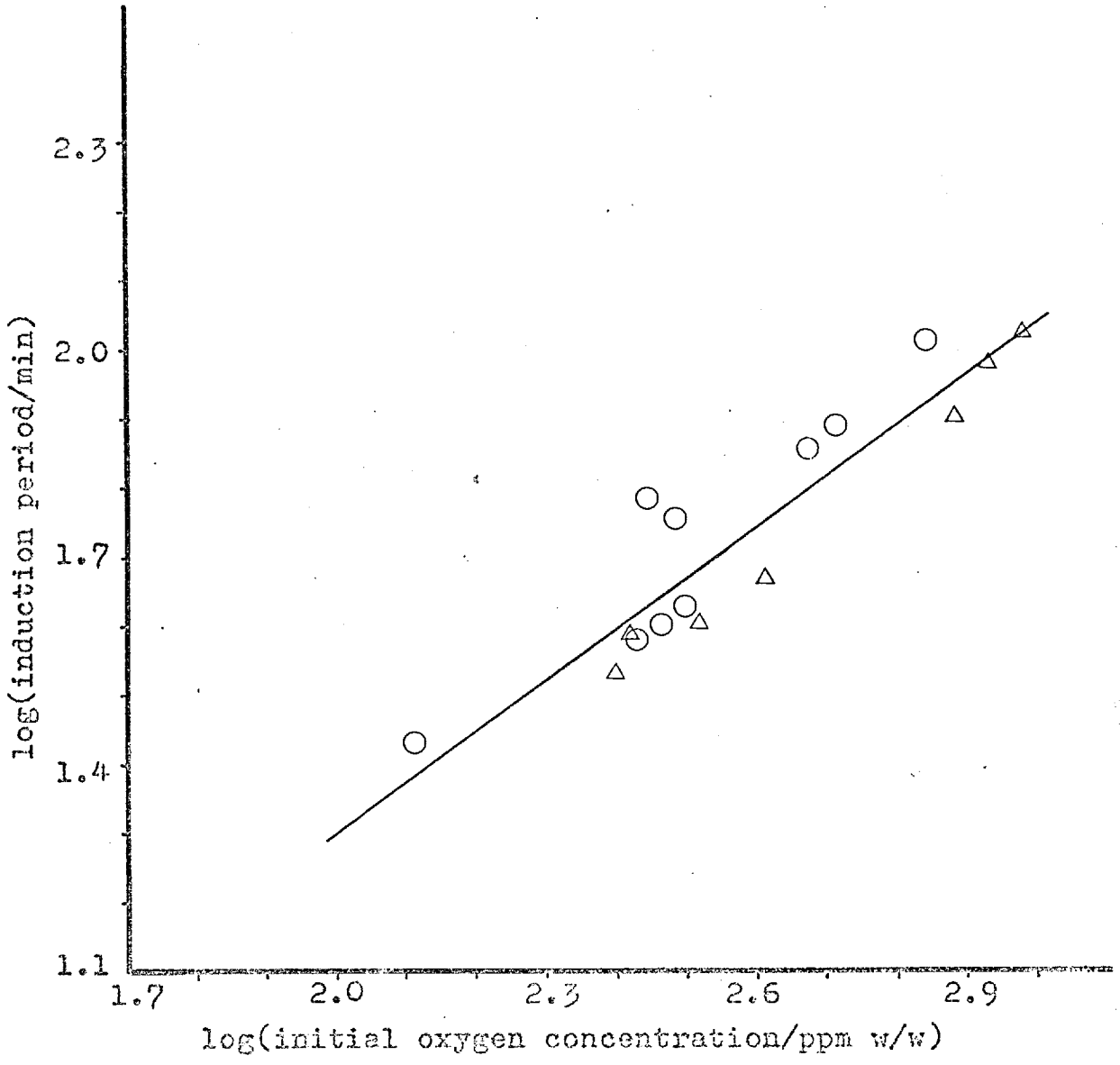


Fig. 10. log(induction period) vs. log(initial oxygen concentration) at 50°C at a constant AIBN concentration of 4×10^{-3} mol dm^{-3}, (○) batch VI and (△) batch VII.

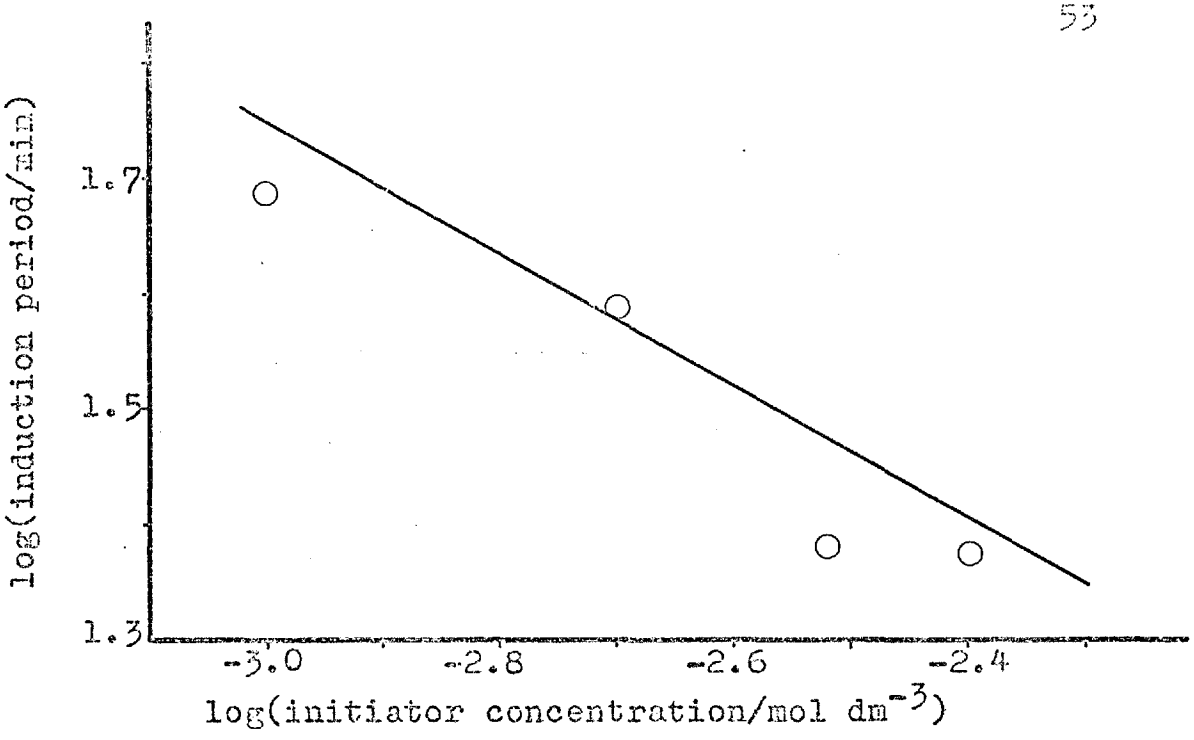


Fig. 11.A. log(induction period) vs. log(AIBN concentration) at 50°C at a constant initial oxygen concentration of 126 ppm w/w.



Fig. 11.B. log(induction period)vs. log(AIBN concentration) at 50°C at a constant initial oxygen concentration of 224 ppm w/w.

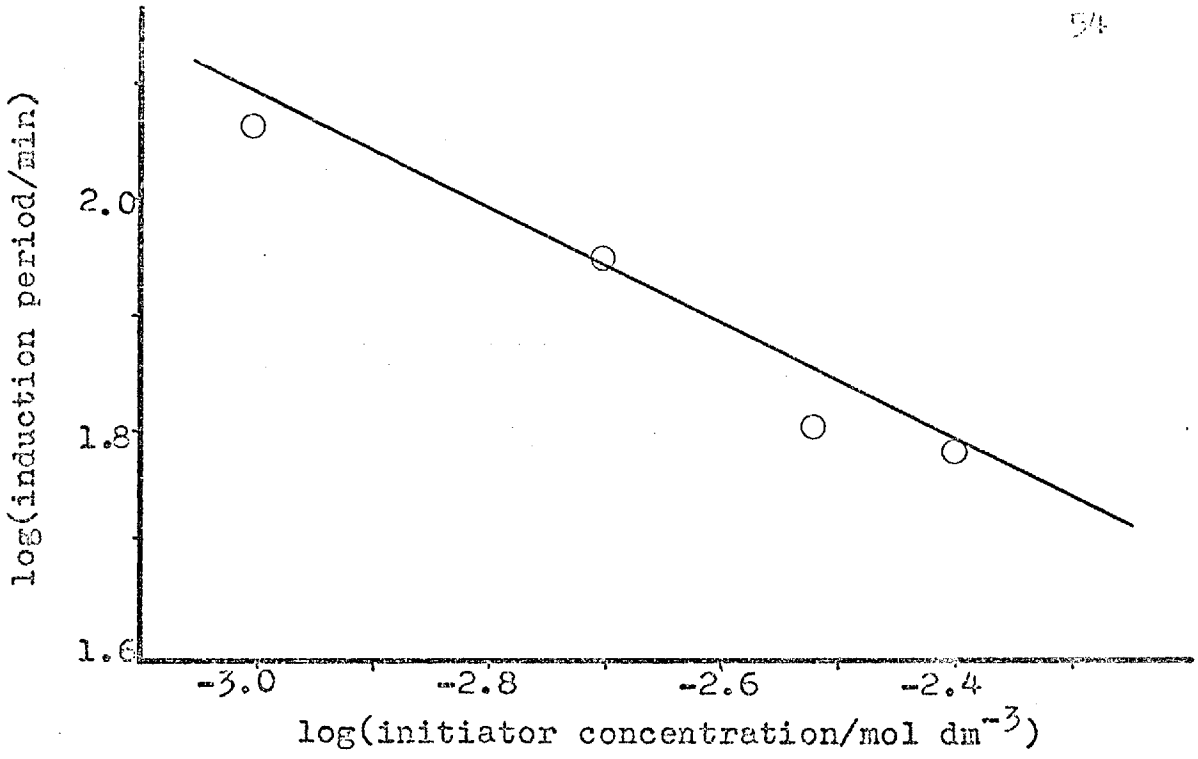


Fig.11.C. log(induction period) vs. log(AIBN concentration) at 50°C at a constant initial oxygen concentration of 447 ppm w/w.

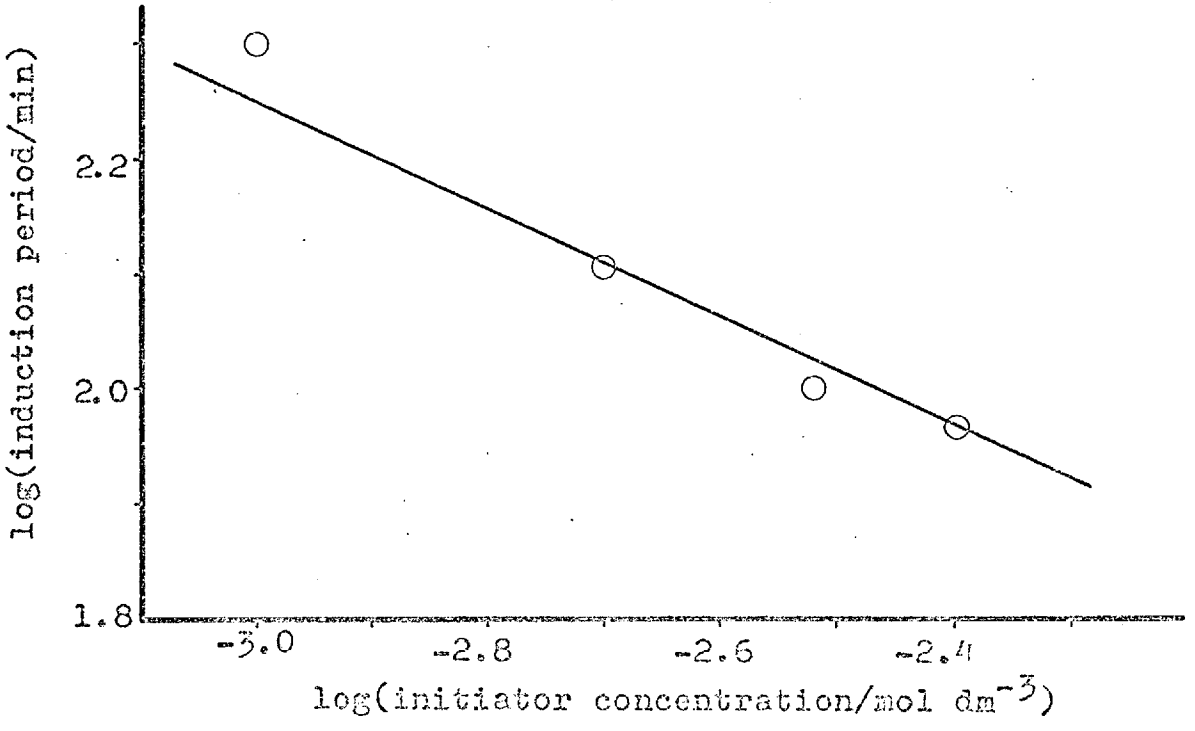


Fig.11.D. log(induction period) vs. log(AIBN concentration) at 50°C at a constant initial oxygen concentration of 794 ppm w/w.

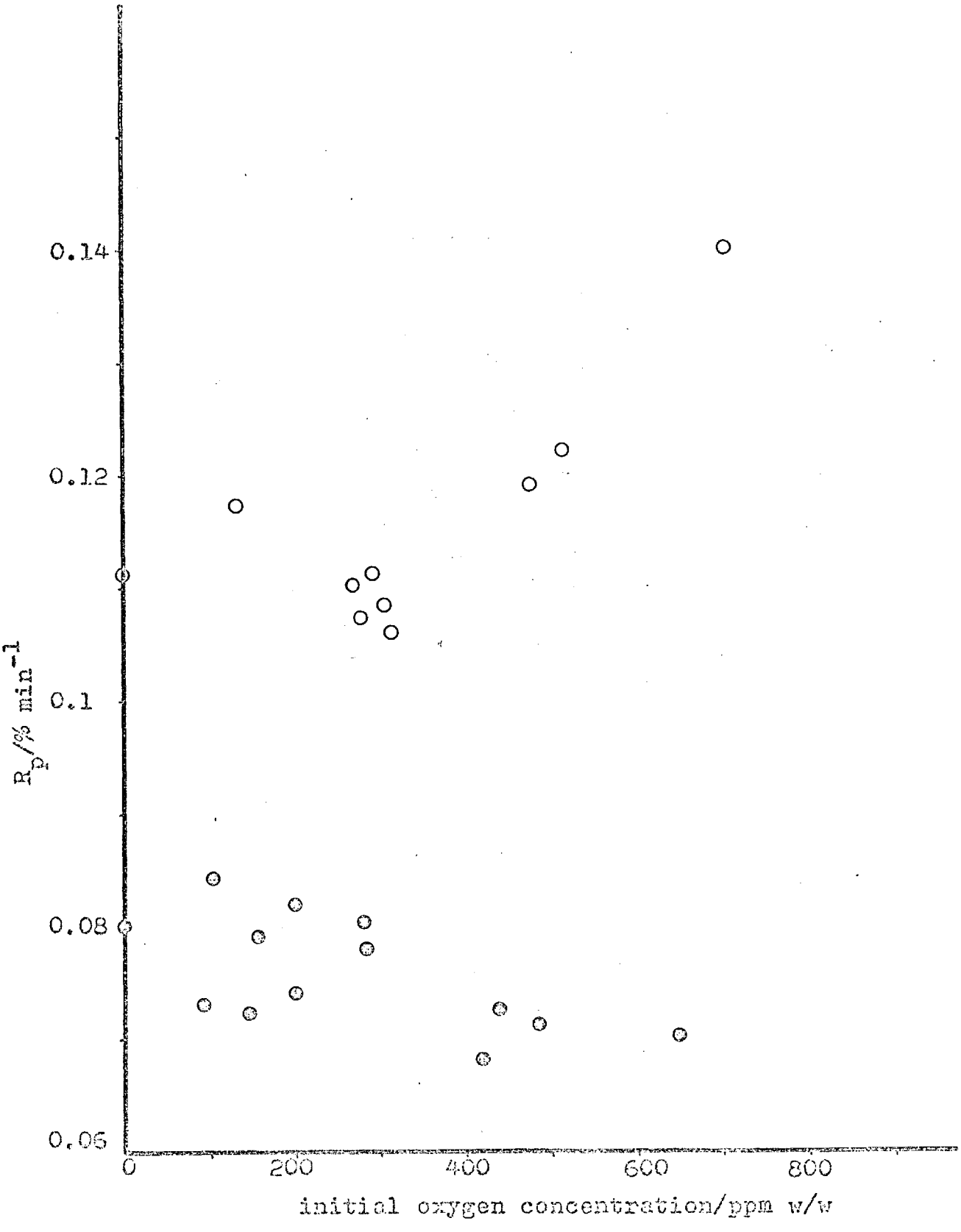


Fig.12. Effect of the initial oxygen concentration on the rate of polymerisation, R_p, at 0.5% conversion at 50°. Concentration of AIBN: (○) 2×10^{-3} mol dm^{-3} and (○) 4×10^{-3} mol dm^{-3}.

2.11 Discussion

The rate of oxygen consumption when all three types of terminations occur concurrently, can be calculated from equations 1.23 and 1.25 (chapter 1):

$$-d[O_2]/dt = \left\{ \frac{fk_d[I]}{k_{t1}+k_{t2}(k_6[O_2]/k_5[M])+k_{t3}(k_6[O_2]/k_5[M])^2} \right\}^{\frac{1}{2}} k_6[O_2] \qquad (2.4)$$

If an infinitesimally small induction period, dIP, is caused by the consumption of an amount of oxygen, $d[O_2]$, then:

$$dIP = d[O_2]/-d[O_2]/dt \quad \ldots \qquad (2.5)$$

Hence, on integration:

$$IP = \int_{\Delta}^{[O_2^{\circ}]} (d[O_2])/-d[O_2]/dt) \quad \ldots \qquad (2.6)$$

where $[O_2^{\circ}]$ represents the initial oxygen concentration and Δ is the lowest concentration of oxygen at which homopolymerization takes place.

If cross termination of alkyl radical and alkyl peroxy radical ($R\cdot + RO_2\cdot$) is predominant, integration of 2.6 by substituting equation 2.4 suitably modified gives:

$$IP = \int_{\Delta}^{[O_2^{\circ}]} (d[O_2])/k_6[O_2]\left\{ \frac{fk_d[I]}{k_{t2}(k_6[O_2]/k_5[M])} \right\}^{\frac{1}{2}} \qquad (2.7)$$

Since [M] and [I] are essentially constant throughout the induction period, equation 2.7 becomes:

$$IP = A[M]^{-\frac{1}{2}}[I]^{-\frac{1}{2}}([O_2^{\circ}]^{\frac{1}{2}} - \Delta^{\frac{1}{2}}) \qquad (2.8)$$

where A is a constant equal to $2\left(\frac{k_{t2}}{fk_dk_5k_6}\right)^{\frac{1}{2}}$.

Equation 2.8 can be simplified by assuming that Δ is very small, whence:

$$IP = A[M]^{-\frac{1}{2}}[I]^{-\frac{1}{2}}[O_2^{\circ}]^{\frac{1}{2}} \qquad (2.9)$$

Therefore, the induction period, IP, is inversely proportional to the square root of the monomer and initiator concentrations and directly proportional to the square root of the initial oxygen concentration. However, since the present study has always been performed with bulk monomer, with negligible change in monomer concentration during induction periods, the $[M]^{-\frac{1}{2}}$ term is effectively constant.

If mutual termination of alkyl peroxy radicals ($RO_2\cdot + RO_2\cdot$) is dominant, by applying the previously described type of analysis, equation 2.4 becomes:

$$IP = \int_{\Delta}^{[O_2^{\circ}]} (d[O_2])/\left| k_6[O_2]\left\{\frac{fk_d[I]}{k_{t3}(k_6[O_2]/k_5[M])^2}\right\}^{\frac{1}{2}} \right| \qquad (2.10)$$

and then,

$$IP = A_1[M]^{-1}[I]^{-\frac{1}{2}}([O_2^{\circ}] - \Delta) \qquad (2.11)$$

where A_1 is $\left(\frac{k_{t3}}{fk_d}\right)^{\frac{1}{2}} \frac{1}{k_5}$.

If Δ is negligible,

$$IP = A_1[M]^{-1}[I]^{-\frac{1}{2}}[O_2^{\circ}] \qquad (2.12)$$

Hence, the induction period is proportional to the initial concentration of oxygen, inversely proportional to the monomer concentration and inversely proportional to the square root of initiator concentration. The third type of termination ($R\cdot + R\cdot$) is not considered to be applicable to the acrylonitrile oxidation under the experimental

conditions employed, i.e., 94-1351 ppm w/w initial oxygen concentration. If such a termination is predominant, according to Schulz and Henrici[35], no inhibition period should be observed. Nevertheless, the possibility of such a termination cannot be totally ignored, particularly towards the end of an induction period when the oxygen concentration and consequently $RO_2^{\bullet}$ concentration becomes extremely low.

In order to simplify the calculations involving induction periods, the fact that the polyperoxide formed during the induction period is capable of initiating a free radical polymerization has not been considered.

As can be seen from table 6 the slopes of the logarithmic plots of the initial oxygen concentration against the induction period are consistently higher than 0.5 which would be expected for the cross termination reaction ($R^{\bullet} + RO_2^{\bullet}$). This appears to be due to the mutual termination of a proportion of the alkyl peroxy radicals rather than to experimental error. The fact that the logarithmic plots of induction period against the initial oxygen concentration in almost all experiments, and particularly in batch IV (figure 7), appear to have some degree of curvature supports this suggestion. Indeed, the occurrence of one type of termination, or a mixture of two, has been observed for a number of vinyl monomers at different oxygen pressures. For instance, in the oxidation of α-methylstyrene at oxygen pressures of up to 40 mm Hg the rate of oxygen uptake has been shown to be proportional to the square root of oxygen

pressure indicating a cross termination reaction[9]. At higher oxygen pressures, the rate increased with increasing pressure but never became completely independent of oxygen pressure below 3200 mm Hg. The latter observation implies that in the oxygen pressure range 40-3200 mm Hg some of the growing radicals with α-methylstyrene end groups participate in a cross termination reaction ($R\cdot + RO_2\cdot$). Styrene exhibited a similar behaviour but over a different range of oxygen pressures. Under 0.5-4 mm Hg pressure of oxygen, the rate of oxygen uptake was proportional to the square root of the oxygen pressure, but it became nearly independent of oxygen pressure above 20 mm Hg.[10] In methylmethacrylate, a mixture of two terminations occurred below 200 mm Hg oxygen pressure[24]. The termination below 25 mm Hg pressure took place exclusively by a cross termination reaction. Such a mixture of terminations has also been considered for oxidation of some unsaturated compounds such as ethyl linoleate and phytene in which even three types of termination take place at certain pressures of oxygen[43].

In the present study, at constant AIBN concentration, from the shapes and the slopes of the logarithmic plots of induction period against initial oxygen concentration, together with the evidence discussed previously, two types of termination, ($R\cdot + RO_2\cdot$) and ($RO_2\cdot + RO_2\cdot$), apparently occur concurrently which give an exponent greater than 0.5. In fact, the predominance of either termination depends on the ratio of concentrations, $[R\cdot]/[RO_2\cdot]$. This ratio, according to equation 1.23

depends on k_5/k_6 as well as the monomer and oxygen concentrations. Thus,

$$[R\cdot]/[RO_2\cdot] = k_5[M]/k_6[O_2] \qquad (2.13)$$

Therefore, one can assume that at high oxygen concentrations, mutual termination by alkyl peroxy radicals, $RO_2\cdot$, tends to take place. As the oxygen concentration decreases due to its consumption, mutual termination of $RO_2\cdot$ radicals becomes less significant, whereas the cross termination becomes more important. In order to make a comparison between this work and the studies of other investigators, it is necessary to calculate the vapour pressure of oxygen above acrylonitrile at 50°C. The enthalpy of evaporization of oxygen has been reported elsewhere[52] :

$$H_v = 9328 - 27.85\ T \quad J\ mol^{-1} \qquad (2.14)$$

and its boiling point, $T_b = 90.18$ K .

These values may be substituted into the Clausius Clapeyron equation, $d(\ln P)/dT = \frac{H_v}{RT^2}$ (2.15)

where P is vapour pressure at temperature T/K. The vapour pressure of oxygen at 50°C, P_1, calculated by integrating equation 2.15 is 109.5 atmospheres. Assuming ideal solution behaviour, the vapour pressure (P) of oxygen above acrylonitrile solution is, according to Henry's law, proportional to its mole fraction (X) in acrylonitrile.

$$P/P_1 = X \qquad \ldots \qquad (2.16)$$

Thus, the calculated vapour pressure of oxygen at 50°C above acrylonitrile solution lies within 13 - 186 mm Hg for initial oxygen concentrations of 94 - 1351 ppm.

This pressure may be lower because of deviations from Henry's law, as the result of polar attraction between oxygen and acrylonitrile and possible formation of charge transfer complexes. Charge transfer complexes have been reported for a number of other vinyl monomers[53]. The range of oxygen pressures calculated above is well within the range of oxygen pressures at which a mixture of two types of termination occurred for the oxidation of styrene, α-methylstyrene and methylmethacrylate.

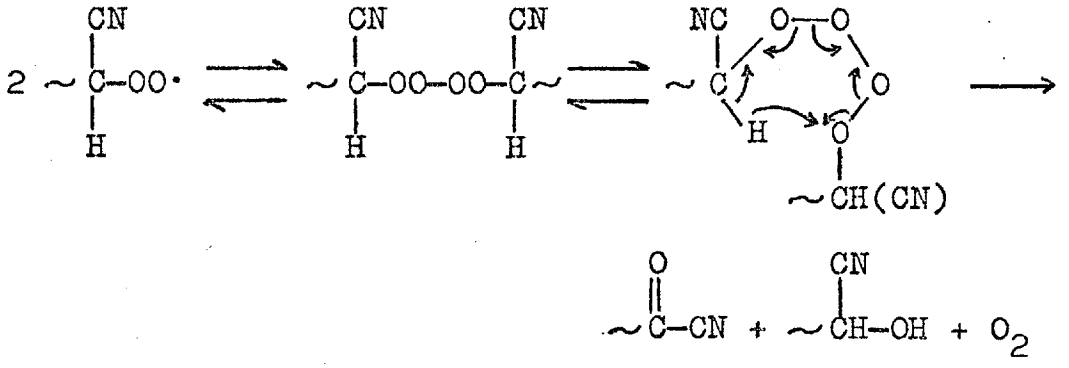
The dependence of the induction period on the concentration of AIBN, at constant oxygen concentration, as shown in table 7 varies slightly with different initial oxygen concentrations. The initiator exponents decrease with increasing initial oxygen concentration in a way that cannot be completely explained. However, all of these initiator exponents are fairly close to the theoretically predicted value of -0.5.

2.11.A <u>The end groups in the polymeric peroxide of acrylonitrile</u>

An IR spectrum of the polymeric peroxide showed adsorption due to groups such as $-\overset{O}{\overset{\|}{C}}-$, OH and $-C\equiv C-$. Nevertheless, data obtained from the IR study should be interpreted cautiously since small amount of impurities, for example, acrylonitrile and formaldehyde also produce similar absorptions.

The $\bar{M}_n$ of the polymeric peroxide is low and the chain transfer reaction to monomer may play a part in determining its chain length with consequent formation

of unsaturated end groups. Transfer to HCHO and particularly to HCN could take place although the concentration of these two compounds is relatively low. The occurrence of such transfer reactions results in the formation of end groups such as -OOH. Transfer reactions similar to those described by Mayo (chapter 1 equations 1.6 - 1.8) for the oxidation of styrene are also feasible for acrylonitrile oxidation. Termination by interaction of two alkyl peroxy radicals might be responsible for the formation of end groups such as $-\overset{O}{\overset{\|}{C}}-$ and -OH.



(2.17)

This reaction (the Russell mechanism)[54] is generally believed to proceed through a cyclic transition state and has been suggested for the oxidation of aralkyl hydrocarbons.

During the preparation of the polyperoxide oxygen was bubbled through the reaction vessel, i.e., high $\sim CH_2-CH(CN)OO\cdot$ concentration, so the latter termination reaction could lead to the formation of such end groups.

2.11.B Polymerization rate data

During the induction period the AIBN decomposes while the polymeric peroxide is produced simultaneously. The concentration of the polymeric peroxide, assuming that all the oxygen is converted into it can be calculated

from the initial oxygen concentration. This concentration lies approximately within the range 2.3 - 33 x 10^{-3} mol dm^{-3} for the various dilatometers used in the polymerization rate measurements. If the low values for the % conversion of oxygen to the polymeric peroxide are correct, then the concentration of the polymeric peroxide is 0.23-3.3x10^{-3} mol dm^{-3}. This is comparable with typical AIBN concentrations of 10^{-3} - 4 x 10^{-3} mol dm^{-3}.

The k_d value for the polyperoxide is higher relative to that of AIBN and it is expected that the presence of the polymeric peroxide would enhance the rate. As seen from figure 12, in spite of the wide scatter of the results, it seems that polyperoxide formation compensates for the loss of AIBN and may slightly increase the rate. This, however, is not unexpected because polymeric peroxides have been shown usually to be poor initiators. In fact the alkoxy radicals produced by cleavage of —OO— bonds depclymerize rather than initiate polymerization.

2.12 Conclusion

The presence of oxygen inhibits the bulk polymerization of acrylonitrile. The length of the induction periods is approximately inversely proportional to the square root of AIBN concentration at constant oxygen concentrations. At constant concentrations of AIBN, the induction periods are directly proportional to the oxygen concentration to a power of 0.66 ± 0.09 - 0.78 ± 0.08. These values are higher than the value of 0.5 expected

for predominant cross termination ($R\cdot + RO_2\cdot$), indicating that mutual termination ($RO_2\cdot + RO_2\cdot$), may also take place. During the induction periods, apart from the polymeric peroxide of low molecular weight, side products such as HCN, HCHO, CO_2 and possibly CO were also formed (chapter 3). The polymeric peroxide appears to be a relatively poor initiator for the polymerization of acrylonitrile compared to AIBN.

