PHOTOPOLYMERISATION OF 1,2-EPOXIDES BY

ARENEDIAZONIUM SALTS

by

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DECLARATION

The material presented in this thesis is entirely original and
has not been presented previously or elsewhere. Where results from
the author's M.Sc. thesis are quoted, a citation is given in every
case.

ABSTRACT

Photo-decomposition ($\lambda >$ 300 nm) of 2,5-diethoxy-4-tolylthiobenzene-diazonium salts (Dz^+X^- where $X^- = SbF_6^-$, PF_6^-, BF_4^- etc.) initiates the polymerisation of 1,2-epoxides, particularly, propylene oxide (PO) and butylene oxide (BuO) which are studied as model compounds for epoxy resins of significance in photo-imaging processes, such as Epikote 828. The extent of polymerisation is strongly dependent on X^-, decreasing in the order $SbF_6^- \gg PF_6^- > PO_412Mo_3xH_2O^{3-} > BF_4^- > SnF_6^- > ZnCl_4^{2-} \approx PO_2F_2^-$.

While the initiation and propagation steps of $Dz^+PF_6^-$-initiated polymerisation of PO are unaffected by added phenol and 2,2-diphenyl-1-picryl-hydrazyl, polymerisation is terminated by Na^+PhO^-, indicating an exclusively ionic mechanism.

The polymerisations of both PO and BuO (as neat liquids) initiated by either $Dz^+SbF_6^-$ or $Dz^+PF_6^-$ yield only high molecular weight ($\bar{M}$) polymer; whereas that of PO initiated by $Dz^+BF_4^-$ gives largely low $\bar{M}$ oligomers, especially $(PO)_4$ (50%).

The polymerisation of neat PO initiated by $Dz^+PF_6^-$ occurs in two stages; Stage I is rapid (duration < 300 s) and results in ca. 15% conversion to polymer (PPO), but Stage II is much slower (duration 6-8 h), being characterised by slight further formation of PPO (i.e. up to 25%) without an increase in its $\bar{M}$ value. In contrast, BuO polymerisation occurs in one stage, similar to Stage I of that of PO. The polymerisation of Epikote 828 in 1,2-dichloroethane proceeds in two stages, indicating that PO is a better model than BuO. The end of Stage I involves transfer processes to existing polymer; however, the overall termination probably involves transfer of fluorine from PF_6^- to propagating species (detected by ^{19}F n.m.r. spectroscopy).

The polymerisations of both neat PO and BuO initiated by $Dz^+SbF_6^-$ have the following features: (i) they lead to much higher conversions than those initiated by $Dz^+PF_6^-$, (ii) pre-polymerised reaction mixtures (of BuO) are further polymerised (ca. two weeks after the original photoinitiation) by adding neat BuO, and (iii) there is virtually no incorporation of fluorine into the growing chains; these observations indicate lack of overall termination.

Polymerisation occurs predominantly by formation of fresh polymer with a minimal increase in its $\bar{M}$ value. The polymerisation kinetics of both neat PO and BuO (by ^{1}H n.m.r. spectroscopy) are complicated by the increasing and very high viscosity of the media, and yield fourth- and seventh-orders of reaction, respectively. The role of viscosity is demonstrated by near-quantitative conversion to polymer obtained (i) when ca. 5% H_2O is added and (ii) with 1,2-dichloroethane as cosolvent. In both of these cases, the reaction mixtures are of relatively low viscosity throughout.

An adiabatic kinetic study of BuO polymerisation (20% in 1,2-dichloro-ethane) initiated by $Dz^+SbF_6^-$ gives (i) a reaction order of one, (ii) an activation energy of 66.9 kJ mol^{-1}, and (iii) an Arrhenius A factor of 3.0 x 10^8 s^{-1}. The reaction order for the heat-generating step is attributed to the unimolecular ring-opening of tertiary oxonium ions.

Addition of H_2O to polymerising PO (initiated by both $Dz^+PF_6^-$ and SbF_6^-) leads to much reduced $\bar{M}$ values due to increased chain-transfer reactions. The effect of cosolvents, however, is more complex; the polymerisation of PO initiated by $Dz^+PF_6^-$ give reduced conversion and $\bar{M}$ values of resultant PPO, and whilst that of BuO in 1,2-dichloroethane initiated by $Dz^+SbF_6^-$ leads to lower $\bar{M}$ values but an increased conversion to polybutylene oxide (PBuO), which is attributed to the viscosity effect discussed above.

Preliminary ^{19}F n.m.r. experiments indicate that in the polymerisations of both neat PO and BuO initiated by $Dz^+SbF_6^-$ there is virtually complete disappearance of the resonance signal due to SbF_6^- upon irradiation. This result suggests that SbF_6^- is not involved as the counter-ion in the propagating species. In contrast, the polymerisation reactions initiated by $Dz^+PF_6^-$ show only a diminished resonance signal due to PF_6^- anions, which is retained throughout reaction.

The British patent 1,376,840 concerning the use of $Dz^+PO_2F_2^-$ as a photo-initiator for the polymerisation of epoxy resins is void because (i) the arenediazonium salt referred to is in fact $Dz^+PF_6^-$ and (ii) authentic $Dz^+PO_2F_2^-$, which has now been prepared, is shown to be absolutely ineffective.

CONTENTS

Glossary of Abbreviations

A:	The Arrhenius pre-exponential or frequency factor
$ArN_2^+X^-$:	Arenediazonium salts (where $X^- = SbF_6^-$, PF_6^-, etc.)
BuO:	Butylene oxide
DPPH:	2,2-Diphenyl-1-picryl-hydrazyl
Dz^+X^-:	2,5-Diethoxy-4-tolylthiobenzenediazonium salts (where $X^- = SbF_6^-$, PF_6^-, etc.)
E_p:	Energy of activation of a polymerisation reaction
EtO:	Ethylene oxide
Et_2O:	Diethyl ether
EtOH:	Ethanol
$Et_3O^+X^-$:	Triethyl oxonium salts (where $X^- = SbF_6^-$, PF_6^-, etc.)
EV:	Elution volume
ΔG_p:	Free energy change of polymerisation
GPC:	Gel permeation chromatography
h:	hours
Hg:	Mercury
H_p or ΔH_p:	Enthalpy change of polymerisation
^1H n.m.r.:	Proton nuclear magnetic resonance
$[I]$:	Initiator concentration
IR:	Infra-red
$[IS]$:	Concentration of injected sample
$I-M^*$:	Propagating or reactive species
$k_{d,i,p\ and\ t}$:	Rate constants for depropagation, initiation, propagation and termination reactions, respectively
k_p^+ and $k_p^\pm$:	Rate constants for propagation reactions by free-ions and ion-pairs, respectively
k_n:	Rate constant for reaction of order of n
k_{tu}:	Rate constant for unimolecular termination reaction
$[M]$:	Monomer concentration
$[M_e]$:	Equilibrium monomer concentration
$[M_f]$:	Final monomer concentration
$[M_o]$:	Initial monomer concentration

$\bar{M}$:	Molecular weight
MD:	Molecular weight distribution
$\bar{M}_{n,\ p,\ v\ and\ w}$:	Number, peak height, viscosity and weight average molecular weights, respectively
Na^+PhO^-:	Sodium phenoxide
Ox:	Oxetane
$(Ox)_n$:	Cyclic oligomer of oxetane (where n = 2, 3, 4 etc.)
$[P^*]$:	Concentration of cyclic oxonium ions
PBuO:	Polybutylene oxide
PEV:	Peak elution volume
PO:	Propylene oxide
$(PO)_n$:	Cyclic oligomer of propylene oxide (where n = 2, 3, 4, etc.)
PPO:	Polypropylene oxide
PPOG:	Polypropylene oxide glycol
PPS:	Polypropylene sulphide
RI:	Refractive index
R_p :	Rate of polymerisation
ΔS_p :	Change in entropy of polymerisation
ΔS_p^o :	Change in entropy of polymerisation for unit molar concentration
$\Delta S_p^{\ddagger}$:	Change in entropy upon activation
s:	seconds
T:	Temperature
T_c:	Ceiling temperature
T_f:	Floor temperature in section (1.2) only
T_f:	Final temperature
t:	Time
THF:	Tetrahydrofuran
$\bar{x}$:	Degree of polymerisation
η_i:	Logarithmic viscosity number (or inherent viscosity)
η_r:	Viscosity ratio (or relative viscosity)
η_{sp} and $\eta_{sp,\infty}$	Specific viscosity and infinity value of specific viscosity
$[\eta]$:	Limiting viscosity number (or intrinsic viscosity)

INTRODUCTION

1.1 THE TECHNOLOGICAL SIGNIFICANCE OF EPOXY COMPOUNDS

The chemical and technological interest in epoxy resins (where 'resin' refers to monomer, oligomer, prepolymer or high polymer species) originates from the wide variety of conditions, both physical and chemical, which can be used to effect their curing and the extensive and varied range of desirable properties which they can attain when polymerised. Two very substantial monographs[1, 2] are devoted to this class of high polymer.

Depending on the epoxy resin, curing agent and conditions, it is possible to obtain mechanical properties ranging from extreme flexibility to high strength and hardness, chemical and heat resistance, high adhesive strength and electrical insulation. Furthermore, no volatile materials are given off during the cure, and the shrinkage is much less than that encountered in the vinyl polymerisation of unsaturated-polyester resins. Consequently, these products are used in protective coatings, adhesives, potting and encapsulation compounds, glass-reinforced plastics, body solders and caulking compounds, low-pressure moulding resins, and stamping dies and patterns. In this thesis, we are particularly interested in their increasing use as components of photo-resists (see Section 1.8).

1.1.1 <u>Definitions</u> The term 'epoxy' (in the American literature)[3, 4] refers to a chemical group consisting of an oxygen atom bonded to two carbon atoms, which are already united in some other (even remote) way, usually to form a cyclic monoether. The three-numbered, or oxirane, ring is called an α-epoxy or 1, 2-epoxy, <u>e.g</u>. ethylene oxide (Fig. 1), while the terms 1, 3- and 1, 4-epoxy are applied to four- (<u>e.g</u>. trimethylene oxide) and five-numbered (<u>e.g</u>. tetrahydrofuran) rings, respectively. However, this usage is not prevalent in the European literature, and in this thesis the terms epoxide or epoxy refer exclusively to the 1, 2-epoxides.

The term 'curing' is used to describe the process by which the low molecular weight resins are transformed into the highly cross-linked network.[5] This conversion is accomplished by the addition of chemically active compounds known as curing agents. Some curing agents act catalytically (<u>e.g</u>. Lewis acids),

whilst others, called hardeners, (e.g. polyamines, polyacids, polymercaptans and polyphenols) which are used in larger quantities, participate directly in the reaction and are chemically bound into the polymer chain. The reactions of hardeners are generally based on the presence of one active hydrogen atom in the curing agent per epoxide group.

The copious literature concerning epoxy compounds covers their chemical synthesis, structure and reactions;[1,2,6-9] additionally there is a large technical literature dealing with the physical and chemical properties of epoxy-based polymers.[1,2] In this thesis we are exclusively concerned with the photo-initiated polymerisation of 1,2-epoxides by arenediazonium salts.

Figure(1)

Bond lengths and bond angles in ethylene oxide[8]
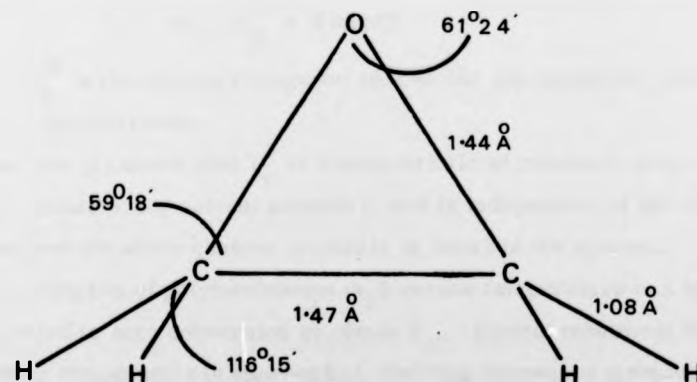
1.2 THERMODYNAMICS OF POLYMERISATION

For polymerisation to occur, (i) a molecule must be functionally capable of reacting with at least two other molecules, (ii) the reaction must be thermodynamically 'allowed' and (iii) there needs to be a route of reasonably low activation energy for this process. The concept of functionality, introduced by Carothers,[10] is fundamental to an understanding of why high polymers may be formed from difunctional molecules (regarding C=C as difunctional on excitation to Ċ-Ċ) and not from those which are monofunctional. Detailed studies of kinetics of polymerisations have led to a general understanding of

their mechanisms. In this section, a brief account of the thermo-dynamics of polymerisation is given. The free energy change (ΔG_p) for any polymerisation is given by:

$$\Delta G_p = \Delta H_p - T\Delta S_p \qquad (1)$$

where ΔH_p and ΔS_p are the changes in enthalpy and entropy, respectively, of the system at temperature T. At a certain critical temperature, the system is at equilibrium, i.e. $\Delta G_p = 0$, and there is no tendency for further polymerisation to occur. This temperature is known as the ceiling temperature (T_c)[11, 12] and can be represented as:

$$T_c = \Delta H_p / \Delta S_p \qquad (2)$$

If the monomer behaves ideally, then under standard state conditions $\Delta S_p = \Delta S_p^o + R\ln[M]$; and thus:[12]

$$T_c = \Delta H_p / (\Delta S_p^o + R\ln[M]) \qquad (3)$$

where ΔS_p^o is the entropy change for unit molar concentration, and $[M]$ is the monomer concentration.

Equation (3) shows that T_c is characteristic of monomer-polymer equilibrium (and the nature of any solvent present), and is independent of the monomer or the nature of the active centres (radicals or ions) in the system. Therefore, the plot of degree of polymerisation $(\bar{x}_n)$ versus temperature can be extrapolated to zero conversion to obtain T_c. Kinetic treatment shows that as the ceiling temperature is approached, the rate decreases steeply. Therefore, the plots of the rate of formation of polymer (R_p)(or average molecular weight of the high polymer, $\bar{M}$) against T,[13, 14] can also be extrapolated to zero rate to obtain T_c.

Depending on the signs of ΔH_p and ΔS_p, four distinct combinations exist:

(i)   When both ΔH_p and ΔS_p are negative (as is usual in addition polymerisation), ΔG_p becomes positive above T_c and hence high polymer is formed only below T_c.

(ii) When both ΔH_p and ΔS_p are positive, polymerisation can only occur above a critical temperature known as the floor temperature (T_f), e.g. as in the polymerisation of S_8 rings.[15]

(iii)   When ΔH_p is positive and ΔS_p is negative, no polymerisation is possible under any conditions.

(iv)   When ΔH is negative and ΔS is positive, ΔG_p is always negative and therefore polymerisation may occur at all temperatures.

A more detailed account of the thermodynamics of polymerisation can be found in two recent reviews by Szwarc[16] and Sawada.[17]

1.3   POLYMERISATION REACTIONS

W.H. Carothers[10] classified polymers into two groups, i.e. condensation and addition polymers. This was amended by P.J. Flory,[18] who placed emphasis on the mechanisms of polymerisation, into step-reaction (condensation) and chain reaction (addition) polymerisations. This classification is also preferred by H. Mark.[19]

1.3.1   Step- reaction Polymerisation

All step polymerisations fall into two groups depending on the type of monomer (or monomers) employed.[20]   The first involves two different polyfunctional monomers in which each monomer possesses only one type of functional group, e.g. the reaction of diamines with diacids to produce a polyamide.

$$n(H_2N - R - NH_2) + n(HO_2C - R' - CO_2H) \rightarrow$$

$$H \{ NH - R - NHCO - R' - CO \}_n OH + (2n-1)H_2O \qquad (4)$$
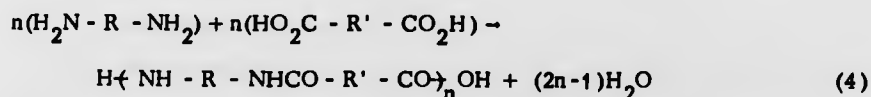
or the reaction of a diol with a di-isocyanate to produce a polyurethane:

$$HO - R - OH + OCN - R' - NCO \rightarrow \{ O - R - O - CONH - R' - NHCO \}_n \quad (5)$$
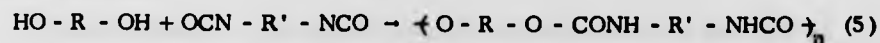
The second type of step polymerisation involves a single monomer containing both types of functional groups, e.g. the polymerisation of an hydroxy-acid to a polyester:

$$n(HO - (CH_2)_x - COOH) \rightarrow H \{ O - (CH_2)_x - CO \}_n OH + (n-1)H_2O \qquad (6)$$

The polymerisation reaction occurs by condensation between two polyfunctional molecules to produce one larger polyfunctional group molecule, with the possible elimination of a small molecule such as water.[21]   The process continues by

stepwise condensation of monomer molecules with dimers, trimers and tetramers, etc. After a short time, most of the original monomer disappears and the reaction then occurs by coupling of low $\bar{M}$ oligomers to give the final high $\bar{M}$ polymer at high conversion. Therefore, the rate of polymerisation, described as the rate of loss of functional groups, is a maximum at the start and decreases rapidly during the reaction as the concentration of functional groups falls.

1.3.ii Chain - reaction Polymerisation

Polymerisation reaction occurs by the propagation of the reactive species (*) which may be a carbenium ion, a carbanion, a free radical, a co-ordination compound or a complex surface compound.[22] Propagation is by the very rapid successive additions of large numbers of monomer molecules to a small number of reactive species. The generally accepted reaction scheme may be represented in its simplest form as follows:[21]

$$I^* + M \rightarrow IM^* \qquad \text{Initiation} \qquad (7)$$

$$IM^* + M \rightarrow IMM^* \qquad \text{Propagation} \qquad (8)$$

$$\text{or, in general } I(M)_n^* + M \rightarrow I(M)_{n+1}^* \qquad (9)$$

$$I(M)_{n+1}^* + X \rightarrow \text{Inactive Polymer} \qquad \text{Termination} \qquad (10)$$
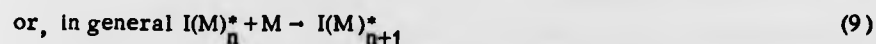
where I is the initiator

* denotes the active centre

M is the monomer

and X is the terminating species which may be another active centre in radical polymerisation.

Characteristics of chain reaction polymerisation are that the high $\bar{M}$ polymer is already present at low conversion, the monomer concentration decreases slowly during the reaction and that, at any instant, the reaction mixture consists almost entirely of high polymer and unreacted monomer, with a tiny ($\sim 10^{-9}$ mol dm^{-3}) concentration of $I-(M)_n^*$. The rate of polymerisation, which is initially zero, rises to a plateau as active centres are formed from the initiator and falls off as initiator is consumed;[20] $\bar{M}$ is relatively unchanged with increased conversion.

The commonest example of chain polymerisation is that of vinyl monomers which are polymerised by radical initiators usually derived from peroxides, such as acetyl and benzyl peroxides:[20]

$$(CH_3COO)_2 \xrightarrow[\text{or } h\nu]{\Delta} 2CH_3CO\overset{\bullet}{O} \longrightarrow 2CH_3^{\bullet} + 2CO_2 \qquad (11)$$

$$(PhCOO)_2 \xrightarrow[\text{or } h\nu]{\Delta} 2PhCO\overset{\bullet}{O} \longrightarrow 2Ph^{\bullet} + 2CO_2 \qquad (12)$$

$$R^{\bullet} \xrightarrow[]{CH_2=CHY} RCH_2\overset{\bullet}{C}HY \xrightarrow[]{CH_2=CHY} RCH_2CHYCH_2\overset{\bullet}{C}HY \text{ etc. } (13)$$

$$R^{\bullet} = CH_3^{\bullet} \text{ or } Ph^{\bullet}$$

Termination of reaction occurs either by combination or disproportionation of two growing radicals.

Whilst almost all monomers undergo radical polymerisation, ionic polymerisation is less universal due to the very strict requirements for stabilisation of anionic and cationic propagating species, Table (1). Anionic polymerisation takes place with monomers possessing electron-withdrawing groups such as nitrile, carboxyl, phenyl and vinyl. Cationic polymerisation is specific to monomers with electron-releasing substituents such as alkoxyl, epoxy, phenyl, vinyl and 1,1-dialkyl.

Table (1)

Types of chain polymerisation processes for various unsaturated monomers[23]

Monomer	Types of Initiation		
	Radical	Cationic	Anionic
Ethylene	+	+	+
1-Alkyl olefins (α-olefins)	-	-	-
1,1-Dialkyl olefins	-	+	-
1,3-Dienes	+	+	+
Styrene, α-Methylstyrene	+	+	+
Halogenated olefins	+	-	-
Vinyl esters (CH_2=CHOCOR)	+	-	-
Acrylates, Methacrylates	+	-	+
Acrylonitrile, Methacrylonitrile	+	-	+
Acrylamide, Methacrylamide	+	-	+
Vinyl ethers	-	+	-
N-Vinyl carbazole	+	+	-
N-Vinyl pyrrolidone	+	+	-
Aldehydes, Ketones	-	+	+

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$$R^{\bullet} \xrightarrow{CH_2=CHY} RCH_2\dot{C}HY \xrightarrow{CH_2=CHY} RCH_2CHYCH_2\dot{C}HY \text{ etc. } (13)$$

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1,1-Dialkyl olefins	-	+	-
1,3-Dienes	+	+	+
Styrene, α-Methylstyrene	+	+	+
Halogenated olefins	+	-	-
Vinyl esters (CH_2=CHOCOR)	+	-	-
Acrylates, Methacrylates	+	-	+
Acrylonitrile, Methacrylonitrile	+	-	+
Acrylamide, Methacrylamide	+	-	+
Vinyl ethers	-	+	-
N-Vinyl carbazole	+	+	-
N-Vinyl pyrrolidone	+	+	-
Aldehydes, Ketones	-	+	+

Ionic polymerisations are still not completely understood, because their investigation is made difficult by their very fast rates which are extremely sensitive to the presence of small concentrations of cocatalysts, impurities and to other factors (e.g. solvents) which make it difficult to obtain reproducible kinetic data. Moreover, heterogeneous inorganic catalysts are often involved. Only propagating ions of fairly high thermodynamic stability have adequate lifetimes to enable growth.[24] Ionic polymerisations are usually carried in solvents of low or moderate polarity such as dichloro-ethane, dichloromethane, pentane and nitrobenzene, where all ionic species are probably in the form of ion-pairs.[20] Termination usually occurs by reaction of the growing chain either unimolecularly or by transfer to monomer or solvent.

1.4 RING-OPENING POLYMERISATION

A wide variety of cyclic monomers, such as cyclic ethers, acetals, esters, amides and sulphides, etc. have been successively polymerised by ring opening polymerisation.[25] Initiation by a catalyst (e.g. Na, RO^-, HO^-, H^+, BF_3, etc.) results in opening of the ring to form an initiator species (IM*) which grows by successive addition of monomer molecules,[20] viz.

$$R - Z + I \longrightarrow IM* \tag{14}$$

$$IM* + n R - Z \longrightarrow IM \{ R - Z \}_n^* \tag{15}$$
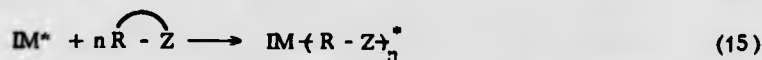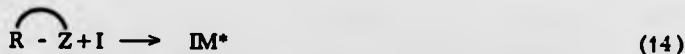
where I is the catalyst and Z is the active functional group.

This process resembles chain polymerisation in that there is no elimination of any small molecule, and the propagation is by addition of monomer only. The classification as a chain or step polymerisation can, however, be made by the experimentally observed kinetic laws, which describe the time distribution in which the high polymer is observed. All ring-opening polymerisations behave as chain polymers in that high $\bar{M}$ polymer is formed throughout the reaction. Many are further complicated by polymerisation-depolymerisation equilibria, section (1.6).

1.4.i Thermodynamics of Ring-opening Polymerisation

The tendency of cyclic monomers to polymerise depends on the reactivity of the functional group, the initiator used, and the ring size.[17]

ΔG_p is affected by (i) angle strain, (particularly in 3- and 4-membered rings), (ii) conformational strain (e.g. that in the completely eclipsed conformation of ten adjacent hydrogen atoms in cyclopentane, which has virtually no angle strain in the planar form) and (iii) the steric effect of side groups (bulky substituents making the free energy of the ring-opening reaction more positive relative to the unsubstituted case).[21]

Ring-opening polymerisation of cyclic compounds usually leads to formation of linear polymers which are virtually free from strain, and therefore ΔH_p provides a direct measure of the strain energy in the monomer ring,[26] Table (2). Thus, in cyclopropane, each bond is distorted[17] by an angle of $49°\,28'$ from the normal angles[27] of a tetrahedral carbon atom.

Table (2)

Heat of polymerisation (ΔH_p) for cyclic monomers[*1]

Monomer	No. of atoms in ring	Standard states [*2]	$-\Delta H_p$ kJ mol^{-1}	Temp/K
Ethylene oxide[26]	3	$g \to g$	104.3	298
		$l \to c$	94.6	298
Propylene oxide[28]	3	$g \to g$	75.4	298
Styrene oxide[26]	3	$l \to c$	101.7	299.9
3-Nitrostyrene oxide[26]			100.9	299.9
Oxetane[29]	4	$s \to s$	80.8	264
3,3-Dimethyloxetane[29]	4	$s \to s$	67.4	264
Tetrahydrofuran[30-32]	5	$g \to g$	12.1	298
		$l \to c$	38.1	298
		$l \to c$	22.2	298
Tetrahydropyran[30, 33]	6	$g \to g$	1.7	293

[*1] For a much extended list, see reference 17, p.133.

[*2] Monomer and polymer states: l, liquid; s, solution; c, condensed; g, gas.

ΔH_p, ΔS_p and ΔG_p, Fig. (2) for the polymerisation of liquid[6] cycloalkanes to linear polymers at 298 K have been calculated by Dainton et al.[12, 34] The ΔH_p and ΔS_p values show that ΔH_p makes the major contribution to ΔG_p for the 3- and 4-membered rings, whereas ΔH_p and ΔS_p are equally important for the 5-, 6- and 7-membered rings. The thermodynamic feasibility of the ring-opening process (for any one size of ring) is greater for the unsubstituted derivative than the substituted. For substituted and unsubstituted 6-membered rings, and the substituted 5-membered rings, ΔG_p is positive, thereby precluding their spontaneous ring-opening polymerisation. Thermodynamic feasibility, however, does not guarantee the practical realisation, and polymerisation of cyclopropane and cyclobutane has not been achieved.[35]

The effect of ring size on ΔG_p for saturated heterocyclic compounds has been considered by Small.[36] For nitrogen- and oxygen-containing compounds, bond lengths and bond angles of C-N and C-O do not differ much from those of C-C bonds, Table (3), and therefore replacement of a carbon atom in a cycloalkane by N or O, Fig.(1), does not produce a large change in angle strain. The C-S bond length, however, is much longer than that of the C-C bond and therefore, produces a considerable change in the structure of the cyclic compounds, as is borne out by the strain energies of cyclic compounds.[37] Strain energies for ethylene and propylene oxides are nearly the same as those for cyclopropane, and that of ethylene imine is only a little lower. However, the strain energy of ethylene sulphide is much smaller than that of cyclopropane.

Table (3)

Bond lengths and bond angles[17]

Single Bond Lengths ($\overset{\circ}{A}$)		Bond Angles
1.54	C - C - C	$109^\circ\ 28'$
1.47	C - N - C	109°
1.44	C - O - C	111°
1.82	C - S - C	100°

Figure (2)

Free-energy of polymerisation of cycloalkanes as a function of the number of atoms in the ring [12]

A: Unsubstituted.   B: Methyl substituted.   C: Dimethyl substituted.
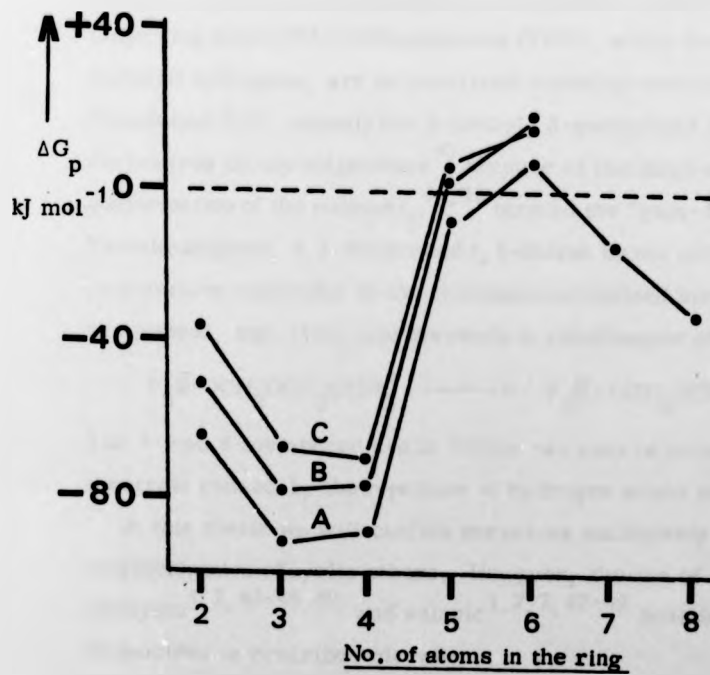
The results of the polymerisation of cyclic ethers, esters, urethans, ureas and imides,[38] and the ΔH_p values[26] for these have been summarised[17] as follows:

(i) The tendency of 5- and 6-membered compounds to polymerise depends markedly on the class of compound.

(ii) The 4-, 7- and 8-membered rings can be polymerised in nearly every case.

(iii) Substituents on the ring decrease the tendency to polymerise.

(iv) In general, substitution of heteroatoms in the ring have little effect on the tendency to polymerise as compared to the parent monomer.

1.4.ii Polymerisation of Cyclic Ethers

The ether function is a strong Lewis base and therefore the ring-opening polymerisation of cyclic ethers is usually initiated by cationic species.[20] However, epoxides[8,39] can also be readily polymerised by anionic initiators due to the high degree of ring strain. Both oxetanes, which possess large ring strain and tetrahydrofuran (THF), which includes repulsion of eclipsed hydrogens, are polymerised smoothly with cationic catalysts. Substituted THF, namely the 2-methyl, 3-methyl and 2-chloromethyl derivatives do not polymerise[40] because of the large steric effects in the conformation of the polymer,[41,42] termed the "gem-dimethyl effect".[17] Tetrahydropyran, 1,3-dioxan and 1,4-dioxan do not polymerise, but trioxan polymerises easily due to the resonance-stabilised initiating and propagating zwitterions, eqn. (16), and the ready crystallisation of polyoxymethylene.[17]

$$F_3\bar{B}\text{-}OCH_2OCH_2OCH_2^+ \longrightarrow F_3\bar{B}\text{-}OCH_2OCH_2\overset{+}{O} = CH_2 \qquad (16)$$
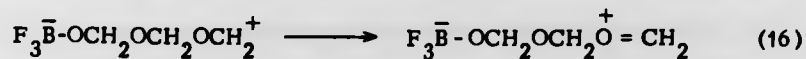
The 7- and 8-membered cyclic ethers can also be polymerised because of the strain caused by the repulsion of hydrogen atoms across the ring.

In this thesis we will confine ourselves exclusively to the cationic polymerisation of cyclic ethers. However, the use of Ziegler-Natta type catalysts[1,2,43-46,49] and anionic[1,2,7,47-49] initiators for the polymerisation of epoxides is described elsewhere.

1.5 CATIONIC POLYMERISATION OF HETEROCYCLIC COMPOUNDS

The   study of cationic polymerisation of heterocyclic compounds has
increased rapidly over the last 15 years, and consequently a vast amount
of literature has accumulated. In this thesis we will summarise only the
results relevant to the present work, and highly detailed accounts of the
present state of knowledge can be found in recent reviews.[21, 49-55].

A variety of initiators have been used for ring-opening polymerisations,
including oxonium salts,[56] protonic acids (superacids) and their derivatives,[57-60]
Friedel-Crafts halides,[49] stable carbenium ion salts[50-52] and arenediazonium
salts.[61] Some of the important monomers which have been studied are
1, 2-epoxides (EtO,[62,63] PO[64,65] and BuO[66,67]), 1,3-epoxides
(e.g.oxetane)[29,68-70] 1, 4-epoxide (THF),[53,71] 1, 2-episulphides[72]
(thiiranes, e.g. propylene sulphide). 1, 3-episulphides[73,74] (thietans, e.g.
3, 3-dimethylthietane), aziridines[74] (e.g. 1-alkylaziridines), azetidines[74]
(e.g. 1-methylazetidines) and the cyclic formals[50] (e.g. 1, 3-dioxolan, trioxan
and 1, 3-dioxepan), lactones and aldehydes.