CHAPTER 3

APPLICATION OF THE MICROWAVE PLASMA DETECTOR (MPD 850) IN THE IDENTIFICATION OF OXIDATION AND REDUCTION PRODUCTS INVOLVING ACRYLONITRILE

3.1 Introduction

Detection of organic compounds in a microwave sustained argon plasma was first carried out by McCormack et al[55]. The argon plasma was subsequently replaced by helium which has a higher ionization potential and does not result in a complex spectrum due to recombination of elemental atoms[55]. Thus in this system an organic compound eluted from a gas chromatograph column disintegrates into its corresponding elements and these elements then absorb energy available in the plasma and subsequently emit light of their characteristic wavelengths. The intensity of each atomic emission is then measured by means of a specific phototube. However, the intensity of atomic emission was found to be linearly proportional to the quantity of the individual element passing through the plasma and independent of the parent compound[57]. Furthermore, the intensity depends on various factors such as tube bore, microwave power, plasma pressure and plasma tube emission profile[57]. The major problem in this system is the relative non-volatility of carbon (m.p.3500°C). Hence, elemental carbon tends to remain in the plasma as a solid deposit on the side of the plasma tube. In order to remove solid carbon from the plasma, application of a scavenger gas, either oxygen or nitrogen, was found to be

necessary[57,58]. These scavenger gases keep carbon in a volatile state by reacting with it:

$$C\ (Solid) + O \longrightarrow CO\ (Gas) \qquad (3.1)$$

$$CO \xrightarrow[energy]{Plasma} C + O \qquad (3.2)$$

3.1.A. Emission characteristics of the helium plasma[57]

Total emission (I_T) is found to be the sum of three components. Steady background emission from the plasma (I_O), atomic emission of element E (I_E) and a steady background emission due to the passage of carbon through the plasma ($I_{C'}$). This component ($I_{C'}$) is due to the tendency of carbon to form small particles in the plasma. These particles absorb energy and emit light throughout the whole visible range and consequently interfere to some extent with all other elemental emissions such as those due to H, Cl, N, O and D. To eliminate this interference a correcting device has been installed in the apparatus and the name "ghost correction" has been given to the correction applied.

3.1.B. Determination of atomic ratio and empirical formula[59]

The ratio of elemental response in the MPD, to the FID response is equivalent to the slope of the graph shown in figure 13.

If the slope is defined as:

$$\frac{\partial C}{\partial FID},\ \frac{\partial H}{\partial FID} \text{ and } \frac{\partial O}{\partial FID}\ . \qquad (3.3)$$

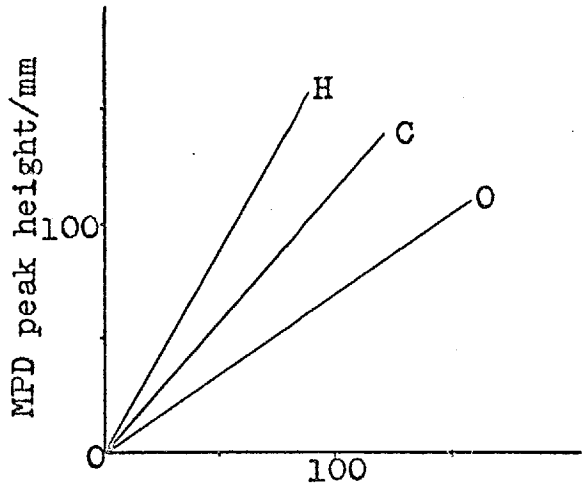


Fig. 13. Plot of the MPD peak height vs. FID peak height for acetone.

For compound X,

$$\left(\frac{\partial C}{\partial FID}\right)_x = \frac{F_{MPD} \times R_c \times n_c \; n_m}{F_{FID} \times \left(R_F\right)_x \times n_m} = \frac{K_c}{\left(R_F\right)_x} \times n_c \qquad (3.4)$$

where $\frac{F_{MPD}}{F_{FID}}$ is the flow rate (splitting) ratio for the two detectors. R_c is the MPD response per gram-atom of carbon, n_c is the number of carbon atoms per molecule, n_m is the number of gram-moles of compound X and $\left(R_F\right)_x$ is the response factor per gram-mole of compound X on the FID. Similarly,

$$\left(\frac{\partial O}{\partial FID}\right)_x = \frac{K_o}{\left(R_F\right)_x} \times n_o \qquad (3.5)$$

and, on division:

$$\left(\frac{\partial O}{\partial C}\right)_x = \frac{K_o}{K_c} \times \frac{n_o}{n_c} = \text{constant X oxygen to carbon atomic ratio.} \qquad (3.6)$$

The constant K_o/K_c is independent of the compound specific response factor of the FID and can be evaluated by reference to any known oxygen-containing compound.

3.2 Experimental

3.2.A. Apparatus

The MPD 850 (Applied Chromatography Systems Ltd., Luton, England) had been interfaced to a gas chromatograph, Model 104 (Pye Unicam Ltd.) (figure 14). In this system, an eluant from a gas chromatographic column is split into two equal streams, one of which passes through a flame ionization detector (FID). The other stream passes through a microwave sustained helium plasma where the compound is fragmented completely into its corresponding atomic species which are excited and then emit their characteristic spectra. The light output from the plasma, after being separated in the spectrometer, is fed into a series of phototubes. Eventually the electrical signals from the phototubes and the FID detector, after being amplified, are passed into two recorders (Omni Scribe$_{TM}$).

3.2.B. Gas supplies

Helium (grade A) was purified by a rare gas purifier (British Oxygen Co.Ltd.) at 700°C. Helium and the scavenger gases, oxygen and nitrogen, were passed through columns containing molecular sieve before entering the apparatus.

Hydrogen and compressed air for the FID were supplied by British Oxygen Co.Ltd.

3.2.C. Gas chromatographic columns

The gas chromatographic columns used in the calibration of the MPD instrument and for the identification

of the oxidation side products were all supplied by Pye Unicam Ltd.

3.2.D. Calibration of the MPD

The major problem in determining the elemental ratios accurately is the interference of carbon particle emission with the emission from other elements (figure 15) which necessitates some corrections. In practice these corrections were made by injecting various amounts of a suitable compound such as CCl_4 for correcting hydrogen, nitrogen and oxygen and $n\text{-}C_5H_{12}$ for correcting chlorine, nitrogen and oxygen. An appropriate solvent, eluting long after the corresponding compound used for correction, was carefully chosen. The right choice of the solvent enables several repetitive injections and facilitates the experimental operation. Eventually carbon responses, in terms of peak heights, were plotted against the peak heights produced by carbon particles emission for each element (figure 16). Since this method was not very satisfactory, a better method was employed by injecting one of the previously mentioned compounds for correction and then adjusting the ghost correcting device until no signal was observed, that is until the weak signal of each element associated with the passage of carbon through the plasma was no longer observed. In order to ensure accurate measurement of the elemental ratios over the permitted concentrations between the plasma over-load threshold and lower limits of detection, the experiment was performed with the highest possible concentration of

the ghost correcting compound. To examine the accuracy of the apparatus and consequently the validity of the results obtained for an unknown compound, samples of various known compounds containing C, H, O, N and Cl were separated on suitable columns such as Porapak Q, PEG 1000 and Squalane (figure 17). Elemental ratios of these known compounds were within ± 4% calculated using the peak heights (tables 8-11). Calibration plots of the theoretical carbon/element ratio against the experimental peak height are shown in figures 18-21 which proves the accuracy and linearity of the apparatus.

3.2.E. Preparation of the oxidation side products

Oxidation side products were prepared by allowing oxygen to react with acrylonitrile, in the presence of AIBN, during the induction period. Acrylonitrile and AIBN were purified in the usual way (chapter 2). AIBN (approximately 30 mg) was dissolved in chloroform and the solution was transferred to a 500 cm^3 round bottomed flask connected to a break seal. Chloroform was then distilled off in vacuo at room temperature and acrylonitrile (approximately 20 cm^3) was distilled into the flask at -76°C. To ensure complete removal of gaseous impurities the solution was degassed once and then medical oxygen at half an atmosphere pressure was admitted into the flask. After sealing off the flask, while its contents were frozen in liquid nitrogen, the flask was immersed in a water bath at 50°C. Stirring was maintained throughout the induction period using a magnetic follower. At the end of the induction period the contents of the flask

were distilled under vacuum into small dilatometers, which were subsequently sealed off and kept in liquid nitrogen until required.

3.2.F. Preparation of the reduction product of the acrylonitrile polyperoxide

Acrylonitrile polyperoxide (about 5g) was treated with a solution of potassium iodide, 5% w/w, in methanol and glacial acetic acid. The liberated iodine was removed from the solution by a double distillation under vacuum at room temperature. The excess acetic acid was neutralized by NaOH and sodium acetate formed was separated by distilling off the volatile products under vacuum at 50°C. $10^{-2}cm^3$ (10 micro-litres) of the distillate was injected into the gas chromatograph, using a Porapak Q column at 215°C. The chromatogram showed that only one reduction product had been formed at a very low concentration. The solvent, methanol, gave a characteristic peak. Since the concentration of the product was low, the excess methanol was separated by fractional distillation and a pure liquid reduction product was isolated (b.p. 163°C).

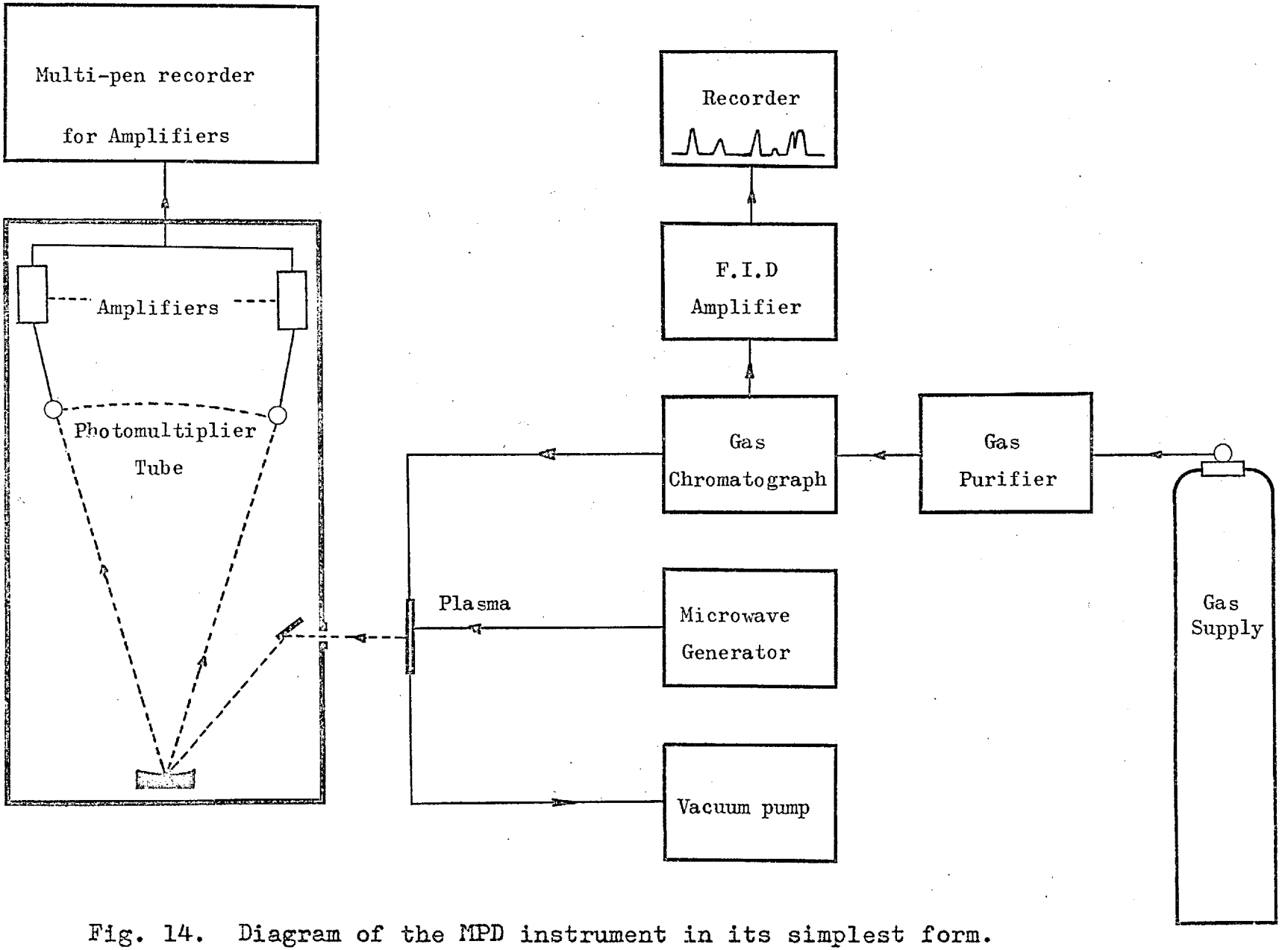


Fig. 14. Diagram of the MPD instrument in its simplest form.

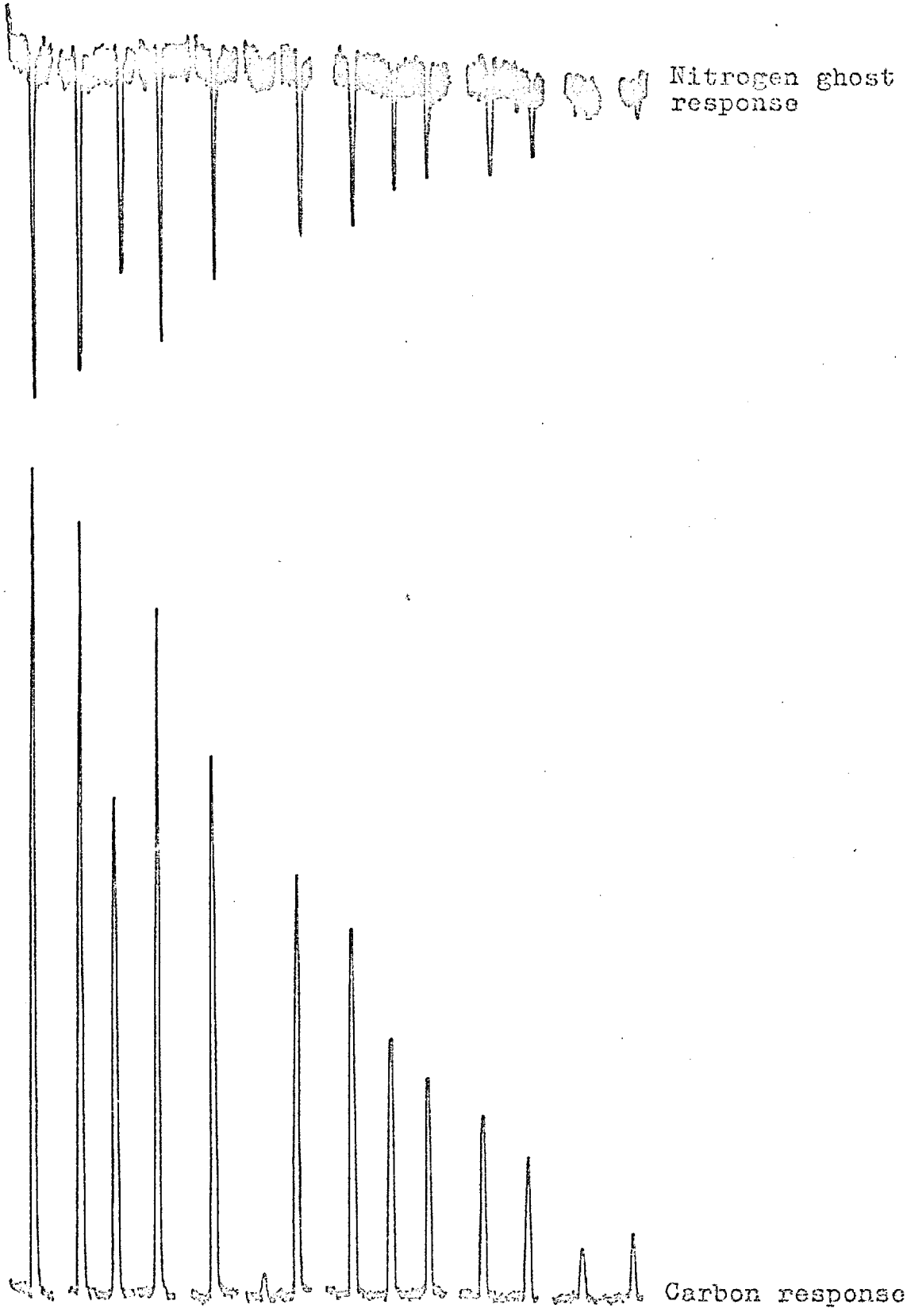


Fig. 15. Typical nitrogen ghost response obtained by injecting CCl_4 into PEG 1000 at 100°C.
[The carbon signal peak height is two thirds of the original height but the nitrogen peak height is unreduced.]

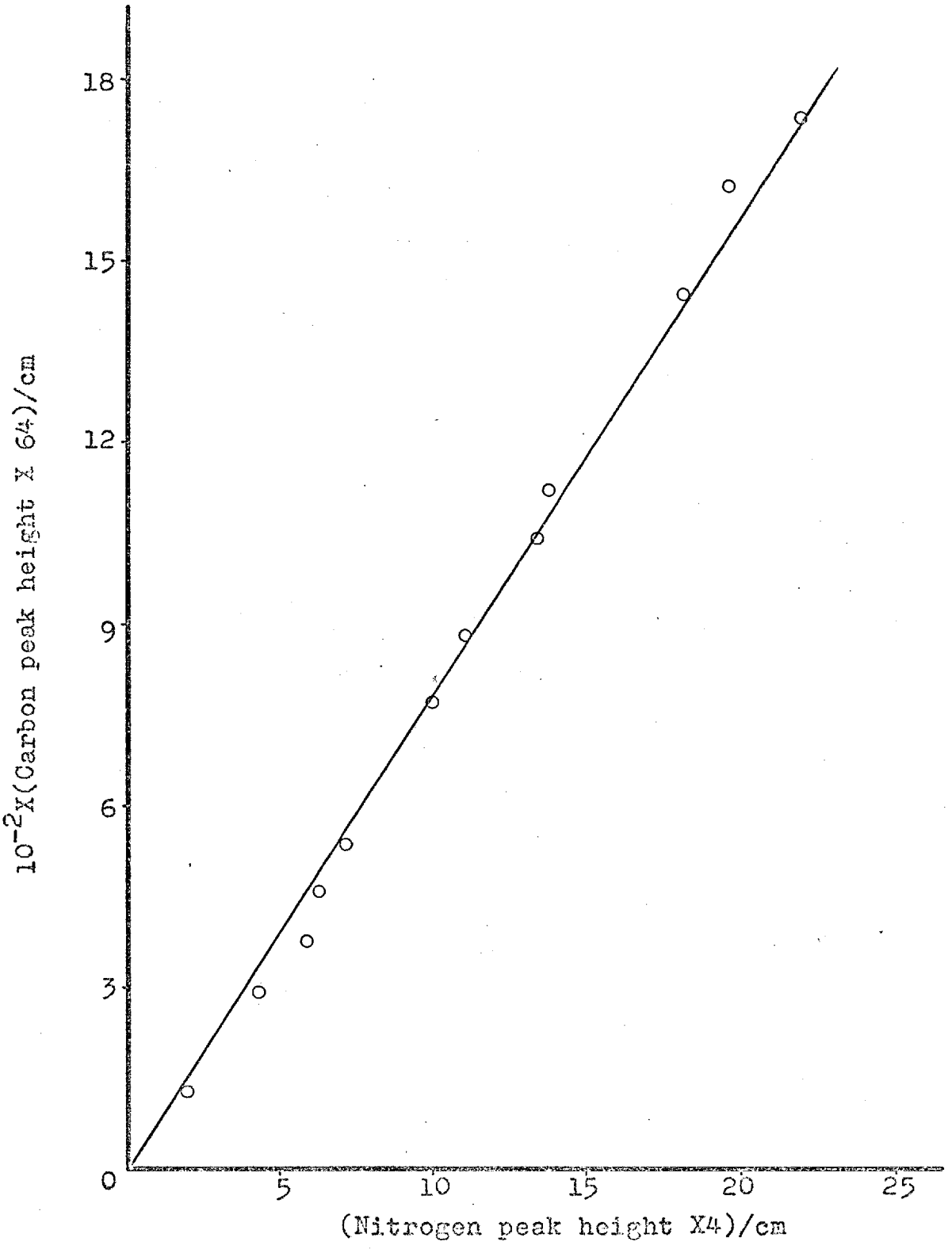


Fig.16. Plot of carbon response against nitrogen ghost response.

Column PEG 1000, temperature 100°C.

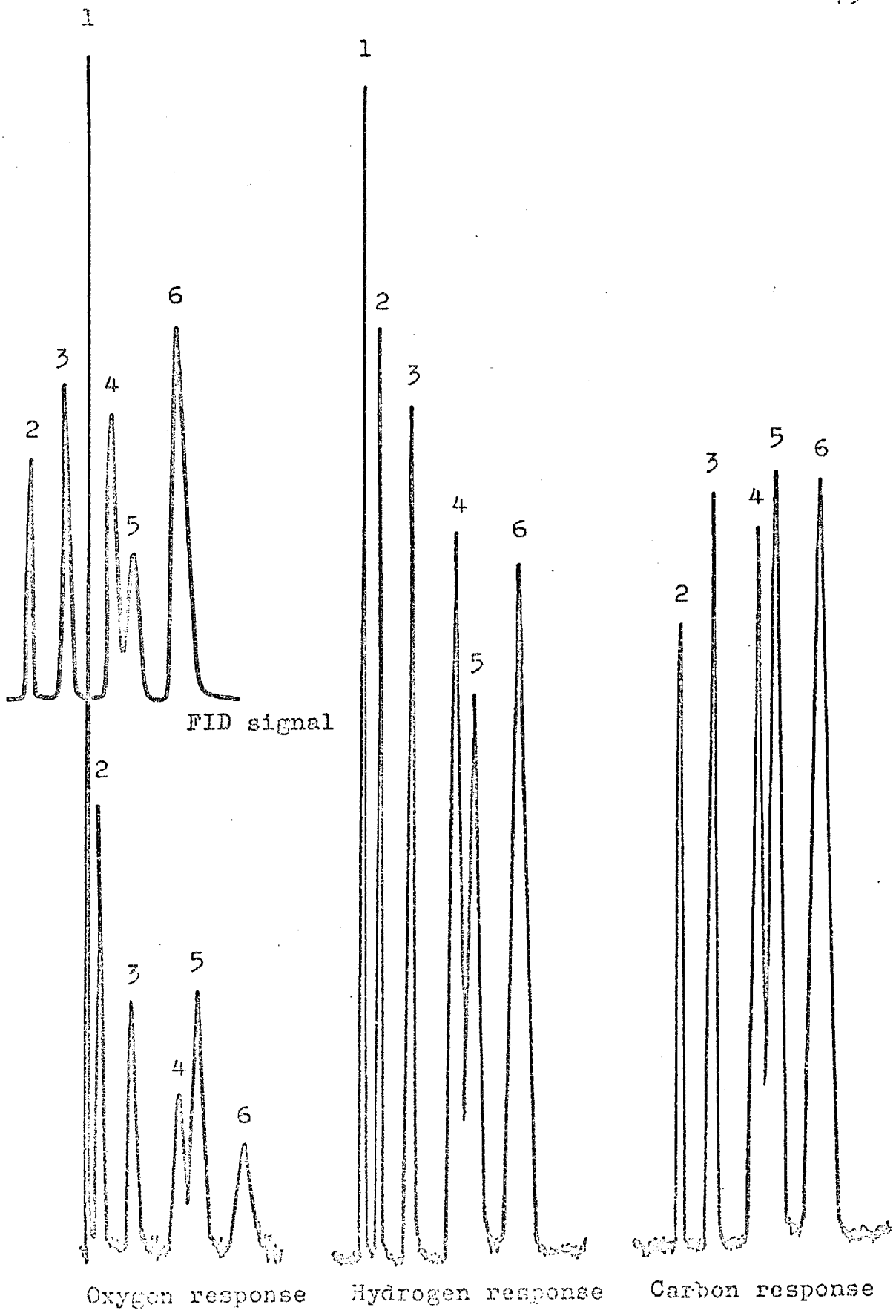


Fig. 17. Separation of C_1-C_4 alcohols and CH_3COOCH_3 on a Porapak Q column (2.1 m x 4 mm) at 180°C. 1=H_2O, 2=CH_3OH, 3=C_2H_5OH, 4=$CH_3CHOHCH_3$, 5=CH_3COOCH_3 and 6=$(CH_3)_3COH$

TABLE 8. C/H ratios of various compounds.

Compound	C/H theoretical	C/H experimental	% error	Conditions*
CH_3OH	0.25	0.247	-1.1	PQ, 190°C
C_2H_5OH	0.333	0.337	+1.2	PQ, 190°C
CH_3NO_2	0.333	0.332	-0.3	PQ, 100°C
$CH_3CHOHCH_3$	0.375	0.370	-1.3	PQ, 190°C
$(CH_3)_3COH$	0.4	0.410	+2.5	PQ, 190°C
$(C_2H_5)_3N$	0.4	0.395	-1.5	PG, 115°C
CH_3COOCH_3	0.5	0.510	+2.0	PQ, 190°C
$CH_3COOC_2H_5$	0.5	0.505	+1.0	PG, 58°C
CH_3CN	0.666	0.646	-3.1	PG, 100°C
$CH_2=CHCN$	1	1.030	+3.0	PG, 100°C

TABLE 9. C/N ratios of various compounds.

Compound	C/N theoretical	C/N experimental	% error	Conditions*
CH_3NO_2	1	1.00	0.0	PG, 100°C
CH_3CN	2	1.93	-3.5	PG, 100°C
$CH_2=CHCN$	3	2.97	-1.0	PG, 100°C
$CH_3(CH_2)_3NH_2$	4	3.91	-2.2	PG, 115°C
$(C_2H_5)_3N$	6	5.80	-3.3	PG, 115°C

* [PQ = 2.1m X 4mm i.d. 85-100 mesh Porapak Q column and PG = 2.8m X 4mm i.d. 10% poly(ethylene glycol) 1000 on 100-120 mesh Diatomite C.]

TABLE 10. C/Cl ratios of various compounds.

Compound	C/Cl theoretical	C/Cl experimental	% error	Conditions*
CCl_4	0.25	0.244	-2.4	SQ, 42°C
$CHCl_3$	0.333	0.324	-2.7	SQ, 42°C
CH_2Cl_2	0.5	0.514	+2.8	SQ, 42°C
C_4H_9Cl	4	4.010	+0.2	SQ, 65°C
C_6H_5Cl	6	5.980	-0.3	SQ, 65°C

TABLE 11. C/O ratios of various compounds.

Compound	C/O theoretical	C/O experimental	% error	Conditions*
CH_3OH	1	0.976	-2.4	PQ. 180°C
$HCOOCH_3$	1	0.961	-3.9	PG, 58°C
CH_3COOCH_3	1.5	1.460	-2.6	PQ, 180°C
CH_3CHO	2	2.050	+2.5	PG, 51°C
C_2H_5OH	2	2.050	+2.5	PQ, 180°C
$CH_3COOC_2H_5$	2	2.040	+2.4	PG, 58°C
CH_3COCH_3	3	2.930	-2.3	PG, 51°C
C_3H_7OH	3	3.070	+2.3	PQ, 180°C
C_4H_9OH	4	4.050	+1.3	PQ, 180°C

* [PQ = 2.1m X 4mm i.d. 85-100 mesh Porapak Q column, PG = 2.8m X 4mm i.d. 10% poly(ethylene glycol) 1000 on 100-120 mesh Diatomite C and SQ = 1.5m X 4mm i.d. 10% Squalane on 100-120 mesh Diatomite C.]

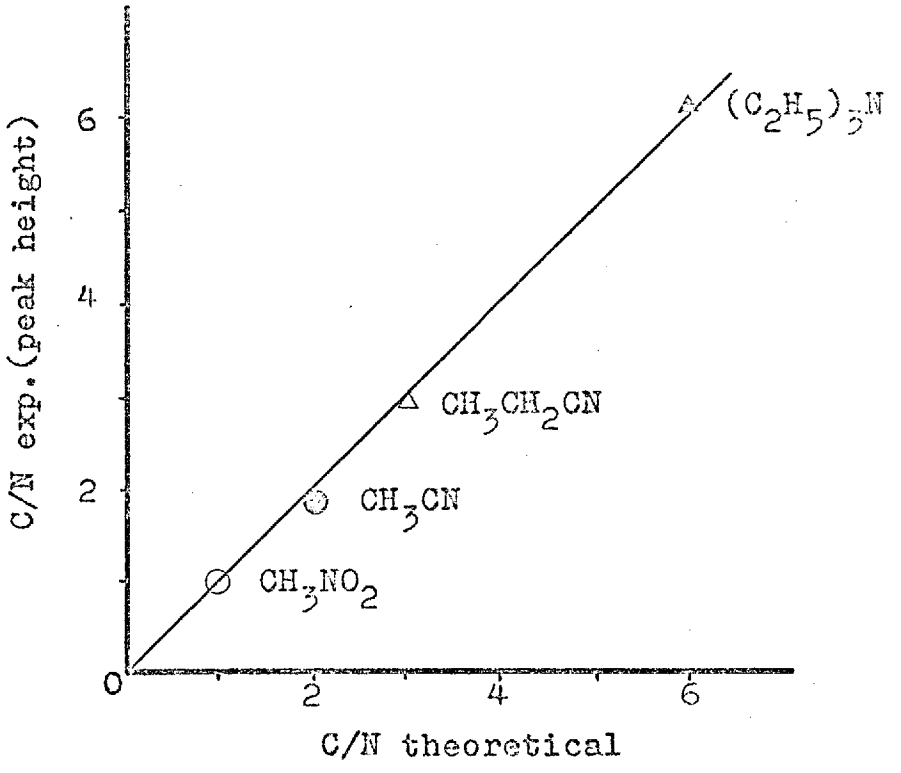


Fig. 18. C/N experimental peak height ratio vs. C/N theoretical ratio.
[C attenuation x 64; N attenuation x 4]

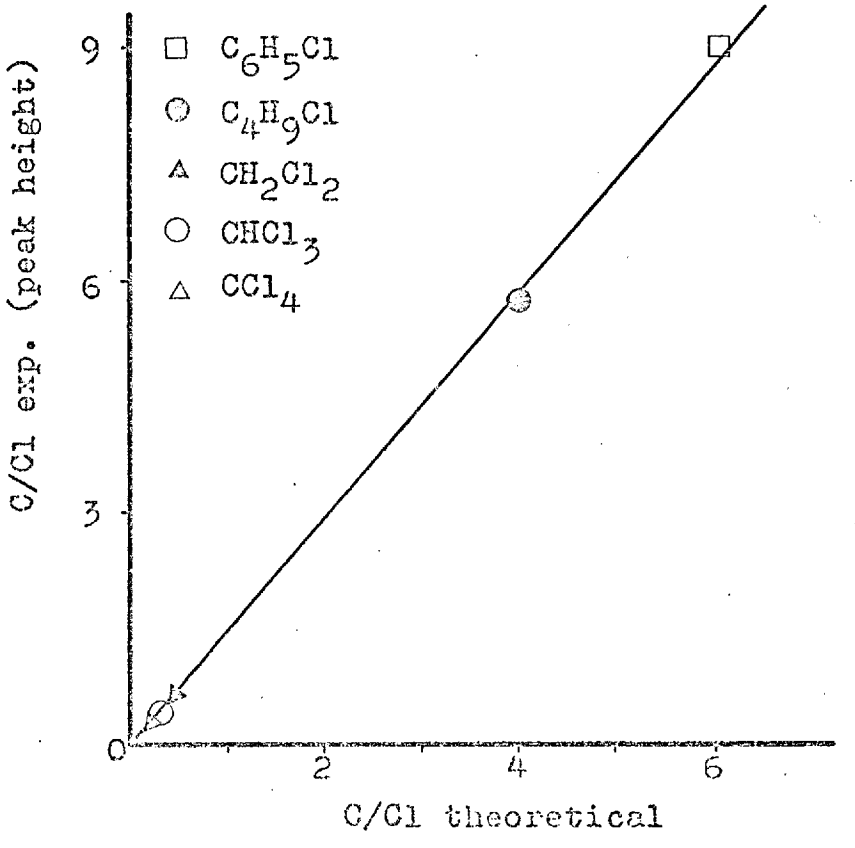


Fig. 19. C/Cl experimental peak height ratio vs. C/Cl theoretical ratio.
[C attenuation x 16; Cl attenuation x 4]

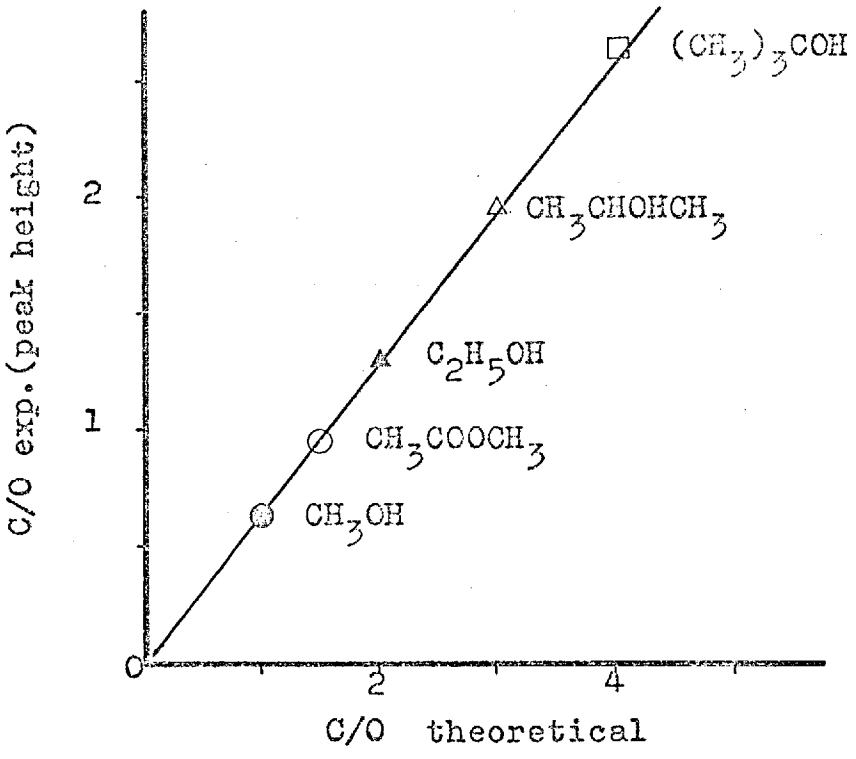


Fig. 20. C/O experimental peak height ratio vs. C/O theoretical ratio.
[C attenuation x 16; O attenuation x 4]

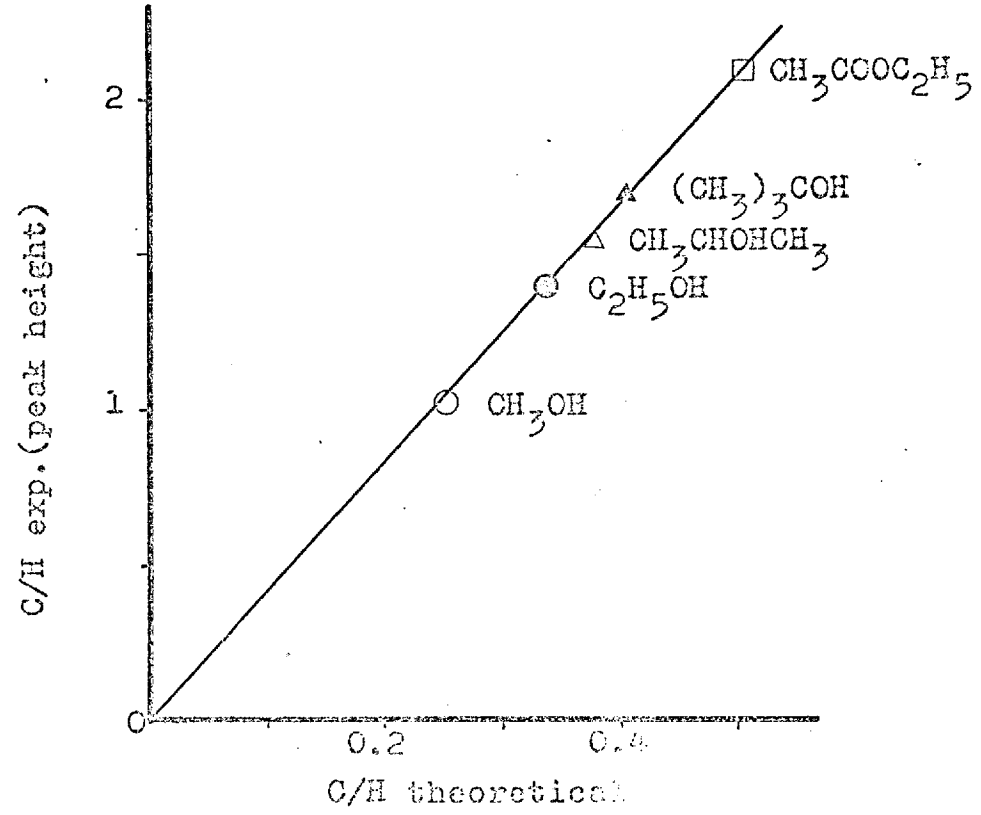


Fig. 21. C/H experimental peak height ratio vs. C/H theoretical ratio.
[C attenuation x 32; H attenuation x 64]

3.3 Results

Identification of the oxidation side products and the reduction product of acrylonitrile polyperoxide.

Samples of about $5 \times 10^{-3} cm^3$ of acrylonitrile before and after treatment with oxygen were injected into a gas chromatograph, using a Porapak Q column. As a result of these experiments, three new compounds designated as X_1, X_2 and X_3 were detected. X_1 eluted before water, which existed as an impurity, did not respond to the FID, and contained C and O only. X_2 eluted after water, gave no response to the FID and contained C, H and O. Finally, X_3 eluted after X_2, responded to the FID and contained C, H and N (figures 22 and 23). Elemental ratios of these unknown compounds were determined against suitable internal standards such as CH_3OH, C_2H_5OH and CH_3CN and are presented in table 12. The three unknown compounds were thus identified as $CO_2(X_1)$, $HCHO(X_2)$ and $HCN(X_3)$. Since acrylonitrile is retained by the Porapak Q column for a longer time than the unknown compounds and all the internal standards, acrylonitrile was used as solvent in all experiments. In order to confirm the results obtained from the MPD, a sample consisting of CO_2, H_2O, HCHO, CH_3OH and C_2H_5OH was prepared and the retention times of these compounds were determined and compared with those of the original oxidation sample under identical conditions (table 13). For the compounds CO_2, H_2O and HCHO which gave no FID signal, retention times were determined from the carbon or hydrogen signal times recorded by the MPD.

Porapak Q is a column from which many common inorganic gases elute before water whereas virtually all organic compounds elute after water. A combination of the FID which does not respond to inorganic compounds, HCHO and HCOOH, and the MPD together with the specific characteristics of a Porapak Q column was thus highly effective in identifying the side products. The other possible oxidation product, CO, was not identified in the reaction liquid phase. This, however, is due to the low solubility of carbon monoxide in organic solvents. When the gas phase of the reaction mixture was injected using a gas sampling valve connected to a $1cm^3$ loop, a very weak carbon signal was observed. Nevertheless, attempts to measure the C/O ratio failed because of the air leak during injection and also due to incapability of the Porapak Q to separate CO from air.

Identification of the reduction product, X_4, of acrylonitrile polyperoxide was carried out, using the same column and procedure (figure 24). Elemental ratios, which are shown in table 14, were determined using three internal standards such as n-C_4H_9OH, CH_3CH_2CN and $HCON(CH_3)_2$. In the experiment involving identification of X_4 the use of a solvent was eliminated by injecting $10^{-4}cm^3$ of a mixture of X_4 and the previously mentioned standards. The purpose of using three internal standards was to ensure that accurate results were obtained by checking the elemental ratios of three standards both with each other and also with the unknown compound, X_4. The validity of the empirical formula, C_4H_7NO, obtained from the MPD was

examined by NMR (figure 25.A) and IR spectroscopy (figure 25.B). These two methods indicated an identical formula for X_4. The mass spectrum of this compound, X_4, gave a molecular weight of 85.

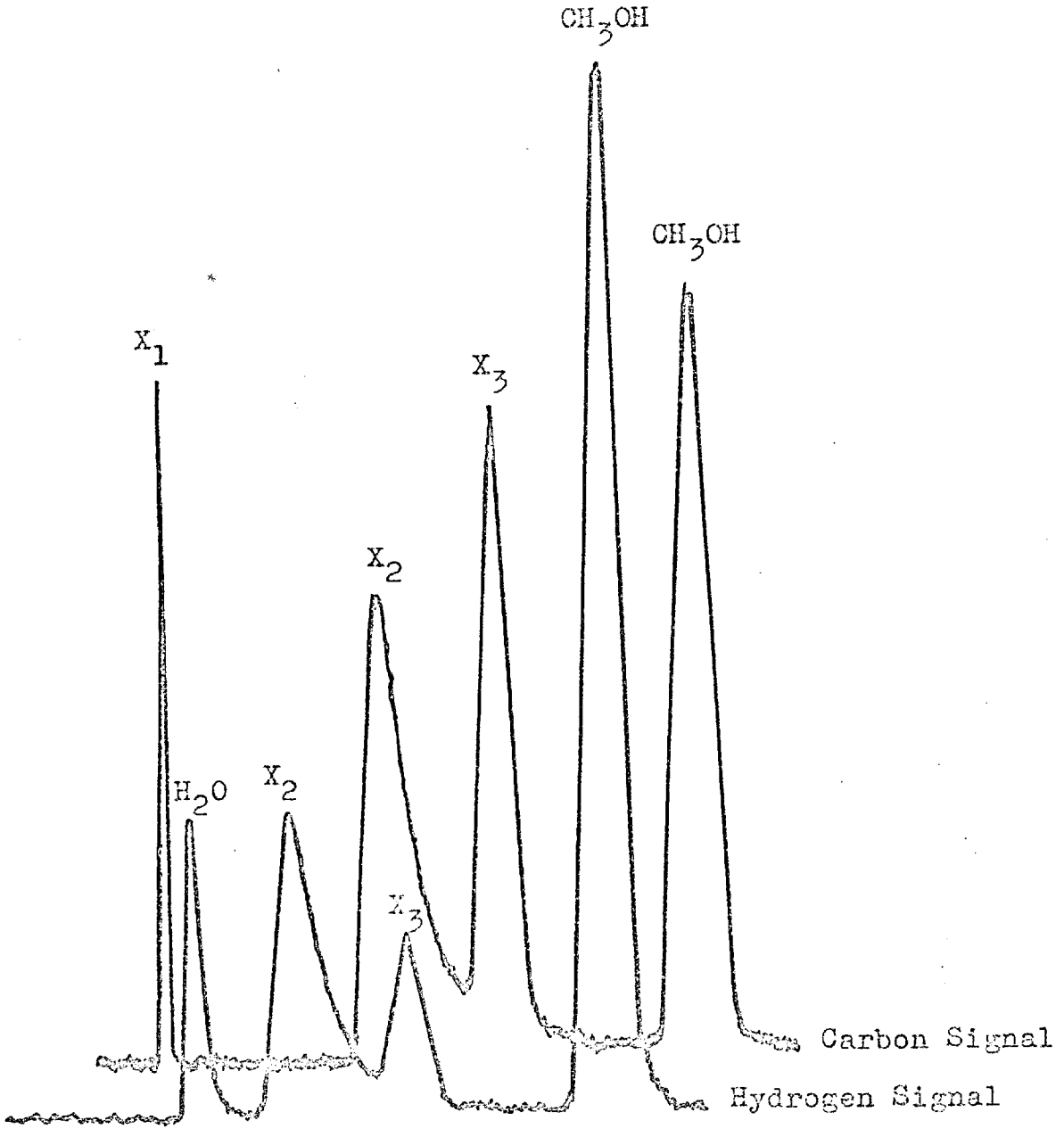


Fig. 22. Separation of the oxidation side products of acrylonitrile on a Porapak Q column (2.1m x 4mm) at 79°C, (experiment h_3).

$X_1 = CO_2$, X_2 = HCHO and X_3 = HCN.

[Carbon and hydrogen attenuations X32.]

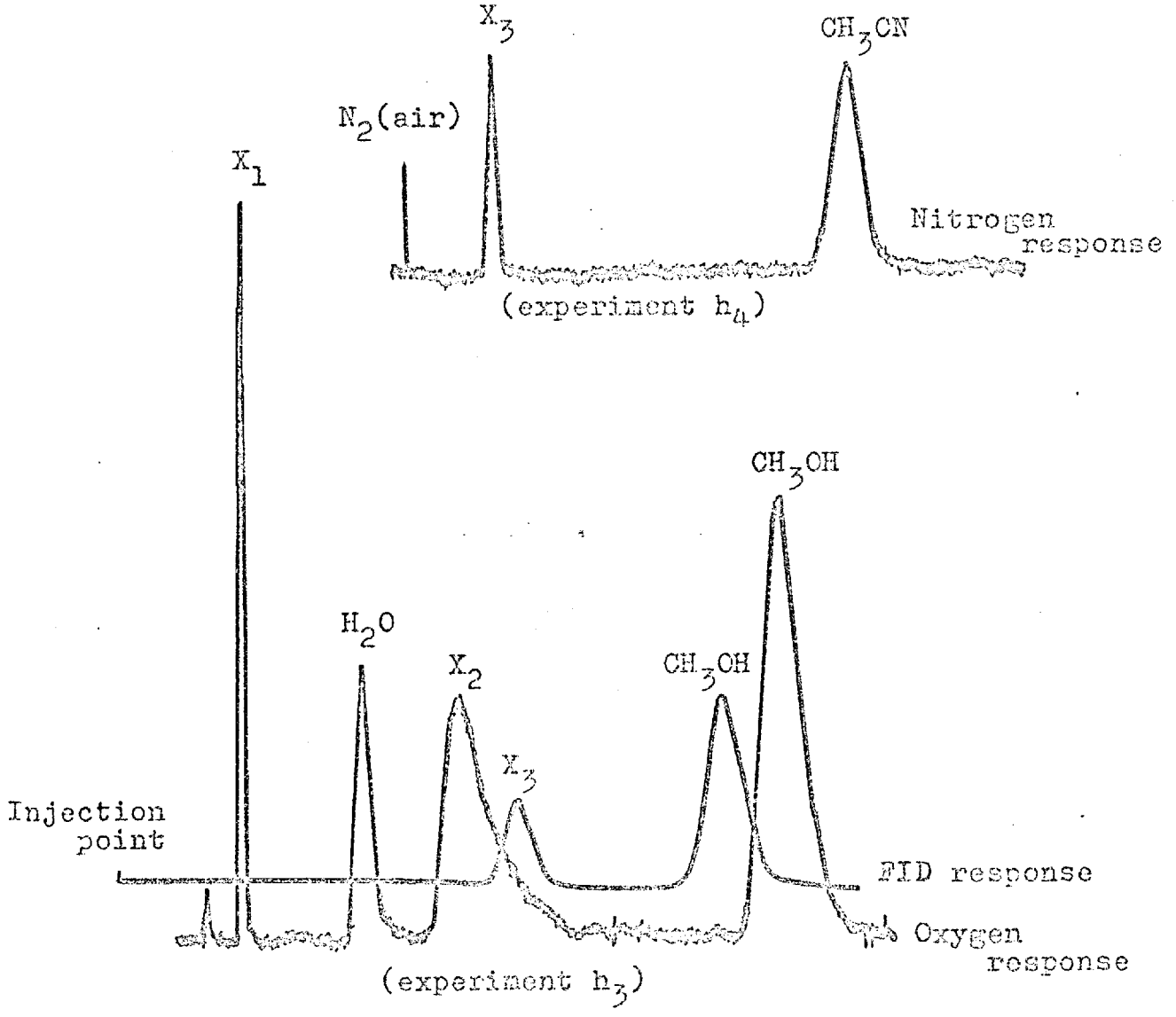


Fig. 23. NPD and FID responses of the oxidation side products of acrylonitrile. Column Porapak Q (2.1m x 4mm), temperatures: 79°C (experiment h_3) and 120°C (experiment h_4)

$X_1 = CO_2$, X_2 = HCHO and X_3 = HCN

[O attenuation x 4; N attenuation x 8.]

TABLE 12

Elemental ratios of the oxidation side products of acrylonitrile

Compound	C/H	C/O	C/N	Internal Standard
X_1	0	0.527	0	CH_3OH
X_2	0.510	1.04	0	CH_3OH
X_3	0.976	0	-	CH_3OH
X_3	0.962	0	-	C_2H_5OH
X_3	-	0	1.02	CH_3CN

TABLE 13

Retention times of the original sample of the oxidation side products, R_{ox}, and the reference sample, R_{ref}.

Compound (oxidation)	R_{ox}/min	Compound (reference)	R_{ref}/min
X_1	1.59	CO_2	1.59
H_2O	3.46	H_2O	3.47
X_2	4.32	HCHO	4.34
CH_3OH †	8.14	CH_3OH	8.18
C_2H_5OH †	20.50	C_2H_5OH	20.58

(† These two compounds added to the oxidation sample for reference purposes.)

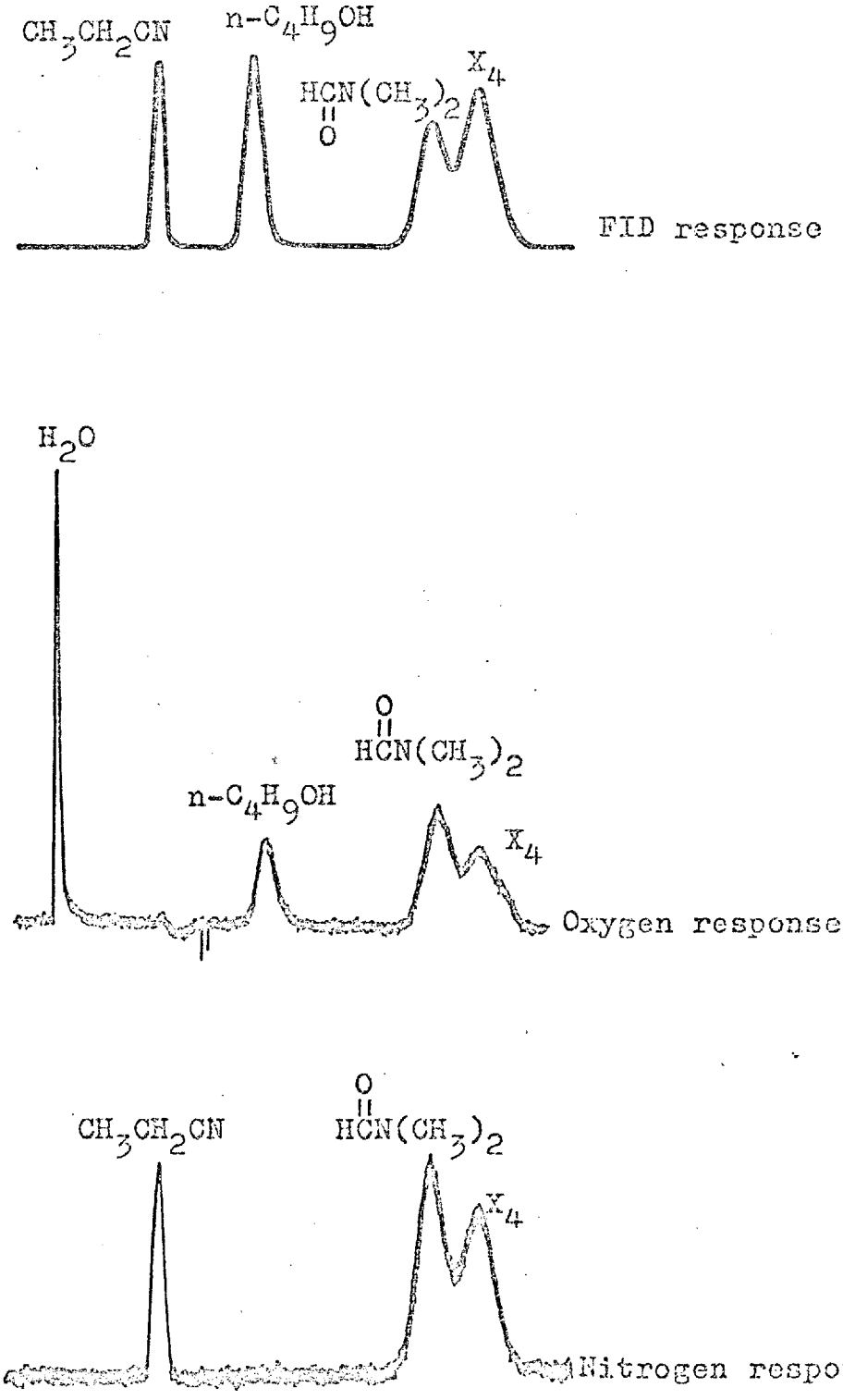


Fig. 24. Separation of the reduction product of acrylonitrile polyperoxide, X_4, on a Porapak Q column (2.1m x 4mm), at 216°C.

[Carbon, hydrogen, nitrogen and oxygen attenuations 32, 16, 4 and 8, respectively.]

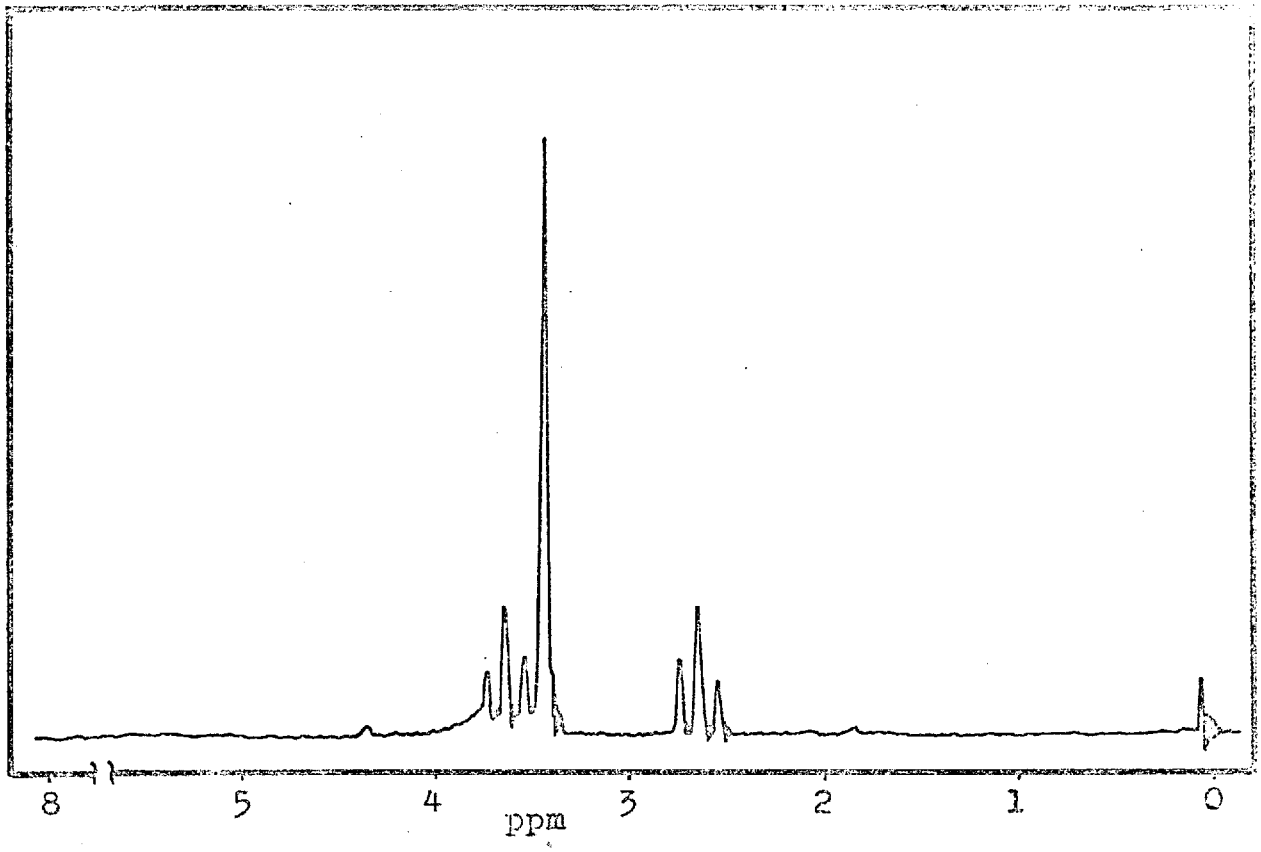


Fig. 25.A. NMR spectrum of the acrylonitrile polyperoxide reduction product, X_4.

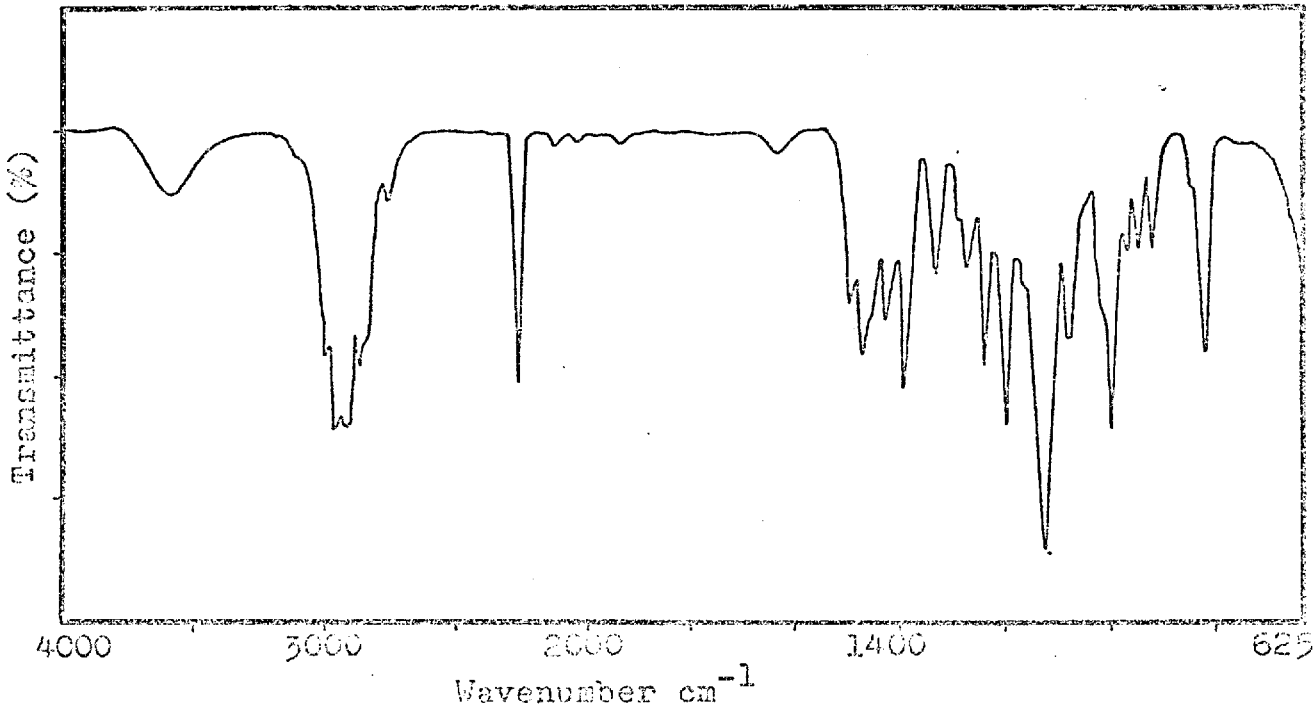


Fig. 25.B. IR spectrum of the acrylonitrile polyperoxide reduction product, X_4.