In general, cationic polymerisations initially involve the generation of a
positively charged species with its attendant counter-ion. Propagation then
occurs through successive additions of monomeric units to the charged or
reactive ends of the growing chains. The most important reactions of the
growing chain are:

(i) propagation (i.e. the addition of further monomer units to the chain),
(ii) chain transfer, in which the reactive entity is transferred to another
    molecule, thereby terminating the former and initiating the latter, and
(iii) termination of the reactive species.

A complete account of the individual steps involved in the cationic
polymerisation of cyclic ethers is given in section (1.6).

1.5.1 Ions and Ion Pairs

One important consideration in the cationic polymerisation of cyclic
ethers is the role of ions (or ion pairs). Winstein[75] has shown that organic
salts can exist in at least three forms. Between the covalent compound (RX)
and the fully dissociated (i.e. solvated) ions (III), there are two types of

Ion pairs, namely the intimate (or tight) ion pair (I) and the solvent-separated (or loose) ion pair (II):

$$RX \rightleftharpoons [R^+X^-] \rightleftharpoons R^+(solv.)X^- \rightleftharpoons R^+(solv.) + X^-(solv.) \qquad (17)$$

I	II	III
Tight ion pair	Loose ion pair	Free solvated ion pair
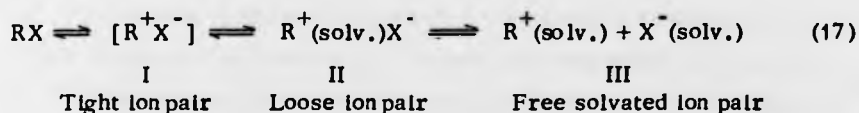
Griffiths and Symons[76] have called the species I a contact (or intimate) ion pair, and have proposed two subspecies in Stage II - solvent-shared (IIa) and solvent-separated (IIb) ion pairs. Although the realisation that these various types of aggregate may have quite different reactivities was recognised relatively recently,[77] the concept of ion pairs was first invoked in 1926. Bjerrum[78] proposed that ions separated by a distance smaller than r_{min}, in equation (18) should be treated as ion pairs:

$$r_{min} = \frac{Z_A Z_B e^2}{2DkT} \qquad (18)$$

where Z_A and Z_B are the ionic charges and e is the electronic charge for a system of spherical, nonpolarisable ions A and B, separated by distance r, in a structureless dielectric medium of dielectric constant D at an absolute temperature T, and k is Boltzmann's constant. Typical values of r_{min} for 1:1 electrolyte are 3.6 Å in water, 45 Å in acetic acid and 120 Å in benzene. Therefore, in media of low polarity (e.g. in solvents such as those commonly used in cationic ring-opening polymerisations[79A]), two ions can be regarded as an ion pair even though they may be separated by a number of solvent molecules.[79B]

1.5.ii Dissociation Constants (K_d) Obtained from Conductance Measurements

The relevant literature concerning the dissociation constants of stable organic cation salts has been recently reviewed by Ledwith and Sherrington.[50] The results can be summarised as follows:

(i) the dissociation constants vary only slightly for different complex anions (e.g. BF_4^-, SbF_6^-, $SbCl_6^-$, ClO_4^- and $SnCl_5^-$) in a given solvent, such as dichloromethane,[50]

(ii) increasing the polarity of the solvent (e.g. from CH_2Cl_2 to liquid SO_2 or $C_6H_5NO_2$) increases the K_d of a given salt,[80, 81]

(iii) for widely different structures of cations of $SbCl_6^-$ salts in CH_2Cl_2, the corresponding K_d values lie within a single order of magnitude,[82]

(iv) the dissociation constants of quaternary ammonium $SbCl_6^-$ salts in CH_2Cl_2 vary little with increasing length of the alkyl substituents,[83] and

(v) the K_d value (4.4×10^{-6} M) for the "living" oligomeric oxonium ion pair derived from THF with BF_4^- counter ion, in CH_2Cl_2 at 272.5 K[84,85] is similar to that obtained from polymerisation kinetics (3.7×10^{-6} mol dm^{-3}). These data are also in good agreement with ion pair dissociations of $Et_3O^+BF_4^-$ (5.4×10^{-6} mol dm^{-3}) and $Et_3O^+PF_6^-$ (8.3×10^{-6} mol dm^{-3}) in CH_2Cl_2 at 273 K.[86]

The general trends in the data justify the assumption that the degree of dissociation of a propagating ion pair, under given conditions, depends only marginally on the counter-ion (providing it is large) and chain length.[50] However, in polymerisation reactions the presence of monomer may have a significant influence on the position of equilibrium between free ions and ion pair species, particularly if the polarity of the monomer differs substantially from that of the solvents.[86,87] The dissociation constant of $Et_3O^+PF_6^-$ in CH_2Cl_2 at 273 K increases by a factor of _ca_. 2 when small quantities of THF are added. THF has a lower dielectric constant than CH_2Cl_2 and, therefore, might be expected to reduce dissociation. These results have been interpreted in terms of specific solvation of the cation by ether molecules, with subsequent reduction in its effective charge density.

1.6 CATIONIC POLYMERISATION OF CYCLIC ETHERS

1.6.1 Tetrahydrofuran

In the cationic polymerisation of THF many systems undergo a relatively fast and quantitative initiation, leading to polymerisation-depolymerisation equilibria,[53] provided that a sufficiently stable complex anion is used (_e.g._ PF_6^-, SbF_6^-, AsF_6^- and OSO_2X^- where X = CF_3 or F).[88,89]

The "living" characteristic of the process has been demonstrated for the bulk polymerisation of THF, using PF_6^- counter ion, giving a value for T_c of $85 \pm 2^\circ$ C.[31,61] ^{14}C-labelled triethyloxonium tetrafluoroborate[90] ($Et_3O^+BF_4^-$), and sodium phenoxide (Na^+PhO^-)-terminated polymer samples[91,92]

have been used to demonstrate the quantitative conversion of catalyst to initiating species.

The triethyloxonium salt $(Et_3O^+X^-)$-initiated polymerisation of THF may be represented as follows:-

$$EtO^+X^- + O \underset{}{\overset{k_i}{\rightleftharpoons}} Et-\overset{+}{O}X^- +Et_2O \qquad (19)$$

$$Et-\overset{+}{O}X^- + O \underset{k_d}{\overset{k_p}{\rightleftharpoons}} Et-O-(CH_2)_4-\overset{+}{O}X^- \qquad (20)$$
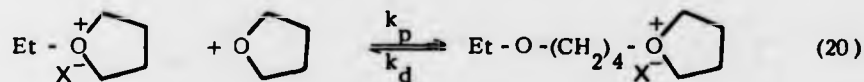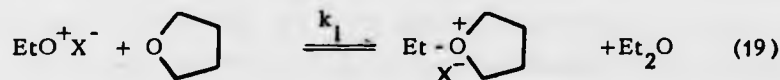
where k_i, k_p and k_d are rate constants for initiation, propagation and depropagation (depolymerisation) respectively.

The k_p values for THF polymerisation in CH_2Cl_2 at 273 K, initiated by triethyloxonium ions are found to be almost independent of the counter-ions, $(BF_4^-, PF_6^-, SbF_6^-$ and ClO_4^-) used.[93] However, much slower apparent rates are found with different cation initiators, namely acetyl hexafluoro-antimonate and 2-methyl-1,3-dioxolenium perchlorate. Sangster and Worsfold,[94] using $Et_3O^+BF_4^-$ initiator, have shown that the rate constants for propagation by free ions $(k_p^+ = 1.0 \times 10^{-2} \, dm^3mol^{-1}s^{-1})$ and ion pairs $(k_p^{\pm} = 1.4 \times 10^{-3} \, dm^3mol^{-1}s^{-1})$ differ by a factor of 7 only , compared with the factor of 10^3 found in the ionic polymerisation of vinyl monomers.[95-97] In the polymerisation of cyclic sulphides[98] the $k_p^+:k_p^{\pm}$ ratio is also found to be low and solvent-dependent, and is ascribed to the attack being on the carbon α to the charged atom instead of on the charged atom as in the anionic case.

The polymerisation of THF initiated by 1,3-dioxolan-2-ylium salts with AsF_6^-, PF_6^- and SbF_6^- anions, and with esters of fluorosulphonic and trifluoromethansulphonic acids (e.g. $CH_3CH_2OSO_2CF_3$) in CCl_4 has recently been studied using ^1H n.m.r. spectroscopy.[89] The THF-CCl_4 system eliminates dissociation of the ion pairs into free ions. The value of $k_p^{\pm}$ $(4.0 \times 10^{-2} \, dm^3mol^{-1}s^{-1}$ at $[THF]_o = 8.0 \, mol \, dm^{-3}$ and at 298 K)

was found to be independent of the counter-ions used, namely AsF_6^-, PF_6^-, SbF_6^- and $CF_3SO_3^-$, but varied according to Laidler and Eyring's expression relating the rate and the dielectric constant of monomer/solvent mixtures. The overall rate of polymerisation with derivatives of CF_3SO_3H is much lower than that of the complex anions because of the reversible conversion of the macroion-pair into the inactive macroester form:

$$\sim\!\!\!\!\overset{+}{O}\!\!\!\!\rangle \quad\Longleftrightarrow\quad \sim\!\!\!O(CH_2)_4\text{-}O\text{-}SO_2CF_3 \qquad (21)$$

$CF_3SO_2O^-$

Macroion   Macroester
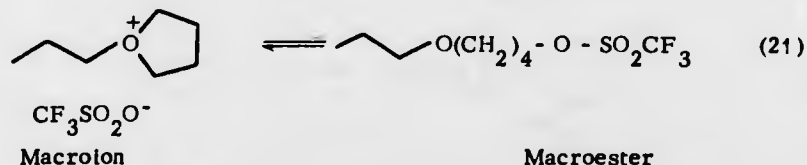
Addition of $Ag^+SbF_6^-$ eliminates internal return from the sulphonate ion pair to its ester, giving an increased overall rate of polymerisation. Polymerisation proceeds on the macroion pairs with SbF_6^-, and is termed a special salt-effect.

(a) <u>Initiation with $Ph_3C^+SbCl_6^-$ and p-ClC$_6$H$_4$N$_2^+$PF$_6^-$</u>

The initiation of THF polymerisation by the triphenyl methyl carbenium ion (Ph_3C^+) involves overall hydride ion (H^-) abstraction[99] to form triphenylmethane (Ph_3CH).[100] H^- transfer has been demonstrated both by the presence of Ph_3CH detected by ^1H n.m.r.[101] and by the formation of chlorobenzene (ClC_6H_5)[61] in the decomposition of p-chloro-benzenediazonium hexafluorophosphate (p-ClC$_6$H$_4$N$_2^+$PF$_6^-$) in 2-MeTHF, rather than p-chlorofluorobenzene (p-ClC$_6$H$_4$F), the normal product of thermal decomposition of this initiator. In the interaction between $Ph_3C^+SbCl_6^-$ and 2-MeTHF or THF, Dreyfuss, Westfahl and Dreyfuss[102] suggest that $HSbCl_6$ and furans are formed in addition to Ph_3CH. The initiation reaction therefore includes the dehydrogenation of THF to a furan or dihydrofuran along with the formation of the free acid of the counter-ion ($H^+PF_6^-$ or $H^+SbCl_6^-$) which is stabilised by complexing with monomer, forming the dietherate complex, (23.I). The mechanism of initiation by diazonium (and trityl) salts as proposed by Dreyfuss et al.[54,56,103] is as follows:-

$$p\text{-}ClC_6H_4N_2^+PF_6^- + \underset{O}{\bigcirc} \xrightarrow[\text{fast}]{\text{THF}} \left[\underset{PF_6^-}{\underset{O}{\bigcirc}}\right]^+ + ClC_6H_5 + N_2 \quad (22)$$

$$\left[\underset{PF_6^-}{\underset{O}{\bigcirc}}\right]^+ \xrightarrow{.\text{THF}} \left[\underset{O}{\bigcirc}\right] + \underset{PF_6^-}{\overset{+}{O}H}\text{-------}O\bigcirc \quad (23)$$

$$(23.\text{I})$$

$$\underset{PF_6^-}{\overset{+}{O}H}\text{-------}O\bigcirc \longrightarrow HO(CH_2)_4\text{-}\underset{PF_6^-}{\overset{+}{O}}\bigcirc \quad (24)$$
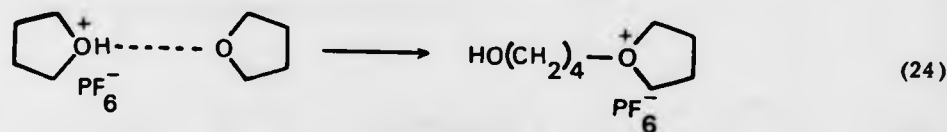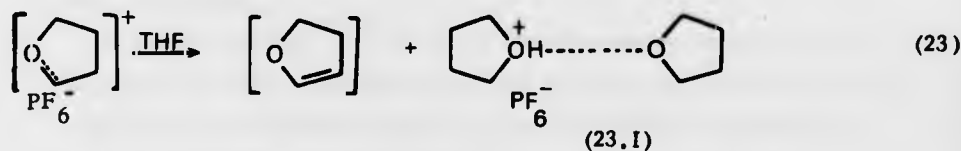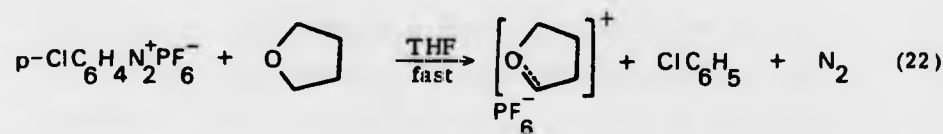
Ledwith and Sherrington,[21] however, suggest that it is equally likely that the primary mode of decomposition of the arenediazonium salt is homolytic, yielding ultimately α-alkoxy radical (26.I) from the cyclic ether, leading to an aldehydic end group (28.I):

$$ArN_2^+X^- \longrightarrow Ar^{\cdot} + N_2 + X^{\cdot} \quad (25)$$

$$Ar^{\cdot} + \underset{O}{\bigcirc} \longrightarrow ArH + \underset{O}{\overset{\cdot}{\bigcirc}} \quad (26)$$

$$(26.\text{I})$$

$$\underset{O}{\overset{\cdot}{\bigcirc}} + ArN_2^+ \longrightarrow \left[\underset{O}{\bigcirc}\right]^+ + Ar^{\cdot} + N_2 \quad (27)$$

$$\left[\underset{O}{\bigcirc}\right]^+ + THF \longrightarrow H\overset{O}{\overset{\|}{C}}(CH_2)_3\text{-}\underset{X^-}{\overset{+}{O}}\bigcirc \quad (28)$$

$$(28.\text{I})$$
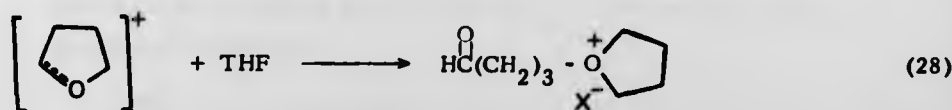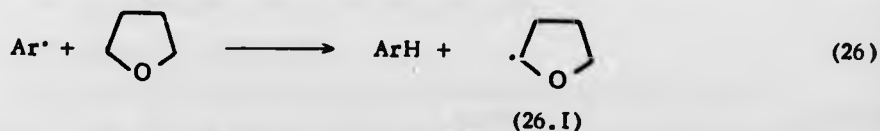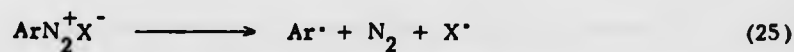
Polymerisation of THF initiated by $Ph_3C^+SbCl_6^-$ gives rate constants (with respect to disappearance of Ph_3C^+ studied spectrometrically) of ca. 6×10^{-3} $dm^3 mol^{-1}s^{-1}$ for $[THF] = 0.4$ mol dm^{-3} in CH_2Cl_2 at 298 K, and ca. 21×10^{-3} $dm^3 mol^{-1}s^{-1}$ for pure THF.[104] In CH_2Cl_2 free ions are thought to be present, and in pure THF (a much less polar solvent) ion pairs are expected to predominate. Here it appears that the free ions may be less reactive than the corresponding ion pairs. Ledwith and Sherrington[50]

also point out that the kinetics of initiation may be further complicated by the carbocation-oxonium ion equilibria which may occur in ether systems.[105]

(b) Propagation

It is now generally[6,106] accepted that propagation occurs by nucleophilic attack at the α-carbon atom of the propagating species (a tertiary oxonium ion) by the lone electron-pair of an incoming THF molecule. This can be represented as follows:-[61]

$$- O \{ CH_2 \}_4 - O \quad \xrightarrow[\text{Depropagation}]{\text{Propagation}} \quad - O \{ CH_2 \}_4 - O \qquad (29)$$
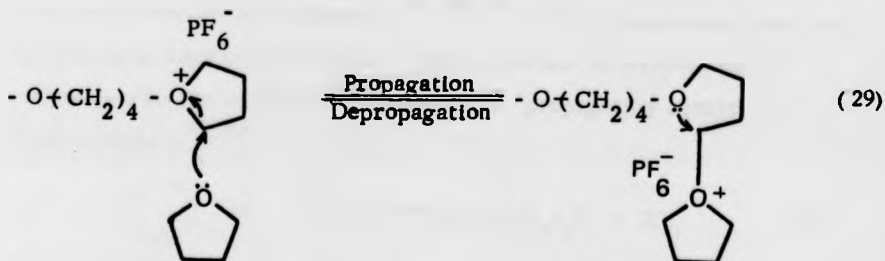
The depropagation reaction occurs by a similar nucleophilic attack by the penultimate oxygen atom in the polymer chain.

(c) Transfer and Termination

Chain transfer reactions to oxygen centres can occur with acyclic ethers[61] (e.g. diethyl ether), orthoesters[61,88] [e.g.$(CH_3O)_3CH$], water[88,108] alcohol[88] and polymer.[61,68,88,89] The transfer reaction with Et_2O has been demonstrated by monitoring the incorporation of ^{14}C-labelled diethyl ether (used as a solvent) into the polymer.[107] The reaction can be represented as follows:-

$$R_1 - O \quad \rightleftharpoons \quad R_1 - O \qquad (30)$$

$$R_1 - O(CH_2)_4 OR_2 + R_3 - O$$
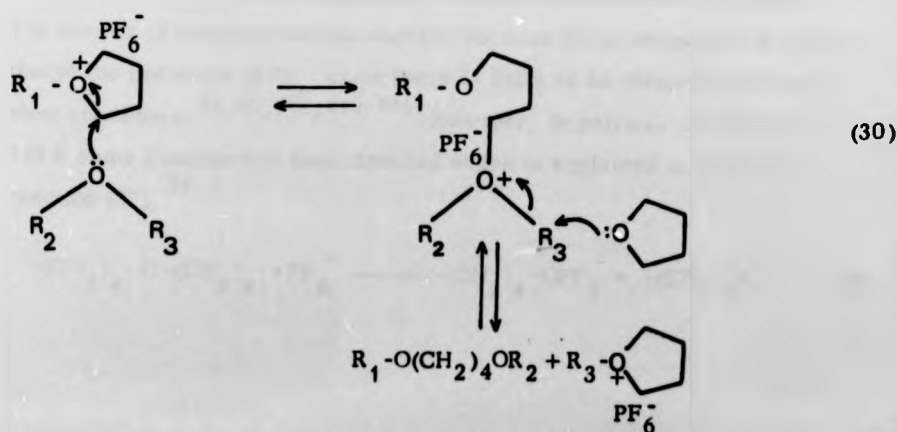
A similar transfer reaction can occur with the oxygen atoms in both the polymer chains and the monomer. The reaction of a polymer oxygen centre in the chain with its growing-end could lead to the formation of a macrocyclic oligomer and a shortened propagating oxonium ion.[88] The formation of cyclic oligomers is discussed in section (1.6.iv).

The kinetics of THF polymerisations carried out with anions such as $AlCl_4^-$, BF_4^- and $SbCl_6^-$, which are highly reactive towards the propagating species, should be described in terms of both reversible propagation and chain termination,[88,90,91] the latter becoming especially significant at high temperatures. The mechanism of termination is assumed to be the self-decomposition of the propagating species by counter anion:-[91,109]

$$\wedge\!\!\wedge\!\!\wedge O^+ \underset{}{\overset{}{\bigcirc}} \quad BF_4^- \xrightarrow{k_t} \wedge\!\!\wedge O(CH_2)_4F + BF_3 \qquad (31)$$
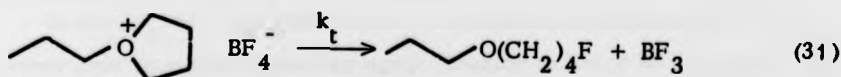
BF_3 (in low concentrations) in the absence of cocatalyst does not initiate further polymerisation of THF.[110] However, similar reactions involving $SbCl_6^-$ and PF_6^- anions will generate $SbCl_5$[109,111,112] and PF_5,[107] which may reinitiate polymerisation, giving essentially a transfer reaction. THF initiation by $SbCl_5$ can be represented as follows:-[111,112]

$$2\left[SbCl_5 \cdot O\bigcirc\right] \longrightarrow SbCl_4O(CH_2)_4\text{-} \overset{SbCl_6^-}{O^+\!\!\bigcirc} \qquad (32)$$
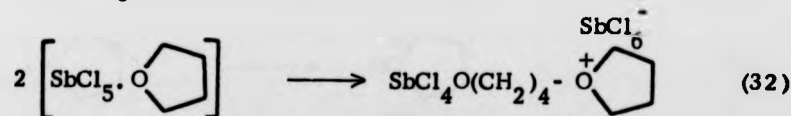
The polymerisation reactions carried out with $SbCl_6^-$ gegenion, particularly at high temperature, give ultimate conversions which fall below the equilibrium conversions, suggesting that some termination must occur.[111-114] The results of polymerisations carried out near room temperature indicate that in the presence of PF_6^- anion there is little or no termination under most conditions.[31,61,109,114-116] However, in polymer produced at 343 K some fluorine has been detected which is explained in terms of reaction (33).[31]

$$-(CH_2)_4\text{-}O\text{-}(CH_2)_4\text{-}+PF_6^- \longrightarrow -(CH_2)_4\text{-}OPF_5^- + -(CH_2)_4F \qquad (33)$$
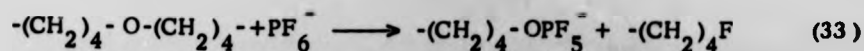
However, reaction similar to that represented by eqn (31) is another possibility, leading to further initiation of polymerisation. In the absence of a cocatalyst, the THF can function as the "promoter" molecule, thus:-[53]

$$\text{(34)}$$
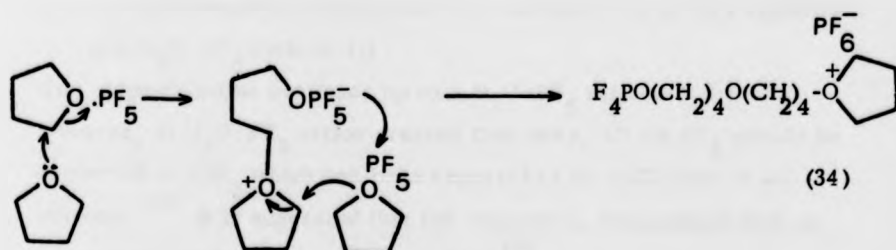
(d) Transfer Reactions Effected by Water

In the BF_3-ECH (epichlorohydrin)-initiated polymerisation of THF, water acts as a chain-transfer agent, leading to lower $\overline{M}$ polymer, but without change in the rate. The following mechanism for the transfer reaction was proposed:-[108]

$$\text{(35)}$$

$$\text{(36)}$$
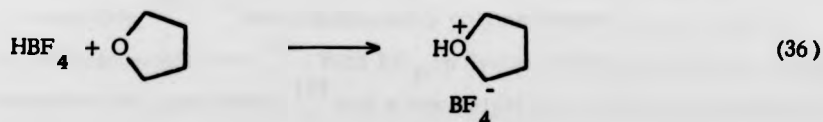
However, this can be written as in eqn. (37) which is analogous both to the reaction with dialkyl ether, eqn. (30), and that with the polymer oxygen centre.[88]

$$\text{(37)}$$
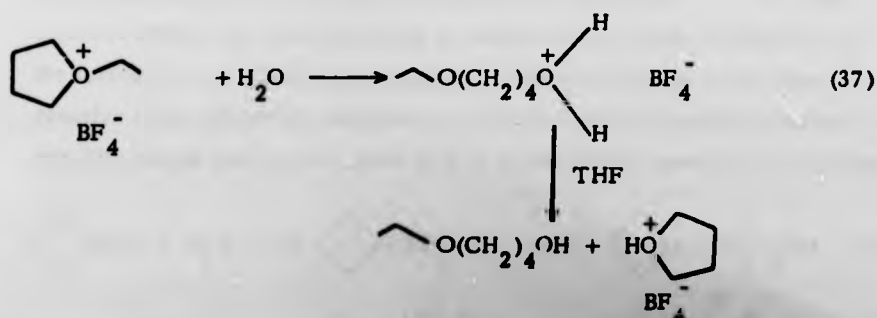
The effect of water upon the PF_5-initiated polymerisation of THF can be summarised as follows:-[107]

(i)   from low concentrations of water, the rate increases to a maximum value at a $H_2O:PF_5$ ratio of ca. 1:6

(ii) at higher water concentrations the rate falls, but is still significant at a $H_2O:PF_5$ ratio of 1:1

(iii) polymerisation continues up to a $H_2O:PF_5$ ratio of 1.3:1

However, at $H_2O:PF_5$ ratios greater than unity, all the PF_5 should be converted to POF_3, which has been reported to be ineffective as an initiator.[116] It is suggested that the reaction is complicated both by cocatalysis and destruction of catalyst.[107]

Bawn et al.[114] have suggested that the transfer reaction in the bulk polymerisation of THF must involve one of the following:-

(i)   hydride ion abstraction from the α methylene of THF or tetramethylene-oxy units in the polymer, or

(ii) degradative oxonium ion formation with ethereal oxygen atoms of polymer chains.

1.6.11   Oxetanes (or Oxacyclobutanes)

The oxygen atom in oxetanes is much more basic than that in 1,2-epoxides,[117, 118] and consequently polymerisation occurs only by the cationic mechanism.[49] With BF_3, polymerisation does not occur under completely dry conditions,[119] and a cocatalyst such as H_2O is necessary for initiation. The rate of polymerisation, which is first-order with respect to monomer, increases to a maximum with added H_2O, and finally decreases with a change in order from one to two.[29,68] The complex effect of H_2O is explained in terms of a two-step initiation, i.e. the formation of a secondary oxonium ion (38.I), which is much less reactive than the tertiary oxonium ion (38.II), and the transfer reaction, eqn.(39), which leads to decrease in $[\eta]$ as the H_2O concentration increases:[29,68]

$$\diamondsuit\!\!-\!OBF_3 + H_2O \longrightarrow \overset{+}{\diamondsuit}\!\!-\!OHBF_3OH^- \longrightarrow \overset{+}{\diamondsuit}\!\!-\!O\,-(CH_2)_3OH \qquad (38)$$

$$(38.I) \qquad\qquad\qquad BF_3OH^-$$

$$(38.II)$$

$$H_2O + \underset{BF_3OH^-}{\overset{+}{\diamondsuit} O} -[(CH_2)_3O]_{n-1}H \xrightarrow{k_{tr}} HO-[(CH_2)_3O]_nH + H^+BF_3OH^- \quad (39)$$
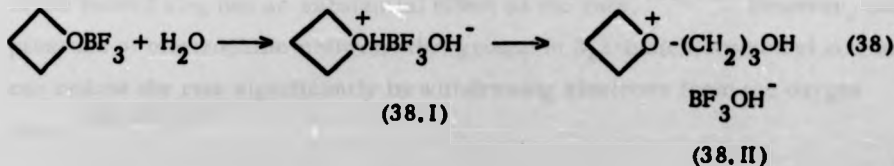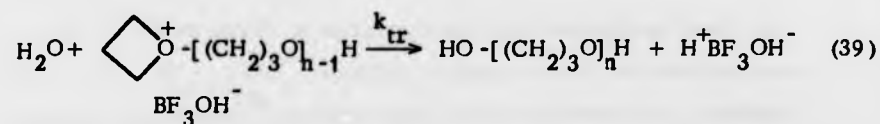
The final products include a cyclic tetramer, the yield of which depends markedly on the temperature of polymerisation. The formation of cyclic oligomers is discussed in section (1.6.iv).

The BF_3-THF complex initiated polymerisation of oxetane in methyl-cyclohexane (which has zero dipole moment[49]) shows a rate of polymerisation about nine times greater than that in CH_2Cl_2.[69, 120] This result is explained in terms of relative solvation of the transition state that is assumed to form in the S_N2 propagation reaction.[120] However, the relative efficiency of the catalyst (as measured in terms of concentration of reactive oxonium ions, $[P^*]$)[121] was reduced to 28-36% in methylcyclo-hexane[120] compared with ca. 80% in CH_2Cl_2,[69] which is attributed to the possible presence of trace water impurity.

The BF_3-THF initiated polymerisation of 3-methyl- and 3,3-dimethyl-oxetane gives $[P^*]$ values which are both solvent- and temperature-dependent. The second-order rate constants (k_p, with respect to monomer and $[P^*]$) are enhanced by substitution at the 3-position, in both solvents. The value of ΔG_p and the activation energy (E_p) change in the opposite sense to increase in k_p, and also the basicity measurements (as measured by the $\Delta\nu_{OD}$ values, i.e. the difference of ν_{OD} of methanol-O-d in benzene (C_6H_6) and ν_{OD} of methanol-O-d and monomer in C_6H_6 is taken as a measure of basicity of monomer) do not correlate with the k_p values.[120] Saegusa et al. concluded therefore that the frequency factor A (i.e. the entropy of activation, $\Delta S_p^{\ddagger}$) increases in the order unsubstituted < monosubstituted < disubstituted, and predominantly governs the reactivity of these monomers.[121] Polymerisation of bicyclic oxetanes (derived from the substitution on the 3-carbon of the oxetane ring) shows that the strain in the second ring has no substantial effect on the rate.[122, 123] However, the presence of electrophilic chloromethyl groups in 3,3-bis(chloromethyl)oxetane can reduce the rate significantly by withdrawing electrons from the oxygen atom.[122, 124, 125]

The polymerisation of oxetane initiated by triethyloxonium salts (with BF_4^-, PF_6^-, $SbCl_6^-$ and SbF_6^- counter-ions) and ethyl trifluoro-methane sulphonate[70] yields not only cyclic tetramer (Ox_4) and high polymer, but also cyclic trimer (Ox_3). The amount and type of oligomer obtained depends on counter-ion, temperature and solvent. $Et_3O^+BF_4^-$ initiator yields as much as 35% oligomer which is predominantly as $(Ox)_4$, and PF_6^-, SbF_6^- and $SbCl_6^-$ salts give insignificant, but detectable, conversion to cyclic oligomers, again with $(Ox)_4$ in greater amounts than $(Ox)_3$. CF_3OSO_2H-initiated polymerisation leads to ca. 15% of almost exclusively trimer. Addition of BF_4^- initiator after complete disappearance of monomer does not cause further conversion to oligomers; the $(Ox)_4$ is stable toward SbF_6^- initiator at room temperature and at 373 K, and cyclic oligomers are only formed when the initiator is added to a mixture containing monomer. Accordingly, cyclic oligomer formation is thought to be a process concurrent with polymerisation.[70] Furthermore, a very much smaller quantity of SbF_6^- salt is required to react all of the monomer, indicating a longer effective lifetime of the active propagating species.

The $Ph_3C^+PF_6^-$-initiated polymerisation of oxetane leads to very rapid and quantitative formation of reactive oxonium ions at low initiator concentrations.[126] This is followed by a very fast propagation reaction which has a half-life of 10 to 20 s as measured by the temperature rise method used by Plesch.[127,128] At the end of the propagation reaction, most of the oxonium ions are still present,and the system is believed to behave as if initially very active chain ends (40. I) are formed which, after a short period of rapid growth, become quiescent and the reaction slowly goes to completion. The results are interpreted in terms of formation of two types of tertiary oxonium ions ; type (40. II) is cyclic and reacts rapidly with more oxetane, and type (40. III) involves an ether linkage, such as in the polymer chain, and reacts only slowly with oxetane:-[126]

$$Ph_3C^+PF_6^- + 2C_3H_6O \xrightarrow{\text{fast}} Ph_3COC_3H_6C\overset{+}{O}\diamondsuit$$ (40)

$$(40.I) \qquad PF_6^-$$

monomer | very fast

$$Ph_3C(OC_3H_6)_n-OC_3H_6-\overset{+}{O}PF_6^-$$

with O, C_3H_6 above and C_3H_6, O below

$$\xleftarrow[\substack{\text{fast} \\ C_3H_6O \\ \text{slow}}]{\text{polymer}} Ph_3C(OC_3H_6)_n\overset{+}{O}\diamondsuit$$

$$(40.III) \qquad \text{Reinitiation} \qquad PF_6^- \qquad (40.II)$$
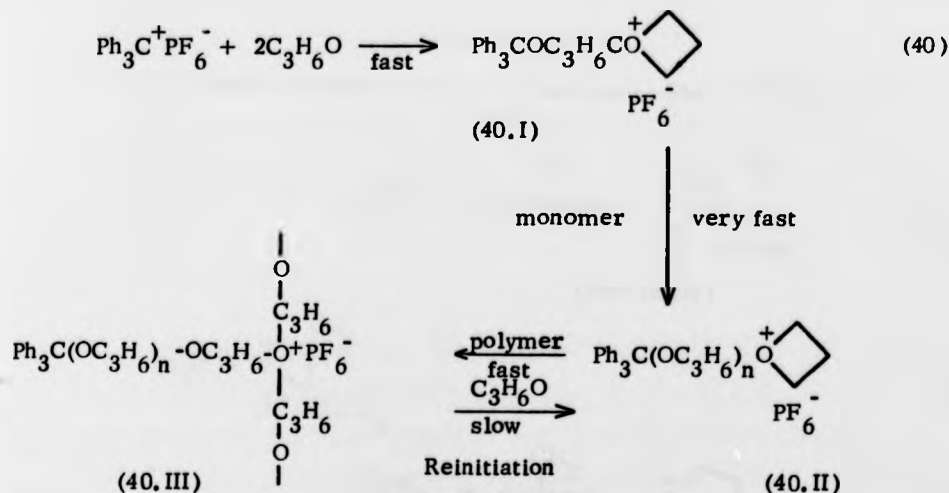
The chain length of polymers formed in the initial rapid stage is an indication of the spurt of propagation by reactive species. At low initiator concentrations the $\bar{M}_w/\bar{M}_n$ ratio may not be unity as in a normal living polymerisation, but it should be close to unity. However, the results indicate that $\bar{M}_w/\bar{M}_n > 2$ except for the two Na^+PhO^--terminated samples after long reaction times.

Polymerisation reactions initiated by $Et_3O^+PF_6^-$ give rates of monomer consumption hundreds of times lower due to the very slow initiation reaction.[126] Values of $\bar{M}$ are found to be independent of initial initiator concentrations. The propagation reaction is assumed to be rapid by analogy with $Ph_3C^+PF_6^-$-initiated polymerisation, with slow reinitiation similar to that shown in eqn. (40).

1.6.iii Copolymerisation of 1,2-Epoxides with Tetrahydrofuran

The polymerisation of THF initiated by $Ph_3C^+SbCl_6^-$ in the presence of 1,2-epoxides (ca. 10 times the initiator concentration or more) gives a several-fold increase in the rate, with no formation of Ph_3CH.[129] The initiation reaction suggested involves the formation of an oxonium ion, viz.

$$Ph_3C^+X^- + CH_3CH\overset{O}{-}CH_2 \longrightarrow Ph_3C-\overset{+}{O}\underset{X^-}{\overset{CH_2}{\underset{CHCH_3}{\diagdown}}}$$ (41)

$$(41.I)$$
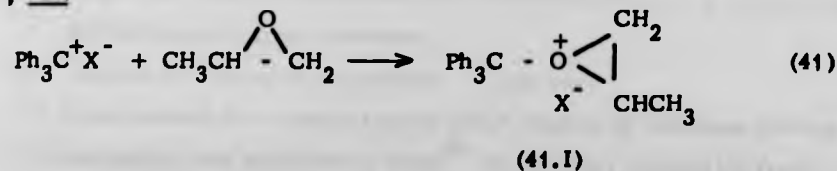
The reactive species (41.I) can now react either with further PO or THF:

(less likely)

$$Ph_3C - O^+ \underset{X^-}{\overset{CH_2}{\triangleleft}} \quad \underset{CHCH_3}{} \tag{42}$$
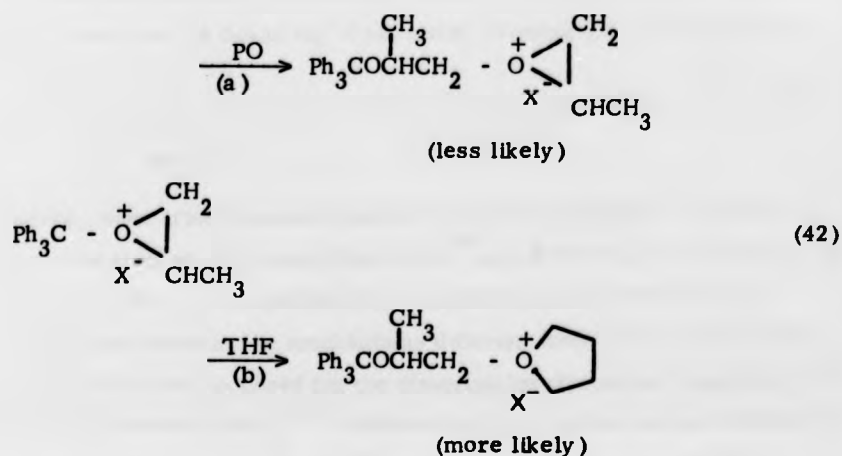
(more likely)

Since THF is a stonger Lewis base than PO,[117] the reactive species (41.I) will be preferentially solvated by THF, and therefore reaction (42.b) is more likely than (42.a). For $Ph_3C^+PF_6^-$-initiated polymerisation,[130] the reactivity ratios for PO ($r_{PO} = 0.26$) and THF ($r_{THF} = 0.80$) show that the two monomers will tend to alternate along the chain. However, the low value for r_{PO} and the fact that no homopolymerisation of THF occurs under similar reaction conditions indicate that blocks of PO are not expected, and only two consecutive units of THF are expected to occur along the copolymer chain.[130] If [THF] >> [PO], then rate of reaction is low due to excess of unreactive double THF chain ends, and if [PO] >> [THF], then polymerisation is much faster, with a tendency to form PO oligomers.

1.6.iv Formation of Cyclic Oligomers

The mechanisms of oligomer formation can be divided into two groups:[55]

(a) a process which is concurrent with polymerisation, i.e. oligomers are formed directly from monomer,

(b) oligomers formed by degradation of polymer.

A mechanism for oligomerisation which occurs by the same process as polymerisation was proposed by Rose[29] for the $(Ox)_4$ formation from

Ox-polymerisation initiated by BF_3 - H_2O, or -EtOH, etc. After the fourth propagation step, the growing species is attacked by the hydroxyl group situated at the beginning of the chain, forming $(Ox)_4$ and initiator:

$$H[O(CH_2)_3]_3 - \overset{+}{\underset{BF_3OH^-}{O}} - (CH_2)_3 \longrightarrow \boxed{[O(CH_2)_3]_4} + BF_3OH^- \ H^+ \quad (43)$$
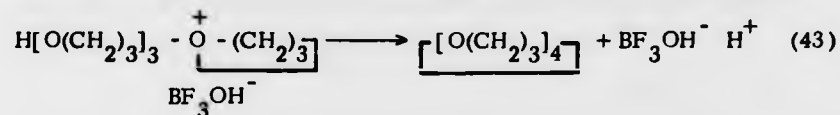
However, when triethyloxonium salts are used as initiators, no hydroxyl groups are formed, but cyclic oligomers[70] are still formed; therefore, the formation of $(Ox)_4$ must proceed by another reaction mechanism.

Oligomer formation by mechanisms different from the polymerisation reaction have been proposed for the dimerisation of styrene oxide (StO),[131] and the formation of $(PO)_4$.[65] Both mechanisms involve initial hydride-ion transfer, and the process for $(PO)_4$ formation can be represented by the solvation of species (II) by three PO units, and its subsequent reaction to give a 12-membered ring.[65]

$$\longrightarrow (PO)_4^+ \qquad (44)$$

$$(PO)_4^+ + PO \longrightarrow (PO)_4 + II \qquad (45)$$

where II =
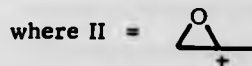
However, polymerisation of 1, 2-butylene oxide (BuO) by $Ph_3C^+AsF_6^-$ does not involve hydride-ion transfer,[67] and in both of the above-mentioned mechanisms degradation of polymer is a possible alternative process.

In the polymerisation of ethylene oxide (EtO), initiated by BF_3 with cocatalysts such as H_2O in 1, 2-dichloroethane,[63] chain growth ceases at $\bar{M}$ ca. 700, and is replaced by the formation of dimer $(EtO)_2$. Dioxan formation is believed to occur by degradation of the polymer, via oxonium

salts, by analogy with the depolymerisation of polyglycols[62] caused by $Et_3O^+BF_4^-$. The mechanism of degradation involves ether-exchange reactions which, firstly, transfer the oxonium ion to the polyglycol chain, eqn. (46), and then eliminate $(EtO)_2$ until the reactive species is destroyed by the termination reactions, eqn. (48).[62]

$$R_3O^+BF_4^- + \text{-O(CH}_2)O(CH_2)_2O\text{-} \longrightarrow R_2O + \text{-O(CH}_2)_2\text{-}\overset{\overset{\displaystyle BF_4^-}{|}}{\underset{\underset{\displaystyle R}{|}}{O}}\text{-}(CH_2)_2O\text{-} \qquad (46)$$

$$(47)$$

$$(48)$$

$$\text{-OCH=CH}_2 + HBF_4 + RO(CH_2)_2O\text{-}$$
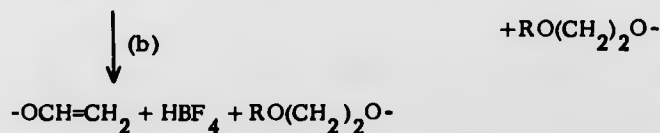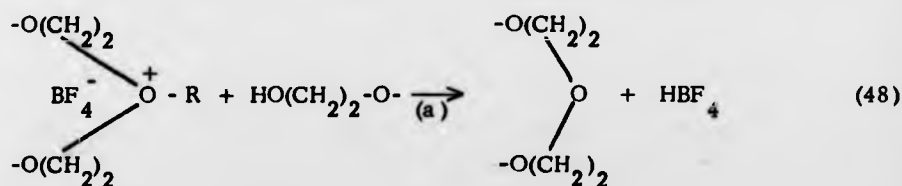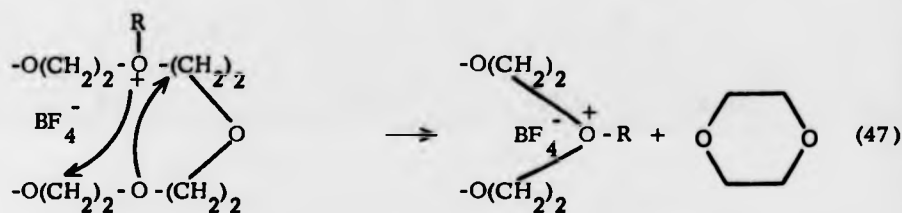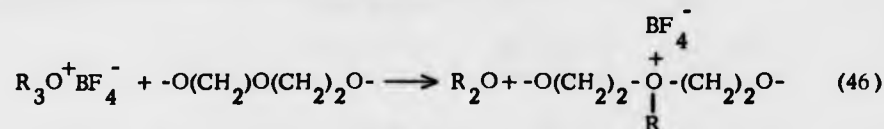
If we consider ring-opening polymerisation as an equilibrium reaction between monomer and polymer, then $[M_e]$ (the equilibrium monomer concentration) will be given by eqn. (49):[12]

$$\ln[M_e] = \Delta G_p/RT = \Delta H_p/RT - \Delta S_p/R \qquad (49)$$

Since the ΔH_p and ΔS_p values have been calculated for a number of ring-opening polymerisations,[132] $[M_e]$ can be calculated, Table (4). The $[M_e]$ values for the 6-membered and some 5-membered rings show that depolymerisation of polymers to form these monomers is thermodynamically

feasible, and will occur provided a suitable mechanism is available.[55] This is demonstrated by the degradation of poly(tetramethylene sulphide), by catalytic amount of $Et_3O^+BF_4^-$, to tetrahydrothiophene.[55]

Table (4)

Estimated theoretical $[M_e]$ values at 300 K [55]

Monomer	Ring strain[133] (kJ mol^{-1})	ΔG_p (kJ mol^{-1})	$[M_e]$ (mol dm^{-3})
▷O	113.0	-87.9	6×10^{-16}
▷S	83.7	-58.6	7×10^{-11}
◇O	106.7	-69.1	10^{-12}
◇S	83.4	-58.6	7×10^{-11}
⬠O	23.4	+1.7	1.9
⬠S	8.4	+16.7	8×10^2
⬡O	-1.3	+25.1	3.6×10^4

All polymers derived from 3-membered heterocyclic monomers have structures which allow the formation of 6-membered rings,[55] by the back-biting mechanism, eqn. (50), which explains the degradation of polyoxiranes, polythiiranes and poly(N-alkylaziridines) to 1,4-dioxans, 1,4-dithians

and dialkylpiperazines, respectively.

$$(50)$$
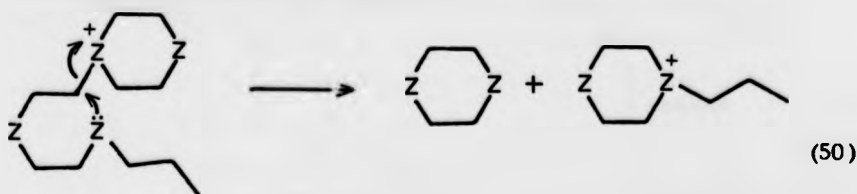
If degradation is not observed, it may be because of the high activation energy for the process, leading to extremely slow reaction, or due to the termination reaction for depolymerisation. Termination of both propagation and degradation reactions have been observed for the polymerisation of propylene sulphide by $Et_3O^+SbCl_6^-$ which is believed to occur between the active sulphonium ions and counter-ions.[73] The polymerisation of N-substituted aziridines stops at limited conversions, but the degradation of the polymer to the corresponding piperazine derivatives (via the quaternary ammonium salts) continues in the presence of unreacted monomer.[134]

In the polymerisation of oxetane, initiated by ethyloxonium salts, and CF_3OSO_2H,[70] section (1.6.11), and that of 3,3-dimethyloxetane, initiated by $Et_3O^+BF_4^-$,[135] oligomer formation is concurrent with polymerisation. Three distinct mechanisms may be put forward to explain this phenomenon:-[55]

(i) polymerisation and oligomer formation occur via two independent routes which cease simultaneously,

(ii) propagation, and degradation of polymer formed, occur simultaneously, but complete conversion to oligomers is prevented by a termination reaction,

(iii) oligomer formation occurs by degradation of polymer, but only in the presence of monomer, e.g.[69]

$$\sim\!\!\text{[O(CH}_2)_3]_3 - \overset{+}{\text{O}}\!\!\square \longrightarrow \sim\!\!\overset{+}{\text{O}}(\text{CH}_2)_3 - [\text{O(CH}_2)_3]_3$$

oxetane   (51)

$$\sim\!\!\overset{+}{\text{O}}\!\!\square \quad + \quad [\text{O(CH}_2)_3]_4$$
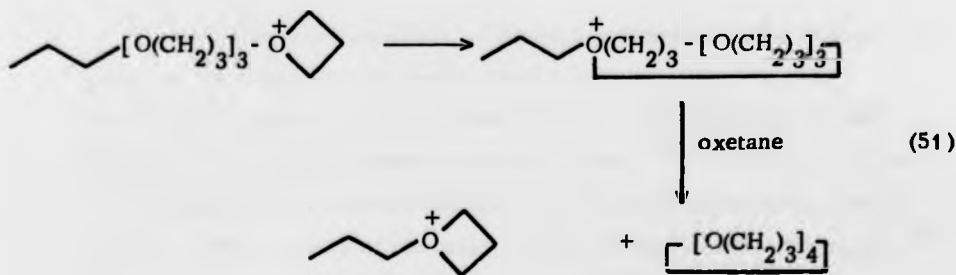
The extent of oligomer formation in the above scheme, which is essentially a transfer reaction, section (1.6.1(c)), will be limited by the availability of monomer. However, at present it is not possible to specify which mechanism operates in tetramer formation from oxetane and 3,3-dimethyloxetane.[69]

Many polymers derived from 3-membered heterocyclic monomers do not degrade to 6-membered rings, and 12-membered or larger rings are formed. The formation of a tetramer from poly(propylene sulphide), (PPS), involves a rapid exchange between sulphonium ions and sulphide functions[136] which ultimately leads to the thermodynamically most stable compound, e.g. $(PO)_4$ is reported to be thermodynamically more stable than either $(PO)_2$ or polymer.[137] The transition state for the formation of 6-membered rings in the back-biting mechanism has been proposed tentatively as follows:-[55]
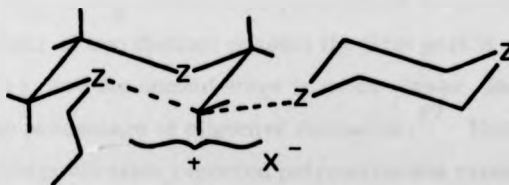
The presence of substituents will result in steric interactions which may lead to formation of larger rings. The importance of configuration in polymer chains is demonstrated by the fact that isotactic PPS will degrade quantitatively to oligomers[138] (predominantly tetramer), whereas PPS obtained by cationic polymerisation does not depolymerise completely,[139] possibly due to the presence of a number of head-to-head structures in this polymer.[140]

In a polymerisation reaction, if the high polymers are the desired products, then oligomer formation must be minimised. However, macrocyclic oligomers such as crown ethers can be useful due to their remarkable complexing power for metal cations.[141, 142] The formation of a complex and its stability depends on the size of crown ether, steric factors, charge density of the cations and solvating power of the media.[141] Therefore, when cyclic oligomers are the desired end-products of polymerisation, then selection of a suitable initiator, solvent and reaction conditions can lead to higher yields.[143-145]

1.6.v 1, 2-Epoxides

In the polymerisation of styrene oxide[131] and α-methylstyrene oxide [146] by $Ph_3C^+SbCl_6^-$, the initiation reaction is explained in terms of α- and β-hydride-ion transfer to the carbocation. However, the alternative mode of initiation for epoxide polymerisation[147] and its copolymerisation with THF[129] is that involving the direct addition of a carbocation to the epoxide, eqn. (41), section (1.6.iii). For the polymerisation of BuO initiated by $Ph_3C^+AsF_6^-$, (i) the UV spectrum of the polymerised products is similar to that of a model compound, $Ph_3COC_2H_5$, rather than that of Ph_3CH, (ii) the ^1H n.m.r. spectrum shows no signal due to C-H of Ph_3CH, indicating that initiation occurs by the direct addition of Ph_3C^+ to the monomer.[67]

$Ph_3C^+AsF_6^-$-initiated polymerisation of BuO is shown by Blanchard et al.[67] to occur in two distinct phases; the first part is very fast (duration of ca. 100 s), and the second stage is much slower, leading to a relatively large percentage of oligomer formation.[67] Blanchard et al.[66] in their earlier publication, reported polymerisation rates which were independent of the counter-ions. (SbF_6^-, PF_6^- and AsF_6^-) with very low percentages of oligomer. A more detailed account of 1, 2-epoxide polymerisation leading to cyclic oligomer formation can be found in section (1.6.iv).

The mechanism of the ring-opening polymerisation of 1, 2-epoxides, prepared by anionic, cationic and co-ordination catalysts, has been shown to proceed almost entirely with inversion of configuration at the carbon atom. Details of the process can be found in references 43, 44 and 148-151.

1.6.vi The Effect of Counter-Ions (AsF_6^-, BF_4^-, SbF_6^-, $SbCl_6^-$ and PF_6^-) upon Polymerisation of Cyclic Ethers

The effect of counter-ions in the cationic polymerisation of cyclic ethers (THF, oxetanes and 1,2-epoxides) may be summarised as follows:-

(i) The polymerisation of THF initiated by 1,3-dioxalan-2-ylium salts, show rates which are independent of the counter-ions[89] (AsF_6^-, PF_6^- and SbF_6^-) and proceed, at room temperature, without termination.[31,61,107,114,15?] The kinetics of polymerisations involving $AlCl_4^-$, BF_4^-[91] and $SbCl_6^-$[111,113] anions should be expressed in terms of both reversible propagation, and termination reactions. Polymers obtained by using kinetically "stable" counter-ions such as PF_6^-[114] and SbF_6^-,[152] give higher conversion to polymer with generally greater $\bar{M}$ values than those obtained with BF_4^-[90,109] and $SbCl_6^-$.[114,152]

(ii) In the polymerisation of oxetane, initiators with BF_4^- anion lead to high percentages of oligomer formation, compared with SbF_6^-, PF_6^- and AsF_6^-. Furthermore, a much smaller quantity of SbF_6^- initiator is required to react all the monomer.[70]

(iii) Polymerisations of 1,2-epoxides by BF_4^- initiators usually give high conversion to oligomers[153] whereas SbF_6^-, PF_6^- and AsF_6^- have been reported to yield polymers of $\bar{M}$ values ranging from 4,500 to 5,500.[66] However, a higher percentage of oligomers may occur with AsF_6^- initiator.[67] Polymerisation of BuO initiated by $Ph_3C^+PF_6^-$, SbF_6^- and AsF_6^- shows very rapid initial reaction, followed by a slower phase, both of which are independent of the counter-ions.[66]

1.7 POLYMER CHARACTERISATION

All polymer molecules, whether natural or synthetic, consist by definition of large numbers of simple repeat units derived from small molecules and joined together by covalent bonds.[154] The final polymer structure can be classified as linear, branched or crosslinked,[20] and is dependent on the chemical properties of the monomer and the process of polymerisation. The polymers which consist of repeating structural units of the same kind (disregarding terminal units) are called homopolymers,

and those with two and three different types of basic units are termed co- and terpolymers,respectively.[155] The copolymers can be random (e.g. vinyl chloride - vinyl acetate), alternating (e.g. maleic anhydride-styrene), block (styrene-butadiene) or graft (poly[styrene-g-acrylonitrile]). In vinyl polymerisation, three arrangements in polymer linkage are possible, namely head-to-tail, head-to-head/tail-to-tail and random.

The polymer structure is further complicated when the backbone molecule contains a carbon atom attached to two different side groups. The configurational arrangements (or tacticity)of such polymers can be regular (tactic) or random (atactic).[156] In tactic polymers the situation where there is a repetition of the same configuration at each progressive asymmetric carbon atom along the chain is called isotactic (e.g. as in polypropylene oxide), and if there is an alternation of configuration it is referred to as syndiotactic (e.g. as in polypropylene).

1.7.i Molecular Weights

A polymer sample in which all the molecules have the same molecular weight ($\bar{M}$) is said to be monodisperse. However, with few exceptions, mainly of biological origin, the occurrence of random processes during polymerisation reactions produce polymer molecules containing varying numbers of repeat units, so that the polymer contains a distribution of molecular weights and is said to be polydisperse. Therefore,it is impossible to characterise completely the polymer by a single $\bar{M}$. Ideally both the average $\bar{M}$ and the $\bar{M}$ distribution (MD) within a polymer are required in order to characterise it fully.

The $\bar{M}$ of a polymer is its most important characteristic. In most instances there is some $\bar{M}$ range for which a given polymer property will be optimum for a particular application, and,therefore,a polymerisation needs to yield a product of sufficiently high and specified $\bar{M}$.[157]

1.7.ii Definition of Molecular Weight Averages

$\bar{M}$ values of polymers can be determined by chemical or physical (UV or visible spectroscopy) methods of functional group analysis, measurement of the colligative properties (membrane osmometry and vapour pressure), light scattering photometry, ultracentrifugation and measurement of dilute

solution viscosity.[158] The most recent method, which has gained the widest usage, is that of gel permeation chromatography (GPC).[159] However, not all of these methods yield the same average $\bar{M}$ because the properties being measured are biased differently towards the different fractions in the sample. This situation leads to definitions of different $\bar{M}$ averages. All $\bar{M}$ averages can be described by equation (52), developed by G. Meyerhoff,[160] as follows:[161]

$$\bar{M}_\beta = \frac{\sum w_i M_i^\beta}{\sum w_i M_i^{\beta-1}} \qquad (52)$$

where the weight fraction $w_i = n_i M_i$ and n_i is the number of molecules whose weight is M_i.

By setting $\beta = 0$, one obtains the equation defining the number averages, $\bar{M}_n$.

$$\bar{M}_{(\beta=0)} = \bar{M}_n = \frac{\sum w_i}{\sum w_i/M_i} \qquad (53)$$

With $\beta = 1$, equation (52) gives the weight averages, $\bar{M}_w$.

$$\bar{M}_{(\beta=1)} = \bar{M}_w = \frac{\sum w_i M_i}{\sum w_i} \qquad (54)$$

The z average molecular weight, which is determined from the sedimentation equilibrium in the ultracentrifuge, can be derived from equation (52) by substituting $\beta = 2$.

1.7.iii The Viscosity Average Molecular Weight ($\bar{M}_v$)

The viscosity of even very dilute solutions of synthetic polymers can be measured easily and with great accuracy. Therefore the viscosity method, introduced by H. Staudinger,[162] has been one of the most commonly used methods of $\bar{M}$ determination. In this work we have monitored the increase in viscosity of polymerising reaction mixtures to indicate the presence of high $\bar{M}$ polymer.

The Hagen-Poiseuille law, eqn. (55), states that with a

$$\eta = \frac{\pi}{8} \cdot \frac{\Delta p}{l} \cdot \frac{r^4 t}{v} \qquad (55)$$

where $\Delta p = \rho g h$ - is the pressure difference

l – length of the capillary

r – radius of the capillary

t – flowtime

v – flow volume

constant flow volume and apparatus (viscometer) dimensions, the viscosity is proprtional to the product of the flowtime (t), through the capillary, and the density of the solution (ρ) or the solvent (ρ_o). For very dilute solutions the densities of solution and solvent can be equated without significant error. Therefore, the relative viscosity (or more correctly the viscosity ratio, η_r) and the specific viscosity (η_{sp}) can be defined as follows:-

$$\eta_{sp} = \eta_r - 1 = \frac{(\eta - \eta_o)}{\eta_o} = \frac{(t\rho - t_o\rho_o)}{t_o\rho_o} \simeq \frac{(t - t_o)}{t_o} \qquad (56)$$

where t – flowtime of solution

t_o - flowtime of solvent

The theoretically derived expression (57), due to Einstein[163] and Simha[164], shows that the relative viscosity of a solution (or dispersion) of spherical, colloidal particles depends only on the volume fraction (φ per cm^3) of the dissolved (or dispersed) phase.

$$\eta_r = 2.5\,\varphi + 1 \qquad (57)$$

The volume which m grams of dissolved macromolecular compound occupy in solution in the form of statistical coils is given by $m/\bar{\rho}_{equ,[\eta]}$, where $\bar{\rho}_{equ,[\eta]}$ is the equivalent density of the empty molecular coils of this compound. φ is then given by eqn. (58) in which V_s is the volume of total solution. Since m/V_s is the concentration in grams per cm^3, then φ is given by eqn. (59).

$$\varphi = (m/\bar{\rho}_{equ,[\eta]})/V_s \qquad (58)$$

$$\varphi = c/\bar{\rho}_{equ,[\eta]} \qquad (59)$$

The Einstein viscosity law, eqn. (57), now becomes:

$$\eta_r = 2.5 \, c/\bar{\rho}_{equ, [\eta]} + 1 \tag{60}$$

Rearranging: $\quad (\eta_r - 1)/c = 2.5/\bar{\rho}_{equ, [\eta]} = \eta_{sp}/c \tag{61}$

where the relative viscosity increase (η_{sp}) is given by eqn. (56). Equation (61) only applies if the dissolved particles do not interfere with one another, i.e. at very high dilutions; therefore, the experimentally determined η_{sp}/c versus c plot is extrapolated to c = 0, to obtain the limiting viscosity number, [η], (or intrinsic viscosity). Various extrapolation procedures are available, the most widely used is the Huggins[165] eqn. (62):

$$\eta_{sp}/c = [\eta] + k_H [\eta]^2 c \tag{62}$$

The logarithmic viscosity number, η_i, (or inherent viscosity) defined as $(\ln \eta_r)/c$ in Kraemer's eqn. (63)[166] is often used for extrapolation in combination with the Huggins equation.

$$\eta_i = (\ln \eta_r)/c = [\eta] + k_K [\eta]^2 c \tag{63}$$

In relatively few cases this combination fails and other extrapolation procedures, such as those proposed by Heller[167] and Martin[168] are required.[169] In our present work, both the Huggins equation and the Schulz-Blaschke[170] eqn. (64) are used section(2.6.1).

$$\eta_{sp}/c = [\eta] + k_{SB} [\eta] \eta_{sp} \tag{64}$$

Also, with solutions of very high molecular weight polymers, the viscosity can depend on the flow gradient G (i.e. on the flow [shear] gradient in the viscometer), and in such cases η_{sp}/c is determined at different G and extrapolated to G = 0.[171] Equation (61) can now be written as:

$$(\eta_r - 1)/c = 2.5/\bar{\rho}_{equ, [\eta]} = \eta_{sp}/c = [\eta] \tag{65}$$

$$\text{Lt}(c \to 0)$$
$$\text{Lt}(G \to 0)$$

With polypropylene oxide (PPO) the G = 0 extrapolation is avoided because the effect is within the error of measurements, which operates particularly with [η] values over 300 $cm^3 g^{-1}$.

Ideal statistical coils in solution show a decrease in their average density with increasing $\bar{M}$ according to Kuhn's law: [172]

$$\bar{\rho}_{coil} = K_\rho \bar{M}^{-0.5} \qquad (66)$$

Substituting eqn. (66) in eqn. (65) gives the Kuhn viscosity law for the 'random-walk necklace model'.

$$[\eta] = 2.5/K_\rho \bar{M}^{-0.5} = K \bar{M}^{0.5} \qquad (67)$$

The exponent is a function of solvent and polymer structure, and is only equal to 0.5 at the well-defined θ conditions (where a Gaussian distribution of the hydrodynamic segments is assumed). [18, 173-176] A theta solvent is a specially selected poor solvent at a particular temperature, called θ- or Flory-temperatures. [18] However, in real systems the coil density decreases generally according to the eqn. (68):

$$\bar{\rho}_{equ, [\eta]} = const. \bar{M}^{-\alpha} \qquad (68)$$

Substitution of eqn. (68) into eqn. (65) gives the general viscosity eqn. (69), called the Mark-Houwink equation, [177] for macromolecular solutions.

$$[\eta] = K \bar{M}_{[\eta]}^{\alpha} \qquad (69)$$

where the exponent α has a limiting value of 0.5 at the theta temperature, rising to an upper limit of 0.9 for good solvent conditions. Eqn. (69) rearranged, and combined with eqn. (65), gives:

$$\bar{M}_{[\eta]}^{\alpha} = [\eta]/K = \eta_{sp}/Kc \qquad (70)$$

For a polydisperse sample, we may assume that the viscosity contributions made by the individual molecules are additive, and that the K and α values of the Mark Houwink equation are independent of values of $\bar{M}$. The specific viscosity of the solution is then given by eqn. (71).

$$\eta_{sp} = \sum_i Kc_i M_i^{\alpha} \qquad (71)$$

Therefore, combining eqn. (71) with eqn. (70):

$$\bar{M}_{[\eta]}^{\alpha} = \frac{\sum Kc_i M_i^{\alpha}}{\sum Kc_i} \qquad (72)$$

Rearranging: $\quad \bar{M}_{[\eta]} = \left[\dfrac{\sum c_i M_i^\alpha}{\sum c_i} \right]^{1/\alpha}$ (73)

When the exponent $\alpha = 1$, the eqn. (73) reduces to eqn. (54), and the viscosity and weight-average values of $\bar{M}$ are equal.

1.7.iv   Relationship between Molecular Weight Averages

The polydispersity, Q, (or dispersion) of the polymer is often used as a simple method of assessing the width of $\bar{M}$ distribution. The $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_z$ are related as follows:-[173]

$$Q = \bar{M}_w / \bar{M}_n \quad \text{and} \quad Q' = \bar{M}_z / \bar{M}_w \qquad (74)$$

For a perfectly uniform or monodisperse polymer $Q = Q' = 1$, but this is not the usual case. Fig. (3) shows a molecular weight distribution curve for a typical synthetic polymer.[178] A high Q ratio points to a low $\bar{M}$ tail, whereas a large Q' value indicates the presence of very high $\bar{M}$ material. Q may range from ca. 1.01 to 100, Table(5).