TABLE 14

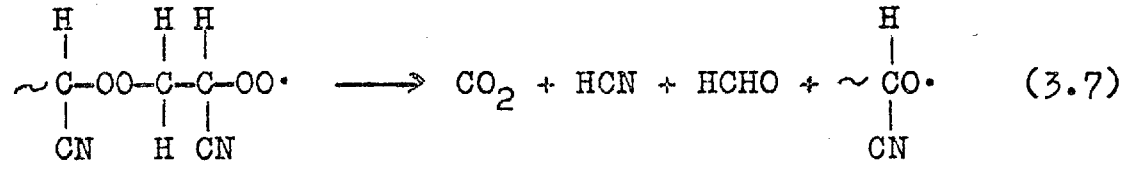
Elemental ratios of the reduction product of acrylonitrile polyperoxide

Compound	C/H	C/O	C/N	Internal Standard
X_4	0.566	-	3.95	CH_3CH_2CN
X_4	0.555	4.00	-	$n\text{-}C_4H_9OH$
X_4	0.568	4.07	3.91	$HCON(CH_3)_2$

3.4 Discussion

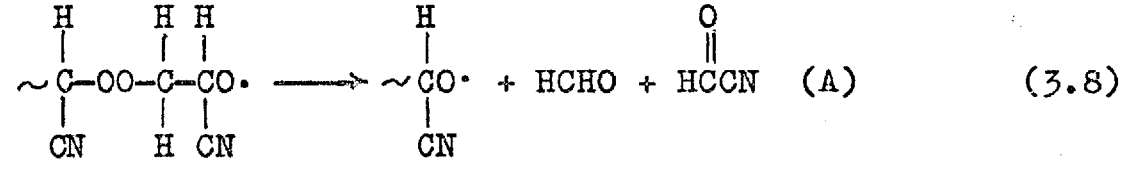
The main oxidation side products from the acrylonitrile - oxygen - initiator system, apart from the polymeric peroxide, were found to be hydrogen cyanide, carbon dioxide, formaldehyde and possibly carbon monoxide. Since no direct injection of the reaction mixture without prior fractionation was made, it is still uncertain whether these are the only products of acrylonitrile oxidation. Direct injection was not carried out mainly because of the presence of the polymeric peroxide in the oxidation mixture which may decarbonize on the gas chromatographic column and consequently impair its performance. Formation of side products such as glycolic acid ($HOCH_2COOH$) and cyanohydrin of glycol aldehyde ($HOCH_2CH(CN)OH$), which have been identified in the course of acrylonitrile oxidation in aqueous solution[16], is not likely in the bulk system since these compounds are produced by the interaction of the growing radicals with water. The exact mechanism of HCN evolution cannot be elucidated because

it is not clear whether its formation is from -H and -CN groups, attached to the same carbon atom or to adjacent carbon atoms. However, on the basis of the results obtained from the MPD 850, the following mechanisms are suggested for the formation of the side products:



(3.7)

the alkoxy radical can either add to another monomer or it can depolymerize further:



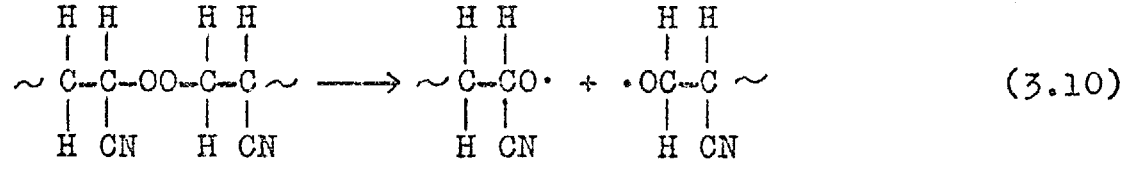
(3.8)

followed by,



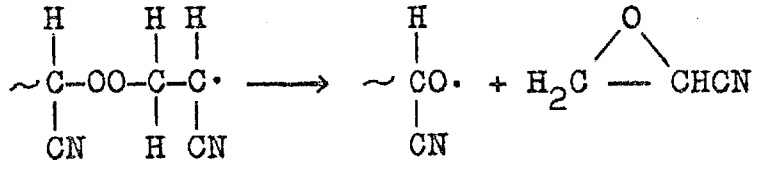
(3.9)

Cyanoformaldehyde, A, could exist as an unstable intermediate in reaction 3.8. Unsuccessful attempts have been made to prepare such a compound (A), but the final products of the reactions have always been carbon monoxide and hydrogen cyanide[60], indicating the instability of such an intermediate. Thus, it appears that cyanoformaldehyde rapidly decomposes to CO and HCN as in reaction 3.9. The alkoxy radicals could either be formed by the unzippering of a growing chain with a peroxidic end group as in 3.7, or could be formed by the homolytic decomposition of a peroxide bond in the polyperoxide.



(3.10)

The other expected cleavage product is glycidonitrile (2,3 epoxy propionitrile) which can be formed by depolymerization of the growing radicals with a monomeric end group:



(3.11)

Attempts to identify such a compound failed, possibly due to its very low concentration in the reaction distillate. In two cases in which epoxides of vinyl monomers have been observed, their concentrations relative to other oxidation products have been demonstrated to be very low, particularly at high oxygen pressures[9,10]. The higher yield of epoxides at low oxygen pressure has been attributed to the longer life of the radical chains with monomeric end groups. In the present study, in order to obtain a sufficient concentration (about 1-4% w/w) of the oxidation side products in acrylonitrile, the preparative reaction was carried out in the presence of relatively large amounts of oxygen. Hence, the concentration of glycidonitrile could well have been too low for detection.

Methoxy propionitrile, $NCCH_2CH_2OCH_3$, was anticipated to be one of the reduction products formed by reaction of the polymeric peroxide with a CH_3COOH-CH_3OH-KI mixture. However, this compound was later thought to be produced by a direct reaction between methanol and acrylonitrile monomer remaining as an impurity in the polymeric peroxide. The identification of methoxy propionitrile indicates the versatility of the MPD apparatus.

3.5 Conclusion

The MPD 850 instrument proved invaluable in the positive identification of several products produced by the interaction of oxygen with acrylonitrile in the presence of a free radical initiator. Future application in polymer chemistry might include:

1) the identification of low molecular weight materials produced in other polymerization systems,

2) studies of the degradation of polymers induced thermally, by light or by atomic radiation, and

3) studies of low molecular weight products produced by fusion reactions of polymers and copolymers.

Positive identification of the chemical nature of the polymers and copolymers is then feasible. In the course of these suggested applications, the deuterium channel could be particularly helpful. For instance, the mechanism of HCN evolution during polyacrylonitrile degradation might be elucidated, using α-deuterated polyacrylonitrile. Similarly, the mechanism of HCN formation throughout the induction period could also be determined using α-deutero acrylonitrile.

CHAPTER 4

A STUDY OF SOME PROPERTIES OF POLYACRYLONITRILE PREPARED IN THE PRESENCE OF OXYGEN

4.1 Introduction

The effect of oxygen on the kinetics of vinyl polymerization has been relatively well studied. However, very little research has been done on the effects of oxygen, incorporated into the polymer back-bone, on the physical and chemical properties of vinyl polymers. Polyvinyl chloride (PVC) appears to be the most studied of the vinyl polymers. Small scale bulk polymerizations under an atmosphere of nitrogen, air, and oxygen, have shown that the presence of oxygen decreases the molecular weight of the polymer samples considerably[61]. The initial rate of HCl evolution of a PVC sample at 175°C, prepared using its own polymeric peroxide as initiator, has been shown to be faster than a commercial PVC sample[62]. Furthermore, the polymer had a low chlorine content, a relatively low molecular weight and exhibited an exceptionally low decomposition point of <60-80°C [62].

Increasing the initial oxygen concentration in a series of bulk polymers indicated that a reduction in the average molecular weight occurred for samples isolated at a constant conversion (~10%)[63]. A study of the effect of initial oxygen concentration on the molecular weight distribution determined by gel permeation chromatography showed that at high conversion (~70%) the proportion of the low molecular weight polymer was independent of the

presence or absence of oxygen. The IR spectrum of a sample of PVC prepared in the presence of oxygen had an absorption band at 1770 cm^{-1}, associated with carbonyl group[63]. The intensity of such a band increased with increasing initial oxygen concentration and decreased with increasing conversion of monomer to polymer. The thermal stability of the bulk polymer samples, at constant conversion, decreased as the initial oxygen concentration increased[63]. Moreover, the thermal stability of PVC samples prepared at constant initial oxygen concentration depended on the degree of polymer conversion.

4.1.A. Dynamic thermogravimetric analysis of polyacrylonitrile (PAN)

Thernogravimetric analysis is the measurement of a change in weight as a function of temperature (DTG) or as a function of time at fixed temperature. The latter method is termed isothermal thermogravimetric analysis (ITG). By applying these techniques to polymers, valuable information concerning thermal stability and kinetics of degradation can be obtained. The advantages of DTG over ITG are that it requires a relatively small amount of sample and is less time-consuming. The thermal stability of PAN has been studied, using DTG, by several investigators[64,65,66,67]. The DTG traces obtained from the degradation of PAN were found to be susceptible to various factors such as sample size, particle size, heating rate, the environment under which degradation takes place and the method of polymer preparation[65]. Sample size when all other conditions were kept constant,

appeared to be the most important factor which influenced the degradation of PAN. In a series of experiments carried out with different sample sizes (1-10 mg), it was demonstrated that the temperature of incipient rapid weight loss increased as the weight of sample decreased. Furthermore, after the sharp initial weight loss, heavier samples continued to lose weight more rapidly. The environment under which degradation was carried out also had a considerable effect. Using identical experimental conditions, the weight losses in air were greater than those in nitrogen in the range 300-330°C. However, the greatest weight losses were observed when the polymer was degraded under vacuum. This most extensive weight loss was attributed to the ready volatization of some degradation products. Heating rate also affected the polymer degradation and an increase in the heating rate increased both the temperature at which rapid degradation started and the extent of the weight loss. The effects of the remaining two factors are not as important as those previously described.

4.1.B. Discolouration and thermal degradation of PAN

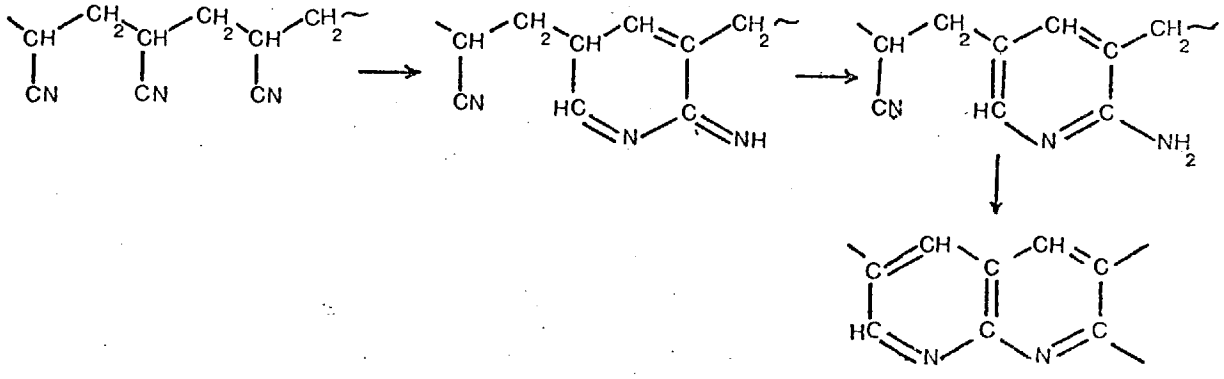
Although extensive research has been performed concerning the thermal degradation of PAN, the mechanism of degradation remains controversial. There have also been many investigations of the discolouration which is noticed when PAN is heated. In this chapter, various mechanistic aspects of the thermal degradation of PAN will first be reviewed and then the thermal stability of PAN samples, prepared in the presence and absence of oxygen, will be examined.

4.1.C. Mechanism of discolouration and thermal degradation of PAN

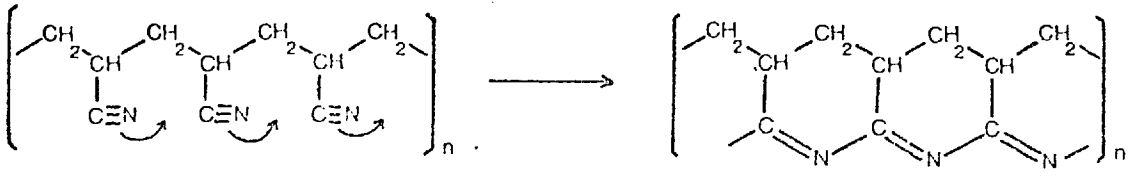
Due to the controversial nature of the degradation reaction involving PAN, the suggestions of some of the main workers in this field will be summarized as follows:

I. Houtz[68] postulated an aromatic naphthyridine structure for the discoloured polymer. The mechanism of the cyclization reaction involves hydrogen transference and elimination, as shown below:

(4.1)



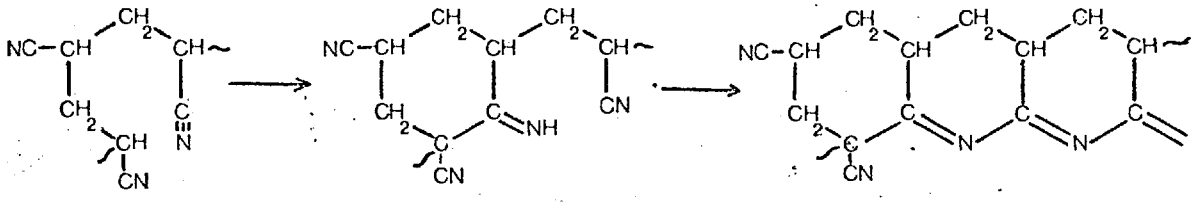
II. A naphthyridine-like structure for the discoloured polymer, formed during alkaline degradation, was first proposed by McCartney[69]. The naphthyridine-like structure was later postulated by Burlant and Parsons[70] for the discoloured residue formed during the pyrolysis of PAN. Accordingly, the mechanism by which this structure is formed is through the cyclization of neighbouring -CN groups:



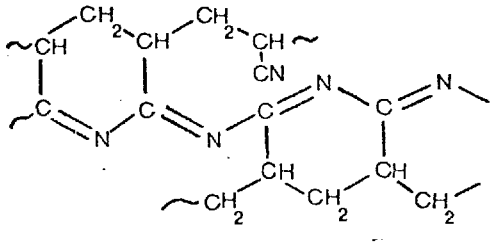
(4.2)

Although the final naphthyridine-like structure has been widely accepted[71,72], there is disagreement about the mechanism involved. The colour formation reaction is likely to be initiated by the tertiary C-H structures[72,73]. If this assumption is correct, then the reaction can proceed either by intermolecular or intramolecular mechanisms. The intramolecular reaction apparently is the predominant one which leads to a structure analogous to that proposed by McCartney[69].

(4.3)

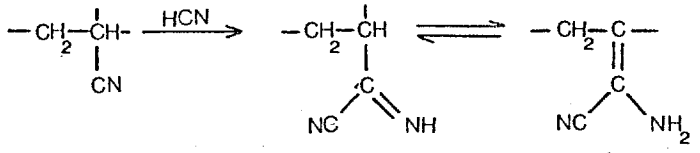


On the basis of the same assumption the rapid development of the insolubility of the polymer was attributed to a cross-linked network formed by some intermolecular reactions:



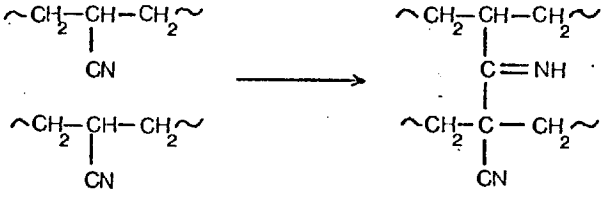
(4.4)

However, since acids are also capable of initiating the discolouration reaction, the other possible source of initiation could be HCN evolved during the thermal degradation of PAN[64].



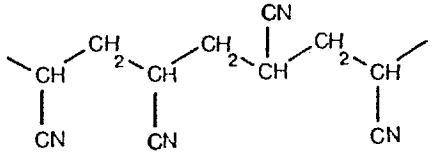
(4.5)

III. Schurz[74], on the basis of spectroscopic data and the reaction of the discoloured polymer with acids, proposed an azomethane linkage between the neighbouring chains. The reaction was suggested to be favoured by the strong attraction between active α-hydrogen atoms and -CN groups.



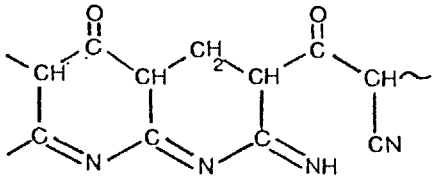
(4.6)

IV. The extent of the cyclization reaction is, according to Watt[75], controlled by the atacticity of the polymer chain.



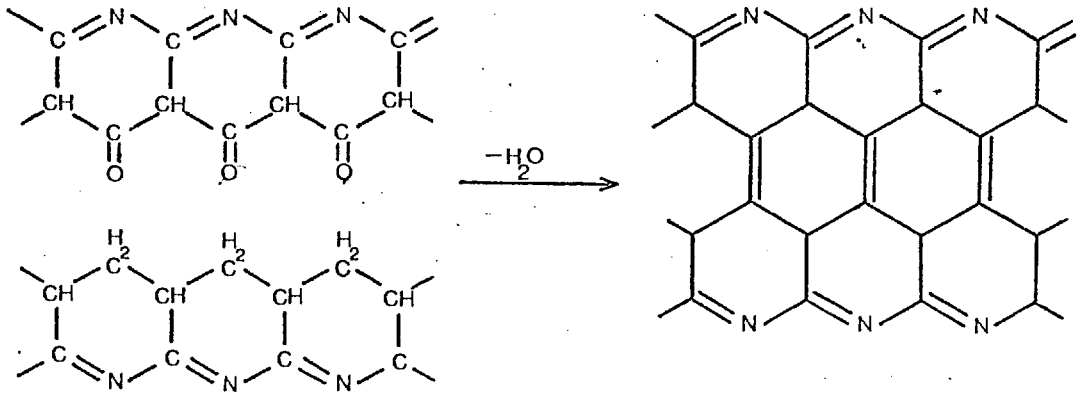
(4.7)

Watt also suggested that when the polymer was heated in air, simultaneous cyclization as well as oxidation of the $-CH_2$ groups took place:



(4.8)

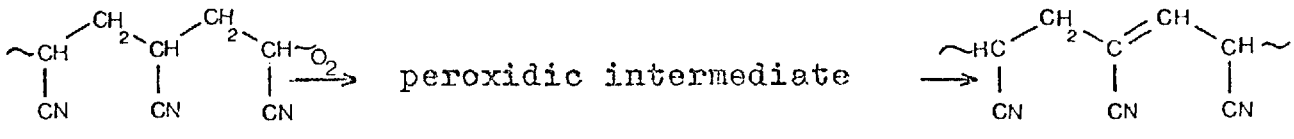
At higher temperature, a highly cross-linked network was formed by intermolecular reaction between the cyclized forms:



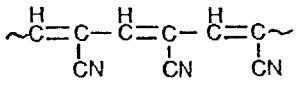
(4.9)

V. A single double bond conjugated with a -CN group was suggested as a precursor to the chromophore[76]. This structure was the decomposition product of a peroxidic intermediate formed during the oxidative degradation of PAN:

(4.10)



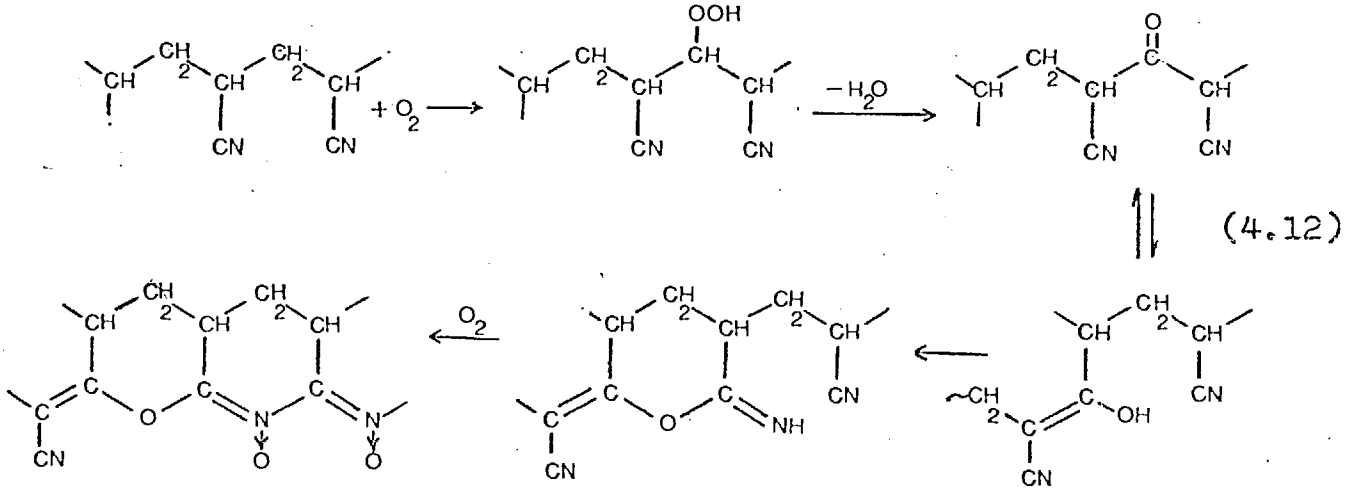
Subsequently, Berlin et al[77] and Fester[78] suggested that a system of conjugated double bonds with pendant nitrile groups could be formed:



(4.11)

Such a linear structure for the discoloured PAN would help to explain its solubility in DMF when degradation is performed in this solvent.

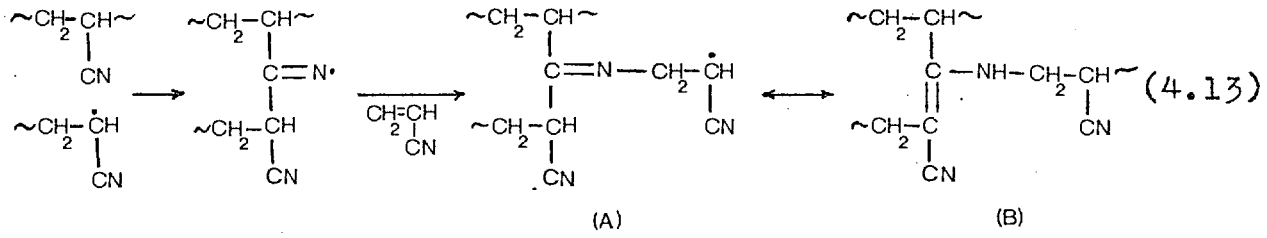
VI. During the oxidation of a series of model compounds, it was demonstrated that methylene hydrogen atoms were more susceptible to oxidation than tertiary hydrogen atoms[79]. On the basis of the data obtained, the following mechanism was suggested for the colour formation process[79,80]:



(4.12)

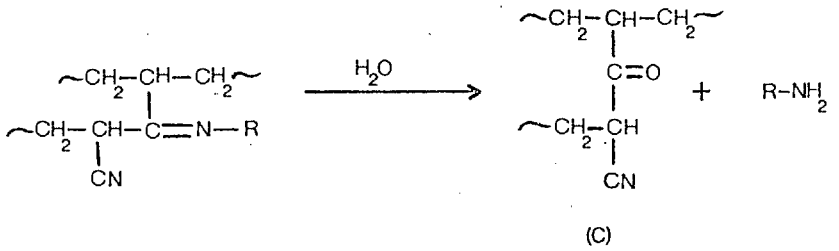
The final structure is a polymer containing imine and nitrone bonds.

VII. The colour formation reaction has also been suggested to take place through the abnormal structures, or defects, which may already exist in PAN[81]. The mechanism of formation of these defects, (A) and (B), during a radical initiated polymerization is as follows:



(4.13)

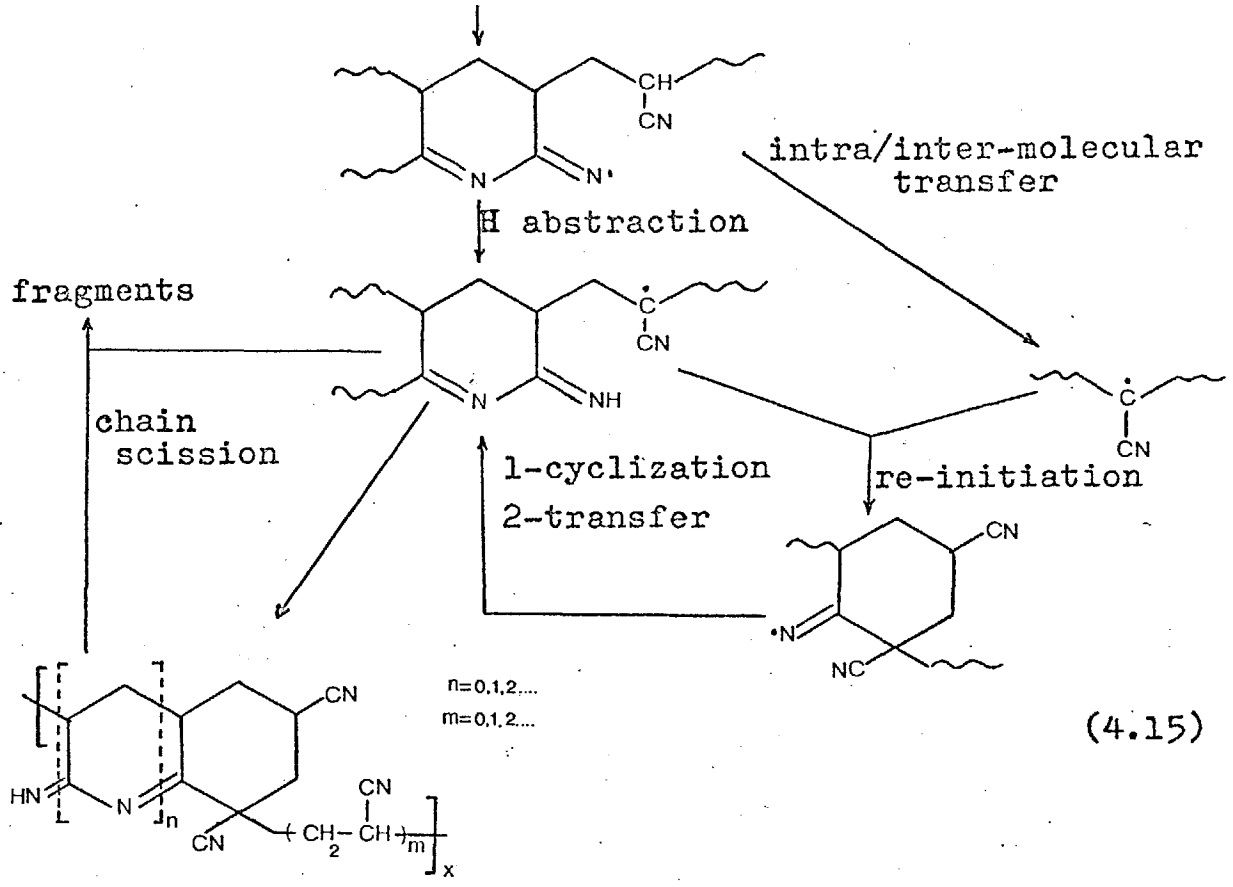
Under suitable conditions, the enamine structure (A) hydrolyses to form a ketonitrile structure (C) :



(4.14)

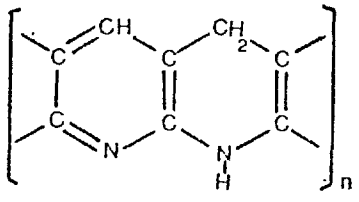
The capability of the enamine defect (A) in inducing colour formation reaction is more than that of the ketonitrile structure (C). The mechanism of colour formation initiated by the above defects involves small cyclized segments linked by segments of unaltered monomer units as shown below[66,82]:

Defects ⟶ cyclization/radicals



(4.15)

VIII. Monahan[83], on the basis of IR absorption and elemental analysis, suggested the following structure for the residue from the degradation of PAN in the temperature region 280-450°C.



(4.16)

4.2 Experimental

4.2.A. Preparation of the polyacrylonitrile sample

AIBN and acrylonitrile were purified by the methods described in chapter 2. Acrylonitrile was distilled under vacuum into a round bottomed flask of known volume and from thence into the main reaction flask containing AIBN with a concentration equal to 2.6×10^{-2} mol dm^{-3} (figure 26). Known volumes of oxygen were introduced into some of the flasks which subsequently were sealed off, after their contents had been frozen in liquid nitrogen, and immersed in a thermostat at $50 \pm 0.2^{\circ}C$. Stirring was maintained throughout the induction period by means of a magnetic follower. At the end of induction period a suitable volume of the reaction mixture was rapidly transferred into the calibrated side-dilatometer. After freezing the dilatometer contents and the remaining solution in the reaction flask, the dilatometer was sealed off and placed vertically in a water bath at $50 \pm 0.02^{\circ}C$. Normal polymerization was allowed to proceed until the polymer at a known degree of conversion had been formed (table 15). At this stage the dilatmeter was broken open and PAN was separated from the monomer by filtration, washed several times with chloroform and was subsequently dried in a vacuum oven at room temperature for several days. All the polymers prepared by this method, regardless of the initial oxygen concentration, were white. No further purification was carried out since the solvents for the polymer such as dimethylformamide are reported to be good initiating agents for the colour formation reaction[72].

4.2.B. Colour formation test

The colour formation examination, based on visual observation was carried out on the polymer samples prepared in the presence and absence of oxygen. Each polymer sample after being ground thoroughly, was loaded into a platinium crucible and placed in an oven. The oven temperature was then increased to 230°C at a heating rate of 10°C per minute. The temperature was maintained at 230°C for a period of four hours and the colour change of the samples was recorded at intervals of time (table 16).

4.2.C. Examination of the thermal stability of the polymer samples using a thermobalance.