Figure (3)

Distribution of Molecular Weights in a Typical Polymer[178]
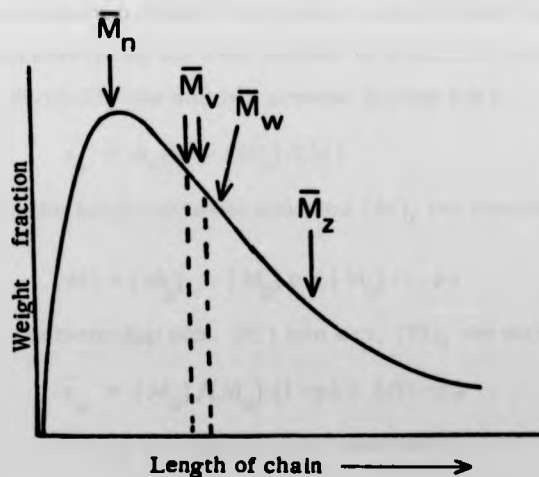
Table(5)

Polydispersity ratios for different types of synthetic polymerisation[158]

Polymer Type	$\bar{M}_w/\bar{M}_n$
Truly monodisperse	1.00
Controlled anionic living polymerisation	1.01 - 1.10
Low conversion addition polymer terminated by combination	1.5
Low conversion addition polymer terminated by disproportionation	2.0
Linear condensation polymer	2.0
High conversion vinyl polymer from free radical process	2.0 - 6.0
Polymer from Ziegler-Natta or other co-ordination system	10.0 - 100.0

The molecular weight of a molecule is defined as the mass of one molecule of the substance divided by 1/12th of the mass of an atom of the isotope carbon-12. In a recent review,[158] Billingham prefers to use molar mass defined as the mass of one mole of the substance. Numerically the molecular weight and the molar mass are identical; however, the former quantity is dimensionless and the latter has units g dm^{-3}.

Instead of $\bar{M}$, one often uses the degree of polymerisation, $\bar{x}_n$, ($\bar{P}$ or $\bar{DP}$ are also employed to signify the number average degree of polymerisation) defined as the average number of structural units in each macromolecule. $\bar{x}_n$ can be represented by the total number of monomer molecules present initially (n_o) divided by the number present at time t (n):

$$\bar{x}_n = n_o/n = [M_o]/[M] \tag{75}$$

where $[M_o]$ is the initial concentration and $[M]$, the concentration at time t, is given by:-

$$[M] = [M_o] - [M_o]p = [M_o](1-p) \tag{76}$$

Therefore, by substituting eqn. (76) into eqn. (75), we obtain the Carothers[179]

$$\bar{x}_n = [M_o]/[M_o](1-p) = 1/(1-p) \tag{77}$$

equation, (77), relating the degree of polymerisation to the extent of reaction (p).

1.8 THE USE OF ARENEDIAZONIUM SALTS IN PHOTOFABRICATION AND PHOTOIMAGING

The photochemical decomposition of arenediazonium salts ($ArN_2^+X^-$), which has been extensively utilised in dyeline reprographic processes,[180] can also be used to polymerise cyclic ethers[181, 182] to provide photo-resists. The commercially available epoxy resins can be photopolymerised to yield polymers with properties (such as high adhesive strength to many substrates, low shrinkage, dimensional stability, high mechanical strength and abrasion resistance, etc.) which are desirable for their application in photofabrication, integrated and printed circuit technology, light-curable protective coatings and lithography.[183]

In the apparent absence of moisture or hydroxyl groups,[183] the cationic polymerisation of epoxy resins is thought to be initiated by the Lewis acids (BF_3, PF_5, SbF_5, AsF_5, $SnCl_4$, $FeCl_3$, $BiCl_3$ and $SbCl_5$)[182, 184] generated upon photolysis of $ArN_2^+X^-$, <u>viz.</u>[183, 185]

$$ArN_2^+BF_4^- \xrightarrow{h\nu} ArF + N_2 + BF_3 \qquad (78)$$

(79)

(80)
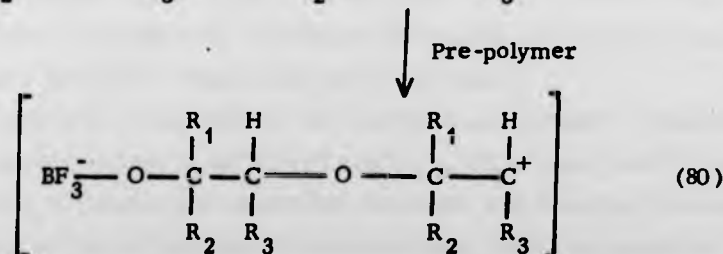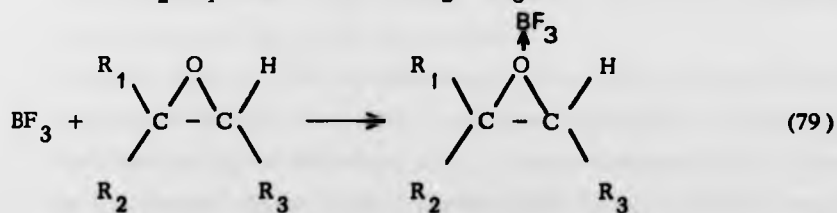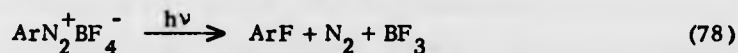
The placement of substituents on the aromatic ring of the diazonium salts can give a range of spectral sensitivity from the UV to the blue region.[185]

The epoxy resin-arenediazonium salt systems show particular promise in lithography, where printing plates of quality equal to, or better than, those available at present can be obtained by choosing an appropriate pre-polymer, and initiator (e.g. 2,5-diethoxy-4-tolylthiobenzene-diazonium hexafluorophosphate, $Dz^+PF_6^-$).[185]

1.8.1 The Procedure for Making Printing Plates

A variety of epoxide materials can be photopolymerised to yield coatings, including phenyl glycidyl ether, polyfunctional glycidyl ethers and esters, bisphenol A-glycidyl ether resins, and epoxidised olefins and polyolefins. While the general applications of these photopolymers are described elsewhere,[185] the principle of the process for preparing printing plates is as follows:[186]

1) The arenediazonium salt and a pre-polymer (e.g. 3:1, Epikote 1004 [Shell Chemicals]: D.E.N. 438 [Dow Chemicals Co.] are dissolved in a suitable solvent (e.g. butanone 20% w/v), and uniformly spread over sheet metal (e.g. aluminium plate).

2) This pre-polymer layer is allowed to dry, and then irradiated through a patterned master transparency with light of suitable wavelength (i.e. that absorbed by the diazonium salt). Polymerisation occurs only in the illuminated regions, with relatively little "creep" into dark regions.

3) The plate is washed with a solvent for the residual pre-polymer which leaves a 'polymeric' negative of the master copy.

4) The metal plate is smeared in ink, and the image printed. Alternatively the exposed surface is etched with acid (e.g. nitric acid), and the photo-resist (i.e. polymer) is removed by treatment with dimethyl formamide,[183] leaving an 'etched' positive of the master copy, which is capable of retaining ink. In offset lithography the process involves the transfer of an image from an inked plate to a roller, and then to a 'receptor' sheet.[180]

1.8.11 Photodecomposition of Arenediazonium Salts

The release of nitrogen (N_2) from arenediazonium salts, termed dediazoniation by H. Zollinger,[187] induced by heat or light occurs via two different mechanisms depending both on the type of substituent present on the benzene ring, and the nature of the solvent,[188] viz. the ionic pathway (leading to an aryl cation)

$$ArN_2^+X^- \longrightarrow Ar^+ + N_2 + X^- \tag{81}$$

the free radical pathway,

$$ArN_2^+X^- \longrightarrow Ar^{\bullet} + N_2 + X^{\bullet} \tag{82}$$
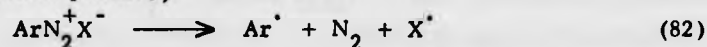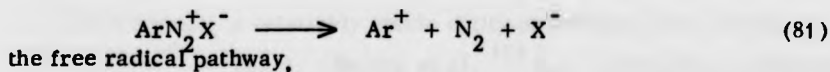
Magnetic susceptibility measurements[189] carried out on the light-induced dediazoniations in aqueous solutions indicate that paramagnetic intermediates must be present in the reaction. However, Calvert et al.[190] detected products of reaction which could be ascribed exclusively to the heterolytic pathway, eqn. (81), and therefore suggested that the magnetic properties must arise from a triplet state of the photoactivated diazonium salt. In alcoholic solutions (e.g. ethanol) the products of photolytic dediazoniation are predominantly due to the homolytic process, eqn. (82), with the formation of small amounts of phenetole (< 5.0 %) which is attributed to the heterolytic reaction.[190]

Thermally-induced dediazoniation in acidic methanol[191, 192] occurs via heterolytic and homolytic pathways in the presence of O_2, and its absence, respectively, and the rates of the two processes differ only by a factor of 2. Homolytic dediazoniation becomes more important with diazonium ions (e.g. 4-nitrobenzene diazonium ion) which are rendered more electrophilic by substitution of the aryl group, whereas with weakly electrophilic arenediazonium ions, the heterolytic mechanism predominates even in the absence of O_2.[187] The formation of diazoaryl[193, 194] and aryl radicals is enhanced by solvents in the following sequence:[187] hexafluoro-isopropanol (HFIP) $\approx$ trifluoroethanol (TFE) $< H_2O$ (acidic) $\approx CH_3OH$ (acidic) $\leq$ DMSO $<$ hexamethylphosphoric triamide; the rate of heterolytic dediazoniation remains fairly constant in solvents such as H_2SO_4 (aqueous), glacial acetic acid, CH_2Cl_2, TFE and HFIP.[195-197]

Furthermore, radical formation in TFE, H_2O and DMSO is enhanced by pyridine, and in H_2O by PhO^-, NO_2^- and OH^-:[187, 194]

$$ArN_2^+ + PhO^- \longrightarrow ArN_2^{\cdot} + PhO^{\cdot} \tag{83}$$
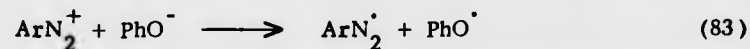
This type of specific nucleophilic solvation is clearly necessary for homolytic dediazoniation; however, the donor species must also be capable of forming a relatively stable entity on release of an electron, (e.g. $NO_2^- \xrightarrow{-E} NO_2^{\cdot}$). Becker et al. [198] have shown that, of the two possible dediazoniation reactions, that reaction is favoured in which the electron required for elimination of N_2 can be supplied with the lowest expenditure of energy; homolytic dediazoniation involves an electron transfer from an external donor, and heterolytic reaction is regarded as "intramolecular" electron transfer, forming an aryl cation from the aryl group with or without participation of an external acceptor solvent.[187]

The photolysis of suitably substituted arenediazonium salts (i.e. those bearing electron donor substituents, particularly in the 4-position) at 77 K yield ground-state triplet aryl cations in polymer films, including the polymer of the diglycidyl ether of bisphenol-A,[199, 200] identified by their highly characteristic e.s.r. spectra.

1.9 THE AIM OF THIS WORK

This is to establish:

(i) the efficacy of the visible-light absorbing arenediazonium salts, especially 2,5-diethoxy-4-tolylthiobenzene diazonium hexafluorophosphate and -difluorophosphate,[201] as photoinitiators for epoxide polymerisation, on a quantitative basis, and

(ii) the principal features of such polymerisation (using propylene oxide and 1,2-butylene oxide as model compounds), as regards initial rates, time for conversion to high yield, $\bar{M}$ changes during the course of polymerisation, and general kinetic character (particularly with reference to additives, e.g. solvents), and to draw conclusions concerning the mechanism from these data.

MATERIALS AND METHODS

2.1 PURIFICATION OF PROPYLENE OXIDE (PO) AND BUTYLENE OXIDE (BuO)

For our previous work,[202] PO (ex-BDH) was distilled either from KOH pellets[45] or from sodium wire.[203] However, more consistent viscometric data, section (3.1.1) are obtained by using PO which has been purified by the following procedure:-

Both PO (ex-BDH) and BuO (ex-Aldrich) are stirred under a N_2 atmosphere with calcium hydride[67, 130] (CaH_2) at room temperature for approximately eight hours, then refluxed overnight. The resultant mixture is fractionally distilled and the middle fraction (b.p. 34.5-36° C, PO) is collected over molecular sieves (3 Å) and stored in brown bottles under N_2 in a dry box.

2.2 PURIFICATION OF 1, 2-DICHLOROETHANE

Dichloroethane is refluxed over CaH_2 for 24 hours and then distilled.[67] The first ca. 10%- and final 15%-fractions are discarded and the middle fraction, b.p. 62.5^o C is collected over molecular sieves (4 Å), in brown bottles and stored in a N_2 dry box.

2.3 PURIFICATION OF ARENEDIAZONIUM SALTS

The 2, 5-diethoxy-4-tolylthiobenzenediazonium hexafluorophosphate ($Dz^+PF_6^-$) salt, supplied as pure by Ozalid Group Holdings Ltd., (Loughton, Essex) was dissolved in a minimum amount of Analar acetone (Hopkin and Williams) and the resulting solution was filtered. The arenediazonium salt was precipitated by adding a large excess of diethyl ether (Et_2O) and filtered, and washed thoroughly. The brightly yellow crystalline compound was firstly air dried and then vacuum pumped (at 0.5 N m^{-2}) for ca. two hours and finally allowed to stand for 24 hours over silica gel in an evacuated desiccator in the dark. The recrystallised salt was collected in a brown container and wrapped in an aluminium foil and stored in a refrigerator (ca. 277 K).

2, 5-diethoxy-4-tolylthiobenzenediazonium hexafluorostannate $[(Dz^+)_2(SnF_6H_2O)^{2-}]$ has a lower solubility,and was dissolved in hot acetone to obtain a saturated solution and then purified by the above procedure.

2,5-diethoxy-4-tolylthiobenzenediazonium phosphomolybdate $[(Dz^+)_3(PO_412MoO_3xH_2O)^{3-}]$ (green colour) has a very low solubility in acetone, and therefore could not be purified by the above procedure. The diazonium salt was found to be virtually insoluble in methanol, cyclohexane and choroform. The salt was simply washed thoroughly with Et_2O and used in photopolymerisation reactions.

2,5-diethoxy-4-tolylthiobenzenediazonium hexafluoroantimonate $(Dz^+SbF_6^-)$ was prepared by the method given in section (3.4.1), and purified by the same procedure as that used with $Dz^+PF_6^-$.

The prepolymer, Epikote 828, supplied by Shell Chemicals Ltd., was used without purification. [204]

2.4 NITROGEN DRY-BOX

The high sensitivity of cationic polymerisations[6, 106] to traces of water necessitate that the reactions be carried out in a moisture 'controlled' environment. Therefore, as far as possible, the polymerisation reactions discussed were carried out in a N_2 dry box.

The box (made in the Engineering Workshop of the University) consists of an aluminium and steel frame with a perspex window, measuring 75 cm in height, 100 cm in width and 62 cm deep at the top and 69 cm at the bottom, with a cylindrical air-lock chamber, 70 cm long and 30 cm in diameter. A circular (5.0 cm diameter) pyrex window at the side of the dry box allows irradiation of polymerisation samples by a mercury vapour lamp, section (2.5).

Nitrogen (N_2) [containing $\sim$ 2-3 ppm moisture and $\sim$ 2 ppm O_2] is passed through a 1.2 m column containing heated (338 K) BASF catalyst to remove trace O_2, and two 0.9 m tubes of KOH (pellets) and silica gel, to remove trace quantities of water before flushing the box. Circulating tubes from a Churchill (Perivale, Middlesex) chiller-thermo circulator are connected into the N_2 dry-box (i) to maintain constant reaction temperatures in optical cells, section (2.6.vi), and (ii) to cool pre-initiation polymerisation reaction mixtures in the optical dewar, section (2.6.vii). A rotary piston vacuum pump (Genevac Ltd., Radcliffe, Lancs.) is also connected to the box to enable evacuation of prepolymer and solvents.

2.5 OPTICAL BENCHES

Two optical benches were used for this work; one for viscometry (OB.I) and the other for direct photolysis in the N_2 dry box (OB.II).

The optical bench OB.I, Fig. (4), consists of a high pressure mercury vapour lamp, Wotan type HBO 200 W, connected to a current-stabilised ($\pm$ 1%) power supply unit type S.C.T. 100-4 supplied by K.S.M. Electronics Ltd., Potters Bar, Hertfordshire. A parallel light beam of suitable wavelength is achieved using quartz lenses and appropriate filter. The sample solution is placed in a quartz cell or an optical cell-viscometer, section (2.6.i), maintained in a bath containing circulating tap water.

The optical bench OB.II which is used for photolysing solutions inside the N_2 dry box, is essentially the same as that shown in Fig.(4), but without a light shield (L) and water bath (W). A quartz cell, with circulating tap water, is mounted in front of the pyrex window on the dry box, and acts as an infra-red filter, section(2.6.vii).

2.6 METHODS FOR FOLLOWING THE COURSE OF POLYMERISATION

The course of polymerisation can be followed by measuring either the rate of reaction or the $\bar{M}$ values of the resulting polymer. Rates of polymerisation can be determined by the measurement of 'extent of reaction' as a function of time. The usual methods[205] for obtaining polymerisation rates are chemical analysis, dilatometry, refractometry and direct weighing of polymer after separation of monomer and solvent; other methods are based on infra-red, n.m.r. and e.p.r. spectroscopy, vapour-phase chromatography,[130] differential scanning calorimetry,[206] and dielectric constant and conductance measurements.

In our previous work,[202, 207] only viscometric and direct weighing methods were used. In the present study, ^{1}H n.m.r. and infra-red spectroscopy, dilatometry and adiabatic reaction kinetics are employed additionally in combination with viscosity meaurements.[208-210]

Figure (4)

The optical bench (OB.I)

Key: A: Adjustment screws (for aligning lamp)

B: Balzer filter

C: Cooling tower

F: Quartz focusing lens

L: Light shield

M: Mercury vapour lamp

P: Quartz plano-convex lenses

S: Shutter

T: Teflon shields

W: Water bath
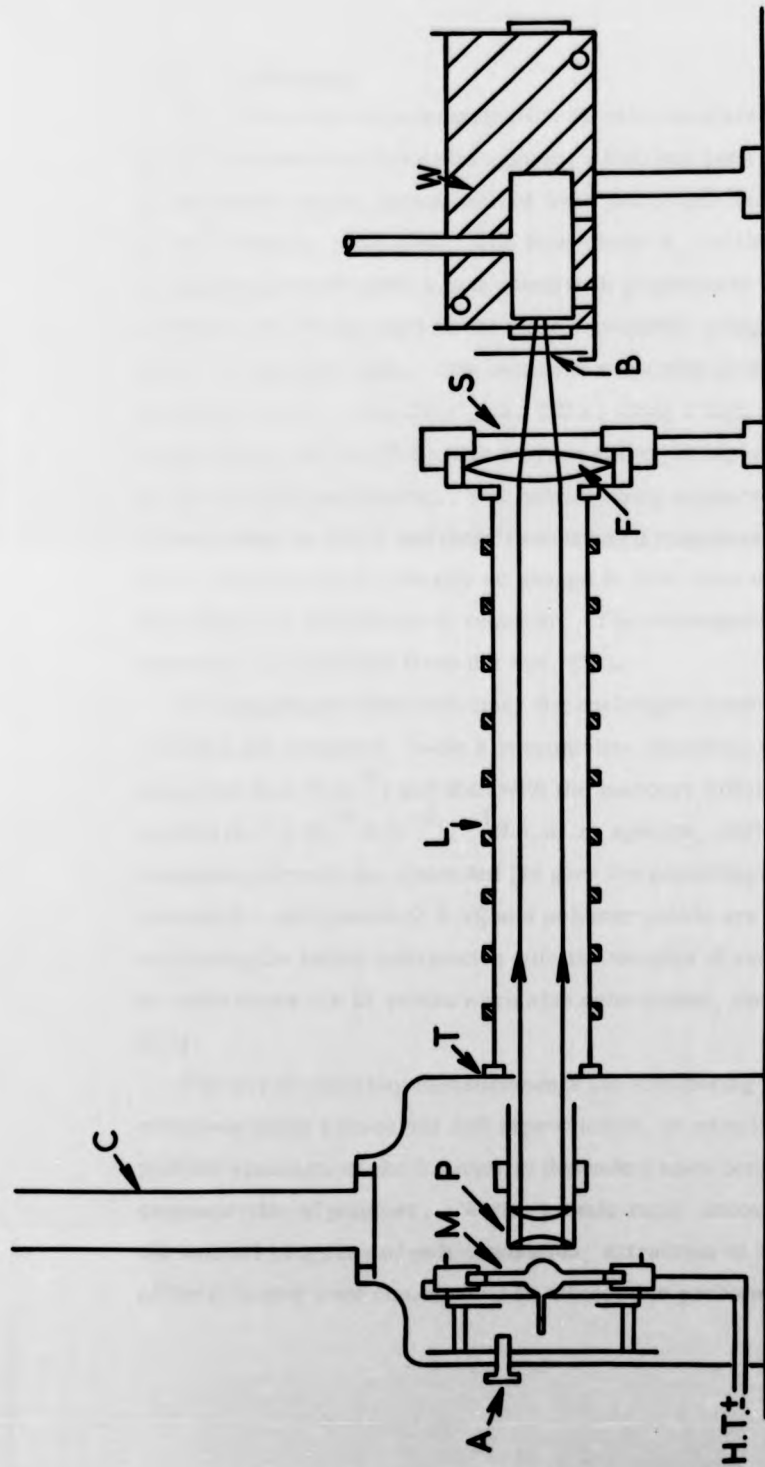
2.6.1 Viscometry

The viscosities of polymerisation reaction mixtures were measured in an Ubbelohde capillary viscometer, which had been modified to incorporate a quartz optical cell of 5 cm pathlength and (nominally) 20 cm^3 capacity, Fig. (5). The flow-times (t_o) of the solutions containing arenediazonium salt catalyst in prepolymer (or in other solvents when these were used) were measured, using a stopwatch, at 298 K in very dim light. The solutions were then photolysed (until the mixtures turned 'colourless', ca. 100 s) using a high pressure mercury vapour lamp, section (2.5), with a pyrex filter, at tap-water temperature, to initiate polymerisation. The polymerising mixtures were placed in a thermostat at 298 K and their flow-times (t) measured at approximately 900 s intervals until virtually no change in flow-time was observed, indicating the completion of reaction. The corresponding specific viscosity is calculated from the eqn. (56).

On completion of the reaction, the unchanged prepolymer and other solvents are removed, using a vacuum-line operating firstly at rotary pump pressure (0.3 N m^{-2}) and then with the mercury diffusion pump in the system (5.0 x 10^{-3} N m^{-2}). ^{1}H n.m.r. spectra, section (2.6.v), of the resultant polymer are recorded [to give the percentage of entrained monomer - see section (2.6.v)] and polymer yields are calculated from combining the latter information with the weights of recovered PPO. In some cases the $\overline{M}$ values were also determined, using GPC, section (2.7).

The use of viscosity measurements for monitoring polymerisation reactions while convenient and reproducible, is complicated by the fact that the viscosity of the solution is dependent upon both the $\overline{M}$ and the concentration of polymer. While "kinetic runs" undoubtedly indicate the overall progress of polymerisation, extraction of overall polymerisation rate constants is an intractable problem.

Figure (5)

The optical-cell viscometer

Viscometer incorporating irradiation cell, obtained
by modifying an Ubbelhode viscometer, Type
BS/1P/SL, Size 1-A.
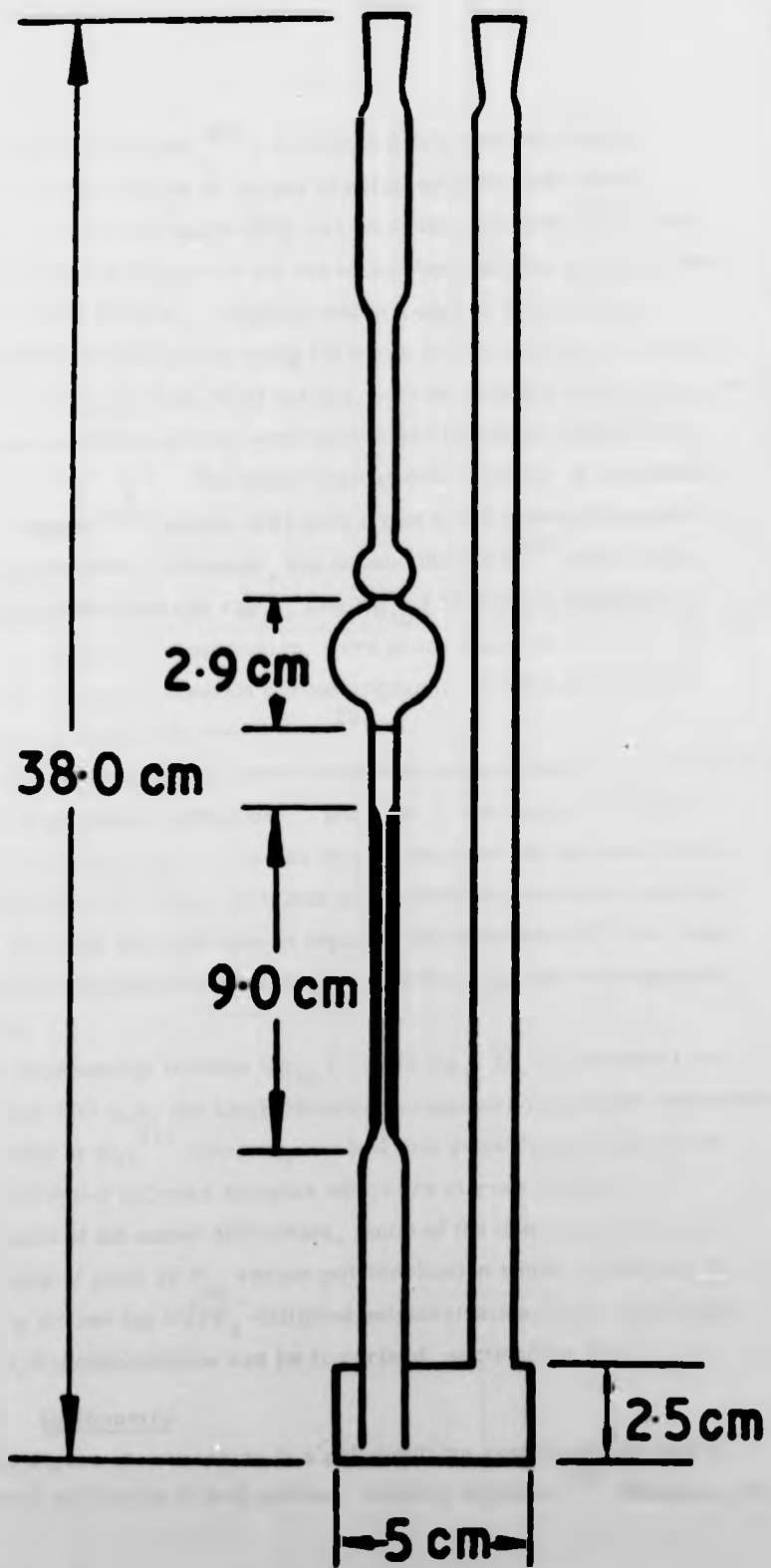
In our previous work, [202] we attempted to relate the limiting viscosity number to the $\bar{M}$ values of polypropylene oxide (PPO), eqn. (69). Propylene oxide (PO) was photoinitiated with $Dz^+PF_6^-$ and the polymerisation reactions monitored by observing the change in the viscosity of the mixture. Samples with a range of final specific viscosities were obtained by using PO which had been distilled in three different ways, i.e. from KOH pellets, sodium wire and CaH_2 [some of the polymerisation reactions were terminated before completion with H_2O, section (3.1.ii)]. For these various PPO samples, it was found that the Huggins[165] equation (62) gave a plot which curves upwards at high concentrations. However, the Schulz-Blaschke[170] relationship, eqn. (64), gives a straight line. The $\log_{10} [\eta]$ values, obtained by the above extrapolation procedure, were plotted against the $\log_{10} \bar{M}_p$, determined by gel permeation chromatography, and the relationship obtained was found to be non-linear. [202]

By contrast, for PPO samples obtained by terminating the polymerisation reaction with sodium phenoxide[121] (PhO^-Na^+), the Huggins[165] plot is a straight line, Fig. (6). This can only be explained by the interference of excess PhO^-Na^+ with the polymer chain conformation when dissolved in PO. We have not been able to separate the unreacted PhO^-Na^+ from the polymerised mixture because PPO is rather miscible with aqueous solvents.

The relationship between $\log_{10} [\eta]$ and $\log_{10} \bar{M}_w$ (in benzene) for crystalline PPO (i.e. the Mark-Houwink parameters) has been determined by G. Allen et al.;[211] however, we feel that these figures may not be applicable to our polymer samples which are viscous liquids.

Because of the above difficulties, much of the data in this thesis is in the form of plots of η_{sp} versus polymerisation time. However, the resulting curves for $Dz^+PF_6^-$-initiated polymerisation of PO, and epikote 828 in 1,2-dichloroethane can be linearised, section (3.1.vii).

2.6.11 Dilatometry

The degree of conversion in a polymerising system can be easily related to the volume of homogenous reaction mixture. [212] However, the

Figure (6)

The Huggins relationship, eqn.(62)

Polymerisation of 2.0×10^{-3} mol dm^{-3} solution of $D\overset{+}{z}PF_6^{-}$ in neat PO (100 cm^3) in a round-bottomed flask inside the N_2 dry box. The polymerisation reaction is terminated with 25.0 cm^3 solution of $PhO^{-}Na^{+}$ (1.0×10^{-2} mol dm^{-3}) at 24 h after initiation. The polymer is separated from the mixture by vacuum pumping on a line at mercury diffusion pump pressure overnight.

A: Plot of η_{sp} versus concentration (c) for PPO in neat PO

B: Huggins[165] plot (η_{sp}/c versus c) for PPO in neat PO
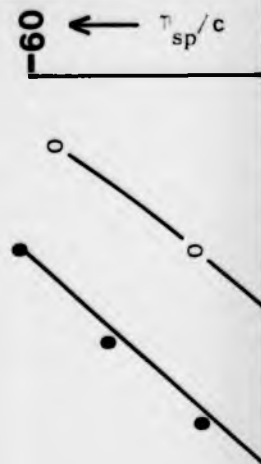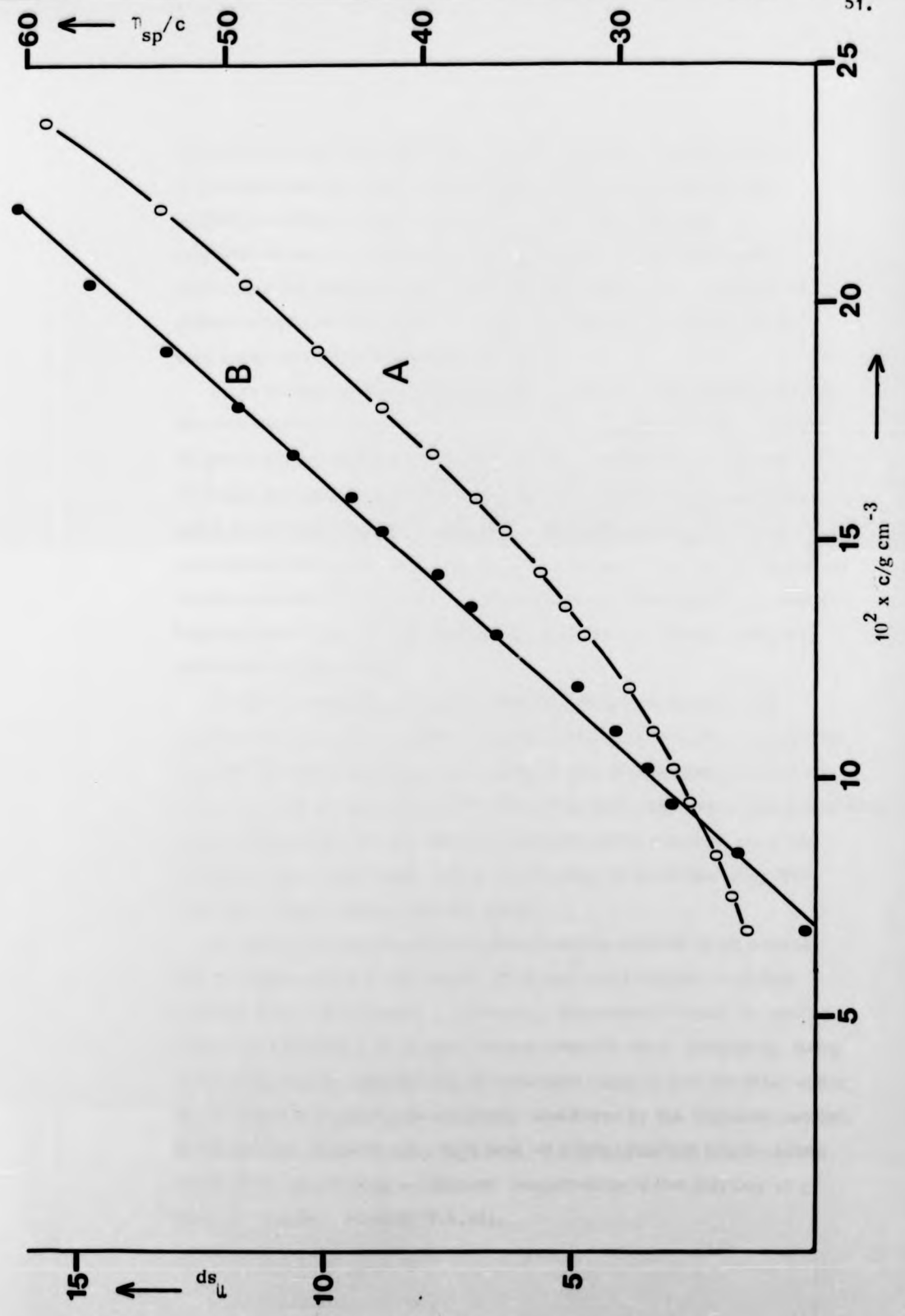
formation of a small molecule as in step-reaction polymerisations can complicate the kinetics and therefore dilatometry is usually applied to addition-reactions only[205] (e.g. vinyl and allyl polymerisations).   Dilatometry is one of the most widely used techniques for following polymerisation reactions, and a number of different types of dilatometers have been devised, including those with automatic recording systems.[212-217]

In the present work, preliminary dilatometric experiments showed that the photolysis of 2.0×10^{-3} mol dm^{-3} solution of Dz$^+$PF$_6^-$ in neat PO gives 80 mm decrease (measured using a cathetometer) in the (1.0 mm diameter) capillary height of the polymerising mixture in 660 s for a total volume of 5.0 cm^3.   When the above solution is photolysed directly in a dilatometer, the nitrogen (N$_2$) bubbles released usually caused a break in the solution stationed in the capillary column. Rigorous degassing of solutions before and after photolysis does not eliminate this problem.

We have attempted to overcome the N$_2$ bubble trapping in the capillary by (i) using a wider (3.0 mm) bore tube, and (ii) to photolyse at lower temperatures (i.e. by cooling in dry-ice/acetone mixture or liquid N$_2$), but to warm up before observing post-irradiation polymerisation. These experiments showed that the polymerisation reaction proceeds through a 'first' fast stage, which is too rapid to be followed by this technique, and a slower 'second' stage.

An alternative approach is to photolyse the solution in an optical-cell (a quartz cell 5.0 cm length, 20.0 cm^3 total volume) and then transfer it to a dilatometer.   However, this method cannot be used to follow the first 900 s of polymerisation reaction after photolysis, owing to the difficulty in transferring the reaction mixture into the dilatometer, and the second stage can be adequately monitored by the viscosity method. Furthermore, there is very high heat of polymerisation which causes difficulty in maintaining a constant temperature of the polymerising reaction mixture, section (2.6.vi).

2.6.iii   Direct Weighing Method

The isolation of polymer, section (2.6.i) , from aliquot samples (usually 1.0cm^3) taken from a polymerising reaction mixture (initiated by 2.0×10^{-3} mol dm^{-3} $Dz^+PF_6^-$ in neat PO, total volume 20.0 cm^3) from an optical-cell thermostat at 298 K, section (2.6.vi.A) shows that about 16% of PO is converted to involatile products within 600 s of the start of photoinitiation (irradiation time $\underline{ca}$. 100 s), which increases to 18-20% after 1,200-1,800 s, with only slight further conversion after 20 h.[202, 207]   Clearly, for this system, polymerisation rates cannot be obtained from the weight yields of the isolated polymer samples.

2.6.iv   Infra-red Spectroscopy

Infra-red (IR) absorption spectroscopy is often used to monitor the degree of cure of epoxy resins by following the disappearance of the epoxy group absorption at 916 cm^{-1}.[218, 219]   The calculations are usually based on the assumption that the epoxy group absorption is unaffected by the change from liquid to solid state, and are often complicated by the severe overlap of the new bands that appear during cure.[219, 220]

This method proved to be unsatisfactory for the $Dz^+PF_6^-$ initiated polymerisation of epikote 828 as a neat liquid and in solution (CCl_4 used as a solvent[221]), because of the following:

(i)   the small change in absorption peak height upon curing,

(ii)   combined effect of high heat of polymerisation[222] and IR absorption results in solvent loss during polymerisation, and

(iii)   each run results in glueing IR plates (NaCl) together.

The IR spectra recorded using Perkin-Elmer 621 and 457 grating infra-red spectrophotometers showed that the change in the absorption peak height occurred within the time taken to scan a small region of the spectrum ($\underline{i.e.}$ 200-300 s from start of irradiation) with only a very small further decrease after 6-8h. The rapid curing of the epoxy resin in this system is indicated by the immediate solidification of the $Dz^+PF_6^-$/epikote 828 mixture when irradiated in a beaker.

The epoxide group absorptions in the near-infra-red,[223] at 6060 and 8628 cm^{-1}, have been used to monitor reaction of epoxy resins with primary amine curing agents.[224] For work in this region of the IR disposable cells, made of commercially available rectangular glass tubing, can be used. However, the technique was rejected because (i) the anticipated small change in the absorption band by analogy with the above work, (ii) the difficulties that will arise in maintaining constant temperature of the polymerising mixture and (iii) the curing reaction appears to be too rapid for application of this method.

2.6.v ^{1}H n.m.r. Spectroscopy

Proton nuclear magnetic resonance (^{1}H n.m.r.) spectroscopy has recently been successfully used to monitor the polymerisation of 3,3-dimethylthietan initiated by triethyloxonium salts[73] because (i) monomer and the corresponding polymer have sufficiently different absorption spectra, and (ii) the polymerisation reaction occurs at a reasonable rate to be monitored by this technique.

We have found that the monomer (PO)[225] and the polymer (PPO) resonances are sufficiently differentiated to allow an in situ determination of the extent of polymerisation. Fig. (7) shows that the monomer protons bonded to the carbon atoms, which are part of the epoxide ring, absorb in the 7-8 τ region and the polymer protons, which are attached to the carbon atoms in the polyether "backbone", resonate at 6.5-7 τ. The integral values obtained for this region of the spectrum can be used to calculate percent conversion to polymer. Methyl group resonances, however, are of little value because of the considerable overlap of signals due to monomer and polymer protons.

^{1}H n.m.r. investigations were carried out using either a Perkin-Elmer model R-12 60 MHz spectrometer or a Bruker WH 90 instrument equipped with Fourier transform facilities enabling fast, repetitive scanning. Samples were irradiated directly in n.m.r. tubes which were inserted into the probe within seconds of the termination of irradiation. Fig. (8) shows a time profile of a photo-polymerising

Figure (7)

[1]H n.m.r. spectra of PO, PPO and PO–PPO mixture

Upper: PO (20% in CCl_4 solvent)

Middle: PPO (15% in CCl_4 solvent)

Lower: Photopolymerised PO (after preliminary removal of unreacted monomer by vacuum pumping on a line at 5.0×10^{-3} N m^{-2} for 1, 800 s; 20% in CCl_4 solvent).

monomer

pure polymer

CH$_2$

residue from photopolymer

6   7

monomer

CH₃

CH₂

CH CH

CH

pure
polymer

CH₂ & CH

CH₃

4

2.5

residue from
photopolymerisation

6   7   8   9   10
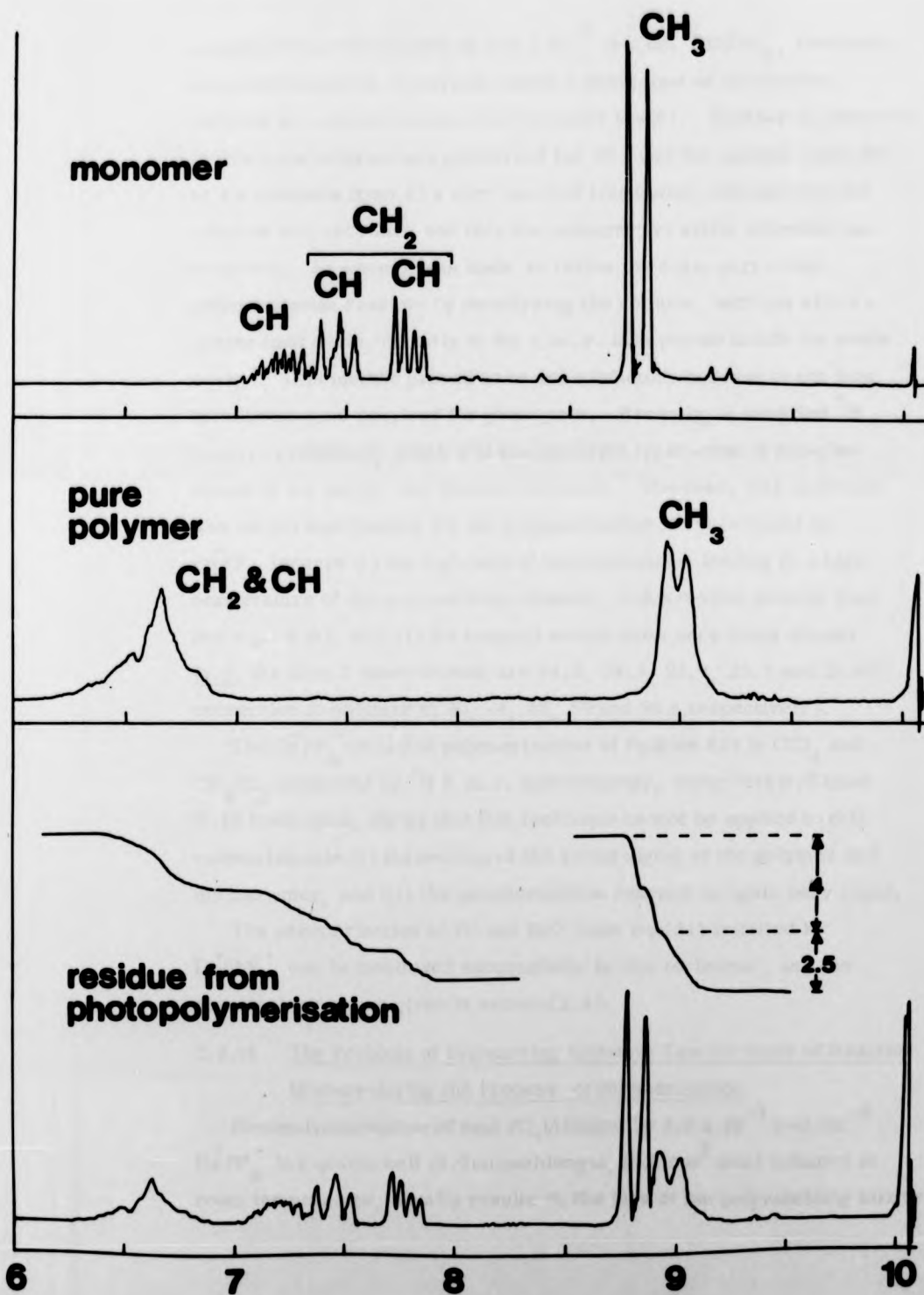
sample of neat PO initiated by 2.0×10^{-3} mol dm^{-3} Dz$^+$PF$_6^-$, indicating the rapid formation of polymer within a short time of irradiation, followed by a static situation (on this time scale). Further experiments in which the solution was photolysed for 25 s and the spectra recorded at 4 s intervals from 40 s after start of irradiation, showed that the reaction was very fast, and only the (apparently) static situation was observed. An attempt was made to follow the early part of the polymerisation reaction by photolysing the solution, with the aid of a quartz light guide, directly in the n.m.r. tube placed inside the probe cavity. This method proved to be unsatisfactory because of the long irradiation time required for photolysis. Recently, a modified ^{1}H n.m.r. probehead, which will enable direct irradiation of samples placed in its cavity, has become available. However, this technique was not pursued further for the polymerisation of PO initiated by Dz$^+$PF$_6^-$ because (i) the high heat of polymerisation leading to a high temperature of the polymerising mixture, which is often greater than the b.p. of PO, and (ii) the integral values show very large scatter (e.g. the first 5 measurements are 34.5, 29.4, 23.9, 25.1 and 20.6% conversion to polymer at 40, 44, 48, 52 and 56 s,respectively).

The Dz$^+$PF$_6^-$-initiated polymerisation of Epikote 828 in CCl$_4$ and CH$_2$Cl$_2$ monitored by ^{1}H n.m.r. spectroscopy, using Perkin-Elmer R-12 instrument, shows that this technique cannot be applied to this system because (i) the overlap of the broad signal of the polymer and the monomer, and (ii) the polymerisation reaction is again very rapid.

The polymerisation of PO and BuO (neat liquids) initiated by Dz$^+$SbF$_6^-$ can be monitored successfully by this technique, and the results obtained are given in section(3.4).

2.6.vi The Problem of maintaining Constant Temperature of Reaction Mixture during the Process of Polymerisation

Photopolymerisation of neat PO, initiated by 2.0×10^{-3} mol dm^{-3} Dz$^+$PF$_6^-$ in a quartz cell (5.0 cm pathlength, 20.0 cm^3 total volume) at room temperature, usually results in the loss of the polymerising mixtures

Figure (8)

^{1}H n.m.r. spectra of polymerising sample of PO

Photopolymerisation of neat PO initiated by 2.0×10^{-3} mol dm^{-3} Dz^{+}PF$_{6}^{-}$ in an n.m.r. tube. Numbers refer to 60 s intervals after initial photolysis (20 s irradiation).
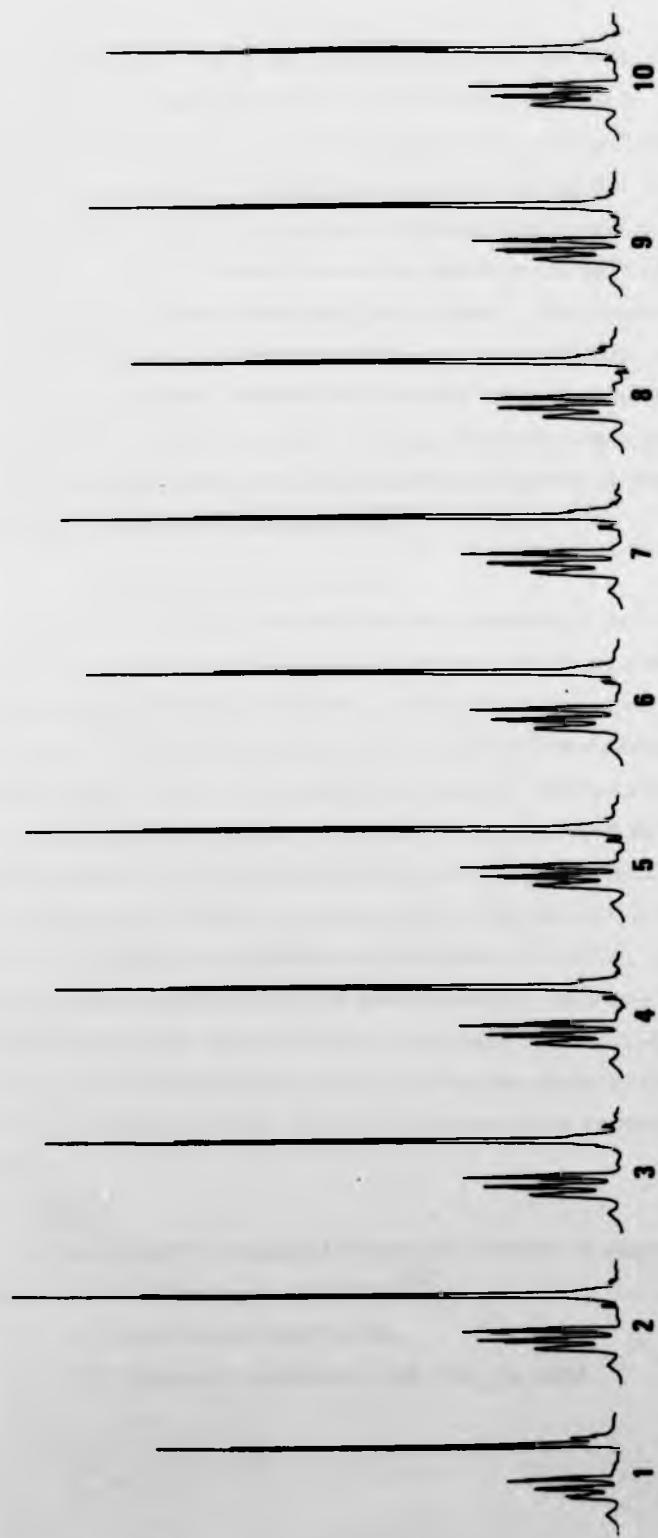
due to ebullition. This is attributed to the formation of N_2 upon photolysis of the arenediazonium salts, and the increase in temperature of the mixture caused by high heats of polymerisation. In order to minimise the temperature increase during the polymerisation process, a number of different thermostat methods were used. Fig. (9) shows plots of temperature change as function of time for the various thermostat procedures. The temperature was measured using a chromium-aluminium thermocouple, enclosed in a thin glass sleeve, attached to a Comark digital thermometer model 5000. It must be noted that during the early stages of the polymerisation reaction, the temperature increases by at least 5 K with all the thermostat methods used.

2.6.vii. Adiabatic Reaction Kinetics

A number of methods are available for measuring rates of fast reactions by monitoring the change in temperature of the reaction mixture under adiabatic conditions. A technique developed by Bell and Clunie[128] involves measurement of very small temperature changes (i.e. 0.01 to 0.1 K) and gives rates for reactions with half-lives in the range 3 to 180 s. However, the method used by Plesch,[127, 226] which assumes that the rate of polymerisation is proportional to the rate of temperature increase, can be applied to reactions with a temperature rise of 1-5 K (for total reaction) and half-lives of 3-300 s. In the present work the photolysis of the arenediazonium salts by a very powerful Hg-vapour lamp is likely to contribute to the temperature increase, and therefore the adiabatic method developed by Gordon,[227, 228] which is concerned with the shape of the temperature versus time curve, is used.

(a) Theory

The mathematical treatment of reaction kinetics of adiabatic systems is based on the following assumptions:[227]

(i) The law of mass action holds.

(ii) The Arrhenius expression, eqn.(84), is valid.

Figure (9)

Increase in temperature of the polymerising reaction
mixture for the various different thermostat procedures

Plots of temperature increase ($\Delta T/K$) versus time.

A: A quartz cell of 5 cm pathlength, total volume 20 cm^3,
    placed in an optical-cell holder,[202] made of copper,
    which is maintained at 298 K by liquid circulated by a
    Churchill thermo-chiller, section(2.4).
    X - the thermocouple is forced out of the reaction
        mixture by ebullition.

B: A quartz cell of 2.0 cm pathlength, total volume 3.5 cm^3,
    with liquid (at 298 K) circulating around the body of the
    cell (except at the windows).

C: The arrangement as in B (above) at 283 K.
    Y - UV lamp switched off.

D: A pyrex cell of 10 cm pathlength and 2.0 cm diameter
    windows, total volume ca. 23 cm^3, maintained at 298 K
    with liquid circulating both around the body of the cell
    (except at windows) and through an internal coil.
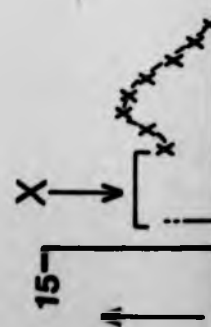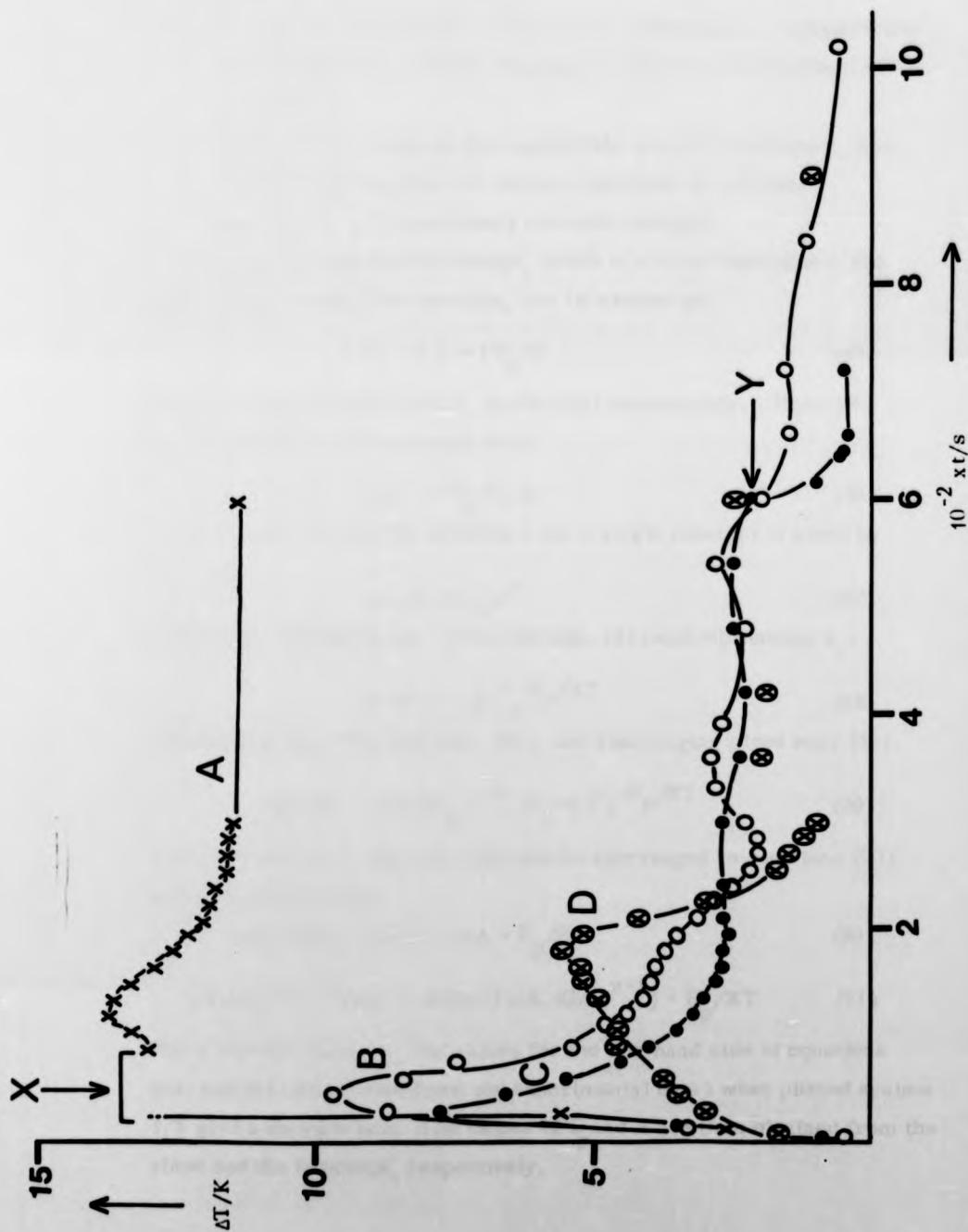
ction
cedures
e.

e 20 cm^3,
copper,
ated by a

ction

me 3.5 cm^3,
body of the

diameter
ed at 298 K
f the cell
oil.

A

X →

B

C

D

Y

$\Delta T/K$

15

10

5

2   4   6   8   10

$10^{-2} \times t/s$

$$k_n = Ae^{-E_p/RT} \tag{84}$$

where k_n is the rate constant for reaction of order n, and A is the pre-exponential frequency factor.

(iii)   The specific heat of the system (C) is independent of temperature and composition, and the enthalpy of reaction is independent of temperature.

(iv)   The enthalpy change is due exclusively to a single reaction, and the catalysing species are neither produced or consumed significantly in the secondary chemical changes.

The rate of temperature change, which is a direct measure of the progress of an adiabatic reaction, can be written as:

$$| T_f - T | = cH_p/C \tag{85}$$

where c in the molality and T_f is the final temperature.   Eqn. (85) can be written in a differential form:

$$\pm dT = H_p/C.dc \tag{86}$$

Since the rate of reaction of order n for a single reactant is given by eqn. (87):

$$-dc/dt = k_n c^n \tag{87}$$

Therefore, combining eqn. (87) with eqn. (84) and eliminating k_n:

$$dc/dt = -Ac^n e^{-E_p/RT} \tag{88}$$

Substituting eqn. (88) into eqn. (86), and rearranging gives eqn. (89):

$$\pm dT/dt = A(C/H_p)^{n-1}. (T_f - T)^n e^{-E_p/RT} \tag{89}$$

For $n = 1$ and $n \neq 1$, the eqn. (89) can be rearranged to equations (90) and (91), respectively.

$$\ln[-d\ln(T_f - T)/dt] = \ln A - E_p/RT \tag{90}$$

$$\ln[d(T_f - T)^{1-n}/dt] = \ln[(n-1).A.(C/H)^{n-1}] - E_p/RT \tag{91}$$

For correctly chosen n, the values for the left-hand side of equations (90) and (91) (calculated from the experimental data) when plotted against $1/T$ give a straight line. The values of E_p and A are then obtained from the slope and the intercept, respectively.

(b) Experimental and Treatment of Results

The polymerisation reactions were carried out inside the N_2 dry box in an optical-dewar, Fig. (10), using 50 cm^3 (total volume) solutions. The temperature increase was monitored by a chromium-aluminium thermocouple and a Comark electronic thermometer, Type 1602, attached to a Servoscribe potentiometric recorder, Type RE 511.

The problems encountered in the adiabatic method of following the photopolymerisation of PO initiated by $Dz^+PF_6^-$ are as follows:

(i) The direct irradiation of the thermocouple causes an immediate rise in temperature, which is not the true measurement of the solution temperature. An attempt was made to overcome this problem by using larger volumes of solution so that the thermocouple may be placed away from the light path, Fig.(10). However, this necessitates stirring of the solution to achieve complete photolysis, which in turn leads to minor fluctuations or "noise" in the temperature versus time traces recorded. Fortunately the response of the thermocouple to irradiation is constant (ca. 5 K) throughout the range of measurements, and therefore the temperature-time plots may be assumed to be displaced by 5 K.

(ii) The heat loss from the polymerising reaction mixture was minimised by (a) using the most efficient of the three optical-dewars, which were used in the preliminary experiments, and (b) limiting the experiments to a small range about room temperature [the pre-initiation reaction mixtures were cooled by using a cold-finger, Fig. (10)].

(iii) Attempts were made to obtain calibration curves, which could be used to compensate for the heat gained or lost by the polymerising solutions. However, the very slow heat loss (and gain) and the relatively large temperature fluctuations in the N_2 dry box rendered this impractical.

(iv) The heat absorbed from the intense irradiation by PO in the absence of arenediazonium salts was minimised by using heat-filters. A quartz cell, ca. 2.5 cm in length, containing either PO or circulating H_2O was mounted in the light path. Both PO and H_2O were equally effective in reducing the rate of temperature increase of PO, but only H_2O was used.

Figure (10)

A: The optical-dewar made by E. Burgess, Glassblowing
Workshop, Department of Chemistry and Molecular
Sciences, University of Warwick.

B: The cold-finger attached to a Churchill thermo-chiller,
which is used to cool the pre-initiation reaction
mixtures.

T: Thermocouple

R: Rubber bung

C: Cork stopper

GS: Glass sleeve

V: Vacuum

S: Initiator and pre-polymer solution

U: Unsilvered surface to allow irradiation of polymerisation
reaction mixture

Note   Diagrams drawn are actual size of apparatus.

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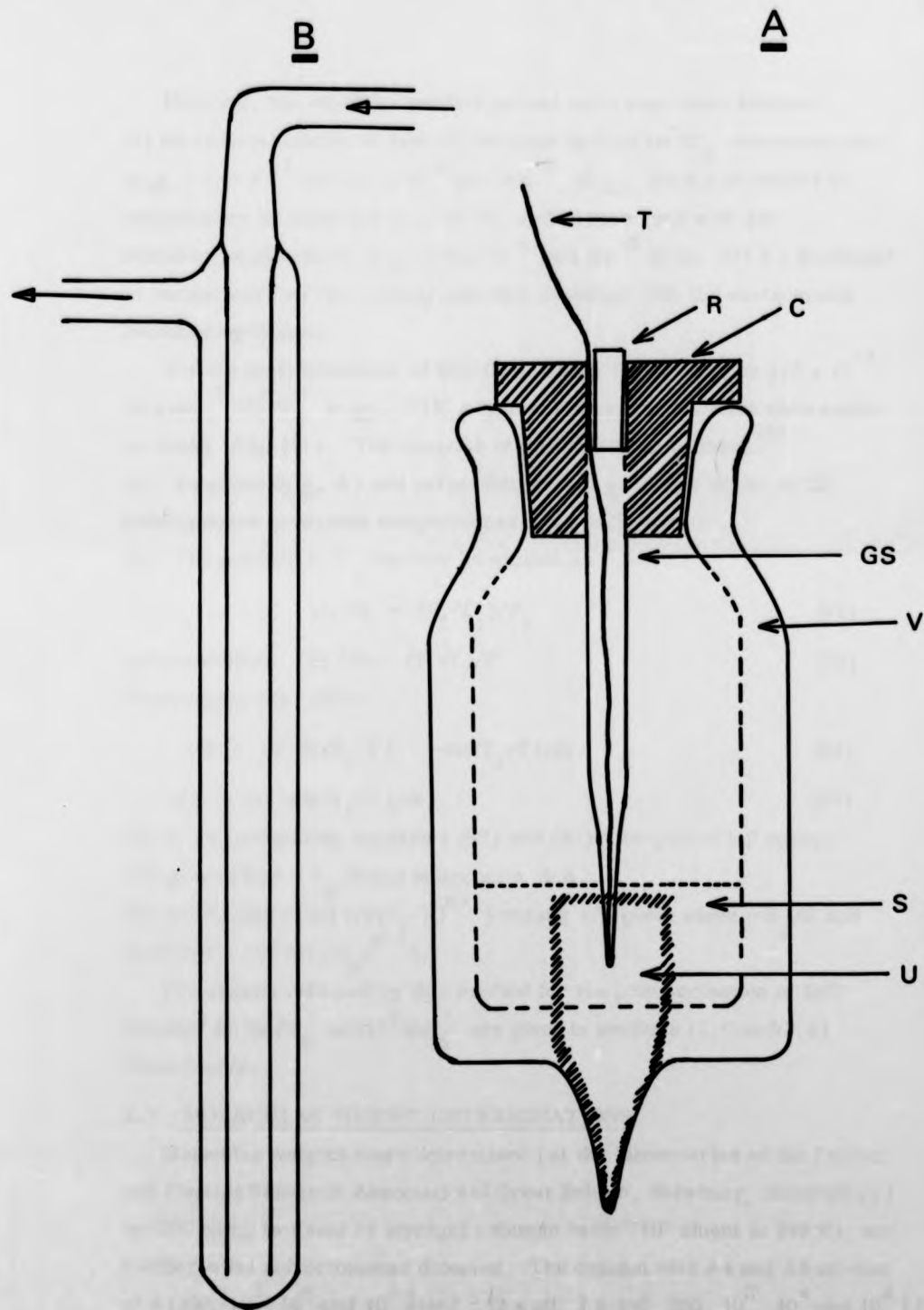
However, the adiabatic method proved to be unsuitable because (i) the polymerisation of neat PO initiated by high $Dz^+PF_6^-$ concentrations (e.g. 1.0×10^{-3} and 8.0×10^{-4} mol dm^{-3}, at ca. 272 K) increased in temperature to above the b.p. of PO, and (ii) the runs with low initiator concentration (e.g. 4.0×10^{-4} mol dm^{-3} at ca. 271 K) increased in temperature so very slowly that heat exchange with the environment becomes significant.

For the polymerisation of BuO (b.p. 345.5 K) initiated by 1.0×10^{-3} mol dm^{-3} $Dz^+PF_6^-$ at ca. 270 K, a typical temperature versus time curve is shown, Fig. (11). The analysis of this plot is as follows:[228]

(i) Tangents (e.g. A) and perpendiculars (e.g. B) are drawn to the heating curve at various temperatures (e.g. at T_1).

(ii) The gradient at T_1 can now be written as:

$$dT/dt = (T_f - T_1)/P_1 \tag{92}$$

and generally:
$$dT/dt = (T_f - T)/P \tag{93}$$

Rearranging eqn. (93):

$$1/P = dT/dt \, (T_f - T) = -d\ln(T_f - T)/dt \tag{94}$$

$$-\ln P = \ln[-d\ln(T_f - T)/dt] \tag{95}$$

For $n = 1$, comparing equations (95) and (90): the plot of $\ln P$ versus $1/T$ gives slope $= E_p/R$ and intercept $= -\ln A$.

For $n \neq 1$, plot of $\ln[1/P(T_f - T)^{n-1}]$ versus $1/T$ gives slope $= E_p/R$ and intercept $= -\ln[A(C/H_p)^{n-1}]$.