The thermal stability of the polymer samples was examined using a Stanton Redcroft TG-750 thermobalance under static air and dynamic nitrogen atmospheres at elevated temperatures. The polymer samples, after being ground thoroughly, were loaded into a sample crucible and the weight of each sample was directly recorded on a recorder. After setting the temperature programming device at a heating rate of 3°C per minute, the experiment was commenced and the weight loss was determined under static air up to 450°C (figure 27). When the experiment was carried out under a nitrogen atmosphere, the apparatus was first flushed with nitrogen at a flow rate of 100 cm^3 per minute for twenty minutes. Moreover, in order to avoid any error due to the presence of moisture in the nitrogen, the nitrogen was first passed through a small column containing phosphorus pentoxide. Finally,

the nitrogen flow rate was reduced to 40 cm^3 per minute and heating was started at a rate of 10°C per minute. The weight loss was recorded up to 720°C at the above constant heating rate (figure 28). During the oxidative degradation as well as the degradation under a nitrogen atmosphere, all the samples prepared in the absence of oxygen lost about 0.5% of their weight by about 130°C. Since no further weight loss was observed until the incipient rapid weight loss, this initial 0.5% weight loss was attributed to the loss of water absorbed during the manipulation of the samples. In oxidative degradation some samples (D, P_1 and R_1) exhibited a sharp weight loss at the start of degradation at about 273°C, but others degraded slowly. In contrast to the oxidative degradation, all samples degraded under the nitrogen atmosphere had a sharp weight loss of about 5% at about 310°C. The sharp weight loss, during degradation of the polymer samples, both under air and nitrogen occurred almost simultaneously with a slight movement of the heat recording pen, indicating an exothermic reaction. No significant relationship was found between the initial oxygen concentration and the temperature of the incipient rapid weight loss which lies within 305-312°C for non-oxidative and 260-270°C for oxidative degradation. Furthermore, the temperature at which the samples lost 50% of their weight did not follow any particular pattern. This latter temperature is an important characteristic of a polymer sample in evaluating its thermal resistance. However it seems that the % weight loss for the polymer

samples prepared in the presence of oxygen depends on the initial oxygen concentration. When the % weight loss of the samples prepared in the presence of oxygen, up to 305°C for non-oxidative degradation and 258°C for oxidative degradation, was plotted against the initial oxygen concentration in the monomer-oxygen-AIBN system, linear relationships were obtained (figures 29 and 30). The effect of the degree of conversion of monomer to polymer on the thermal stability of samples prepared under a constant initial oxygen concentration was found to be small (figure 31). Since the effect of the sample size has been reported to be important, in determining the extent of polymer weight loss, attempts were made to use the polymer samples with an initial weight of 8-9 mg [64].

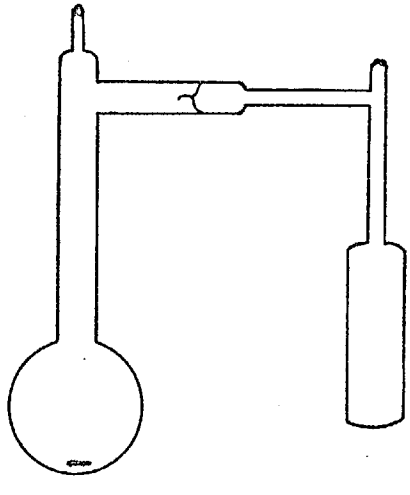


Fig. 26. Apparatus for the preparation of PAN samples.

4.2.D. Examination of the polymer samples by IR spectroscopy

IR absorption spectra of the polymer samples before and after prolonged heating at 230°C were recorded using a Perkin-Elmer model 157 G grating infrared spectrophotometer. Potassium bromide (BDH, for IR spectroscopy) was dried in a vacuum oven for 24 hours at 150°C. An intimate mixture of about 2% w/w PAN in KBr was obtained by grinding the polymer and KBr thoroughly using a pestle and mortar. After drying the mixture in a vacuum oven for several days at room temperature, a disc of PAN incorporated into KBr was prepared and its IR spectrum was recorded. For the PAN prepared in the absence of oxygen (figure 32), the absorption bands such as those at 2950, 2250, 1460, 1365 and 1080 cm^{-1} have been assigned to vibrations due to, for example, -CH, -CN and C-CN[84,85,86]. The band at 1630 cm^{-1}, reported in all the IR spectra of PAN in the literature, has been attributed to traces of impurity in PAN[86]. The polymer samples prepared in the presence of oxygen exhibited all the characteristic absorption of a normal PAN except for an extra absorption in the region 1750 cm^{-1}, possibly due to the presence of $-\overset{O}{\overset{\|}{C}}-$ groups (figure 33). The intensity of this band relative to -CN stretching ($-\overset{O}{\overset{\|}{C}}-/-CN$) had a linear relationship with the initial oxygen concentration in the reaction flask (figure 34).

On heating at 230°C for 30 minutes, the IR spectrum of the pure sample (P_2) did not vary appreciably, whereas the sample prepared under oxygen (H) displayed

two new bands in the region 1600 and 1725 cm^{-1}. After 3½ hours heating at 230°C, the major changes for both samples, prepared in the presence and absence of oxygen, were the formation of an intense band at 1600 cm^{-1} and a relatively weak band at 815 cm^{-1}. The intensity of absorptions due to C–H and –CN in these spectra, compared with those before heating, was reduced. Moreover, the intensity of the previous new absorptions relative to that of –CN for the sample H was higher than those for the sample P_2. All the new absorption bands described above were present in the IR spectra of the two samples (P_2 and H) after 7½ hours heating at 230°C. A new shoulder in the region 1660 cm^{-1} appeared in the spectra of both samples. The relative intensity of this new shoulder in the sample H was more than that of the sample P_2 (figure 34).

The IR spectra of the heat treated polymers are consistent with those reported for PAN undergoing oxidative degradation[66,72,76,87]. The absorption bands at about 1720, 1600 and 815 cm^{-1}, have been assigned to $-\overset{O}{\overset{\|}{C}}-$, either $\leftarrow C{=}C\rightarrow_x$ or $\leftarrow C{=}N\rightarrow_x$, and $=\overset{|}{C}-H$, respectively[64]. A broad band with a maximum at about 3450 cm^{-1} was also noticed for all thermally degraded polymers. This latter band (3450 cm^{-1}) has been assigned to a =NH vibration[64] but such an assignment might be invalid in the present study due to possible traces of water.

TABLE 15. Bulk PAN samples prepared at 50°C at various initial oxygen concentrations.

Sample	(Initial oxygen conc.)/ ppm w/w	(Induction period)/ min	Conversion/ %
P_1	0	0	2.44
P_2	0	0	1.22
P_3	0	0	0.65
M	374	20	1.17
R	771	38	1.00
H	1376	50	1.00
D	2633	120	1.87
R_1	771	36	3.59

TABLE 16. Colour formation test of various PAN samples heated at 230.

time/min / Sample	30	60	120	240
P_1	Light yellow	Dark yellow	Brown	Dark brown
P_2	Light yellow	Dark yellow	Brown	Dark brown
P_3	Light yellow	Dark yellow	Brown	Dark brown
M	Light brown	Brown	Dark brown	Black
R	Light brown	Brown	Dark brown	Black
H	Light brown	Brown	Dark brown	Black
D	Light brown	Brown	Dark brown	Black
R_1	Light brown	Brown	Dark brown	Black

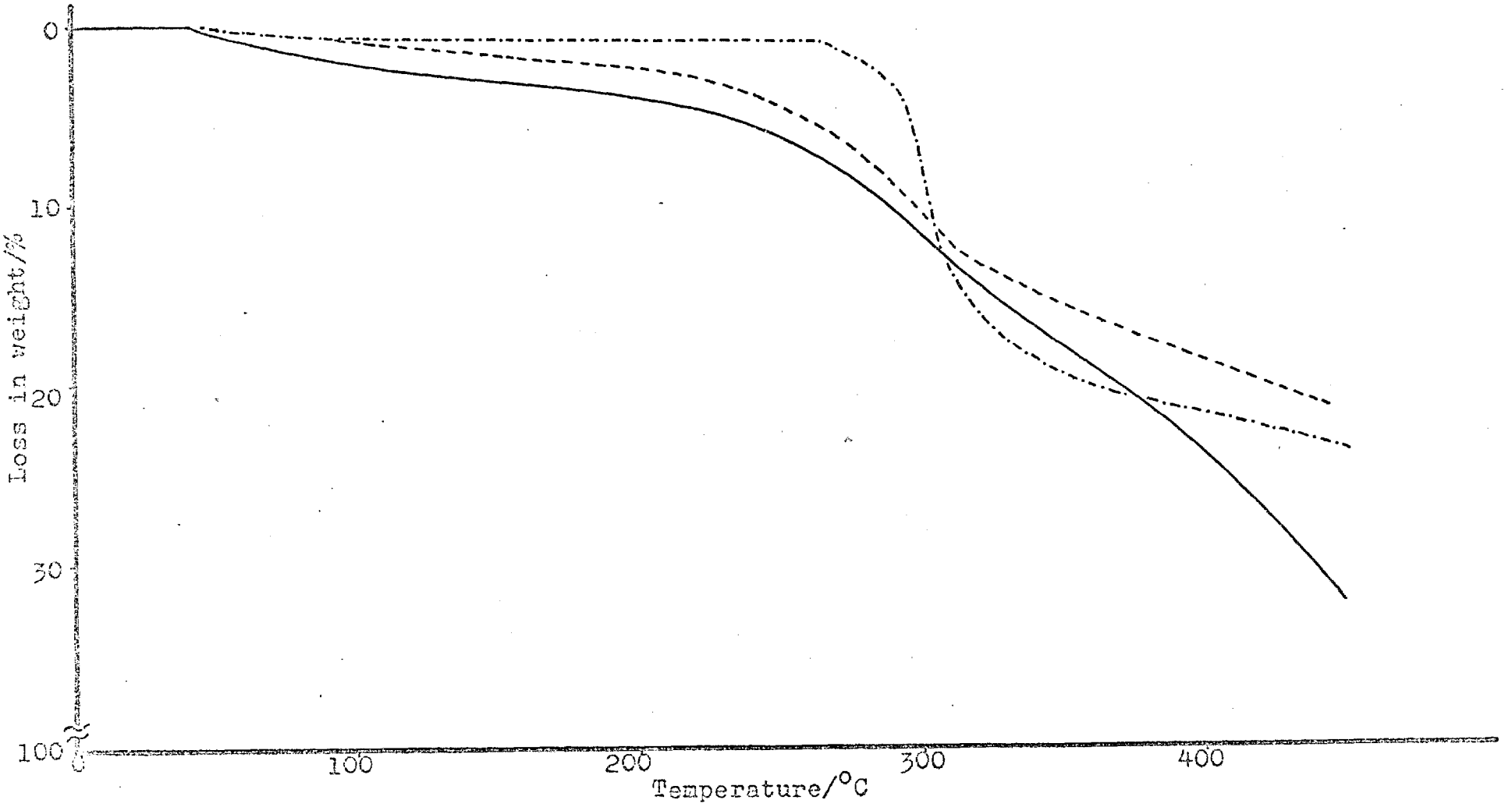


Fig. 27. Degradation of PAN samples prepared at 50°C using AIBN and with various initial oxygen concentrations; (-·-) 0 ppm w/w, (- -) 771 ppm w/w and (-) 1376 ppm w/w. Atmosphere static air. Heating rate 3°C min^{-1}.

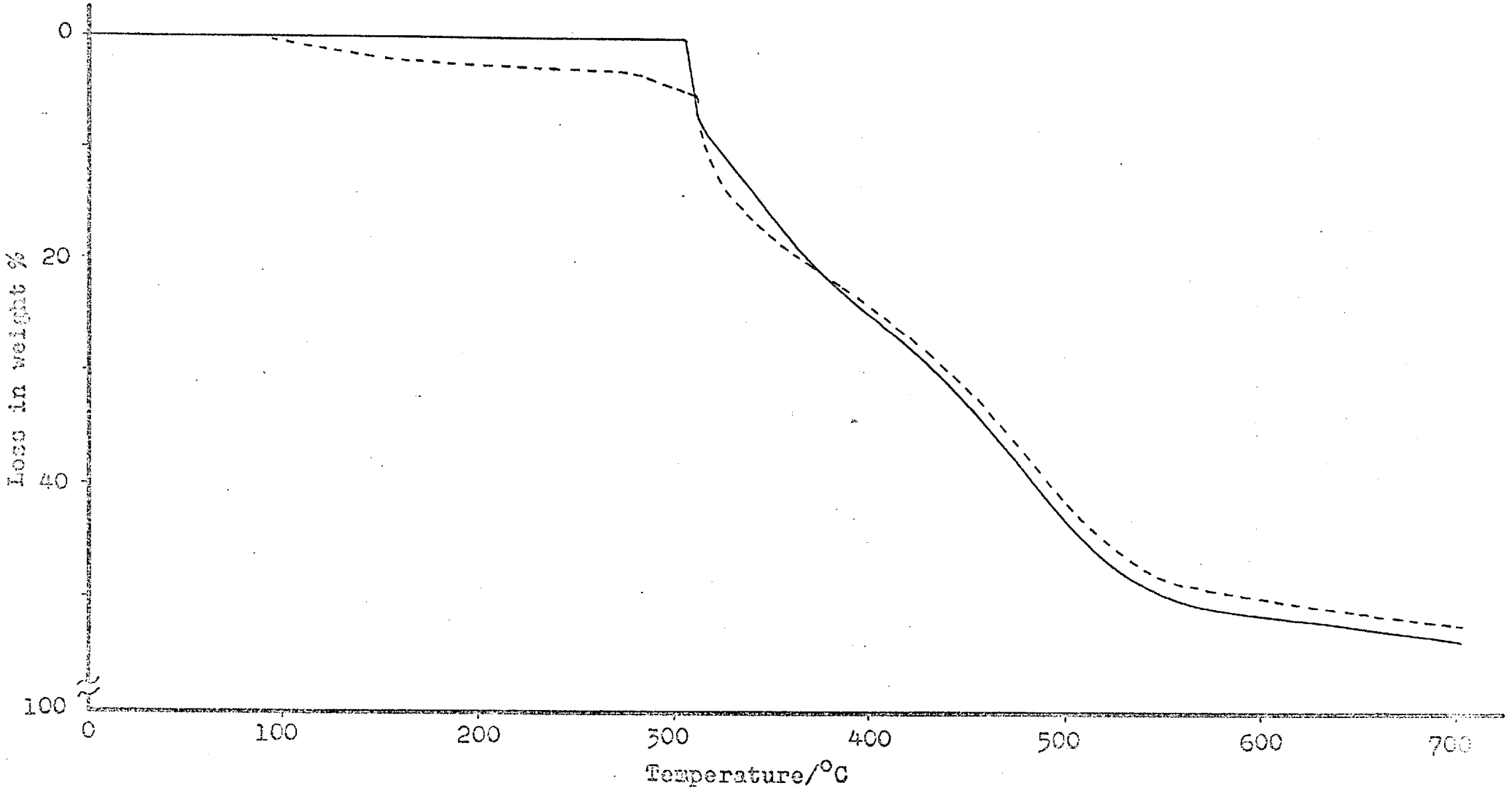


Fig. 28. TG of PAN samples prepared under vacuum (–) and under oxygen with an initial concentration of 1376 ppm w/w (---).
Atmosphere; nitrogen at a flow rate of $40^{o}cm^{3}min^{-1}$. Heating rate $10^{o}C\ min^{-1}$.

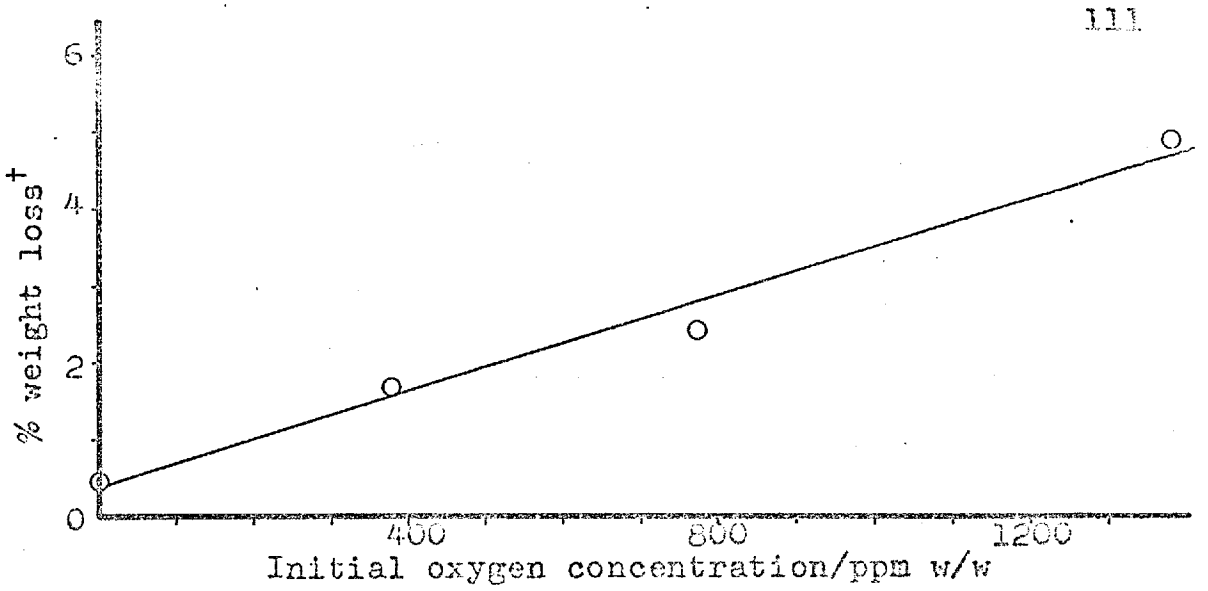


Fig. 29. Effect of the initial oxygen concentration on the thermal stability* of PAN samples degraded under a nitrogen atmosphere.

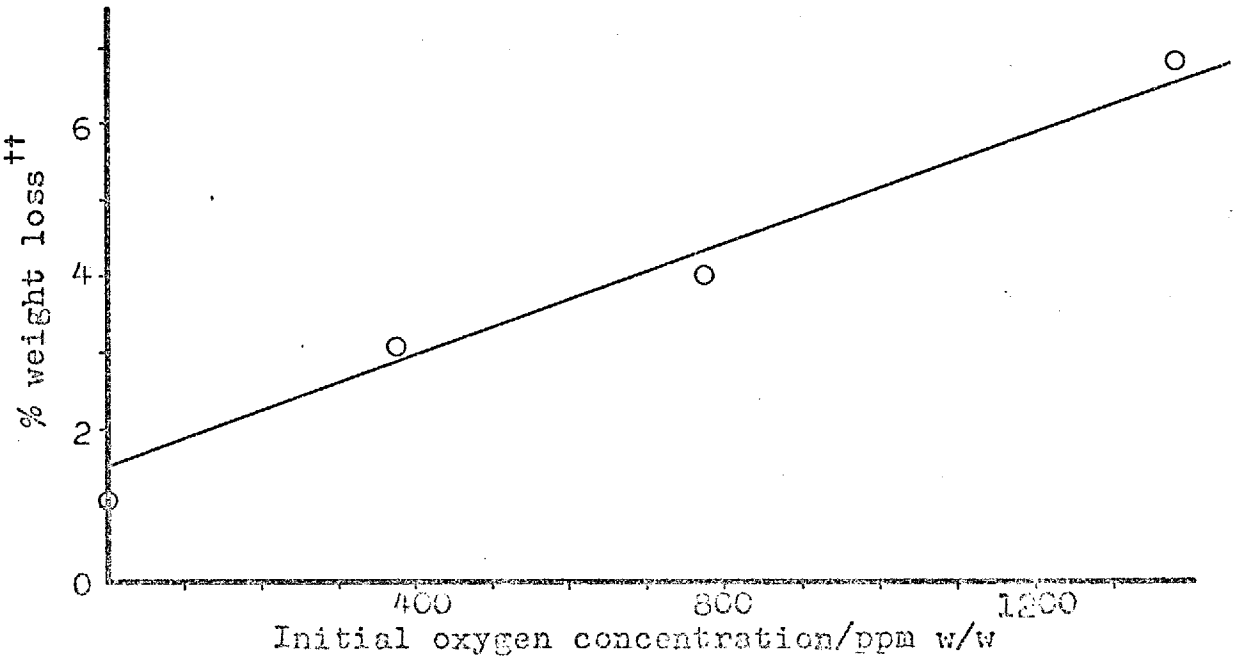


Fig. 30. Effect of the initial oxygen concentration on the thermal stability* of PAN samples degraded under static air.

* The % weight loss was calculated as that occurring before the onset of rapid degradation of the PAN samples.

† up to 305°C ; †† up to 258°C.

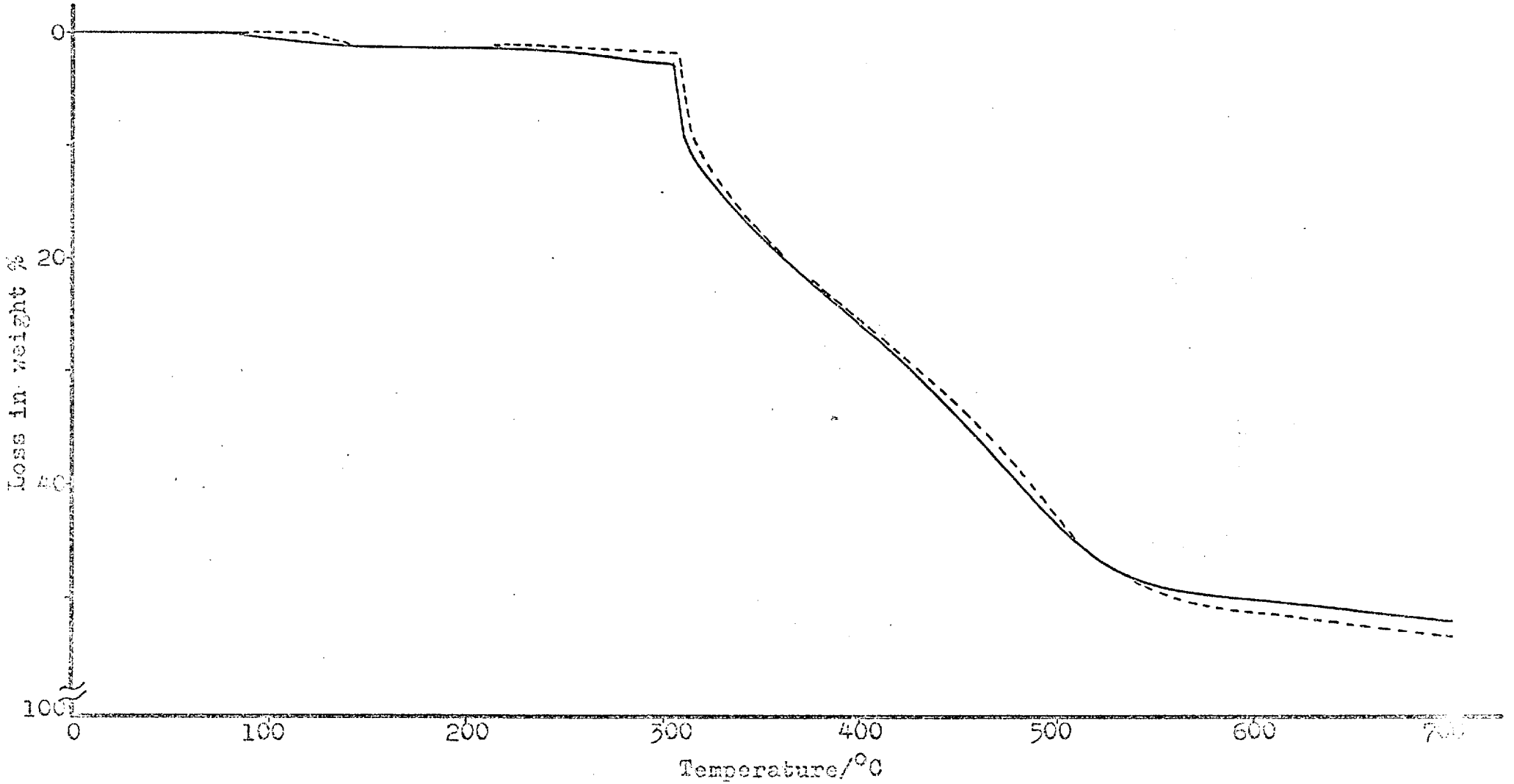


Fig. 31. Effect of the degree of conversion of monomer on the thermal stability of PAN samples prepared at 50°C using AIBN, at a constant initial oxygen concentration of 771 ppm v/v. (–) 1% conversion and (– –) 3.59% conversion.

Atmosphere, nitrogen at a flow rate of 40 cm^3 min^{-1}. Heating rate 10°C min^{-1}.

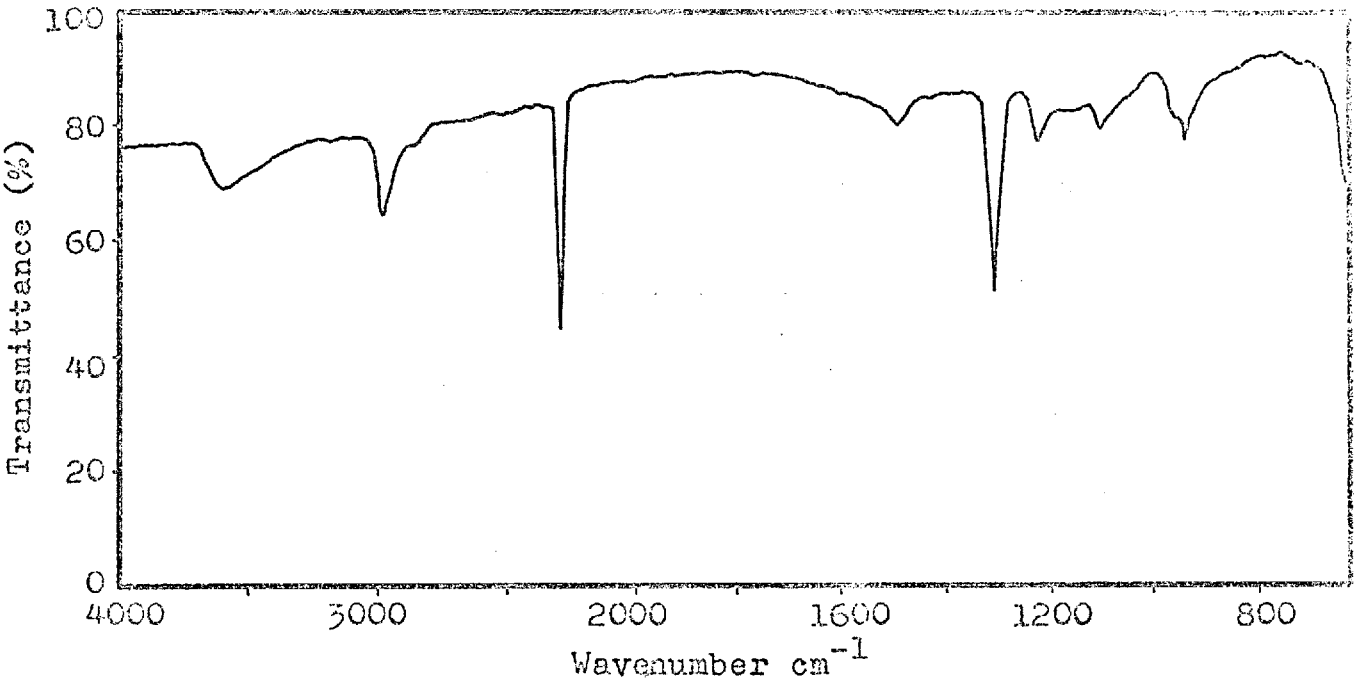


Fig. 32 IR spectrum of PAN prepared in the absence of oxygen.

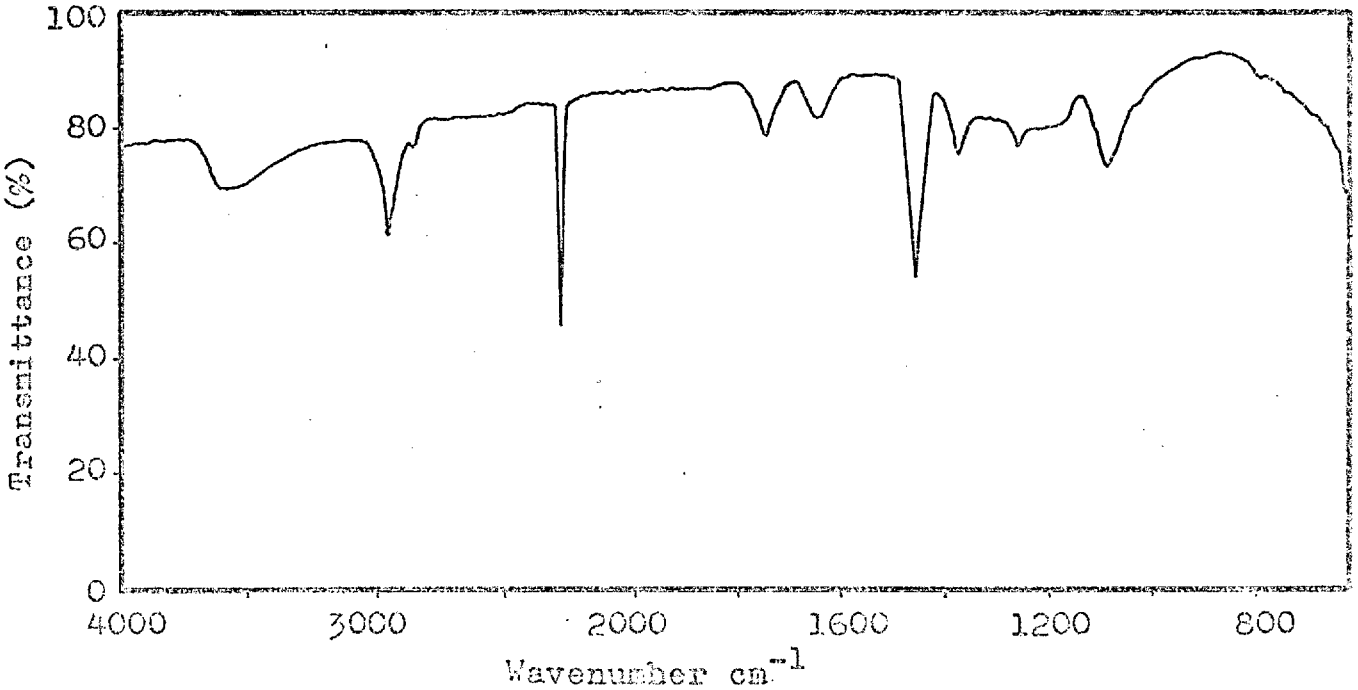


Fig. 33 IR spectrum of PAN prepared with an initial oxygen concentration of 1376 ppm w/w.