The results obtained by this method for the polymerisation of BuO initiated by $Dz^+PF_6^-$ and $Dz^+SbF_6^-$ are given in sections (3.1) and (3.4) respectively.

2.7 MOLECULAR WEIGHT DETERMINATIONS

Molecular weights were determined [at the laboratories of the Rubber and Plastics Research Association of Great Britain, Shawbury, Shrewsbury] by GPC using two sets of styragel columns (with THF eluent at 298 K), and a differential refractometer detector. The column sets A4 and A8 consist of 4 (200, 10^3, 10^4 and 10^5 Å) and 8 (2 x 60, 2 x 100, 200, 10^3, 10^4 and 10^5 Å) columns, respectively.

Figure (11)

Adiabatic reaction kinetics

Polymerisation of BuO initiated by 1.0×10^{-3} mol dm^{-3} Dz$^+$PF$_6^-$, at ca. 270 K.

I   - start of irradiation

TI   - termination of irradiation

T_f - final temperature

A   - tangent at T_1

B   - perpendicular from T_f to T_1

P_1 - distance between the intercepts of A and B at T_f along the time axis.

m^{-3} Dz$^+$PF$_6^-$,

T$_f$ along

10^{-2} x t/s

TI

T$_1$

A

P$_1$

I

B

X

Y

T$_f$

280   300   320

Temperature/K
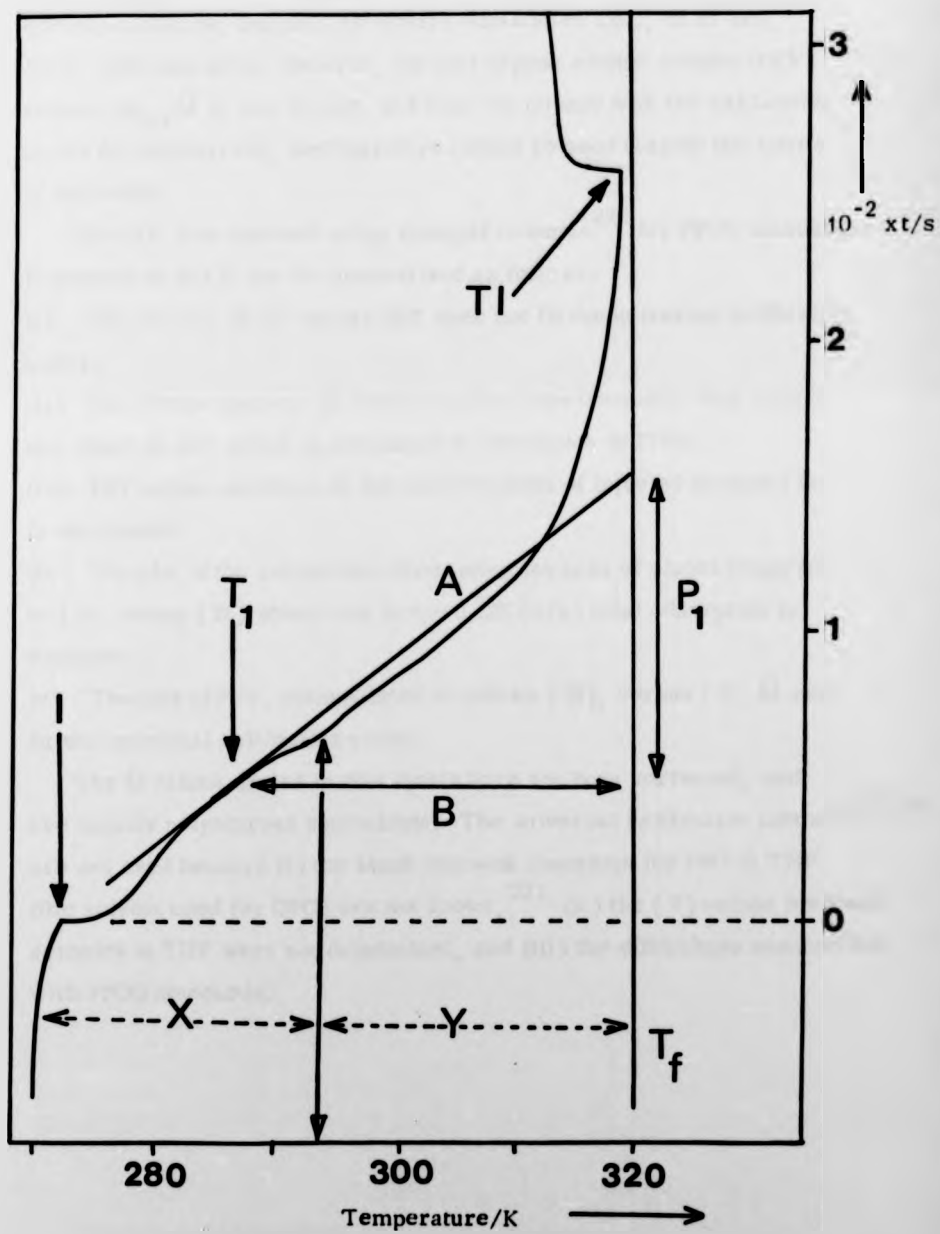
The data obtained assumes that the samples are of polystyrene and is in the form of $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_v$ and $\bar{M}_z$. An attempt was made to obtain calibration curve, Fig. (12), using polypropylene oxide glycol (PPOG) standards, supplied by Waters Associates Ltd., of $\bar{M}$ 800, 1200, 2000 and 4000. However, the plot of peak elution volume (PEV) versus $\log_{10} \bar{M}$ is non-linear, and does not concur with the calibration curve for polystyrene, and therefore cannot be used outside the limits of 800-4000.

The GPC data obtained using styragel columns[229] for PPOG standards in toluene at 303 K can be summarised as follows:

(i) The plot of $[\eta] \bar{M}$ versus PEV does not fit the universal calibration curve.

(ii) The chromatograms of these samples show unusually long tails to the lower $\bar{M}$ end, which is attributed to adsorption of PPOG.

(iii) PEV values increase as the concentration of injected sample [IS] is decreased.

(iv) The plot of the ratio of the chromatogram area of eluted material to [IS] versus [IS] shows that below 0.2% (w/v) total adsorption is expected.

(v) The plot of PEV, extrapolated to infinite [IS], versus $[\eta] \bar{M}$ may fit the universal calibration curve.

The $\bar{M}$ values quoted in this thesis have not been corrected, and are merely polystyrene equivalents. The universal calibration methods[158,230] are not used because (i) the Mark-Houwink constants for PPO in THF (the solvent used for GPC) are not known,[231] (ii) the $[\eta]$ values for these samples in THF were not determined, and (iii) the difficulties encountered with PPOG standards.

Figure (12)

A GPC calibration curve for the set "A8" columns

Plots of peak retention volume counts versus $\log_{10} \bar{M}$.

A: Polystyrene

B: PPOG standards (Waters Associates, Ltd.).

The PPOG standards run in THF solvent at 298 K, 0.2%

(w/v) concentration of injected samples.

4·5

4·0

$\log_{10} \bar{M}$

3·5

3·0
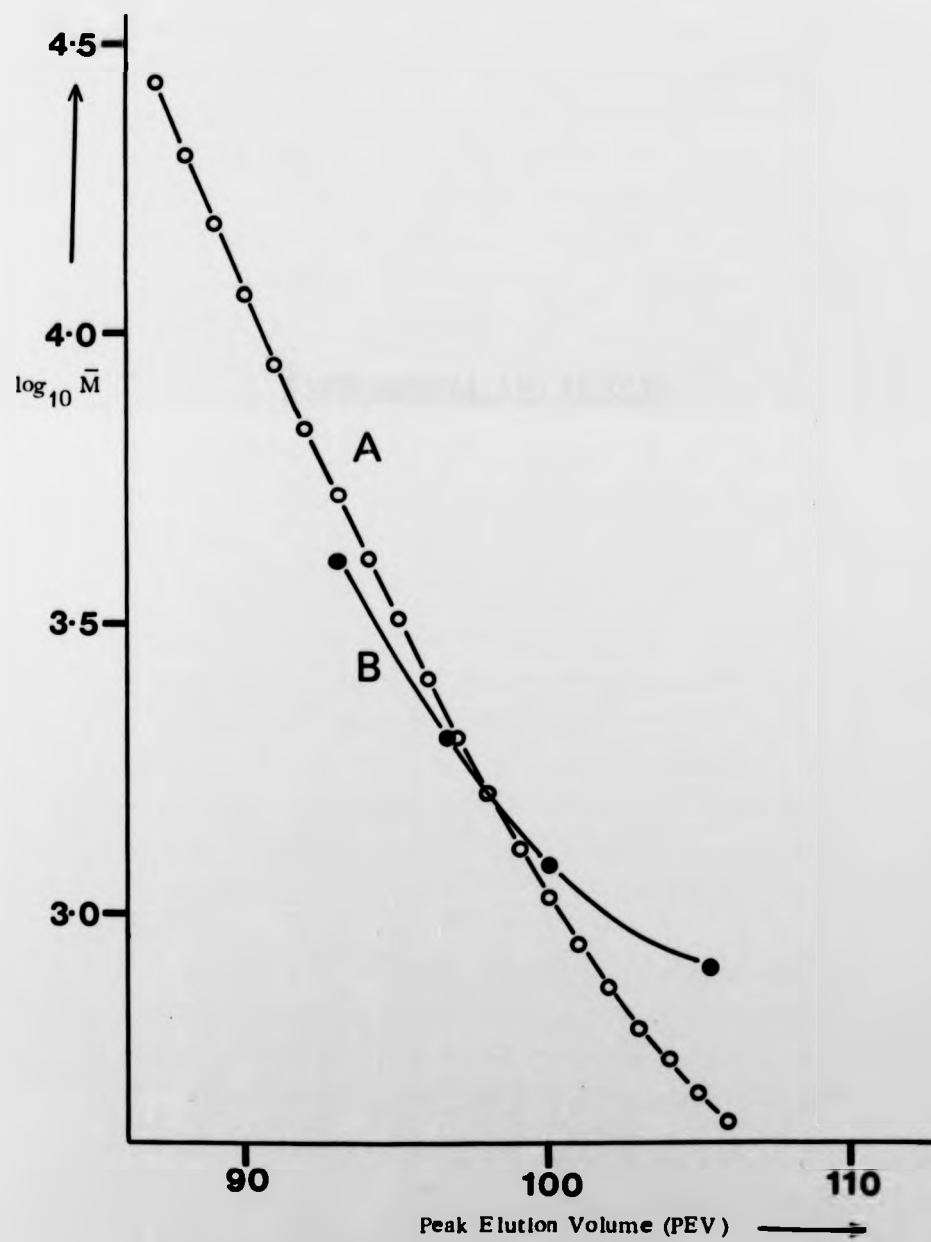
EXPERIMENTAL AND RESULTS

3.1 PHOTOPOLYMERISATION OF PO, BuO AND EPIKOTE 828 INITIATED BY $Dz^+PF_6^-$

3.1.1 Reproducibility of the Viscometric Runs

In our previous work (presented in the M.Sc. thesis) we found that the polymerisation of PO initiated by $Dz^+PF_6^-$ showed considerable irreproducibility with respect to the final η_{sp}. The highest η_{sp} value was obtained with PO which had been freshly distilled from sodium wire.[61, 203]

By using PO which is distilled from CaH_2 section(2.1), we have been able to obtain much more consistent viscometric data. Fig. (13) shows two pairs (A1, A2 and B1, B2) of η_{sp} versus time curves measured on two successive days, i.e. A1 and A2 were run simultaneously on one day and B1 and B2 on the next. Fig. (14) shows similar plots recorded two months earlier.

Polymerisation of Epikote 828 monitored by the viscometric method is also reproducible as shown by the η_{sp} versus time plots in Fig. (23) and Fig. (26).

3.1.11 Effect of Water upon PO Polymerisation

We have previously[202] shown that (i) rigorous drying of the monomer leads to a greater degree of polymerisation characterised by the higher final η_{sp} values and larger $\bar{M}$ of the resultant polymer, (ii) the addition of H_2O to the arenediazonium salt-PO mixture during the pre-initiation or polymerisation periods gives much lower η_{sp} and $\bar{M}$ values, and (iii) the polymerisation reactions terminated in the plateau region of η_{sp}-time curves (with H_2O) show a subsequent decrease in η_{sp} as a function of time.

The IR spectra of PPO (recorded using a Perkin-Elmer 457 instrument) which was obtained by terminating the polymerisation reaction with H_2O, shows a much larger band in the hydroxyl absorption region than the PPO which is isolated from the reaction mixture that is allowed to go to completion. The absorption in the hydroxyl region can either be due to the terminal-OH group or the hydrogen-bonded H_2O molecule.

Figure (13)

Reproducibility of viscometric runs

Plots of η_{sp} versus reaction time for the polymerisation of neat PO initiated by 2.0×10^{-3} mol dm^{-3} Dz$^+$PF$_6^-$.

A1 and A2: Polymerisation reactions carried out simultaneoulsy on day 1.

B1 and B2: Polymerisation reactions carried out simultaneoulsy on day 2.

	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A1	8,598	21,020	2.44
A2	9,959	21,330	2.14
B1	8,400	17,860	2.12
B2	12,440	26,290	2.11

84

eat PO initiated

lsy on day 1.

lsy on day 2.

$\bar{M}_w/\bar{M}_n$

2.44

2.14

2.12

2.11

B1

B2

A1

A2

80

20

15

$10^{-3} \times t/s$

10

5

η_{sp}

30

20

10
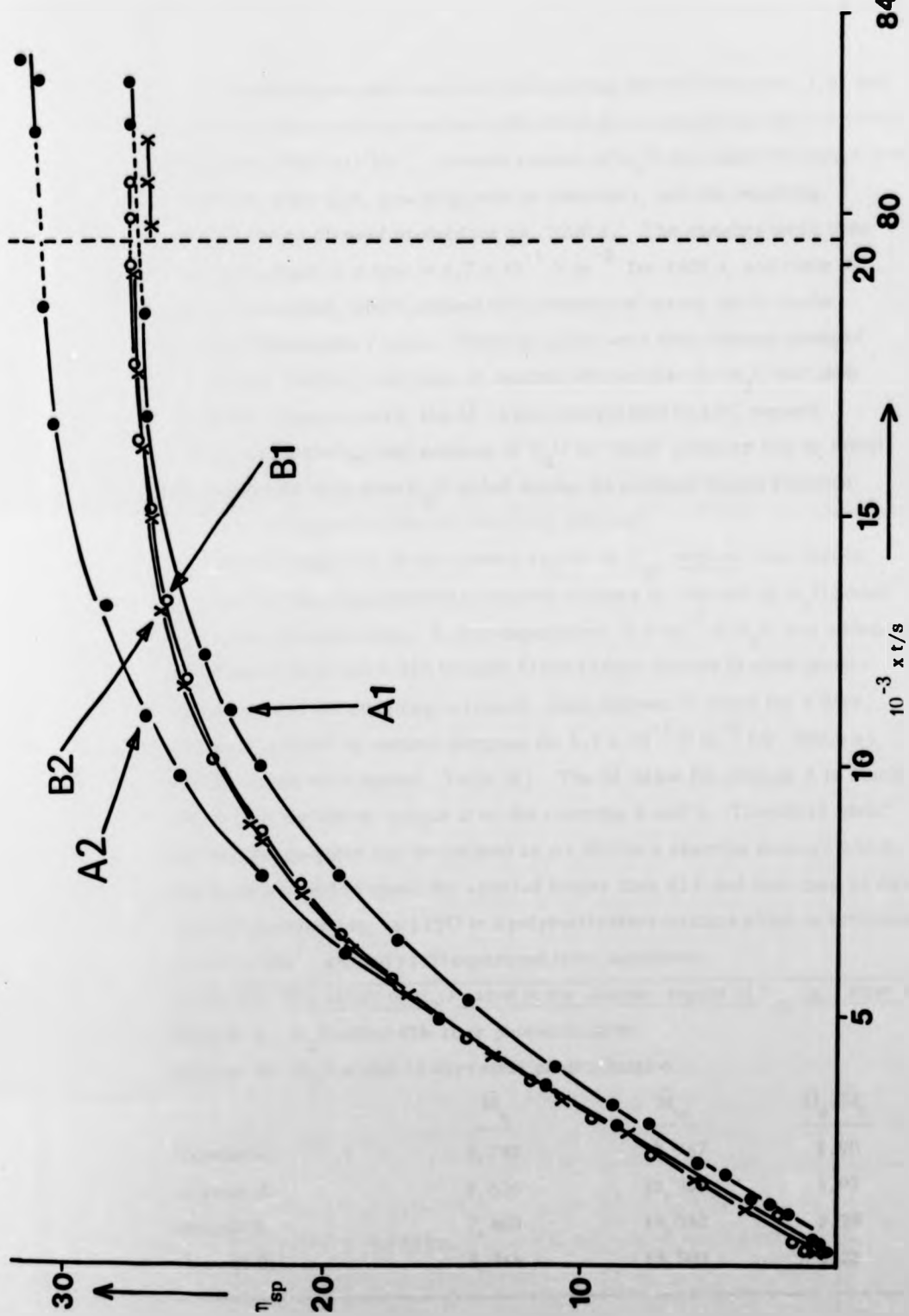
A control experiment was carried out using two PPO samples, i.e. one in which polymerisation had been allowed to go to completion and the other terminated with PhO^-Na^+. A small amount of H_2O was added to components of both samples (i.e. retaining part as controls), and the resulting mixtures were allowed to stand for ca. 7200 s. The samples were then vacuum-pumped on a line at 6.7×10^{-1} N m^{-2} for 1800 s, and their IR spectra recorded, which showed the presence of strong bands in the hydroxyl absorption region. These samples were then vacuum-pumped for further 21600 s, and their IR spectra showed that the H_2O had been removed. Furthermore, the $\bar{M}$ values determined by GPC remain unchanged, indicating that addition of H_2O to "dead" polymer has no effect. These results show that H_2O added during the polymerisation reaction becomes incorporated into the resulting polymer.

The investigations of the plateau region of η_{sp} versus time curves showed that the polymerisation reaction mixture is affected by H_2O added 42 h after photoinitiation. In this experiment, 0.5 cm^3 of H_2O was added to ca. 3.0 cm^3 of reaction mixture 42 h (sample A) and 14 days (sample B) after photo-initiation, and the resulting mixtures were allowed to stand for 4 days. PPO was isolated by vacuum pumping (at 6.7×10^{-1} N m^{-2} for 21600 s), and $\bar{M}$ values determined, Table (6). The $\bar{M}$ value for sample A is much lower than for either sample B or the controls A and B. Therefore 'dead' or inactive polymer can be defined as (i) PPO in a reaction mixture which has been allowed to stand for a period longer than 42 h and less than 14 days after photoinitiation, (ii) PPO in a polymerisation mixture which is terminated with PhO^-Na^+, and (iii) PPO separated from monomer.

Table (6) The effect of H_2O added in the plateau region of η_{sp} vs. time curves

Sample A - H_2O added 42 h after photoinitiation

Sample B - H_2O added 14 days after photoinitiation

	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
Sample A:	5,797	10,987	1.90
Control A:	8,526	16,837	1.97
Sample B:	7,803	15,083	2.28
Control B:	8,311	18,500	2.23

The effect of H_2O on the polymerisation of PO is summarized as follows:-

(i) Rigorous drying of PO increases the extent of polymerisation leading to higher per cent conversion and $\bar{M}$ of PPO.

(ii) Addition of H_2O prior to photoinitiation reduces the extent of polymerisation giving lower per cent conversion and $\bar{M}$ of PPO (e.g. 0.2 and 0.02 cm^3 of H_2O added to 20.0 cm^3 of polymerisation reaction mixture yields 24.9 and 30.1% of PPO respectively).

(iii) Addition of H_2O during polymerisation reaction reduces the $\bar{M}$ of the resultant PPO, Table (6).

(iv) H_2O added in (ii) and (iii) becomes incorporated into the resultant PPO.

3.1.iii Effect of 2.2-Diphenyl-1-Picrylhydrazyl (DPPH)

The effects[202] of added ethanol (EtOH), phenol (PhOH) and PhO^-Na^+ can be summarised as follows:-

(i) The effect of EtOH is very similar to that of H_2O.

(ii) PhOH added prior to initiation or during polymerisation produces no perceptible effect on the course of the reaction.

(iii) PhO^-Na^+ causes complete and immediate termination of polymerisation.

Addition of 1.0 cm^3 solution of 4.0 x 10^{-2} mol dm^{-3} DPPH (in PO) to 20.0 cm^3 polymerising reaction mixture, initiated by 2.0 x 10^{-3} mol dm^{-3} $Dz^+PF_6^-$, has virtually no effect on (i) the course of the reaction, Fig. (14), (ii) the percentage yield of PPO and (iii) the $\bar{M}$ of the resultant polymer. The complete lack of effect of DPPH, which is a free radical, indicates that the polymerisation reaction (the stage monitored by the viscometry method) is exclusively ionic.

3.1.iv Effect of Solvents: Dichloromethane (CH_2Cl_2), Dichloroethane (ClH_2CCH_2Cl) and Cyclohexane (C_6H_{12}) on Polymerisation of PO

The viscometry method showed that the polymerisation of PO in CH_2Cl_2, ClH_2CCH_2Cl, C_6H_{12} and benzene (C_6H_6), used as cosolvents leads to much smaller final η_{sp} values.[202] Table (7) and Fig. (15) show that this is due both to the lower percentage yield and $\bar{M}$ of the resultant polymer.

Figure (14)

Effect of DPPH upon polymerisation of PO initiated by 2.0×10^{-3}
mol dm^{-3} Dz$^+$PF$_6^-$

1.0 cm^3 solution of 4.0×10^{-2} mol dm^{-3} DPPH (in neat PO) is added
to 20.0 cm^3 polymerising reaction mixture 1800 s after start of
initiation.

A: Control - 1.0 cm^3 PO is added at X.

B: 1.0 cm^3 solution of DPPH is added at X.

2.0 x 10^{-3}

t PO)is added

r start of

η$_{sp}$

A

B

X

30

20

10

20

15

10

5

10^{-3} x t/s
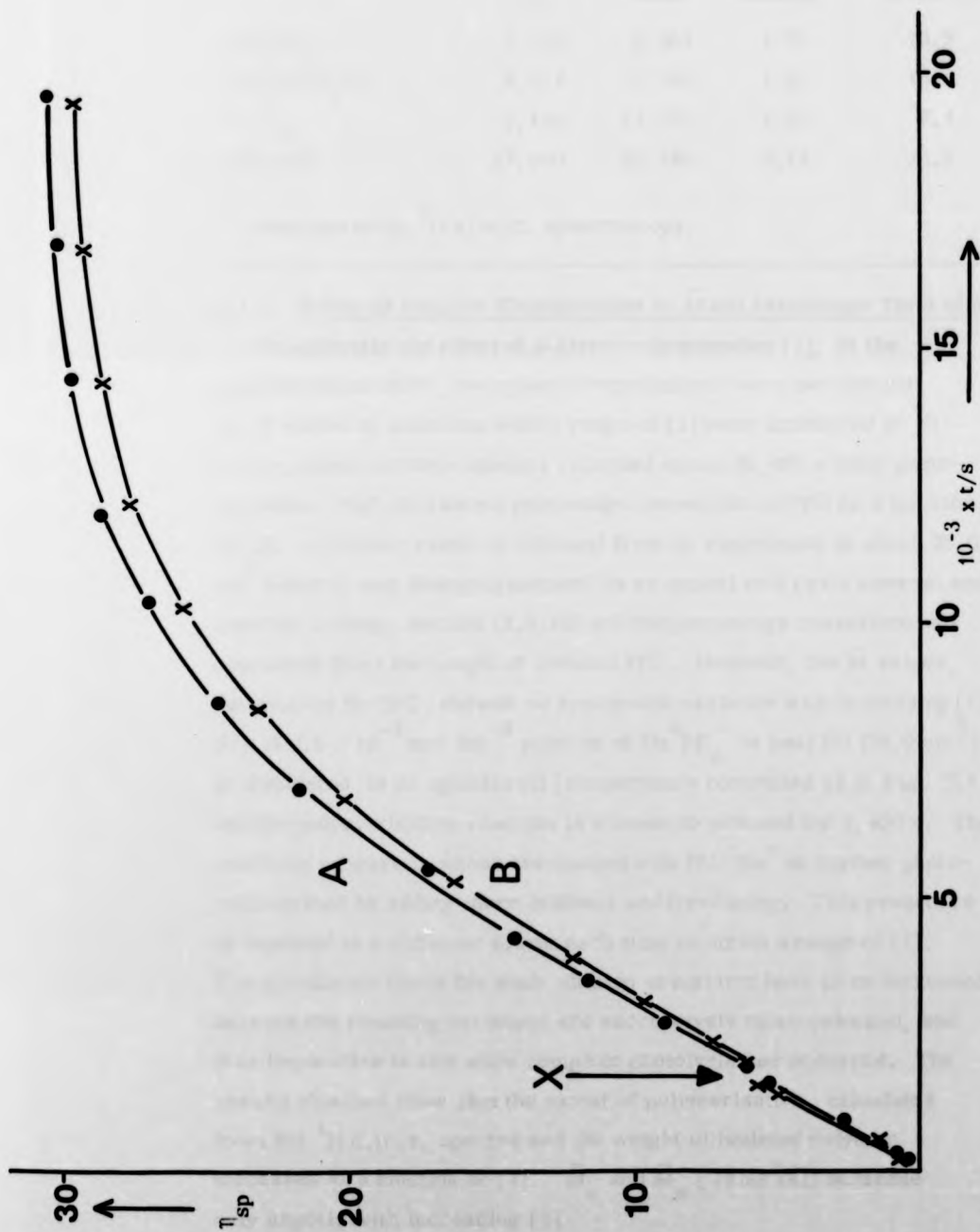
Table (7)

Effect of solvents

	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	% yield of PPO*
CH_2Cl_2	3,732	6,362	1.70	15.9
ClH_2CCH_2Cl	4,574	7,348	1.61	16.4
C_6H_{12}	6,181	11,720	1.90	7.4
Neat PO	17,960	38,440	2.14	23.9

* Determined by [1]H n.m.r. spectroscopy.

3.1.v Effect of Initiator Concentration on $\bar{M}$ and Percentage Yield of PPO

To ascertain the effect of initiator concentration [I], on the polymerisation of PO, two types of experiments were carried out:

(i) A series of solutions with a range of [I] were irradiated in [1]H n.m.r. tubes and their spectra recorded at ca. 86,400 s after photo-initiation. Fig. (16) shows percentage conversion to PPO as a function of [I]. A similar result is obtained from an experiment in which 25.0 cm^3 solution was photopolymerised in an optical cell [with internal and external cooling, section (2.6.vi)] and the percentage converison was calculated from the weight of isolated PPO. However, the $\bar{M}$ values, determined by GPC, showed no systematic variation with increasing [I].

(ii) A 2.0×10^{-3} mol dm^{-3} solution of $Dz^+PF_6^-$ in neat PO (20.0 cm^3) is irradiated in an optical cell [temperature controlled as in Fig. (9)A], and the polymerisation reaction is allowed to proceed for 1,400 s. The resulting mixture is either terminated with PhO^-Na^+ or further photo-polymerised by adding more initiator and irradiating. This procedure is repeated to a different extent each time to obtain a range of [I]. The irradiation times for each addition of initiator have to be increased because the resulting mixtures are successively more coloured, and it is impossible to say when complete photolysis has occurred. The results obtained show that the extent of polymerisation, calculated from the [1]H n.m.r. spectra and the weight of isolated polymer, increases as a function of [I]. $\bar{M}_n$ and $\bar{M}_w$ [Table (8)] decrease only slightly with increasing [I].

Figure (15)

Molecular weight distribution (determined by GPC) of PPO samples recovered from polymerisation of PO and its mixtures with solvents (50:50)

		$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	%Yield of PPO
A:	CH_2Cl_2	3,732	6,362	1.70	15.9
B:	ClH_2CCH_2Cl	4,574	7,348	1.61	16.4
C:	C_6H_{12}	6,181	11,720	1.90	7.4
D:	Neat PO	17,960	38,440	2.14	23.9

B   C   D

15
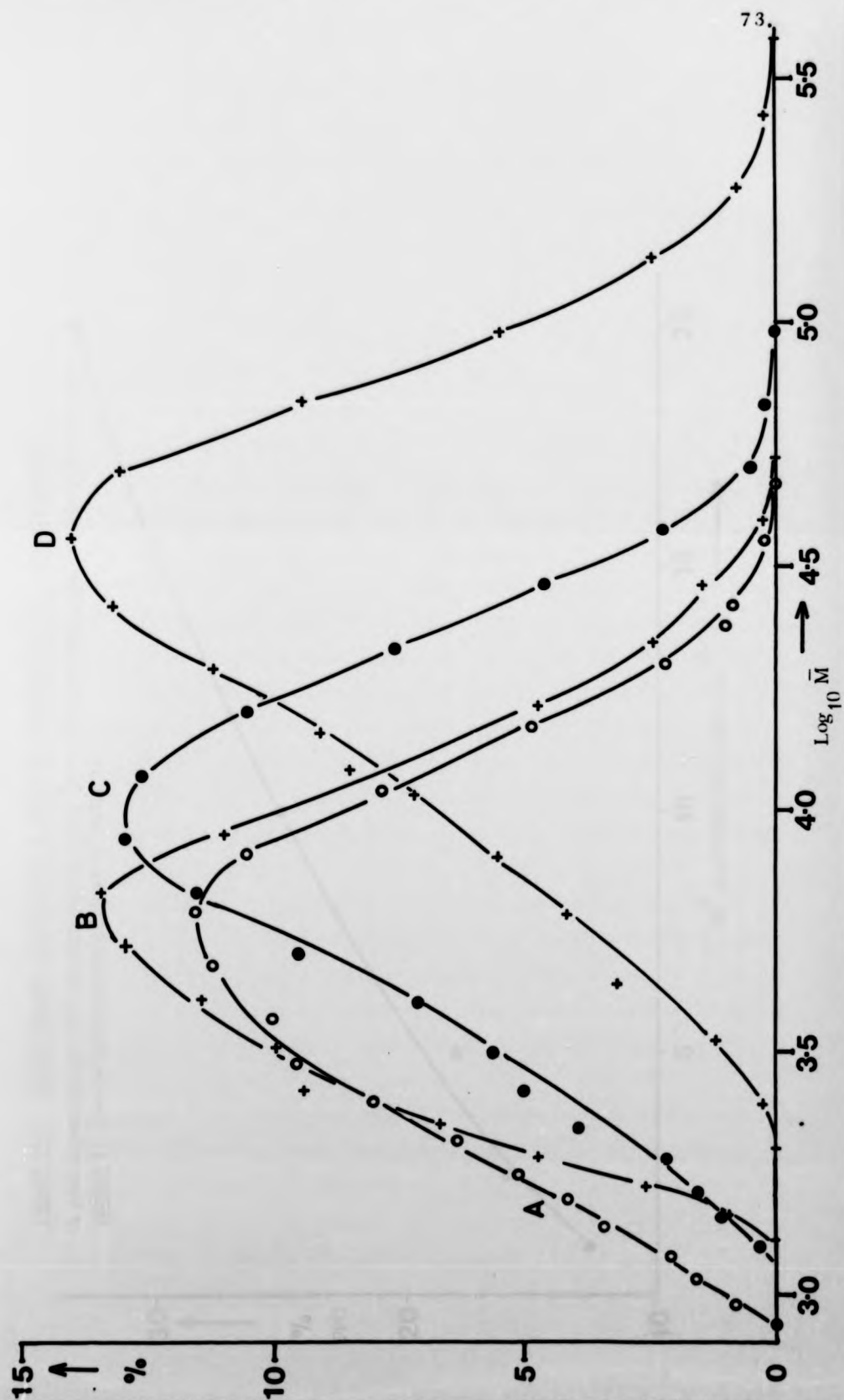
Figure (16) Extent of polymerisation as a function of initial $Dz^+ PF_6^-$ concentration.

A plot of percentage PPO (determined by using ^{1}H n.m.r. spectroscopy, Perkin-Elmer R-12) versus [I] in the polymerised mixture of neat PO.
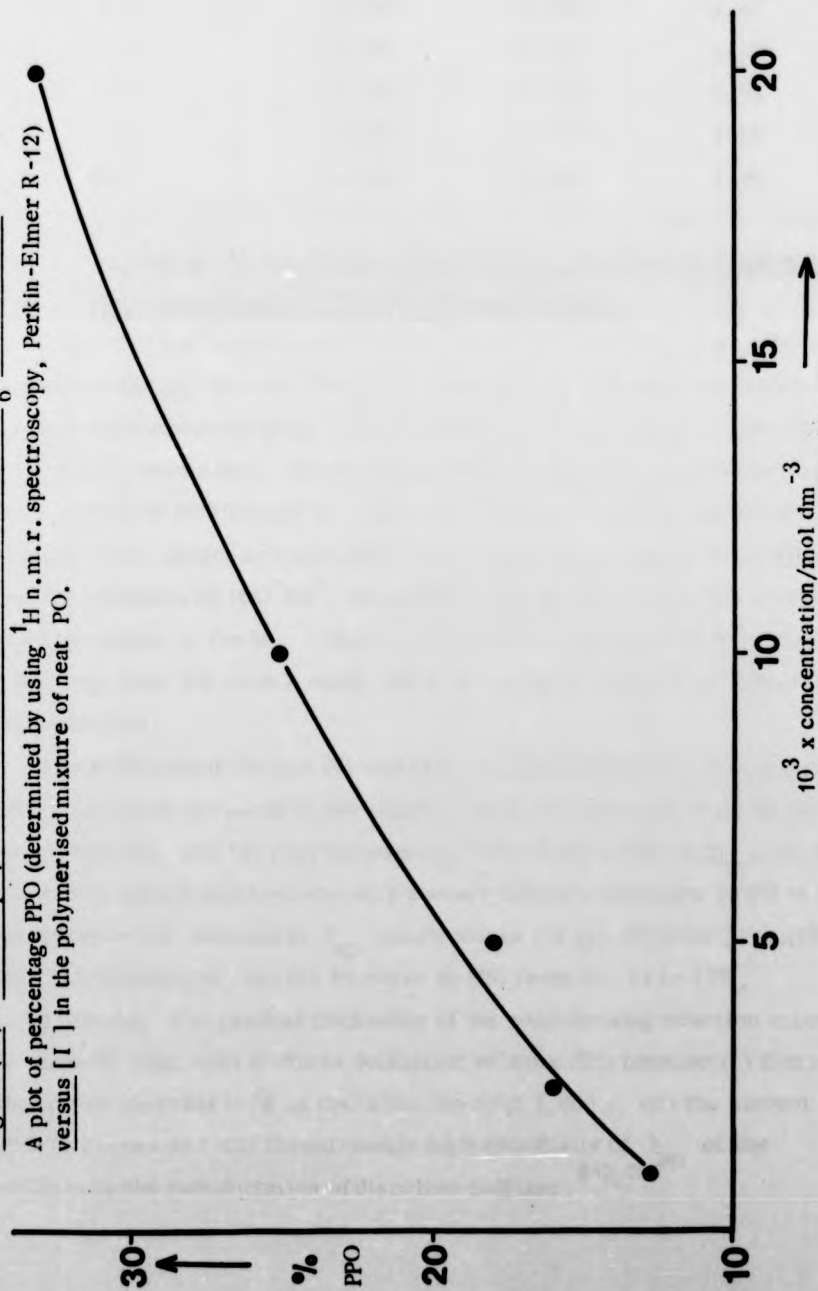
Table (8)

Effect of $Dz^+PF_6^-$ concentration on $\bar{M}$ of the resultant PPO

$10^3[Dz^+PF_6^-]$ mol dm^{-3}	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
2.0	19,460	48,070	2.47
2.0	23,320	40,170	1.72
6.0	21,580	41,170	1.91
8.0	17,800	33,340	1.87
10.0	16,940	33,570	1.98

3.1.vi Percentage Conversion and $\bar{M}$ of PPO as a Function of Time elapsed after Photoinitiation of Polymerisation Reaction

A 0.3-0.5 cm^3 solution of 2.0×10^{-3} mol dm^{-3} $Dz^+PF_6^-$ in neat PO was irradiated for ca. 20 s in ^1H n.m.r. tubes, and its spectrum recorded at various time intervals using a Perkin-Elmer R-12 instrument. The data in Table (9) shows that, despite fluctuations, there is an overall increase in the amount of PPO formed as a function of time. The $\bar{M}$ values of PPO, isolated from aliquot samples taken from polymerising reaction mixtures and terminated with PhO^-Na^+, are given in Table (10). Only run B shows a small increase in the $\bar{M}_w$ values as a function of time up to 600 s, and the remaining data, for runs A and B, form no regular trend with polymerisation reaction time.

From the data in Tables (9) and (10), it is concluded that the polymerisation reaction proceeds in two stages. Stage I is characterised by (i) its short duration and (ii) conversion of ca. 14% of PO to PPO of $\bar{M}_w \approx 27,000$. Stage II is slower and involves only a small further conversion of PO to PPO as shown by the increase in η_{sp} which occurs for ca. 20,000 s [Fig.(13)] after photoinitiation, and the increase in PPO from ca. 14 to 23%, respectively. The gradual thickening of the polymerising reaction mixture in Stage II, Fig. (13) is due to formation of more PPO because (i) there is no further increase in $\bar{M}$ of PPO after the first 1,000 s, (ii) the amount of PPO increases and (iii) the extremely high sensitivity of η_{sp} of the solution to the concentration of dissolved polymer.[202, 207]

Table (9)

Percentage conversion to PPO, determined by ^{1}H n.m.r. spectroscopy as a function of time for the polymerisation of neat PO initiated by 2.0×10^{-3} mol dm^{-3} Dz$^+$PF$_6^-$.

Run A		Run B	
t/s	%PPO	t/s	%PPO
540	14.4	1140	13.0
725	18.6	2100	14.4
960	20.3	3000	14.3
1690	20.0	4980	14.7
4410	19.8	7500	16.4
14400	22.9	11310	18.2
64800	22.2	14220	18.5
		16860	15.4
		20460	15.6
		23100	16.2
		25980	15.8
		83760	18.0
		99540	16.7
		106560	19.7

3.1.vii Linearisation of η_{sp} versus Time Curves

The specific viscosity versus time curves of the type shown in Fig. (13) can be linearised by obtaining an extrapolated infinity value for η_{sp} and using this to calculate $\log_{10}(\eta_{sp,\infty} - \eta_{sp})$. The first order relationship represented by the $\log_{10}(\eta_{sp,\infty} - \eta_{sp})$ versus time plots, Fig. (17), yields gradients which are independent of $\eta_{sp,\infty}$ values and $\bar{M}$ of the resultant PPO. The linearisation may be fortuitous because the viscosity of the polymer solution combines the influences of both the increase in $\bar{M}$ of PPO being formed and percentage PO conversion. However, we have already

Table (10) $\bar{M}$ values of PPO (determined by GPC) as a function of time for the polymerisation of neat PO initiated by 2.0 x 10^{-3} mol dm^{-3} DZ$^+$PF$_6^-$.

A 1.0cm^3 aliquot sample taken from runs A and B[at 298 K, see Fig. (9)A] and terminated with 1.0 cm^3 solution of 2.0 x 10^{-3} and 1.0 x 10^{-2} mol dm^{-3} PhO$^-$Na$^+$ (in neat PO), respectively.

	Run A				Run B		
time/s	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	time/s	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
166	15,990	32,380	2.03	100	12,360	26,980	2.18
191	15,870	34,830	2.20	145	13,720	28,010	2.04
218	13,410	29,180	2.18	165	12,580	28,770	2.29
251	11,500	25,030	2.18	185	12,440	30,250	2.43
302	13,330	33,560	2.52	208	12,440	30,250	2.43
488	12,930	30,370	2.35	301	13,490	32,660	2.33
528	13,530	31,360	2.32	420	14,420	33,640	2.89
600	13,830	32,440	2.35	600	12,910	37,320	2.80
720	13,450	32,280	2.40	840	11,560	32,420	3.24
900	13,490	30,530	2.26	1,200	11,230	36,390	3.19
1,140	12,810	29,780	2.32	1,800	10,350	33,080	2.37
1,455	16,310	31,840	1.95	3,180	16,500	39,100	4.23
1,980	12,330	29,030	2.35	6,120	8,605	36,440	3.08
3,300	13,110	31,030	2.37	14,820	11,880	36,580	2.20
7,200	14,080	30,160	2.14				

shown that the $\overline{M}$ of the polymer does not change during Stage II (i.e. that monitored by the viscosity method) of polymerisation reaction, section (3.1.vi). Therefore, during stage II, the polymerisation reaction must proceed by either a 'spurt' of very rapid propagation (analogous to stage I) of reactive species which are formed in very low concentration by a rate-determining step, leading to PPO units which have essentially the same $\overline{M}$ as those formed at the end of stage I, or a slow propagation occurs but the concentration of the propagating species is so very low that it does not contribute perceptibly to the $\overline{M}$ values obtained from a single polymerisation run as a function of time, Table (10).

The rate at which the η_{sp} of the polymerising solution increases is independent of the $\overline{M}$ value of PPO formed, and the rate constant for this change must constitute the rate of formation of the reactive species which forms the resultant polymer in stage II.

3.1.viii Molecular Weights of PPO

GPC traces [of which Fig. (18) is typical] for PPO samples show the presence of high $\overline{M}$ polymer at low elution volume (EV) between 82 and 105, counted from time of injection. The collection of small peaks beyond EV 115 and before the toluene marker (T) are due to low $\overline{M}$ impurities, and are a common feature of gel chromatograms[158].

An attempt was made to detect the presence of low $\overline{M}$ PPO by distillation of a polymerised reaction mixture, obtained from the polymerisation of PO (100 cm^3) in a round-bottomed flask, initiated by 2.0×10^{-3} mol dm^{-3} Dz$^+$PF$_6^-$. However, no fractions other than PO were collected at 2.7 N m^{-2} and 440 K (oil bath temperature).

3.1.ix Polymerisation of BuO

The differences between the Dz$^+$PF$_6^-$-initiated polymerisations of BuO and PO are as follows:-

(i) A lower final conversion to polymer is obtained with BuO [Table (11)] compared with PO [Table (9)].

(ii) At the end of stage I, the extent of polymerisation (determined by ^{1}H n.m.r. spectroscopy) is equal for BuO [Table (11)] and PO [Table (9)] at 2.0×10^{-3} mol dm^{-3} Dz$^+$PF$_6^-$.

Figure (17)

Linearised η_{sp} versus time curves

Plots of $\log_{10}(\eta_{sp,\infty} - \eta_{sp})$ versus time for the polymerisation of PO initiated by 2.0×10^{-3} mol dm^{-3} Dz$^+$PF$_6^-$.

	$\eta_{sp,\infty}$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	10^5 x gradient/s^{-1}
A:	72.5	18,140	43,250	2.38	-5.35
B:	31.0	8,400	17,860	2.13	-6.05
C*:	7.4	(6,680)	(13,940)	2.09	-5.59

* These $\bar{M}$ values are from a sample with $\eta_{sp,\infty} \approx 15$ because the GPC data for the original sample are not available.

The PO used in runs A, B and C were purified by distillation from Na-wire, CaH$_2$ and KOH pellets, respectively, section (2.1).

2·0-

1·5-

$\text{Log}_{10}[\eta_{sp,\infty} - \eta_{sp}]$

1·0-

·5-
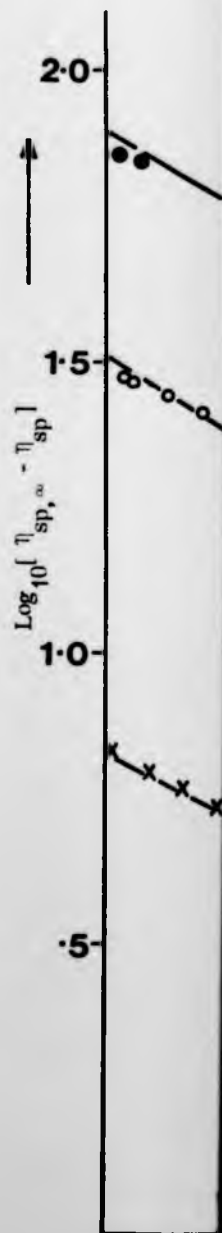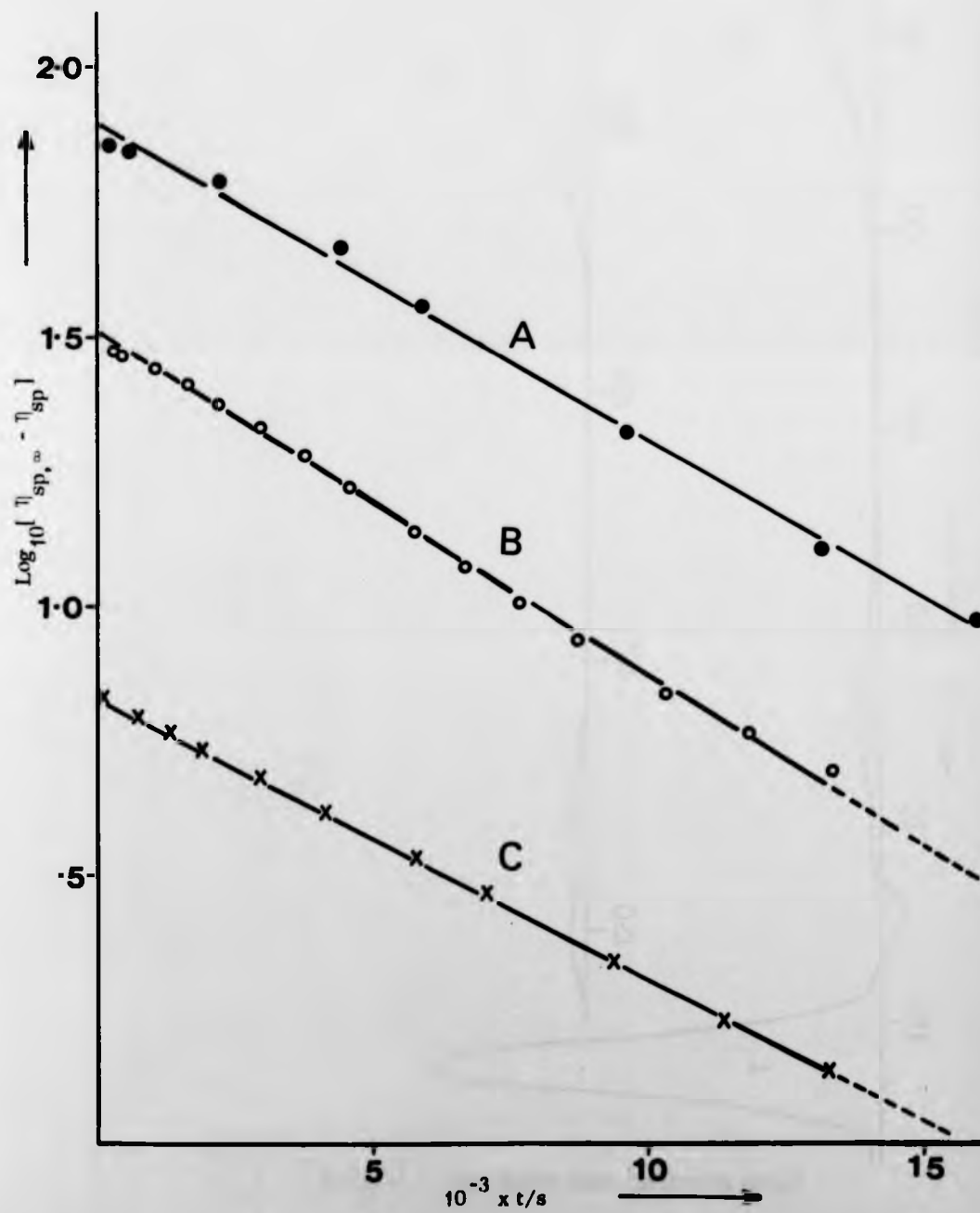
risation

gradient/s^{-1}

-5.35

-6.05

-5.59

use the GPC

from Na-wire,

Figure (18)   Typical GPC traces for PPO and PBuO obtained from polymerisations initiated by $Dz^+PF_6^-$

	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
A: PBuO	12,640	24,020	1.90
B: PPO	6,056	22,810	3.77

T: Toluene marker

A

B

T

Elution volume

80 90 100 110 120 130 140

Refractive index (arbitrary units)
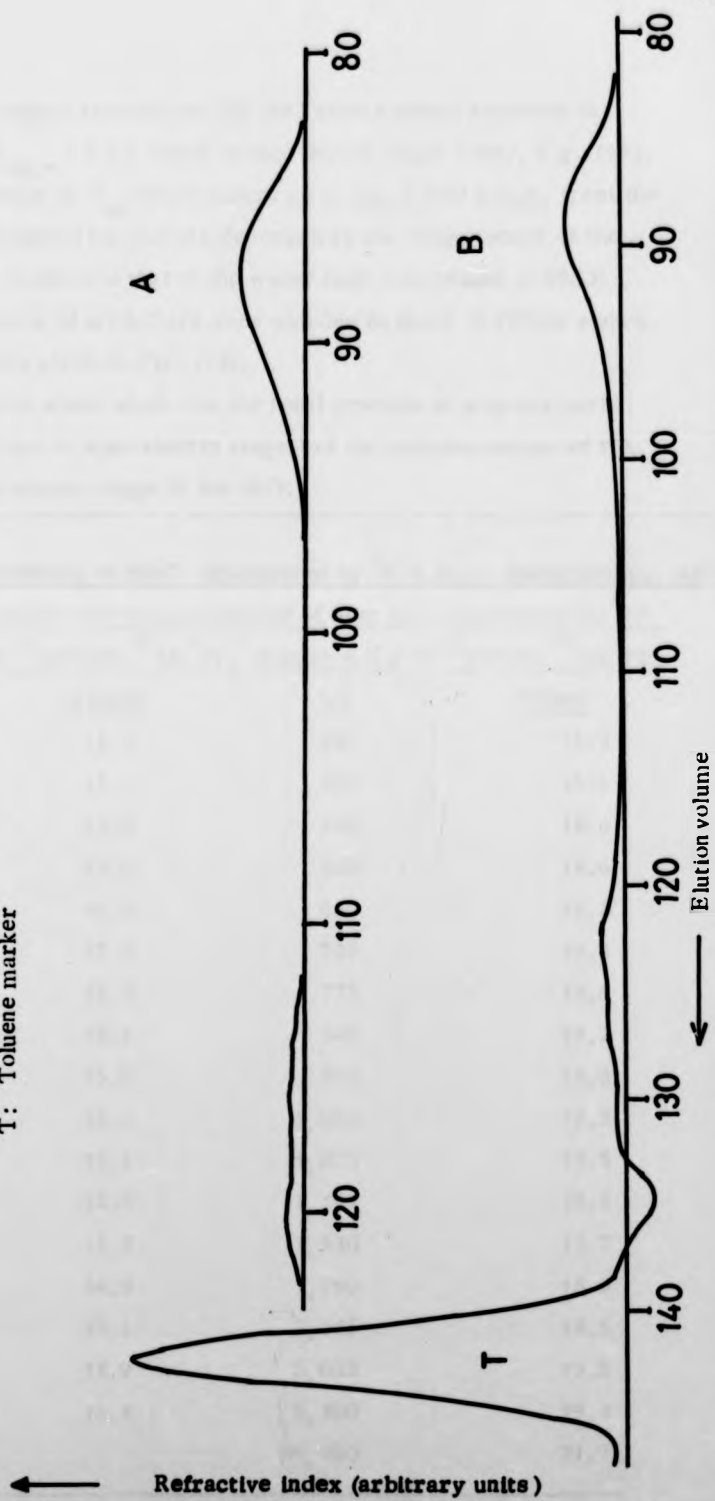
(iii) The η_{sp} _versus_ time curves for BuO show a small increase in viscosity (_ca_. $\eta_{sp, \infty} = 1.0$) which occurs during stage I only, Fig. (19). The slight increase in η_{sp} which occurs up to _ca_. 2,000 s (_i.e._ from the start of photoinitiation) is due to a decrease in the temperature of the polymerisation mixture to that of the water bath maintained at 298 K .

(iv) The values of $\bar{M}$ of PBuO are very similar to those of PPO as shown by the GPC traces given in Fig. (18).

The data given above show that the total process of polymerisation of BuO is rapid and is equivalent to stage I of the polymerisation of PO, _i.e._ there is _no_ slower stage II for BuO.

Table (11)

Percentage conversion to PBuO , determined by [1]H n.m.r. spectroscopy, as a function of time for the polymerisation of neat BuO initiated by $Dz^{+}PF_{6}^{-}$

Run A: 2.0×10^{-3} mol dm^{-3} $Dz^{+}PF_{6}^{-}$ Run B: 4.0×10^{-3} mol dm^{-3} $Dz^{+}PF_{6}^{-}$

t/s	%PBuO	t/s	%PBuO
251	14.3	345	16.9
325	15.1	405	16.6
400	15.5	480	18.6
470	15.6	560	18.6
575	16.5	640	18.8
705	15.5	705	19.4
783	15.9	773	18.6
858	15.1	840	19.2
945	15.6	913	18.3
1,013	15.4	1,003	19.5
1,128	15.2	1,075	18.5
1,200	15.3	1,147	19.1
1,639	15.2	1,530	18.7
1,705	14.9	1,760	18.3
3,346	15.1	3,605	18.5
3,760	14.9	5,032	19.5
86,400	16.4	5,400	19.8
		86,400	21.7

Figure (19)

Viscometric runs for the polymerisation of neat BuO initiated by 2.0×10^{-3} mol dm^{-3} Dz^{+}PF$_{6}^{-}$

Plots of η_{sp} versus reaction time

Sample	Monomer	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A:	BuO	10,800	25,100	2.32
B:	BuO	12,640	24.020	1.90
C:	BuO	14,080	25,950	1.84
D:	PO	-	-	-

BuO initiated by

$\overline{M}_w/\overline{M}_n$

2.32

1.90

1.84

-

C
B
A
D

259

73 74

15

$10^{-3} \times t/s$

10

5

η_{sp}

1·5

1·0

·5
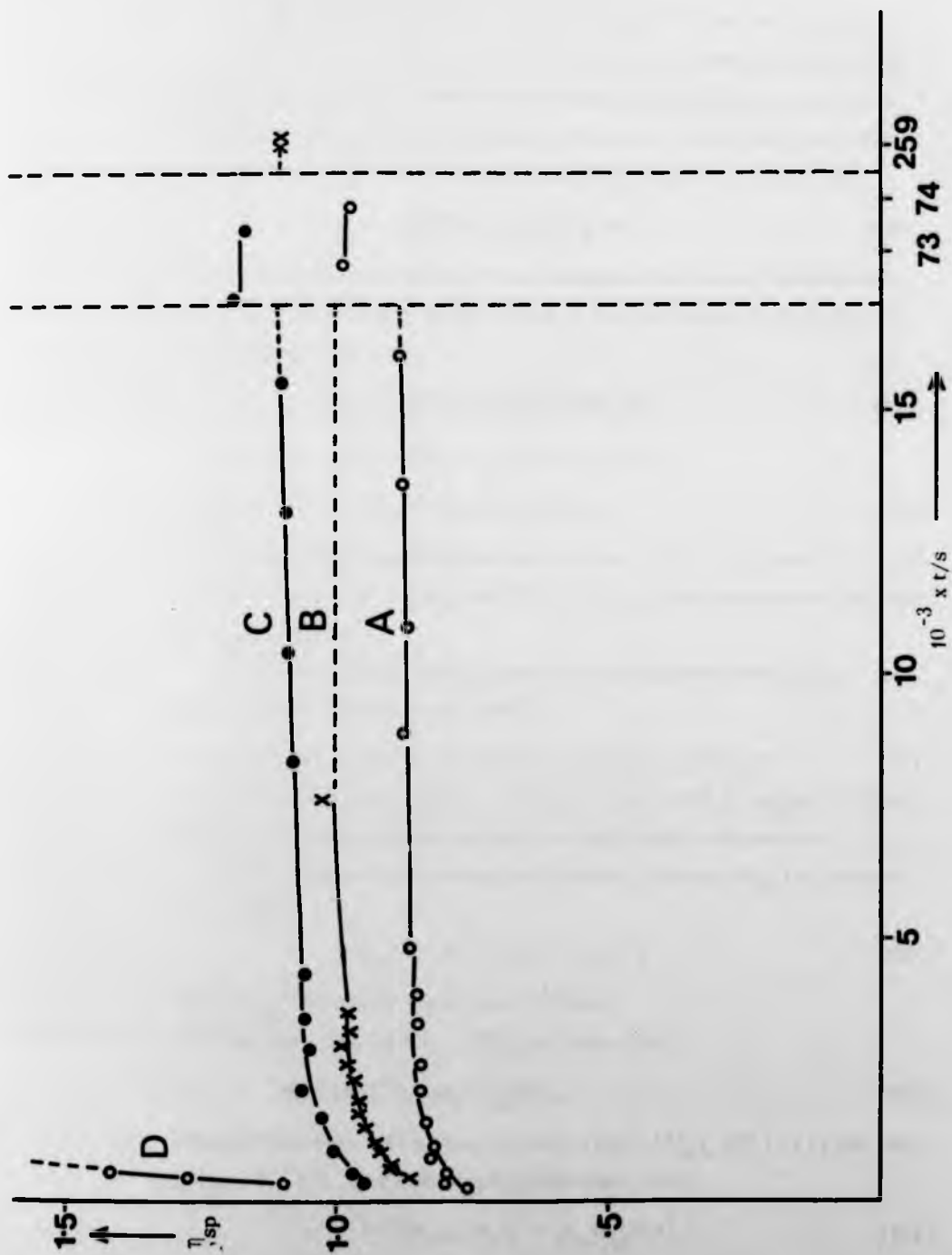
3.1.x Nature of the Termination Process

The mechanism (proposed by E.J. Glethals[73]) for the cationic polymerisation of cyclic sulphides, initiated by triethyloxonium salts, features two types of termination reaction (intermolecular and intra-molecular) depending on ring-size, presence of substituents and the counter-ions. The rate of propagation (R_p) is given by eqn. (96).

$$R_p = -d[M]/dt = k_p[P^*][M] \tag{96}$$

The rate of termination (R_t) for a reaction which occurs between the growing chains and the oxygen atoms of the polymer already formed is given by eqn. (97).

$$R_t = -d[P^*]/dt = k_t[P^*][M_o-M] \tag{97}$$

Dividing eqn. (96) by eqn. (97) gives eqn. (98).

$$d[M]/[P^*] = (k_p/k_t)\{[M_o]/[M_o]-[M]\} \tag{98}$$

At the beginning of polymerisation reaction, $[M] = [M_o]$ and $[P^*] = [I]$, and at the end, $[M] = [M_f]$ and $[P^*] = 0$, (i.e. for quantitative initiation and termination).

Integration of eqn. (98) between the limits given above, and rearrangement leads to eqn. (99).

$$\ln\{[M_o]/[M_f]\} - \{[M_o] - [M_f]\}/[M_o] = (k_p/k_t)\{[I]/[M_o]\} \tag{99}$$

Thus a plot of $\ln\{[M_o]/[M_f]\} - \}[M_o] - [M_f]\}/[M_o]$ versus $[I]/[M_o]$ should give a straight line through the origin with a slope equal to k_p/k_t.

For a unimolecular termination reaction, the rate (R_{tu}) is given by eqn. (100).

$$R_{tu} = -d[P^*]/dt = k_{tu}[P^*] \tag{100}$$

where k_{tu} is the first-order rate constant.

Dividing eqn. (96) by eqn. (100) gives eqn. (101)

$$d[M]/d[P^*] = (k_p/k_{tu})[M] \tag{101}$$

Integration of eqn. (101) between limits $[M] = [M_o]$, $[P^*] = [I]$ and $[M] = [M_f]$, $[P^*] = 0$, and rearranging gives eqn. (102).

$$\ln\{[M_o]/[M_f]\} = (k_p/k_{tu})[I] \tag{102}$$

Thus a plot of $\ln\{[M_o]/[M_f]\}$ <u>versus</u> [I] should give a straight line through the origin with a slope equal to k_p/k_{tu}.

Plots A and B of Fig. (20) are drawn according to eqns. (102) and (99), respectively, for the polymerisation of BuO initiated by $Dz^+PF_6^-$. Plot B is linear and passes through the origin, and therefore the termination reaction for this system must occur between the growing chains and oxygen atoms of the already formed polymer.

For the polymerisation of PO initiated by $Dz^+PF_6^-$, the plots according to eqns. (102) and (99) are shown in Fig. (21) as A and B, respectively. For this system, plot B is a straight line but does <u>not</u> pass through the origin. This is not surprising because the polymerisation of PO occurs in two stages and probably involve <u>two</u> types of termination reaction. However, since plot B is a straight line and passes very close to the origin, the termination reaction for the polymerisation of PO during stage I is likely to be the same as that for BuO. An account of the mechanisms of these reactions can be found in chapter (4).

3.1.xi The Adiabatic Reaction Kinetics of $Dz^+PF_6^-$ initiated Polymerisation of BuO

The temperature <u>versus</u> time curve, Fig. (11), for the polymerisation of BuO initiated by $Dz^+PF_6^-$ can be divided into two parts (X and Y). Analysis of this curve by the procedure described in section (2.6.vii) gives the results shown in Fig. (22); the first-, second- and third-order plots (A, B and C, respectively) show discontinuity expected from the original curve [Fig. (11)]. The first-order plot is a curve and second- and third-order graphs are straight lines.

In terms of polymerisation reaction mechanism, these results seem difficult to explain at first sight. However, possible explanations are as follows:-

(i) The assumption that the enthalpy is due exclusively to a single reaction, and the catalysing species are neither produced or consumed significantly in the secondary chemical changes, [section (2.6.vii)] are not valid.

(a) The initiation step may be exothermic.