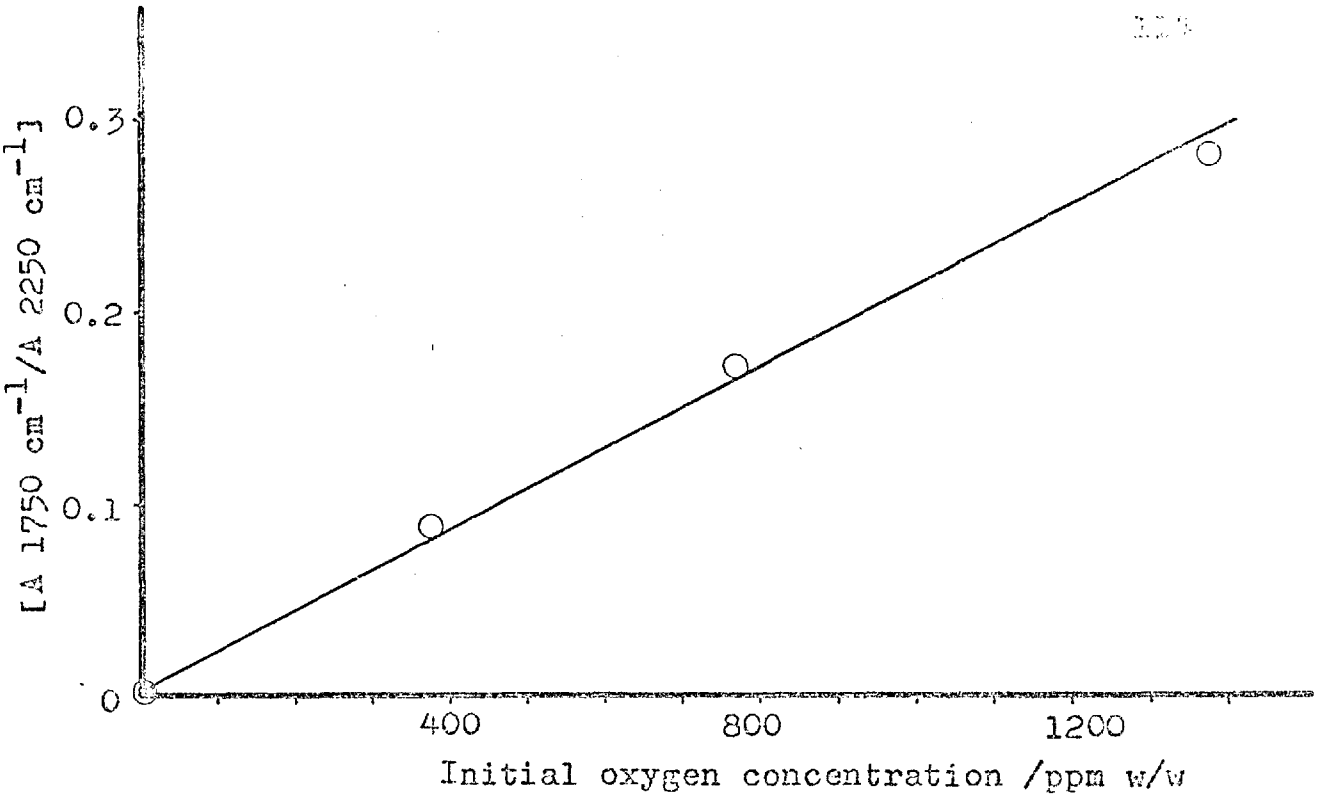


Fig. 34. Plot of [A 1750 cm^{-1}/A 2250 cm^{-1}] vs. initial oxygen concentration.

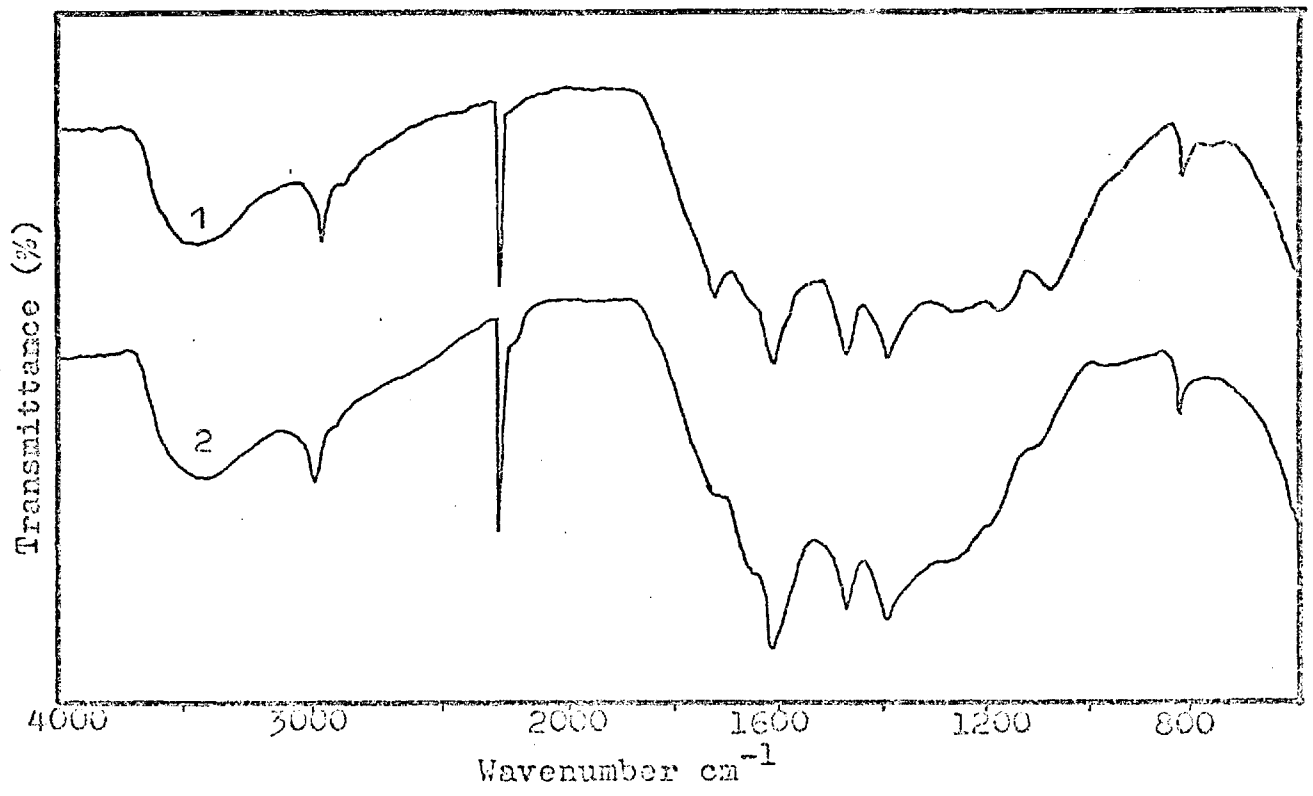


Fig. 35. IR spectrum after 7½ hours heating at 230°C. (1) Sample H(1376 ppm w/w initial oxygen concentration and (2) sample F_2 (prepared in the absence of oxygen).

4.3 Discussion

From DTG, IR spectroscopy and visual discolouration examinations of the PAN samples, it appears that samples prepared in the presence of oxygen discolour and degrade more rapidly than those prepared in the absence of oxygen. Two explanations can be given for the relative initial instability of PAN samples isolated after an inhibition period produced by oxygen; (I) the presence of the polyperoxide existing in PAN as an impurity initiates radical degradation and (II) incorporation of the peroxide bonds in PAN back-bone which also promotes degradation.

However, the existence of polyperoxide as an impurity in PAN is very unlikely since the acrylonitrile polymeric peroxide is highly soluble in the monomer and thus would be expected to be completely removed on filtration. The polyperoxide may be incorporated into PAN back-bones in two different ways: (I) near the end of the induction periods when the oxygen concentration is extremely low and the growing polyperoxidic radicals begin to add to monomer, and (II) through initiation by an alkoxy radical produced by the cleavage of a peroxide bond of a polymeric peroxide chain after the induction periods:

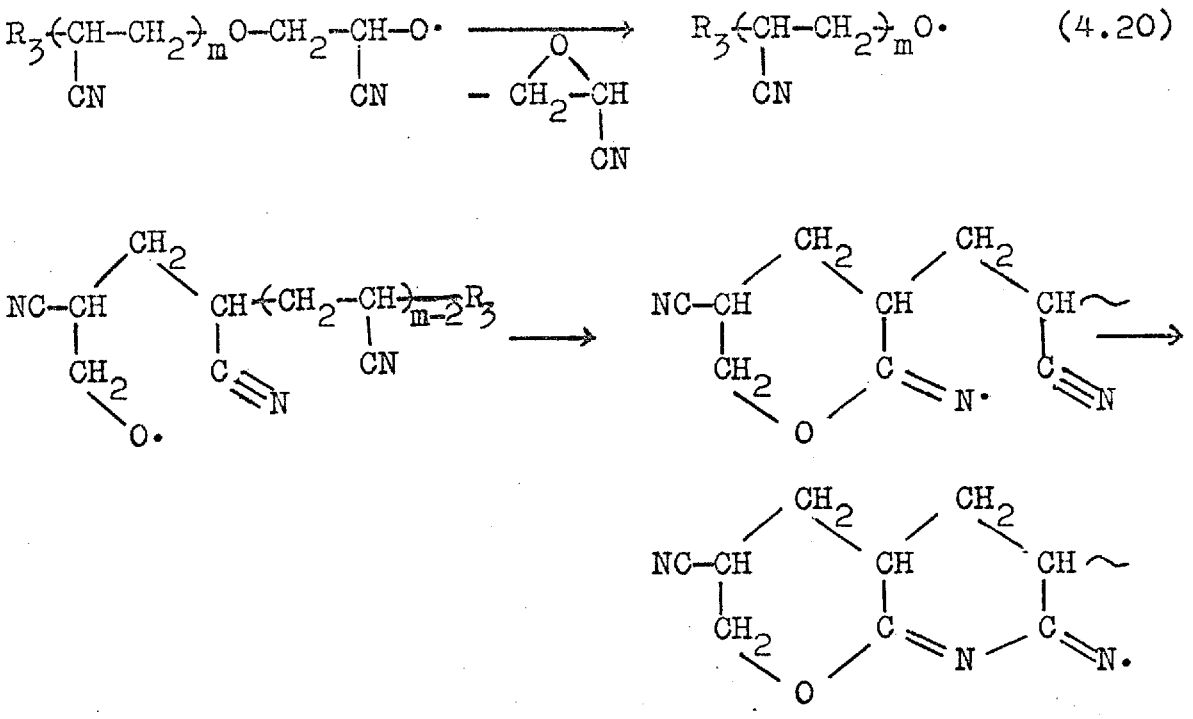
$$R_1\text{-}(OOCH_2\text{-}\underset{CN}{CH})_n OO(CH_2\text{-}\underset{CN}{CHOO})_{n_1} R_2 \longrightarrow R_1\text{-}(OOCH_2\underset{CN}{CH})_n O\cdot + \cdot O(CH_2\text{-}\underset{CN}{CHOO})_{n_1} R_2 \qquad (4.17)$$

$$R_1\text{-}(OOCH_2\text{-}\underset{CN}{CH})_n O\cdot + mCH_2{=}CHCN \longrightarrow R_1\text{-}(OOCH_2\text{-}\underset{CN}{CH})_n O(CH_2\text{-}\underset{CN}{CH})_m R_3 \qquad (4.18)$$

where R_1, R_2 and R_3 represent the appropriate end groups. For the sake of simplification, it has been assumed that after the peroxidic cleavage, the alkoxy radical does not undergo depolymerization. Furthermore, considering the relatively low molecular weight of the initially formed polymeric peroxide, the polymeric peroxide fragments incorporated into the polymer by reaction 4.18 must be of very short chain length. The peroxidic linkages along the PAN chains can be regarded as structural defects in the free radically prepared PAN under an oxygen atmosphere. Since the bond dissociation energy for a peroxidic bond is comparatively low ($-\overset{|}{\underset{|}{C}}-OO-\overset{|}{\underset{|}{C}}- \equiv 8.96$ kJ mol^{-1})[98], facile thermal or photochemical cleavage of this bond would be expected. The early scission of peroxide bonds on heating, could produce initiating centres which initiate the discolouration reaction and the degradation. On the basis of these observations and particularly the IR spectral data for the discoloured polymer, the following mechanism is proposed:

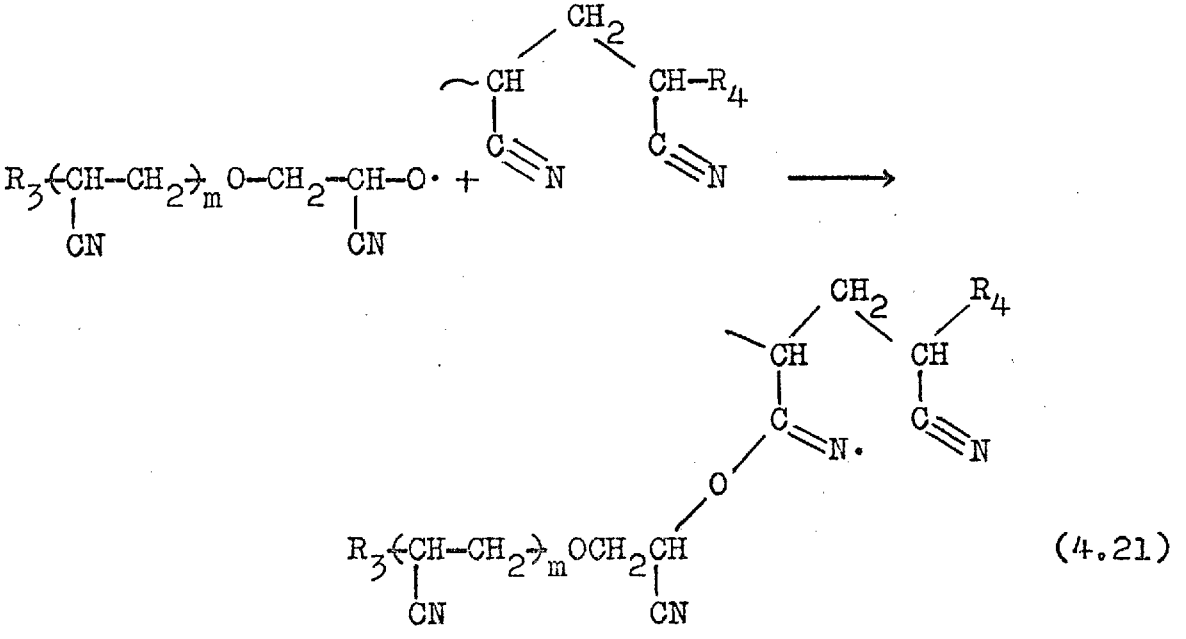
$$R_1\text{-}(OOCH_2\text{-}\underset{CN}{CH})_n O\text{-}(CH_2\text{-}\underset{CN}{CH})_m R_3 \longrightarrow R_1\text{-}(OOCH_2\text{-}\underset{CN}{CH})_{n-1} O\cdot + \cdot OCH_2\text{-}\underset{CN}{CH}\text{-}O\text{-}(CH_2\text{-}\underset{CN}{CH})_m R_3 \quad (4.19)$$

The peroxidic alkoxy radical would probably depolymerize to give products similar to the side products of the acrylonitrile oxidation (chapter 3). Assuming that the discoloured polymer has a cyclized structure, the colouration reaction may be written:



(4.20)

Intramolecular reaction by the initially formed radicals can also take place:



(4.21)

Since the polymeric peroxide fragments are unstable, complete decomposition will probably occur before the start of the rapid weight loss noticed in DTG experiments. This suggestion seems possible because PAN samples prepared in the presence of oxygen showed a relatively higher initial volatization.

The fact that the intensity of IR band at 1725 cm^{-1}, on heating at 230°C, increases with time implies that oxygen is incorporated as $-\overset{O}{\overset{\|}{C}}-$ groups in the polymer back-bone during the oxidative degradation. The mechanisms of this reaction could be similar to those previously described for the oxidative degradation of PAN (introduction to this chapter).

However the mechanism of degradation may not be as simple as that proposed and various other degradative reactions reviewed in the introduction to this chapter could occur simultaneously. While the mechanism suggested for the degradation of PAN samples prepared in the presence of oxygen is in good agreement with DTG and IR spectroscopy results, it must be considered tentative due to insufficient data obtained. Indeed the main reason for the controversy concerning the thermal degradation of PAN is the insolubility of the degraded polymer which has limited studies to IR spectroscopy and elemental analysis.

4.4 Conclusion

The presence of traces of oxygen during the bulk polymerization of acrylonitrile initially reduces the thermal stability of the resulting polymers compared to that of polymers prepared in the absence of oxygen. This reduction in thermal stability of the polymer samples is apparently due to the incorporation of oxygen as peroxidic linkages in the polyacrylonitrile back-bones.

CHAPTER 5

EFFECT OF OXYGEN ON THE SOLUTION POLYMERIZATION OF VINYLIDENE CHLORIDE

5.1 Introduction

It was intended initially that the study of the effect of oxygen on bulk vinylidene chloride polymerization should be carried out dilatometrically, but no induction period was observed under various experimental conditions such as using different temperatures, initial oxygen concentrations and initiator concentrations. This observation was in accord with other reports on vinylidene chloride which state that the reaction of oxygen with the monomer to form polyperoxide is often accompanied by polyvinylidene chloride precipitation[88,89]. Burnett and Melville[90] also did not report an induction period in the photopolymerization of pure vinylidene chloride samples saturated with oxygen at atmospheric pressure. Furthermore, they found an approximate 15% increase in the polymerization rate of such samples compared with the rate for the pure monomer. Razuvaev and Minsker[17], who studied the effect of oxygen on the bulk polymerization of this monomer, attributed the appearance of the turbidity to the limited solubility of the polymeric peroxide in the monomer. Nevertheless, in the same paper, they reported the isolation of a sample of the polymeric peroxide which was not completely disintegrated by an acetic acid solution of KI in methanol. The residue was proved by micro-analysis to be pure polyvinylidene chloride.

However, according to all the information available in the literature[91,92], as well as peroxide tests carried out on the dilatometers contents described previously, it seems that vinylidene chloride like many vinyl monomers reacts with molecular oxygen to form a polymeric peroxide. Since the initial concentration of oxygen in dilatometric experiments is relatively low, the appearance of a white precipitate on heating initially is most likely due to polyvinylidene chloride precipitation. It was, therefore, not feasible to measure induction periods dilatometrically so in order to clarify the problem and to suggest a kinetic interpretation for the unusual behaviour of this monomer, it was decided to carry out oxygen uptake experiments in chlorobenzene. Chlorobenzene has a relatively low vapour pressure at 40°C and is a solvent for the polymeric peroxide.

5.2 Experimental

5.2.1. Materials

(I) Vinylidene chloride

Vinylidene chloride (Koch-Light Laboratories Ltd.) was freed from inhibitor by twice washing with 20% w/v aqueous NaOH followed by distilled water. It was dried over calcium hydride, distilled over calcium hydride in vacuo and was collected in cleaned vessels which were subsequently sealed off at the temperature of liquid nitrogen. The vessels were then stored in liquid nitrogen until required.

(II) Chlorobenzene

Chlorobenzene (Hopkin and Williams Ltd., GPR grade) was dried overnight over calcium hydride. It was then fractionally distilled under vacuum, the middle fraction was collected and kept over molecular sieve until required.

(III) Other reagents

All other reagents were purified as described in chapter 2.

5.2.2. Methods

(I) Oxygen uptake measurements using vinylidene chloride

All experiments were carried out in an apparatus similar to that used by Bovey and Kolthoff (figure 36). The reaction vessel consisted of a 100 cm^3 round bottomed flask joined to a condenser. A gas burette with a total

volume of 137.5 cm^3 was connected to a main mercury reservoir, A, by means of which certain volumes of oxygen at atmospheric pressure could be introduced into the reaction vessel. The total volume of the apparatus enclosed between the reaction flask and stopcock T_2, stopcocks T_2 and T_1 and stopcocks T_2 and T_3 was measured (205 cm^3) several times by introducing known volumes of oxygen from the gas burette into the apparatus.

AIBN was transferred to the reaction vessel as a solution in chloroform. After complete removal of the solvent in vacuo, 50 cm^3 of a solution of vinylidene chloride (0.5-2 mol dm^{-3}) in chlorobenzene at 20°C was quickly pipetted into the reaction flask. The solution was frozen in liquid nitrogen and was degassed by closing T_1 and opening T_2 and T_3. The solution was degassed once more and with T_1 open to the atmosphere, the gas burette was filled completely with mercury by lifting the mercury reservoir. An oxygen cylinder was then connected to the apparatus and after pumping out the connecting tube, oxygen was allowed into the gas burette. With T_3 closed and the reaction flask still in liquid nitrogen, oxygen was introduced from the gas burette into the calibrated apparatus. After closing T_1, the solution was thawed and the reaction flask was immersed in a thermostat at 40 ± 0.2°C. Eventually, when the solution attained thermal equilibrium, the rate of oxygen uptake was measured using a cathetometer to record the height of the mercury meniscus. Readings were taken at 5-30 minute intervals, depending on the speed of the uptake rate.

Stirring throughout the reaction was maintained by a magnetic stirrer and a magnetic follower covered with teflon. Since the volume of the reaction mixture was small, stirring was considered to be quite efficient. Assuming that monomer depletion during the reaction is negligible, the volume of oxygen consumed at any time can be calculated. Typical plots are shown in figures 37-39. The polyperoxide formed during the reaction accelerates the rate of the oxygen uptake and consequently the initial slopes of the uptake curves were used in all calculations. Oxygen reacts with vinylidene chloride in the absence of added initiator so the rate of the purely thermal oxidation was also measured at 40°C (figures 40 and 41). If one assumes the following equation for the rate of oxygen consumption in the presence of an initiator,

$$-d\left(P_{O_2}\right)/dt = k\left(P_{O_2}\right)^{a}\,[I]^{b}[M]^{c} \qquad (5.1)$$

where P_{O_2} is the initial oxygen pressure, [I] is the initial initiator concentration, [M] is the initial monomer concentration and k is a constant, then:

$$\log\left\{-d\left(P_{O_2}\right)/dt\right\} = \log k + a\log\left(P_{O_2}\right) + b\log[I] + c\log[M] \qquad (5.2)$$

The values of a, b and c were determined from plots of $\log\left\{-d\left(P_{O_2}\right)/dt\right\}$ against the logarithm of one variable, keeping the other two variables constant (figures 42-44).

(II) Determination of vinylidene chloride densities

Densities of vinylidene chloride at various temperatures were determined by measuring the monomer volumes at different temperatures using a dilatometer.

Five dilatometers with known bulb volumes, 3-6 cm^3, and 2 mm i.d. 'Veridia' precision bore capillary were prepared. Calibration of the dilatometers was carried out using distilled water. After drying the dilatometers, purified vinylidene chloride was condensed into the dilatometers in vacuo at the temperature of a mixture of solid CO_2 and methylated spirits. The dilatometers were sealed off when their contents had been frozen in liquid nitrogen. The monomer in each dilatometer was thawed and its weight was determined gravimetrically. Finally, the dilatometers were immersed in a thermostat at 20 ± 0.02°C. The increase in the height of the monomer meniscus in the capillary at higher temperatures was measured using a cathetometer. In order to allow the monomer to attain true thermal equilibrium, each dilatometer was left in the thermostat for at least 20 minutes. Densities at 0°C and -76°C were measured by placing the dilatometers in Dewer flasks at these temperatures. When the monomer had reached thermal equilibrium, the level of the monomer in the capillary was marked by a diamond pencil after removing the dilatometers momentarily. The mean densities, calculated from the individual experiments agreed satisfactorily with the values in the literature when comparison was possible (table 17).

(III) <u>% Conversion of oxygen to the vinylidene chloride polymeric peroxide</u>

In order to estimate the amount of oxygen converted to the polyperoxide, solutions of vinylidene chloride (1-2 mol dm^{-3}) in chlorobenzene in the presence

of AIBN were allowed to react with oxygen. After consuming various volumes of oxygen the reaction flask was pumped out under vacuum for fifteen minutes at room temperature to remove the remaining vinylidene chloride and some solvent. The residual solution was transferred into the simple apparatus shown in figure 2 (chapter 2). The polyperoxide solution, after purging with nitrogen, was reduced by the method I described in chapter 2. The liberated iodine was titrated against N/10 $Na_2S_2O_3$ solution, using starch as an indicator. From the volume of oxygen absorbed by vinylidene chloride and the volume of $Na_2S_2O_3$ solution consumed, the % conversion of oxygen to polyperoxide was calculated. The results are shown in table 18.

(IV) Identification of the oxidation side products of vinylidene chloride

The identification of the oxidation side products was carried out essentially in the same way as described in chapter 3. Oxidation side products were prepared by allowing the monomer to react with oxygen in chlorobenzene, in the presence of AIBN at 40°C. The cleavage products, the monomer and some chlorobenzene were separated by distillation in vacuo at room temperature and injections were made into a Porapak Q column connected to the MPD 850. Among the oxidation side products only formaldehyde and carbon dioxide were positively identified. Possible chlorinated compounds, such as HCl and $COCl_2$ were not detected.

(V) Initiation abilities of vinylidene chloride polyperoxide and AIBN in vinylidene chloride solution polymerization

Since the oxidation of vinylidene chloride was auto-accelerating both in the presence and absence of AIBN, it was therefore necessary to examine the initiating capability of the polymeric peroxide of vinylidene chloride. In order to prepare pure polymeric peroxide, a solution of purified vinylidene chloride at a concentration of 2.5 mol dm^{-3} at 20°C in chlorobenzene was transferred to a round bottomed flask. After degassing the solution, a known volume of oxygen was admitted to the flask and the flask was subsequently sealed off while cooled in liquid nitrogen. The reaction was then allowed to proceed at 40 ± 0.2°C until all the oxygen was consumed. At this stage, the flask was taken out of the thermostat, broken open and some of its contents were transferred to calibrated dilatometers which were later degassed and sealed off in vacuo. The rest of the solution, after removal of vinylidene chloride by evacuation for about twenty minutes, was used for the estimation of the polymeric peroxide concentration by the iodometric method.

The rate of polymerization of vinylidene chloride in chlorobenzene solution containing polymeric peroxide at different concentrations was measured at 70°C using the values of 1.126 and 1.67 g cm^{-3} as the densities of the monomer and polymer, respectively. These rates were then compared to the rate of polymerization induced by AIBN (2.4×10^{-2} mol dm^{-3} at 70°C), using the same

concentration of monomer. The slight depletion of the monomer concentration during the oxidative preparation of the polyperoxide was considered to be negligible. As can be seen from figure 45 the polymerization reaction rate, in spite of heterogeneity, does not accelerate within the % conversion range studied.

(VI) Determination of k_d for the decomposition of the polyperoxide of vinylidene chloride in chlorobenzene at 40°C

A sample of polyperoxide was prepared by treating a solution of vinylidene chloride (2 mol dm^{-3}) in chlorobenzene, with oxygen, in the presence of AIBN (10^{-4}mol dm^{-3}) at 40°C. When about 80 cm^3 of oxygen at one atmosphere had been absorbed, the solution was quickly transferred to a 250 cm^3 flask. Vinylidene chloride was then removed by bubbling a stream of oxygen through the well stirred solution at 40°C for a period of an hour. The contents of the flask were diluted with chlorobenzene and equal volumes (10 cm^3) were transferred into some dilatometers. The dilatometers were degassed twice, sealed off and stored in liquid nitrogen. The initial concentration of the polymeric peroxide was determined in one of the dilatometers using method I described in chapter 2. The remaining dilatometers were wrapped in aluminium foil and immersed in a thermostat at 40 ± 0.02°C. The concentration of the polymeric peroxide in the dilatometers was determined at various intervals of time. Assuming that the rate of decomposition of a peroxidic bond, ⊣ O–O ⊢ , is of the first order, one can write:

$$-O-O- \xrightarrow{k_d} 2\text{-}O^{\bullet} \longrightarrow \text{Other products} \qquad (5.3)$$

$$-\frac{d[-O-O-]}{dt} = k_d\,[-O-O-] \qquad \ldots \qquad (5.4)$$

and upon integration between the initial concentration at zero time and the concentration at time t, equation 5.4 becomes,

$$k_d = \frac{1}{t} \ln \frac{[-O-O-]_o}{[-O-O-]_t} \qquad \ldots \qquad (5.5)$$

or,

$$\log[-O-O-]_t = \log[-O-O-]_o - \left(\frac{k_d}{2.303}\right) t \qquad (5.6)$$

Since one mole of -O-O- liberates one mole of iodine which in turn reacts with two moles of sodium thiosulphate, the concentration of $[-O-O-]_t$ is proportional to the volume of $Na_2S_2O_3$ consumed. Thus, k_d of the polyperoxide was obtained by plotting the logarithm of $Na_2S_2O_3$ volume against time (figure 46). The slope of the straight line is equal to $-k_d/2.303$.

(VII) Determination of k_d for AIBN decomposition in chlorobenzene at 40°C

In order to make a comparison between the values of k_d for the polymeric peroxide of vinylidene chloride and AIBN in the same solvent, the decomposition of AIBN was examined in a solution of chlorobenzene at 40°C. The decomposition rate of AIBN was determined by measuring the pressure of nitrogen evolved in a suitable apparatus shown in figure 47. The volume of the apparatus, between the two calibration marks was carefully measured and then a U-shaped one mm i.d. bore capillary was joined to the

apparatus. The manometer was filled with mercury to a total length of about 80 cm and 50 cm^3 of a solution of AIBN (3 g dm^{-3} at 20°C) in chlorobenzene was pipetted into the flask. The flask contents were twice degassed and the apparatus was subsequently sealed off. The apparatus contents were thawed and the flask was immersed in a thermostat at 40 ± 0.02°C. After about one hour, the initial height of the mercury meniscus was recorded, using a cathetometer. The level of water in the thermostat was continuously maintained at 1 cm above the height of the solution in the flask. One source of error in this method is the solubility of nitrogen in chlorobenzene. Therefore, a correction for this was made by measuring the solubility of nitrogen at various partial pressures of nitrogen, using the apparatus described previously in this chapter (figure 36). Assuming that each mole of AIBN evolves one mole nitrogen, the k_d value of AIBN can be determined by plotting $\ln(P_\infty/P_\infty - P_t)$ against time, where P_∞ is the maximum pressure exerted by the nitrogen at infinite time and P_t is the pressure of the apparatus at any time t (figure 48). In practice, P_∞ was determined indirectly by calculation.

(VIII) Oxidizability of vinylidene chloride

Enough data is now available to compare the relative oxidizability of vinylidene chloride, using its known Q and e values, with some other vinyl monomers. This type of comparison was first carried out by Bailey[93] who plotted the relative rate of oxidation of some vinyl monomers and chloroprene to that of styrene, against the

value of $\log Q - 0.5(e + 0.8)$ for each corresponding monomer. All the measurements of the rate of oxygen uptake were carried out under identical conditions, i.e., 1 mol dm^{-3} monomer, initiated by 0.01 mol dm^{-3} AIBN in chlorobenzene under atmospheric pressure of oxygen at 50°C. The rate of oxygen uptake for a concentration of AIBN of 0.01 mol dm^{-3}, in the present work, was calculated from the initiator concentration-initial rate logarithmic plot (figure 42). The value obtained is for an initial pressure of oxygen equal to 60.8 cm Hg, so a correction to atmospheric pressure must be made. Upon applying all the corrections, the rate of oxidation of vinylidene chloride at 40°C is 161×10^{-4} mol dm^{-3} h^{-1} which is considerably higher than that of styrene at 50°C (table 19 and figure 48). Since the rate of AIBN decomposition at 50°C is approximately 4.6 times that at 40°C, this correction makes the oxidation rate even higher. The relative high oxidizability of vinylidene chloride is difficult to explain on the basis of the present results.

TABLE 17

Densities of vinylidene chloride at various temperatures

Temperature/°C	Density/g cm^{-3}	Density*/g cm^{-3}	Reference
-76	1.380		
0	1.250	1.2516	94
20	1.215	1.2129	95
25	1.206	1.2087	95
30	1.197		
40	1.180		
45	1.171		
50	1.161		
55	1.152		

* values in the literature.

TABLE 18

% conversion of oxygen to the vinylidene chloride polyperoxide

(Oxygen uptake)*/ cm^3	N/10 $Na_2S_2O_3$/ cm^3	Active oxygen content/cm^3	% Conversion
21.0	16.4	9.2	43.7
28.1	18.1	10.1	36.0
35.7	28.4	15.9	44.5
53.7	36.6	20.5	38.1
61.9	42.8	24.0	38.7
66.0	44.5	24.9	37.7

* [Volumes of oxygen were measured at 1 atm. pressure and 20°C.]

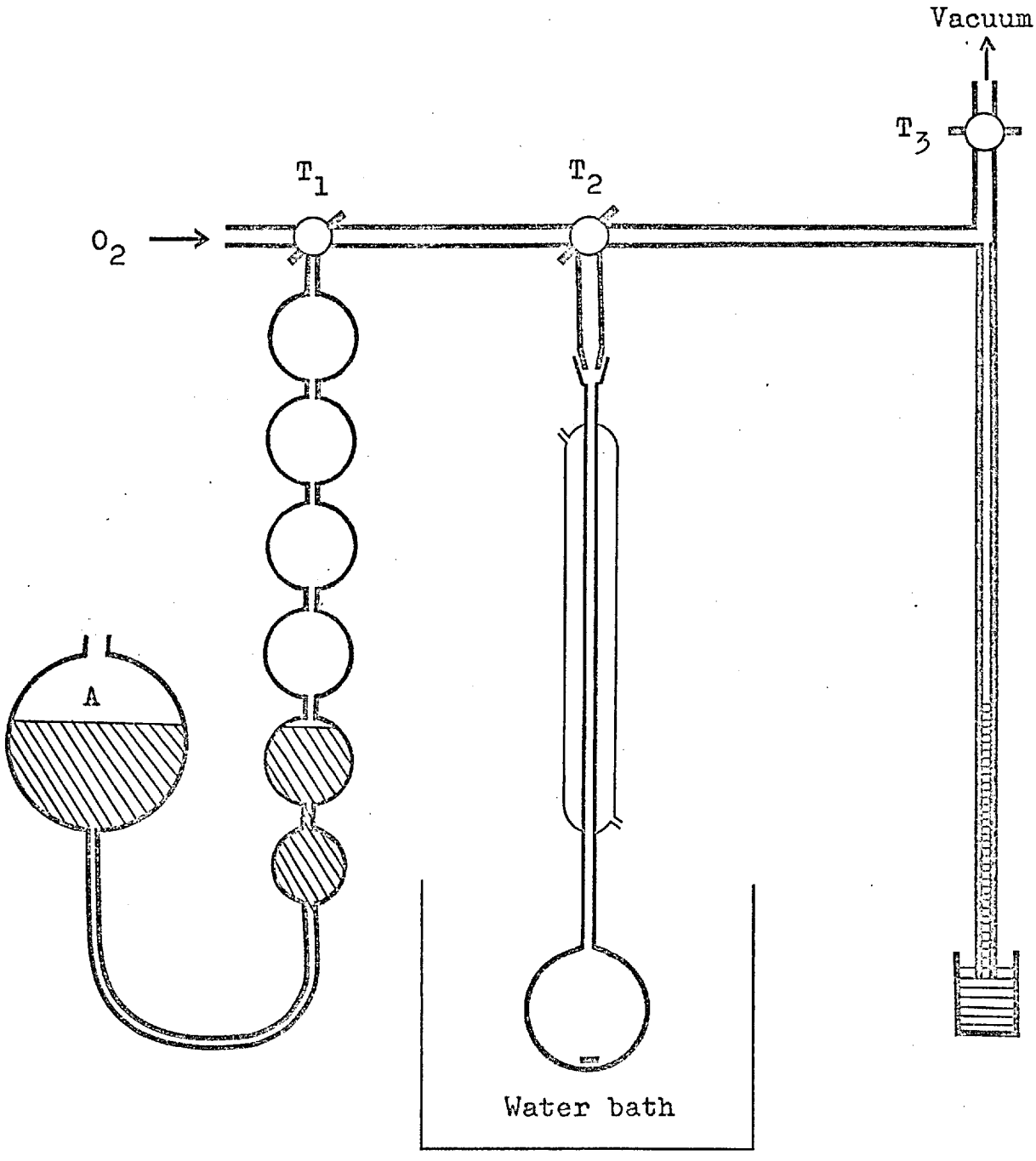


Fig. 36. Apparatus for the measurement of the rates of oxygen consumption.

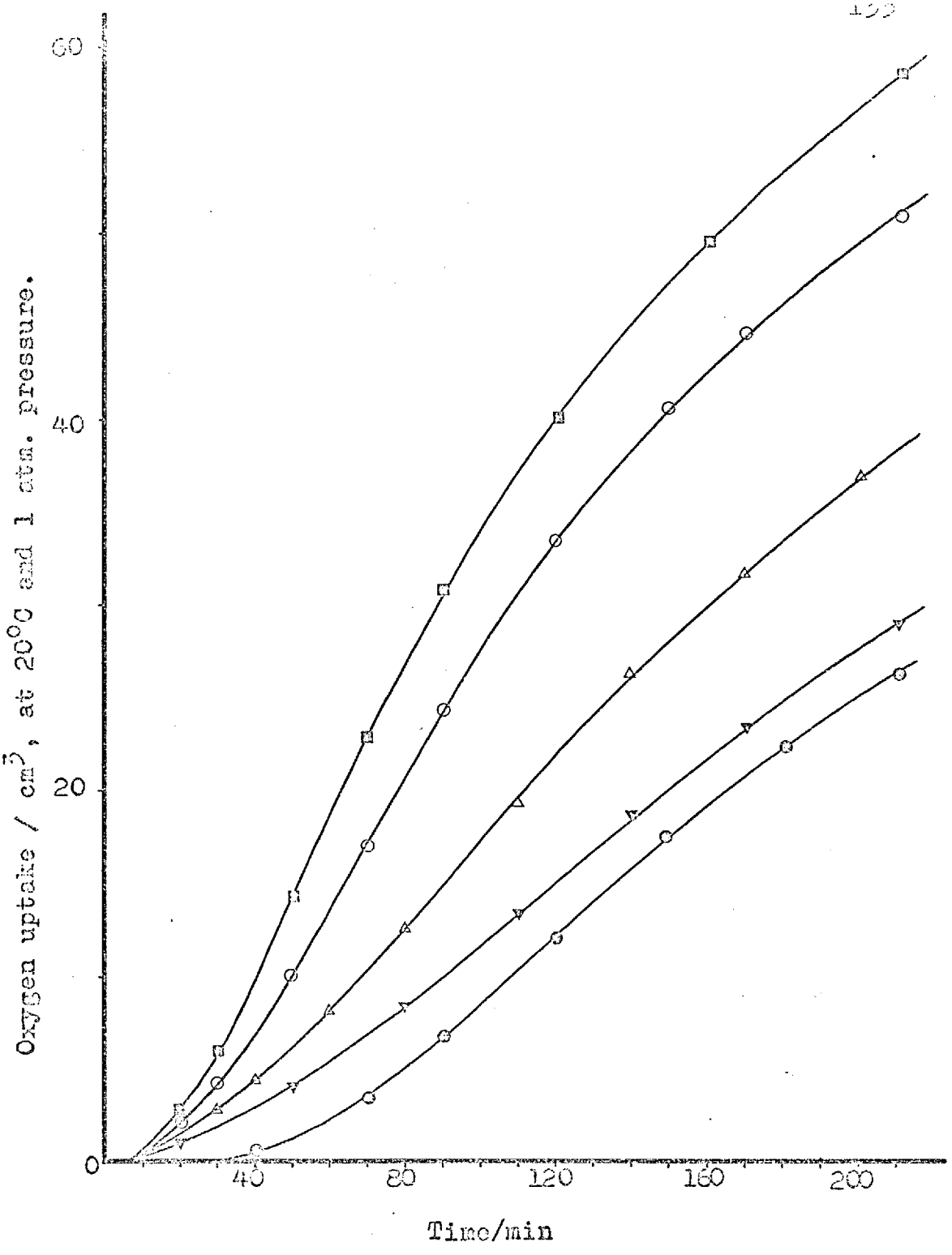


Fig. 37 Oxygen uptake as a function of time at 40°C at a constant concentration of vinylidene chloride of 1 mol dm^{-3} and a constant initial oxygen pressure, P_{O_2} = 60.8 cm Hg, at various concentrations of AIBN; (o) 2.5x10^{-4} mol dm^{-3}, (▲) 5 x 10^{-4} mol dm^{-3}, (△) 10^{-3} mol dm^{-3}, (○) 2 x 10^{-3} mol dm^{-3} and (□) 4 x 10^{-3} mol dm^{-3}.

[P_{O_2} is calculated assuming that the oxygen occupies only the gas phase in the apparatus.]

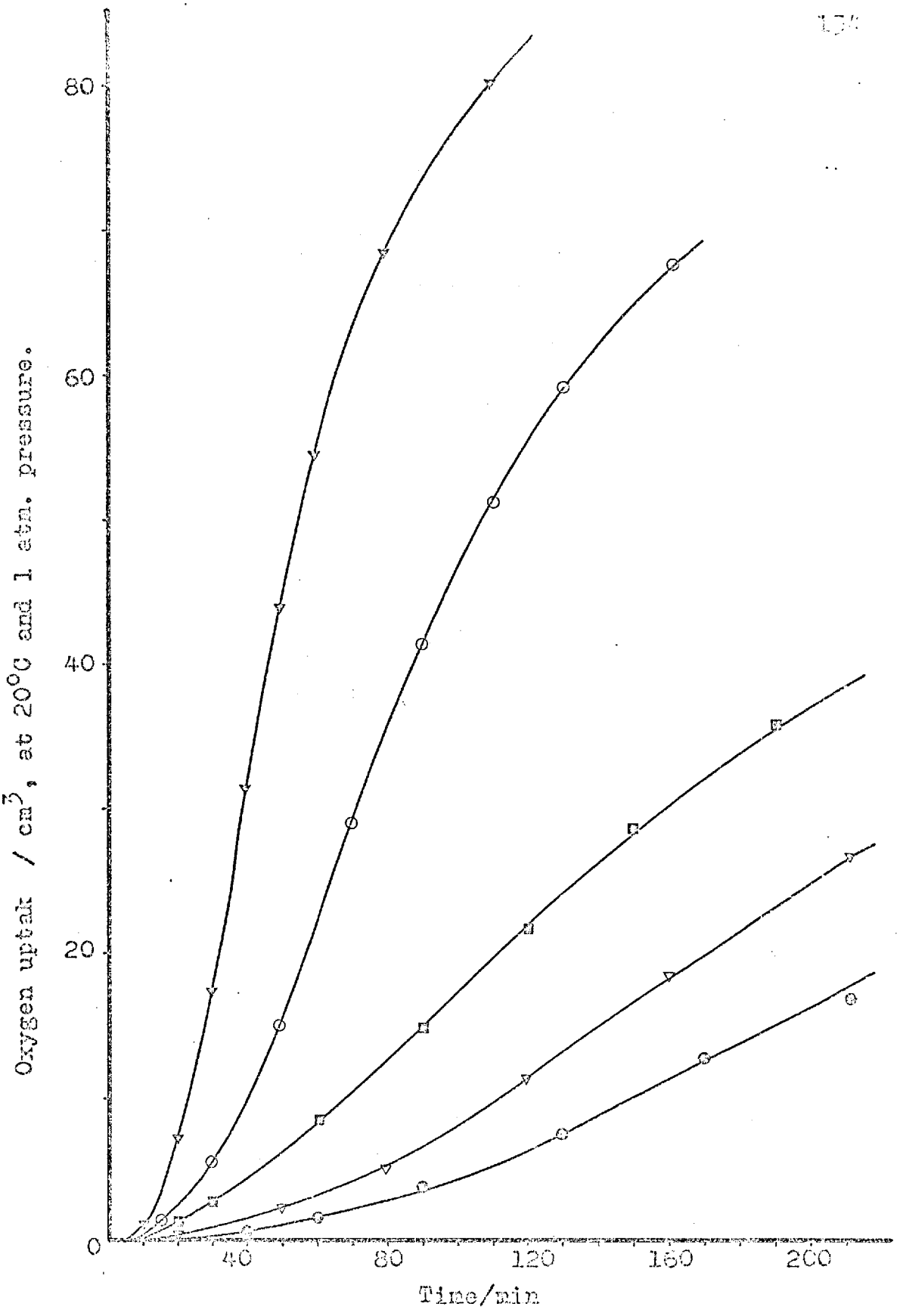


Fig.38 Oxygen uptake as a function of time at 40°C at a constant initial oxygen pressure of 60.8cm Hg and a constant AIBN concentration of 10^{-3} mol dm^{-3}, at different vinylidene chloride concentrations; (o) 0.5 mol dm^{-3}, (Δ) 0.75 mol dm^{-3}, (□) 1 mol dm^{-3}, (○) 1.5 mol dm^{-3} and (▲) 2 mol dm^{-3}.

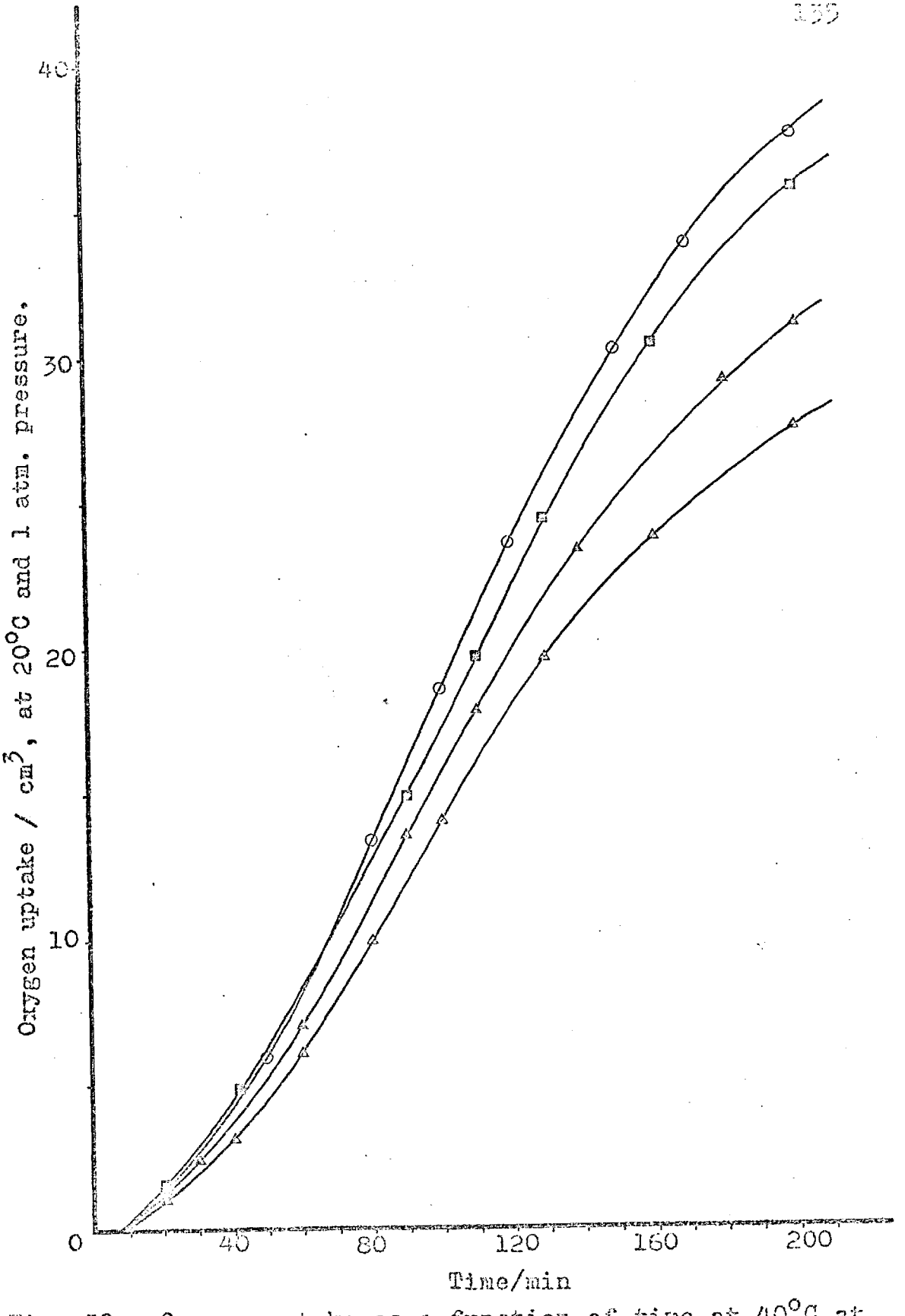


Fig. 39. Oxygen uptake as a function of time at 40°C at constant AIBN and vinylidene chloride concentrations of 10^{-3} mol dm^{-3} and 1 mol dm^{-3}, respectively, under various initial pressures of oxygen; (△) 36.5cm Hg, (▲) 48.6cm Hg, (▪) 60.8cm Hg and (○) 66.9cm Hg.

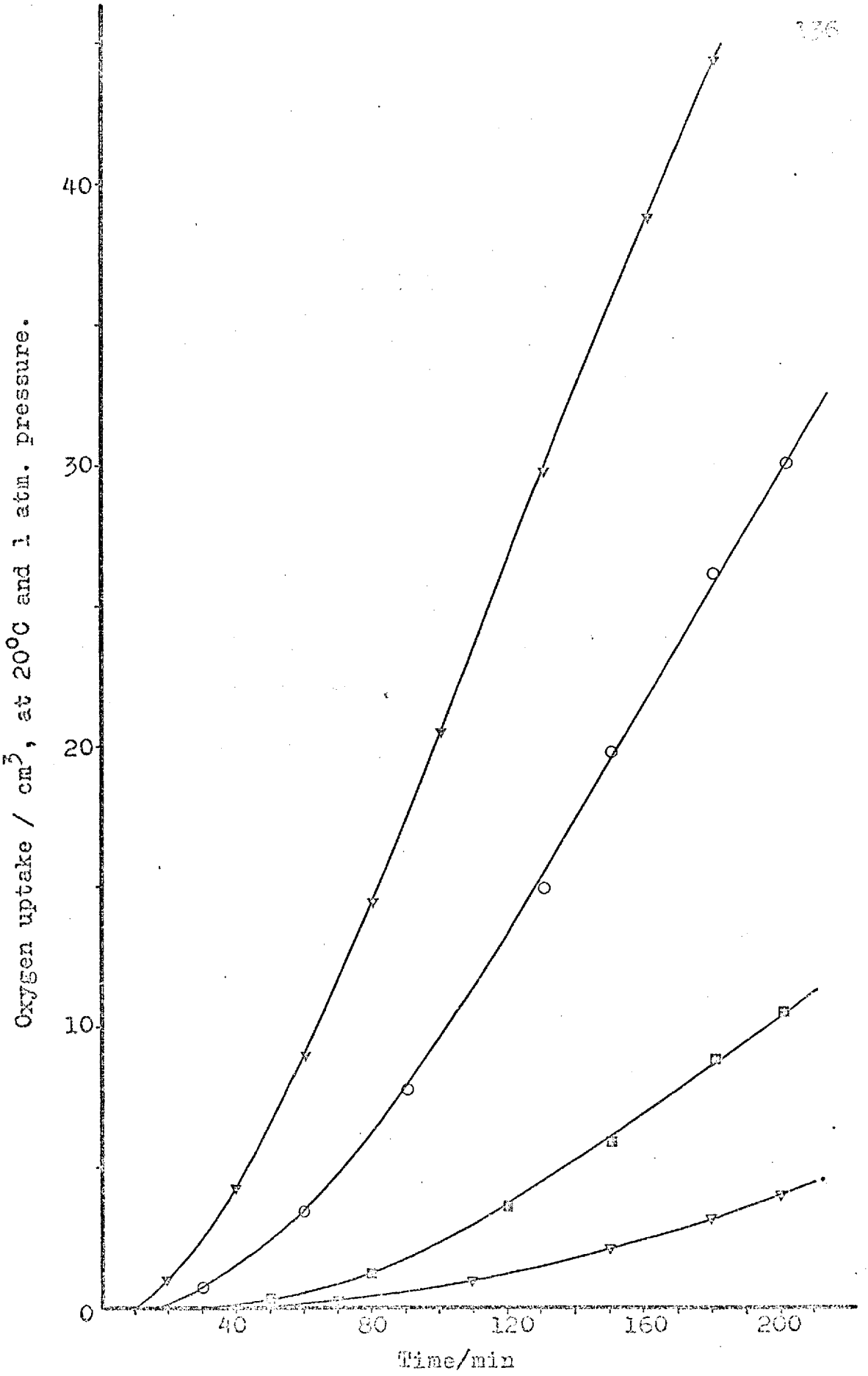


Fig. 40. Oxygen consumption at 40°C in the absence of added initiator at a constant initial pressure of oxygen of 60.8 cm Hg.

Concentrations of vinylidene chloride: (△) 0.75 mol dm^{-3}, (□) 1 mol dm^{-3}, (○) 1.5 mol dm^{-3} and (▽) 2 mol dm^{-3}.

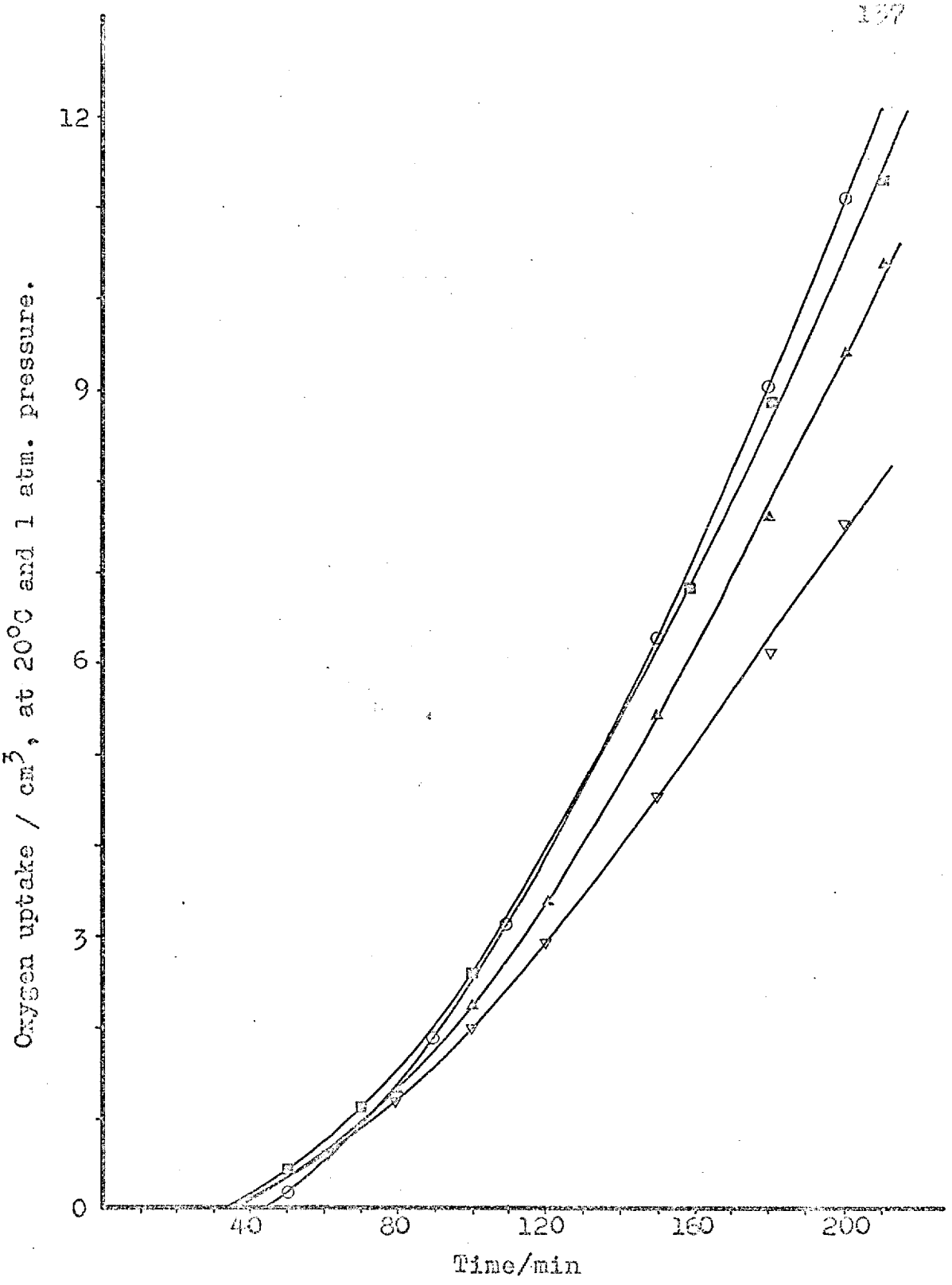


Fig. 41. Oxygen consumption at 40°C in the absence of added initiator at a constant vinylidene chloride concentration of 1 mol dm^{-3}. Initial pressures of oxygen; (△) 36.5 cm Hg, (▲) 48.6 cm Hg, (■) 60.8 cm Hg and (○) 66.9 cm Hg.

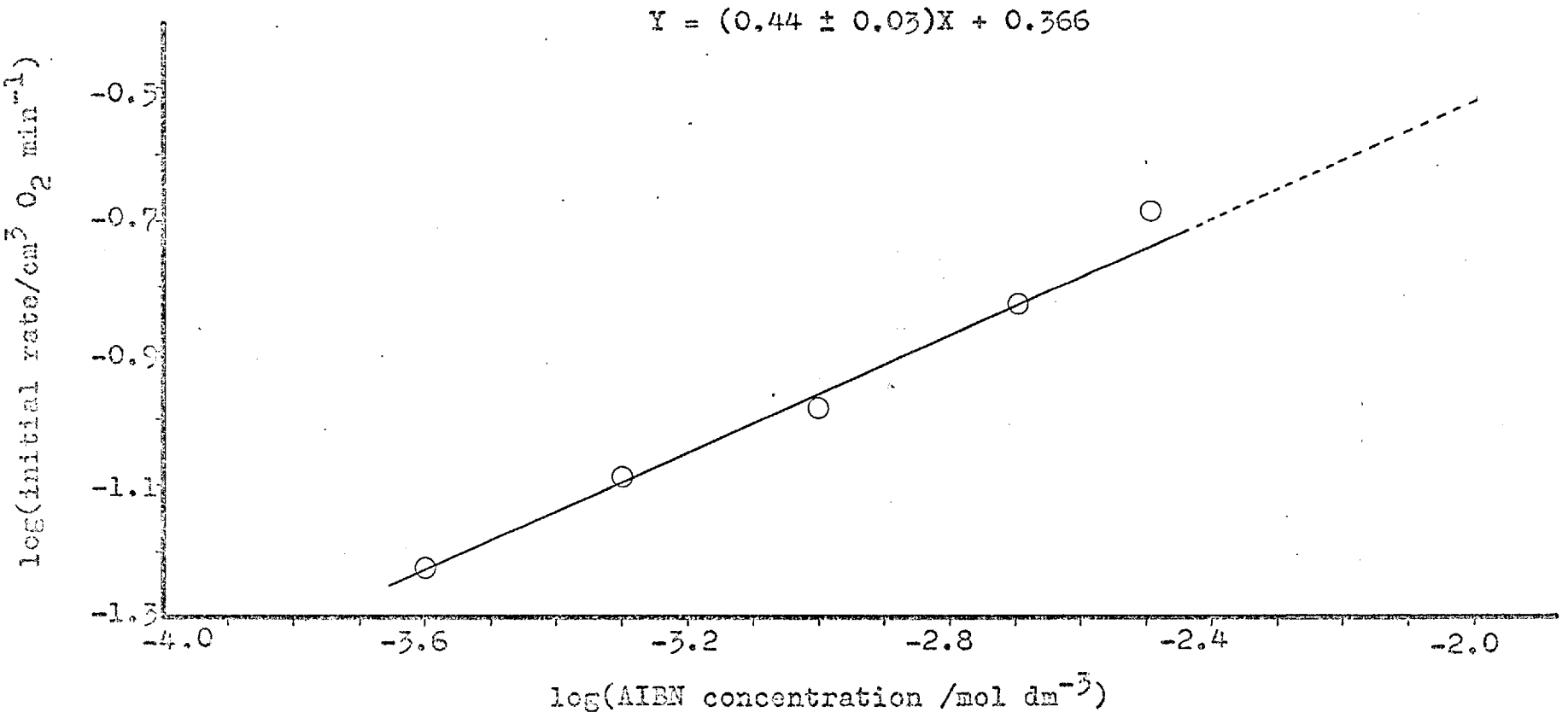


Fig. 42. Dependence of the rate of oxygen consumption on the initiator concentration.

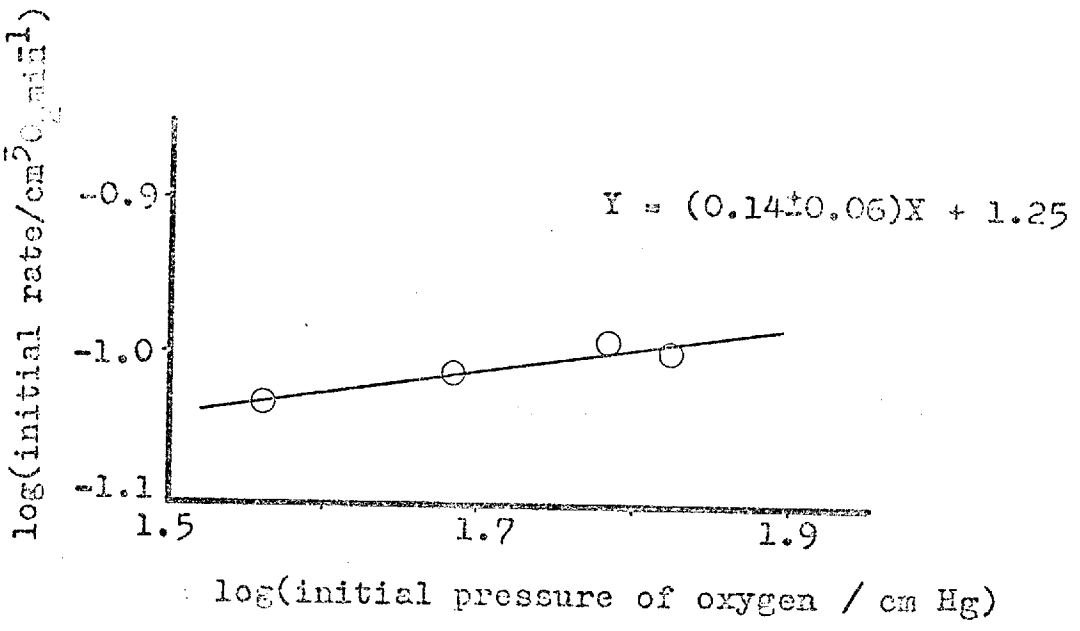


Fig. 43. Plot of the initial pressure of oxygen vs. initial rate of oxygen uptake.

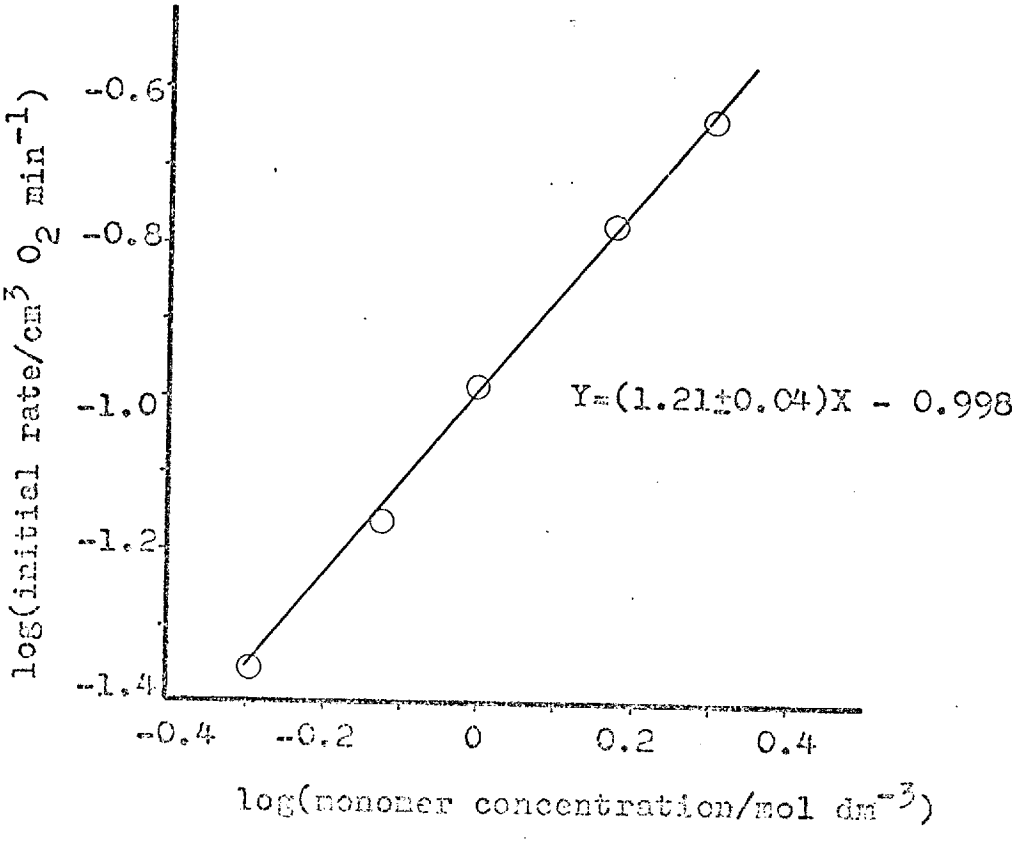


Fig. 44. Dependence of the initial rate of oxygen absorption on the concentration of vinylidene chloride.

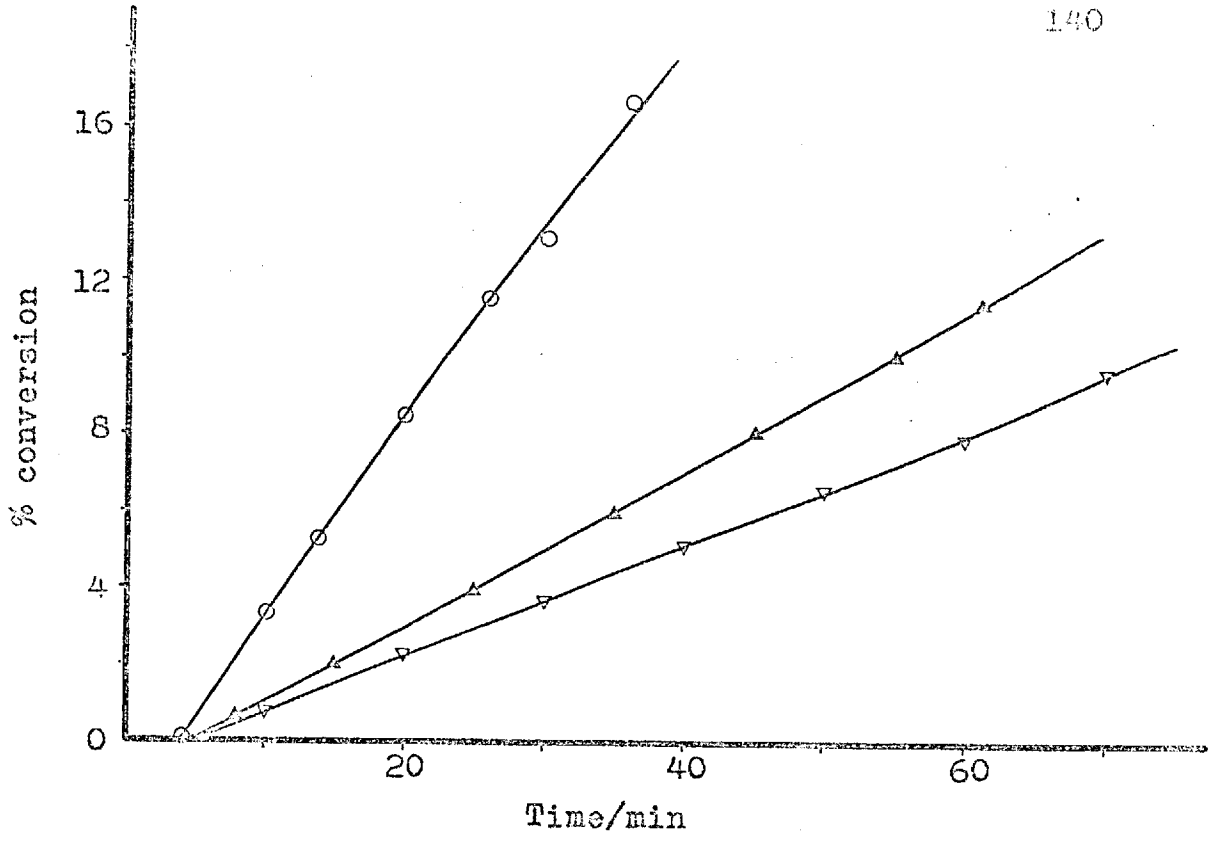


Fig. 45. Rate of polymerization of vinylidene chloride (2.5 mol dm^{-3}) in chlorobenzene, at 70°C. Initiated by AIBN at a concentration of 2.4×10^{-2} mol dm^{-3} (o) and by the polymeric peroxide alone at a concentration of 2×10^{-2} mol dm^{-3} (▲) and 0.7×10^{-2} mol dm^{-3} (△).

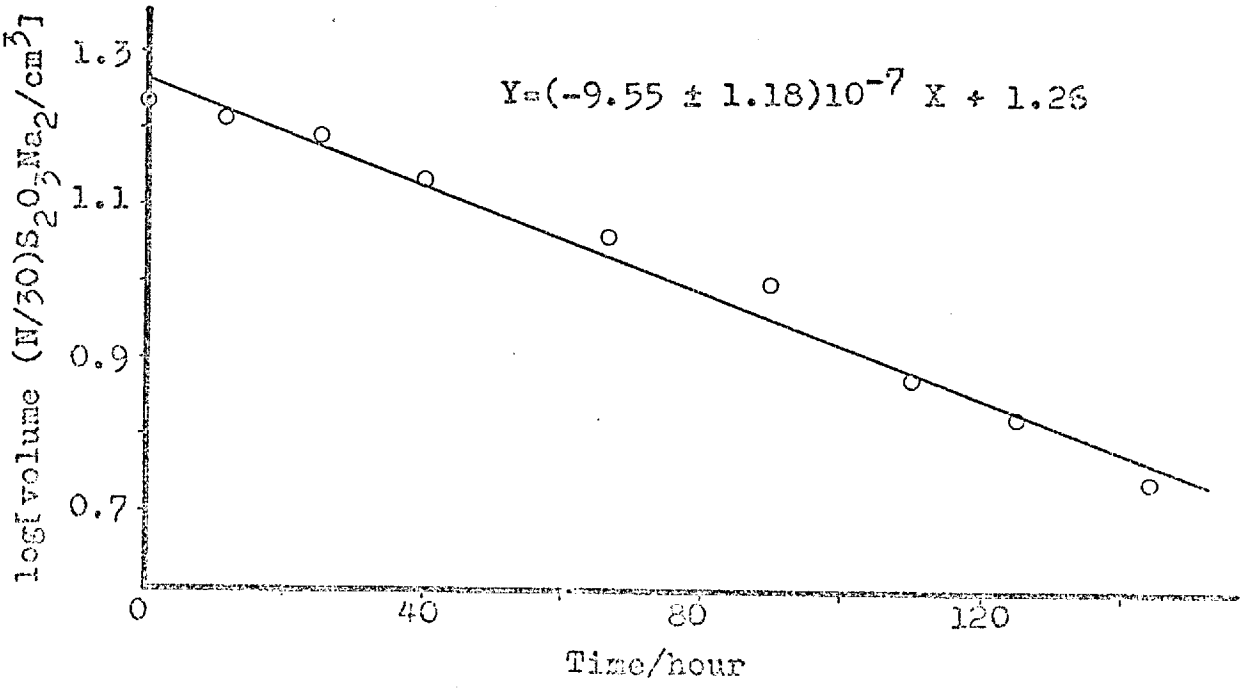


Fig. 46. Vinylidene chloride polyperoxide decomposition in chlorobenzene at 40°C.

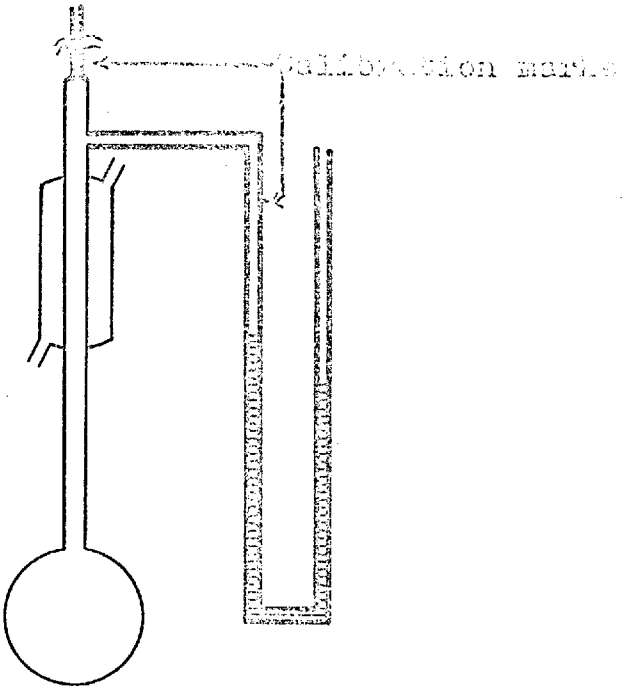


Fig. 47. Apparatus for the determination of the k_d value of AIBN.

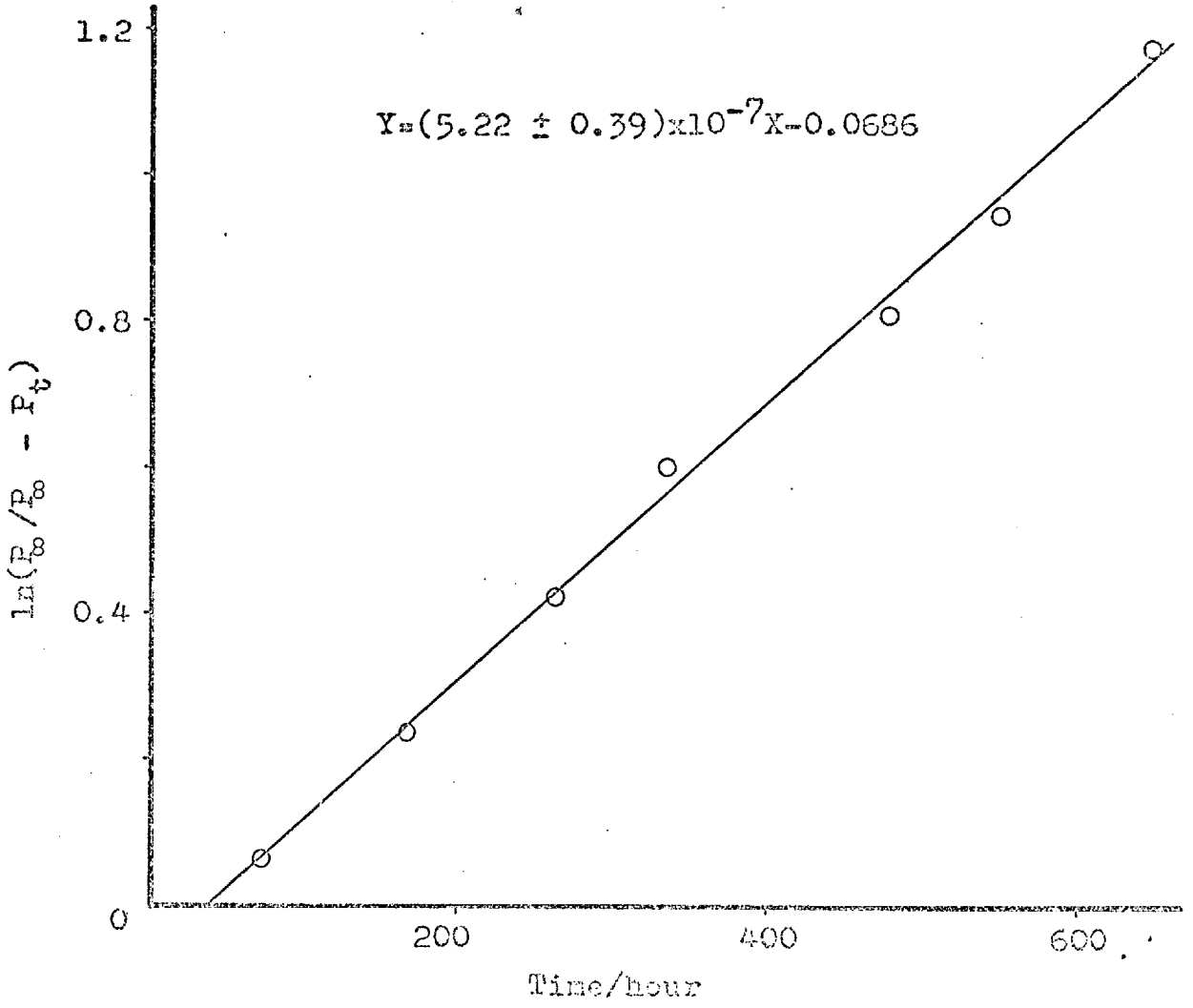


Fig. 48. Decomposition of AIBN in chlorobenzene at 40°C

TABLE 19. Rate of oxidation, R_o, of 1 mol dm^{-3} monomer initiated with 0.01 mol dm^{-3} AIBN, in chlorobenzene, at 50°C.

Monomer	Q	e	$10^4 R_o$/ mol $dm^{-3} h^{-1}$	log Q-0.5(e+0.8)
Chloroprene	7.26	-0.02	290	0.471
Styrene	1	-0.8	71	0
Acrylonitrile	0.6	1.2	14	-1.221
Methylvinyl ketone	0.69	0.68	9.6	-0.901
Vinyl acetate	0.026	-0.22	2.3	-1.875
Butyl acrylate	0.5	1.06	1.9	-1.231
Acrylic acid	0.3	0.77	1.8	-1.308
Vinylidene chloride	0.22	0.36	161	-1.23

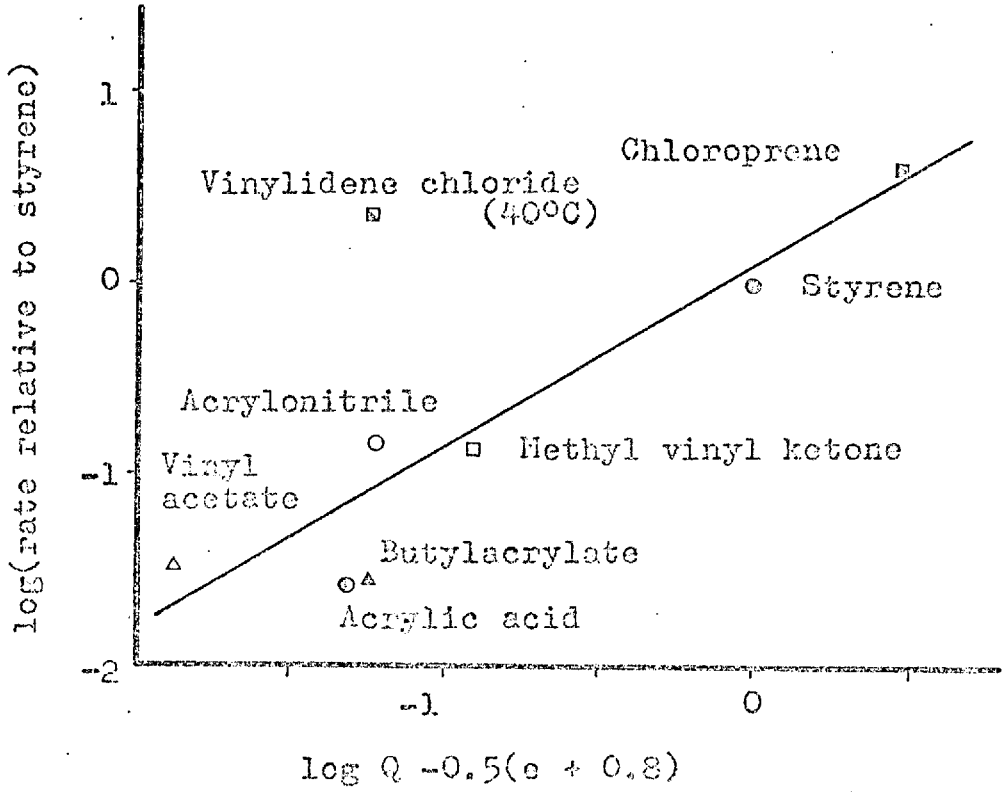


Fig. 49. Relative rates of initiated oxidation of monomers by AIBN at a concentration of 10^{-2} mol dm^{-3} at 50°C.

5.3 Discussion

As was described in chapter one, the final expression for [RM·] including the three types of termination is:

$$[RM\cdot] = \left\{ \frac{k_d f[I]}{k_{t1}+k_{t2}(k_6[O_2]^1/k_5[M])+k_{t3}(k_6[O_2]^1/k_5[M])^2} \right\}^{\frac{1}{2}} \quad (5.7)$$

where $[O_2]^1$ is the concentration of oxygen in the reaction liquid phase (vinylidene chloride in chlorobenzene). The concentration of oxygen in the reaction mixture at any time may be related to the total amounts of oxygen in the system:

$$[O_2]^1 = kP_{O_2} \quad (5.8)$$

where k is an equilibrium constant and P_{O_2} is the partial pressure of oxygen in the gas phase. Moreover one can write:

$$NO_2^1 = [O_2]^1 \cdot V^1 \quad (5.9)$$

and,

$$NO_2^g = (P_{O_2}/RT)V^g \quad (5.10)$$

$$NO_2 = NO_2^1 + NO_2^g \quad (5.11)$$

where NO_2^1 and NO_2^g are the number of moles of oxygen in the liquid phase and gas phase, respectively, V^1 is the volume of the liquid phase and V^g is the volume of gas phase. NO_2 represents the total number of moles of oxygen in any experiment. Substituting equations 5.9 and 5.10 into equation 5.11 gives:

$$NO_2 = [O_2]^1 \cdot V^1 + (P_{O_2}/RT)\cdot V^g \quad (5.12)$$

Thus from 5.8 and 5.12,

$$[O_2]^1 = \frac{NO_2}{V^1 + (V^g/kRT)} = SNO_2 \qquad (5.13)$$

where S is $1/[V^1 + (V^g/kRT)]$.

The rate of oxygen uptake may be written as follows:

$$-\frac{1}{V^1}\frac{dNO_2}{dt} = k_6\,[RM\cdot][O_2]^1 \qquad (5.14)$$

Substituting from equations 5.7, 5.13 and 5.14 :

$$-\frac{dNO_2}{dt} = k_6 \cdot S \cdot NO_2 \cdot V^1 \left\{ \frac{k_d f[I]}{k_{t1} + k_{t2}(k_6 SNO_2/k_5[M]) + k_{t3}(k_6 SNO_2/k_5[M])^2} \right\}^{\frac{1}{2}} \qquad (5.15)$$

If the mutual termination of the alkyl peroxy radicals ($RO_2\cdot + RO_2\cdot$) is predominant, equation 5.15 becomes

$$-\frac{dNO_2}{dt} = k_5[M] \cdot V^1 \cdot (k_d f[I]/k_{t3})^{\frac{1}{2}} \qquad (5.16)$$

From equation 5.16 the rate of oxygen consumption should be independent of the oxygen concentration, directly proportional to the monomer concentration and to the square root of the initiator concentration. From the logarithmic plots (figures 42-44) it appears that the oxidation of vinylidene chloride in chlorobenzene approximately obeys equation 5.16. The dependence of the reaction rate on the initiator concentration gives an exponent of 0.44 which is in agreement with this expression within experimental error. The dependence of the uptake rate on the monomer concentration is slightly in excess of unity (exponent 1.2). This is possibly caused

by the relatively higher rates of oxygen uptake for the solutions at higher monomer concentrations. A similar type of phenomenon has been noticed for some vinyl monomers undergoing polymerization in solution for which excessively low rates have been recorded at low monomer concentration. Jenkins[96] has reviewed the results of three polymerization systems and has commented on the pronounced deviation at monomer concentrations of less than about 2 mol dm^{-3}.

Using labelled initiator, Bevington[97] demonstrated that the efficiency of AIBN in the polymerization of styrene decreased when the concentration of styrene was below 1 mol dm^{-3}. At styrene concentration of 0.5 mol dm^{-3} the AIBN efficiency was about 85% of the value at 1 mol dm^{-3}. Owing to the relatively high partial pressure of vinylidene chloride at 40°C and the type of apparatus employed, a study of the effect of the monomer concentration on the uptake rate was limited to an upper concentration of monomer of about 2 mol dm^{-3}. The dependence of the initial uptake rate on the initial oxygen pressure (exponent 0.14) can be seen from the logarithmic plot (figure 43) and this result deviates slightly from the corresponding kinetic expression, equation 5.16. This deviation might still be due to insufficient stirring of the system. The relatively high rate of oxygen consumption may exhaust the oxygen dissolved in the solution, so that equilibrium cannot be maintained. Consequently some polyperoxy radicals ending in a monomer unit could participate in the termination processes.

A possible explanation can now be given for the lack of any noticeable induction period for vinylidene chloride in the dilatometric work. As can be seen from figure 38 a solution of chlorobenzene containing only two mol dm^{-3} of vinylidene chloride consumed about 3.5 cm^3 oxygen after fifteen minutes, at an initiator concentration approximately equal to that employed in the bulk systems. Thus in a bulk monomer system, with about 1-2 cm^3 of oxygen added, the consumption of oxygen may be so fast that homopolymer precipitates almost immediately.

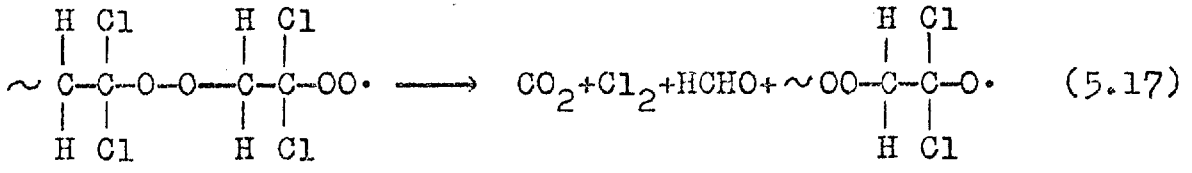
The rate of oxygen consumption in the absence of AIBN were calculated from the initial slopes of the appropriate uptake curves. This purely thermal rate still depends on the oxygen pressure (exponent $\sim$ 0.12) and is proportional to the monomer concentration to the power $\sim$1.15. The unusual shape of the uptake curves is due to two factors, (A) acceleration by polymeric peroxide and later, (B) deceleration due to depletion of the reactants, which is particularly drastic for oxygen.

From the oxygen uptake curves, and studies of the polymerization of the monomer by its own polymeric peroxide, it appears that vinylidene chloride polymeric peroxide is a relatively efficient initiator compared to polymeric peroxides of most vinyl monomers. The acceleration in the rate of oxygen uptake similar to that observed in the present work has not been reported for other vinyl monomers in the literature. The k_d value of polymeric peroxide, $(22 \pm 2.71) \times 10^{-7}$ s^{-1} at 40°C, is higher than that of AIBN, $(5.22 \pm 0.39) \times 10^{-7}$ s^{-1} at 40°C. However,

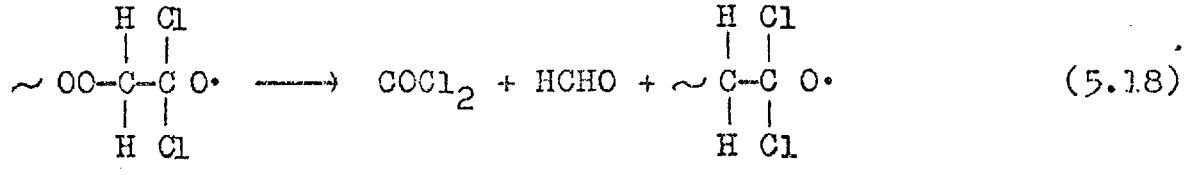
assuming that the overall rate of vinylidene chloride polymerization in chlorobenzene is approximately proportional to the square root of AIBN concentration, the rate of polymerization initiated by AIBN with a concentration equal to that of the polymeric peroxide is about 2.4 times higher. Therefore, the initiator efficiency of the polymeric peroxide must be considerably lower than that of AIBN.

Formation of the oxidation side products

Due to the fact that not all the possible clevage products were identified, any suggestion concerning the mechanism of the side products formation is difficult. Nevertheless, from the results of the present work and other reports, a tentative mechanistic scheme can be proposed. Phosgene, $COCl_2$, has been reported as one of the products of the thermal decomposition of the polymeric peroxide and may also be one of the oxidation side products[88]. Indeed, in the case of many vinyl monomers, oxidation side products are often the same as those formed from the thermal decomposition of the corresponding polymeric peroxides. Assuming that apart from CO_2, and HCHO, phosgene and chlorine are among the cleavage products, the following mechanisms are proposed.



(5.17)



(5.18)

The mode of formation of HCl, which has been reported both as a direct oxidation product and as a product of the thermal decomposition of the polymeric peroxide is uncertain [17,88].

5.4 Conclusion

Vinylidene chloride reacts with oxygen to form a polymeric peroxide and some other side products of which HCHO and CO_2 were positively identified using the MPD 850. The exceptional feature of the reaction of vinylidene chloride with oxygen is the acceleration in the rate of oxygen consumption which was considered to be due to the formation of a relatively reactive polyperoxide. Furthermore, the initial rate of the oxygen uptake appears to be in poor agreement with the Q and e scheme.

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