Figure (20)

Nature of the termination process for the polymerisation of BuO

Plots of:-

A: $\ln\{[M_o]/[M_f]\}$ <u>versus</u> $[I]$

B: $\ln\{[M_o]/[M_f]\} - \{[M_o]-[M_f]\}/[M_o]$ <u>versus</u> $[I]/[M_o]$

  k_p/k_t = slope = 79.0

$10^2 \times (\ln\{[M_o]/[M_f]\})$

25—

20—

15—

10—

5—

merisation of BuO

s [Ɲ]/[M$_o$]
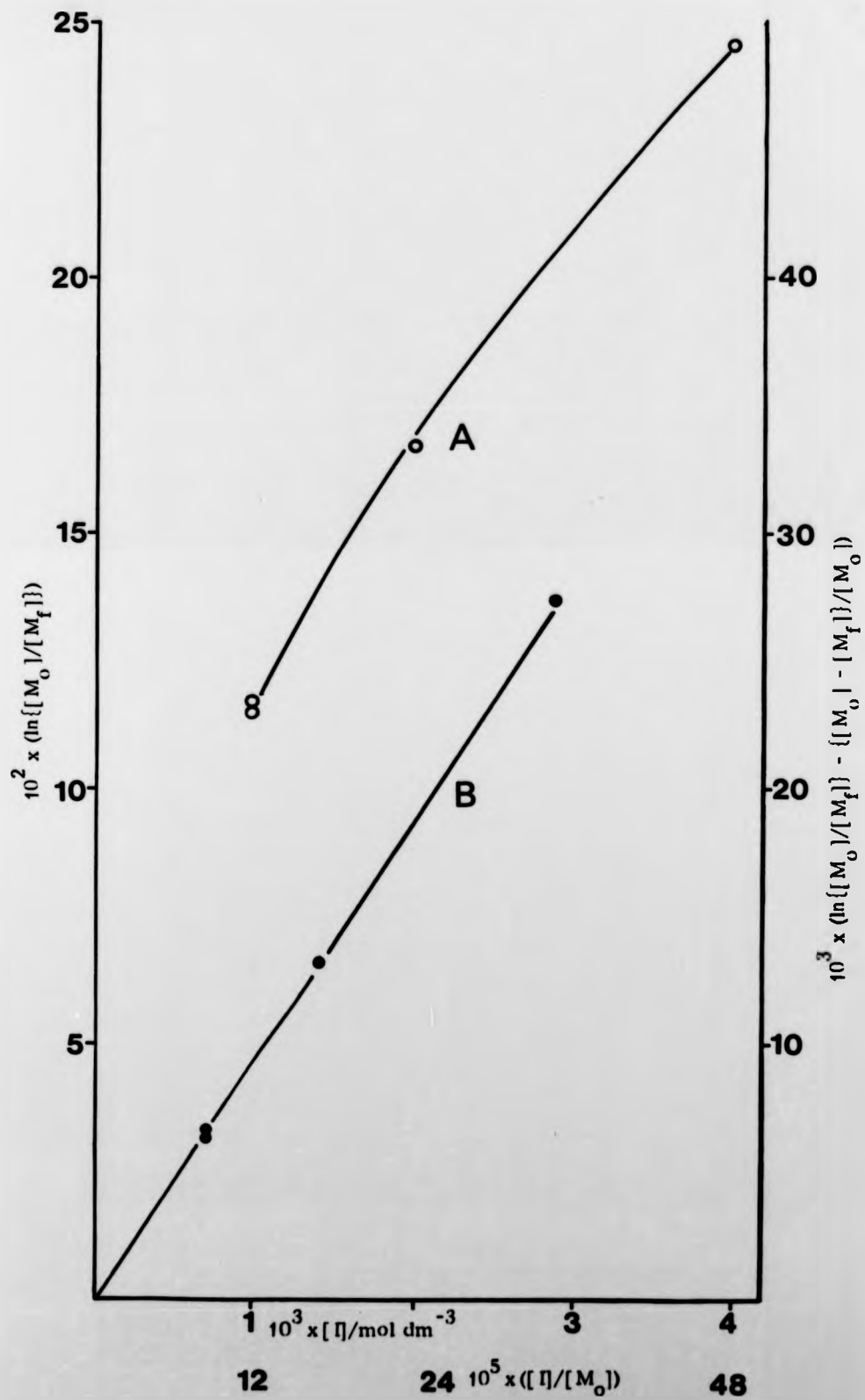
Figure (21)

Nature of the termination process for the polymerisation of PO

Plot of:-

A: $\ln\{[M_o]/[M_f]\}$ <u>versus</u> $[I]$

B: $\ln\{[M_o]/[M_f]\} - \{[M_o] - [M_f]\}/[M_o]$ <u>versus</u> $[I]/[M_o]$

merisation of PO

rsus $[I]/[M_o]$

Axis labels:
- y-axis (left): $\ln\{[M_o]/[M_f]\}$
- y-axis (right): $10^2 \times (\ln\{[M_o]/[M_f]\} - \{[M_o] - [M_f]\}/[M_o])$
- x-axis (lower): $10^3 \times [I]/\text{mol dm}^{-3}$
- x-axis (upper): $10^4 \times ([I]/[M_o])$

Curves labelled A and B.
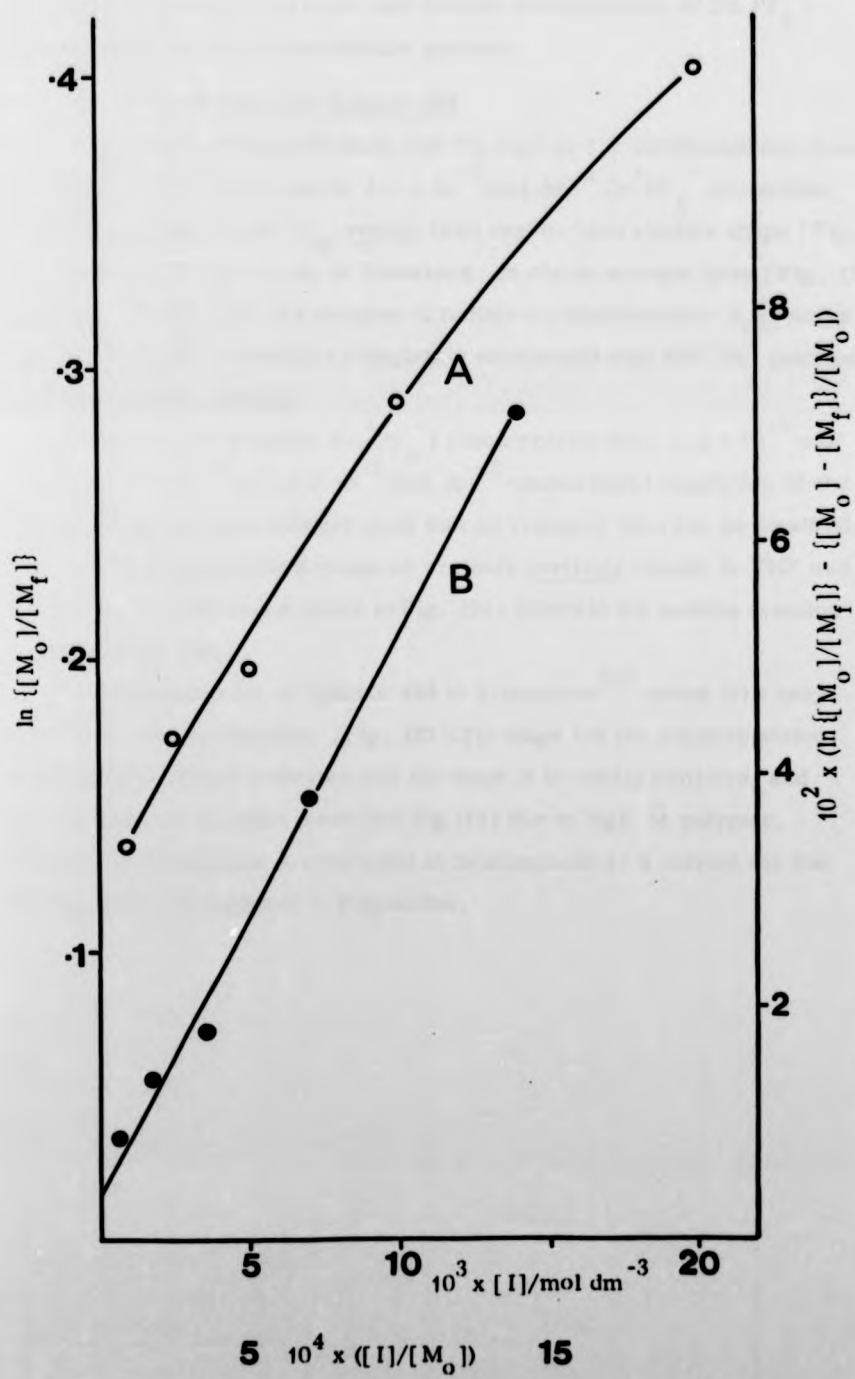
(b)   The termination reaction has been shown in section (3.1.x) to be significant and may also contribute to the temperature increase.

(ii)   In Part X of the temperature $\underline{versus}$ time curve, initiating species are probably formed (by photo- and thermal decomposition of $Dz^+PF_6^-$) concurrent with the polymerisation process.

3.1.xii   Polymerisation of Epikote 828

The polymerisation of Epikote 828 (10.0 g) in 1,2-dichloroethane (total volume 25.0 cm^3) initiated by 2.0×10^{-3} mol dm^{-3} $Dz^+PF_6^-$ resembles that of PO in that (i) the η_{sp} $\underline{versus}$ time curves have similar shape [Fig. (13) and Fig. (23)] and can be linearised to obtain straight lines [Fig. (17) and Fig. (23.I)], and (ii) the post-irradiation polymerisation (i.e. stage II monitored by viscometry) is completely terminated with PhO$^-$Na$^+$ [section (3.1.iii) and Fig.(23)D].

An increase in initiator ($Dz^+PF_6^-$) concentration from 2.0×10^{-3} mol dm^{-3} to 1.0×10^{-2} or 5.0×10^{-3} mol dm^{-3} causes rapid congealing of the polymerising reaction mixture such that no viscosity data can be obtained. The resultant polymerised mixtures are only $\underline{partially}$ soluble in THF and, therefore, the GPC trace shown in Fig. (24) refers to the soluble fraction of polyepikote 828.

The polymerisation of Epikote 828 in 2-butanone[201] shows (i) a very small increase in viscosity [Fig. (23)C] in stage I of the polymerisation reaction only, which indicates that the stage II is totally inhibited, and (ii) the absence of peaks A and B in Fig (24) due to high $\bar{M}$ polymer. Therefore, 2-butanone is concluded to be unsuitable as a solvent for the cationic polymerisation of 1,2-epoxides.

Figure (22)

Adiabatic reaction kinetics of polymerisation of neat BuO initiated by 1.0×10^{-3} mol dm^{-3} Dz$^+$PF$_6^-$.

A: First-order plot of $\log_{10} P$ versus $1/T$

B: Second-order plot of $\log_{10}[P(T_f-T)]$ versus $1/T$

C: Third-order plot of $\log_{10}[P(T_f-T)^2]$ versus $1/T$

4·0.

2·4

$\log_{10} P$
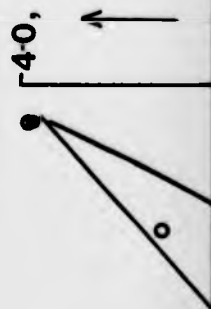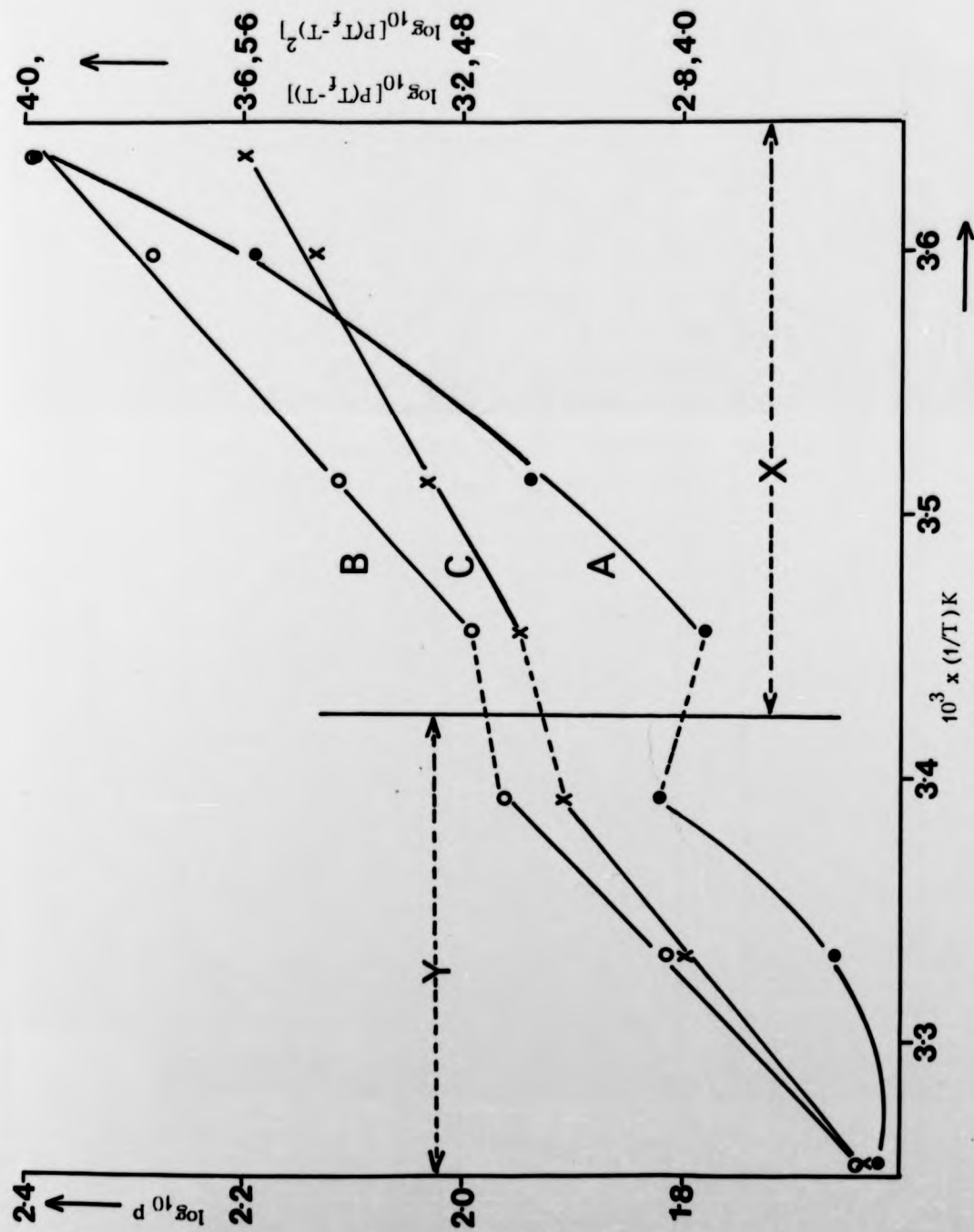
of neat BuO

s 1/T

us 1/T

Figure (23)

Viscometric runs for the polymerisation of Epikote 828 initiated by
$Dz^+PF_6^-$.

Polymerisation of Epikote 828 (10.0 g) in 1, 2-dichloroethane (total
volume 25.0 cm^3) initiated by 2.0 x 10^{-3} mol dm^{-3} $Dz^+PF_6^-$.

A and B: Controls

C: 2-Butanone used as a solvent

D: Effect of PhO$^-$Na$^+$. 1.0 cm^3 saturated solution of PhO$^-$Na$^+$
          in 1, 2-dichloroethane added at X and Y.

ote 828 initiated by

hloroethane (total
$^{-3}$ Dz$^+$PF$_6^-$.

olution of PhO$^-$Na$^+$
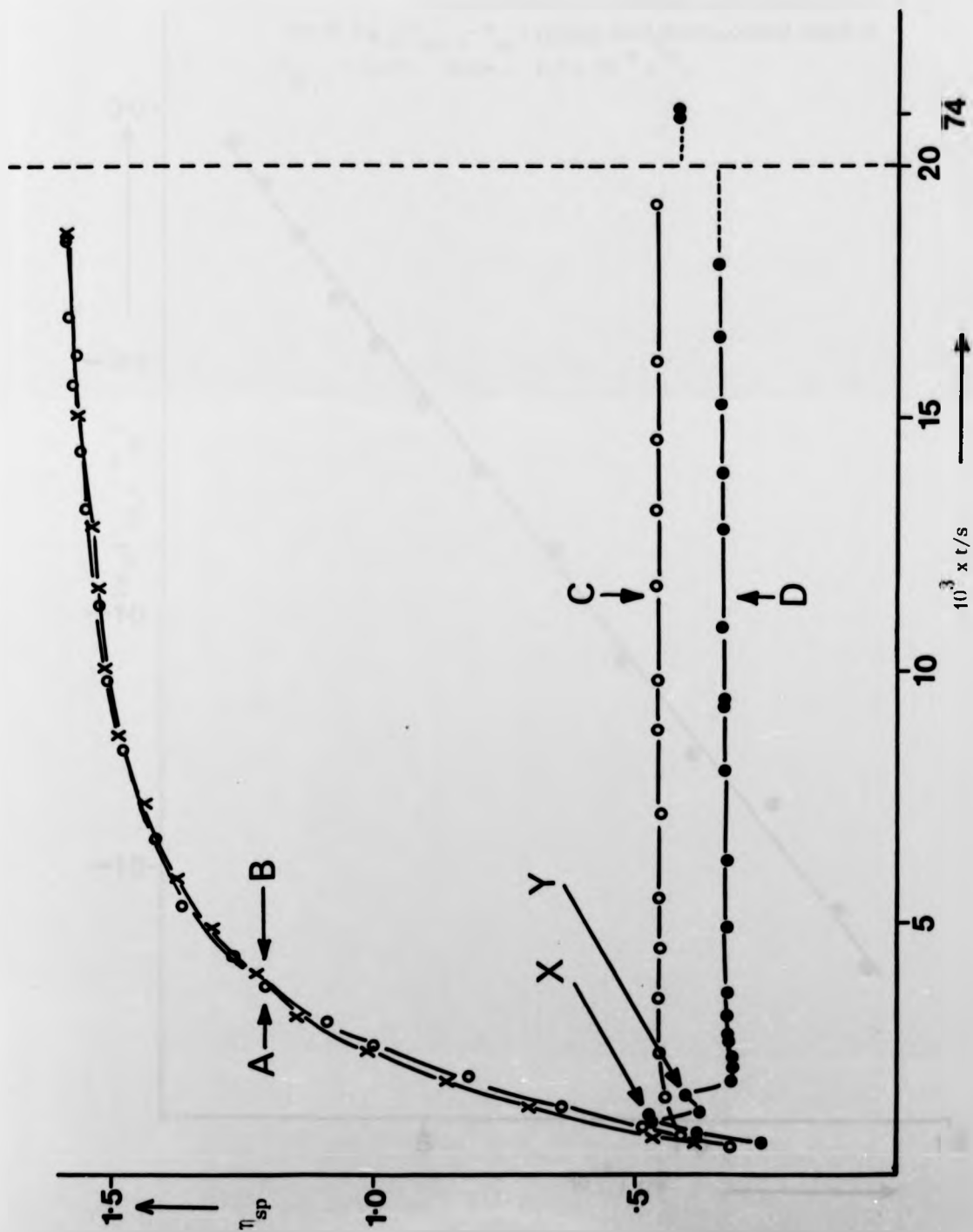
Figure (23.I)   Linearised η_{sp} versus time curve for the polymerisation of Epikote 828 initiated by $Dz^+PF_6^-$

Plot of $\log_{10}(\eta_{sp,\infty} - \eta_{sp})$ versus time, (extrapolated value of $\eta_{sp,\infty} = 1.57$).   Slope $= -1.3 \times 10^{-4} \, s^{-1}$.

Figure (24)

A typical GPC Trace for Polyepikote 828 sample obtained from the polymerisation of Epikote 828 initiated by $Dz^{+}PF_{6}^{-}$.

Polymerisation of Epikote 828 (10.0g) in 1,2-dichloroethane (total volume 25.0 cm^{3}) initiated by 2.0×10^{-3} mol dm^{-3} $Dz^{+}PF_{6}^{-}$. The sample includes the solvent 1,2-dichloroethane.

Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A	17,790	39,930	2.24
B	3,922	9,248	2.36
C	980	1.327	1.35
D	345	353	1.02
E	218	219	1.00
F	176	177	1.00

Figure (24)

A typical GPC Trace for Polyepikote 828 sample obtained from the polymerisation of Epikote 828 initiated by $Dz^+PF_6^-$.

Polymerisation of Epikote 828 (10.0g) in 1,2-dichloroethane (total volume 25.0 cm^3) initiated by 2.0×10^{-3} mol dm^{-3} $Dz^+PF_6^-$. The sample includes the solvent 1,2-dichloroethane.

Peak	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A	17,790	39,930	2.24
B	3,922	9,248	2.36
C	980	1,327	1.35
D	345	353	1.02
E	218	219	1.00
F	176	177	1.00

ple obtained from
$Dz^+PF_6^-$.

-dichloroethane (total
dm^{-3} $Dz^+PF_6^-$.
oroethane.

$\overline{M}_w/\overline{M}_n$
2.24
2.36
1.35
1.02
1.00
1.00

A

B

C

D

E

F

Elution volume

Refractive index (arbitrary units)
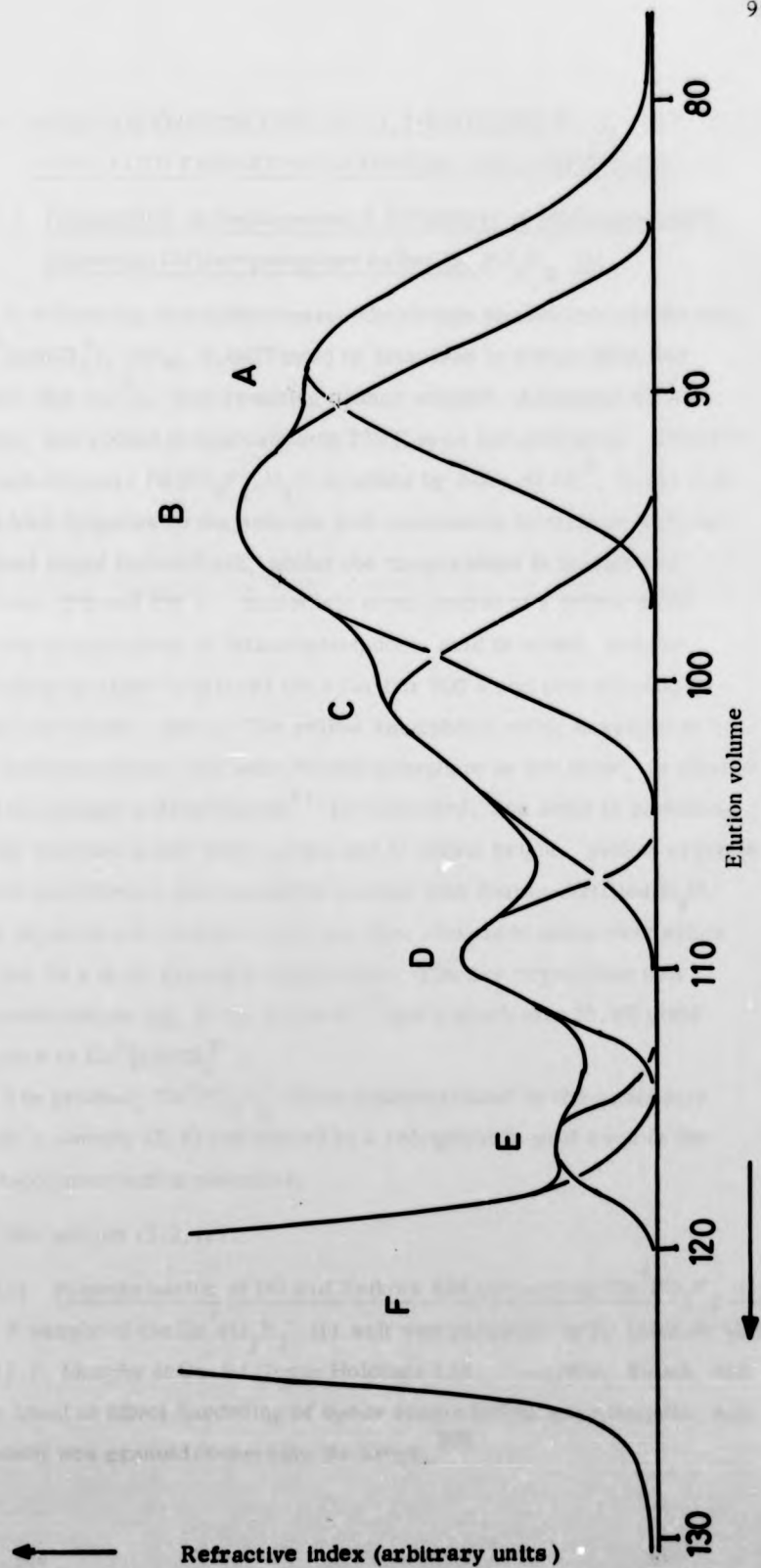
3.2 PHOTOPOLYMERISATION OF 1,2-EPOXIDES BY 2,5-DIETHOXY-4-TOLYLTHIOBENZENEDIAZONIUM DIFLUOROPHOSPHATE

3.2.1 Preparation of the Supposed 2,5-Diethoxy-4-tolylthiobenzene-diazonium Difluorophosphate called $Dz^+PO_2F_2^-$ (I)

2,5-Diethoxy-4-tolylthiobenzenediazonium tetrachlorozincate salt, $Dz^+\frac{1}{2}(ZnCl_4^{2-})$, (20 g, 0.0477 mol) is dissolved in doubly-distilled water (500 cm^3). The resulting orange solution is filtered through celite, and cooled to approximately 272 K in an ice-salt bath. Difluoro-phosphoric acid ($2HPO_2F_2.H_2O$ supplied by Alfa; 30 cm^3, 0.461 mol) is added dropwise to the solution with continuous stirring in a three-necked round bottom flask, whilst the temperature is maintained between 272 and 276 K. Immediate precipitation of a yellow solid occurs as each drop of difluorophosphoric acid is added, and the resultant mixture is stirred for a further 900 s and then allowed to stand for about 1,800 s. The yellow amorphous solid, assumed to be the arenediazonium salt with difluorophosphate as the anion, is filtered and the orange-yellow filtrate[*1] is discarded. The solid is broken up under distilled water with a glass rod to obtain bright yellow crystals which are filtered and thoroughly washed with doubly-distilled H_2O. The crystals are first air-dried and then allowed to stand over silica gel for 24 h in an evacuated desiccator. The dry crystalline salt obtained weighs ca. 5.0 g (1.2×10^{-2} mol) which is a 25.2% yield relative to $Dz^+\frac{1}{2}(ZnCl_4^{2-})$.

The product, $Dz^+PO_2F_2^-$ (I) is recrystallised by the procedure given in section (2.3) and stored in a refrigerator until used in the photopolymerisation reactions.

[*1] See section (3.2.iv).

3.2.ii Polymerisation of PO and Epikote 828 initiated by $Dz^+PO_2F_2^-$ (I)

A sample of the $Dz^+PO_2F_2^-$ (I) salt was prepared by P. Pinot de Moira and J.P. Murphy at Ozalid Group Holdings Ltd., Loughton, Essex, and was found to effect hardening of epoxy resins following photolysis, and a patent was granted concerning its usage.[201]

We were concerned to demonstrate quantitatively the superiority of $Dz^+PO_2F_2^-$ (I) over its hexafluorophosphate analogue by comparing the rates of polymerisation (and $\bar{M}$ of the resultant polymer) of PO and Epikote 828 using these catalysts under controlled conditions. The rate was followed using the viscosity method, section (2.6.1) and $\bar{M}$ of the resultant polymer was determined by GPC, section (2.7). The polymerisation of neat PO and Epikote 828 (in 1,2-dichloroethane) initiated by $Dz^+PO_2F_2^-$ and $Dz^+PF_6^-$ give (i) the same shape of η_{sp} versus time curves [but lower $\eta_{sp,\infty}$ values are obtained with $Dz^+PO_2F_2^-$ (I)] and (ii) similar molecular weight distributions of resultant polymer.

3.2.iii Analysis of $Dz^+PO_2F_2^-$ (I)

In the early stages of this work the arenediazonium salts used were analysed for purity by the nitrometer method[232] at Ozalid Group Holdings Ltd. and the $Dz^+PO_2F_2^-$ (I) was found to be less than 90% pure even after careful purification, Table (12).

Table (12)

Percent purity of arenediazonium salts determined by the nitrometer method[*1]

Sample	$Dz^+PF_6^-$	$Dz^+PO_2F_2^-$ (I)
(1)	88.8[*2]	87.1
(2)	96.6	88.6
(3)	98.9	89.1

[*1] Analysis is usually duplicated and an average result is given

[*2] Result from a single analysis because the amount of sample was too small for duplication

After a period had elapsed, it was decided to check the purity of the $Dz^+PO_2F_2^-$ (I) sample by microanalysis for C, H and N. The figres, Table (13), indicated that the material was either very impure or was not what it was claimed to be. A fresh sample was prepared by the procedure described in section (3.2.1) and an identical analysis

for C, H and N was returned, Table (14). Dr. H.B. Ambroz of this laboratory attempted to synthesise a different arenediazonium difluorophosphate by the same method. The results of all the micro-analyses could only be explained in terms of the material being the hexafluorophosphate salt.

Following this, we submitted a sample of $Dz^+PO_2F_2^-$ (I) for F analysis and the results, Table (14), indicated unequivocally that all samples are in fact hexafluorophosphate salts. This conclusion was confirmed by IR spectroscopy, see section (3.2.v).

Table (13)

Microanalysis of $Dz^+PO_2F_2^-$ (I) and <u>bona fide</u> $Dz^+PF_6^-$

		Carbon		Hydrogen		Nitrogen	
	Sample	%EX	%F	%EX	%F	%EX	%F
$Dz^+PF_6^-$	(2)	44.35	44.53	4.16	4.21	6.08	6.15
$Dz^+PF_6^-$	(2)	44.35	44.53	4.16	4.22	6.08	6.12
$Dz^+PO_2F_2^-$ (I)	(2)	49.04	44.30	4.60	4.17	6.73	6.13
$Dz^+PO_2F_2^-$ (I)	(3)	49.04	44.38	4.60	4.22	6.73	6.13

where %EX is % expected and %F is % found.

<u>Note</u> In analyses of C, H and N the absolute difference in percentages aimed for is ±0.15.   C.H.N. Analysis Ltd., Leicester.

Table (14)

Microanalysis of the freshly prepared $Dz^+PO_2F_2^-$ (I)

	Carbon		Hydrogen		Nitrogen		Fluorine[1]	
	%EX	%F	%EX	%F	%EX	%F	%EX	%F
$Dz^+PO_2F_2^-$ (I)	49.04	44.38	4.60	4.12	6.73	6.24	9.13	24.3:
$Dz^+PF_6^-$ [2]	44.35	-	4.16	-	6.08	-	24.76	

[1] Butterworth Laboratories Ltd., Teddington, Middlesex.

[2] This is included for comparison.

The fact that $Dz^+PF_6^-$ is formed by the procedure given in section (3.2.i) we attribute to the presence of a small amount of HPF_6 in the HPO_2F_2 as supplied,[233] and the pronounced insolubility of the PF_6^- salt which results in its being preferentially precipitated. We therefore

believe that there is a strong possibility that the material referred
to in British Patent 1,376,840 is in reality the hexafluorophosphate
salt.

3.2.iv Preparation of Genuine 2,5-Diethoxy-4-tolylthiobenzene-diazonium Difluorophosphate called $Dz^+PO_2F_2^-$ (II)

The first part of the procedure is the same as that given in
section (3.2.i), but in this preparation 10.0 g (2.39×10^{-2} mol)
$Dz^+\frac{1}{2}(ZnCl_4^{2-})$ and 15.0 cm^3 (2.31×10^{-1} mol) difluorophosphoric
acid is used. The orange yellow filtrate, [*1] section (3.2.i) obtained
after filtering off the PF_6^- salt is extracted with dichloromethane;
the colour is taken up by the organic layer almost immediately. The
solution is washed thoroughly three times with doubly-distilled water;
each time the aqueous layer is slightly coloured. The organic
solution is evaporated to dryness at 308-313 K on a Buchi rotatory
evaporator, to obtain a yellow-brown solid. The product is vacuum-
pumped overnight at 6.0×10^{-1} N m^{-2}, giving 2.5 g (6.0×10^{-3} mol)
of the salt, i.e. 25% yield relative to the starting $Dz^+\frac{1}{2}(ZnCl_4^{2-})$.
The yellow-brown solid, when scraped from the sides of a round-
bottom flask gives lighter colour, yellow-orange material. The
infra-red spectrum of the compound, section (3.2.v) shows it to be
the difluorophosphate salt. The $Dz^+PO_2F_2^-$ (II) was recrystallised,
by the procedure given in section (2.3) for $Dz^+PF_6^-$, to yield ca. 1.0 g
(2.4×10^{-3} mol) of the purified salt which was analysed for C, H, N,
F and Cl, Table (15). This data shows that the material is in fact
difluorophosphate salt with a trace impurity of the starting tetrachloro-
zincate.

Table (15)

Analysis of $Dz^+PO_2F_2^-$ (II) for C, H, N, F and Cl

		C	H	N	F	Cl
$Dz^+PO_2F_2^-$ (II)	%F	49.09	4.57	6.84	9.36	0.19
$Dz^+PO_2F_2^-$	%EX	49.04	4.60	6.73	9.13	-
$Dz^+PF_6^-$	%EX	44.35	4.16	6.08	24.76	-
$Dz^+\frac{1}{2}(ZnCl_4^{2-})$	%EX	48.73	4.57	6.69	-	16.92

3.2.v   Infra-red Spectra of Arenediazonium Salts

The IR spectra of $Dz^+PF_6^-$, $Dz^+PO_2F_2^-$ (I) and (II), $Dz^+\frac{1}{2}(ZnCl_4^{2-})$, $Dz^+BF_4^-$ and $Dz^+SbF_6^-$ were recorded (in nujol mull) using either Perkin-Elmer 457 or 621 instruments. The spectra of $Dz^+PF_6^-$ and $Dz^+PO_2F_2^-$ (I) are identical, and are characterised by the absorption peaks[234, 235] at ca. 552 and 838 cm^{-1}. Whilst the spectrum of $Dz^+PO_2F_2^-$ (II) (i.e. the authentic salt of difluorophosphate) shows absorption peaks[235] at ca. 491, 512, 1140 and 1324 cm^{-1}, Fig. (25), the tetrachlorozincate salt (starting material for the syntheses) shows absorption peaks[236, 237] at 262, 278 and 290 cm^{-1} which are strong but not well-resolved, and at 378 cm^{-1}. The anions of $Dz^+BF_4^-$[238] and $Dz^+SbF_6^-$[234, 239] salts were also identified by IR spectroscopy.[240]

3.2.vi   Attempted Polymerisation of PO and Epikote 828 by $Dz^+PO_2F_2^-$ (II)

A 2.0×10^{-3} mol dm^{-3} solution of $Dz^+PO_2F_2^-$ (II) in neat PO was prepared and irradiated in an optical-cell viscometer; complete decolouration occurs within ca. 120 s. However, no change in viscosity was found to occur after 24 h. A more concentrated solution (2.0×10^{-2} mol dm^{-3}) was irradiated for ca. 720 s in the same way as above. [When photolysing solutions of this strength, it is impossible to define when complete photolysis has taken place because the decomposition products impart a dark orange colour to the reaction mixture]. Again no increase in viscosity of the solution was observed, and the ^{1}H n.m.r. spectra of the solutions showed that no polymerisation had occurred.

Similarly, 2.0×10^{-3} and 1.0×10^{-2} mol dm^{-3} solutions of $Dz^+PO_2F_2^-$ (II) in Epikote 828 (10.0 g) and 1,2-dichloroethane (total volume 25.0 cm^3) were prepared, and irradiated in the optical-cell viscometers, for 240 and 2,160 s respectively. Virtually no increase in viscosity of the solution was observed 24 h after photoinitiation, indicating that no polymerisation had occurred.

We conclude that $Dz^+PO_2F_2^-$ is ineffective as a photoinitiator for epoxide polymerisation and that the patent referring to its usage is probably void.
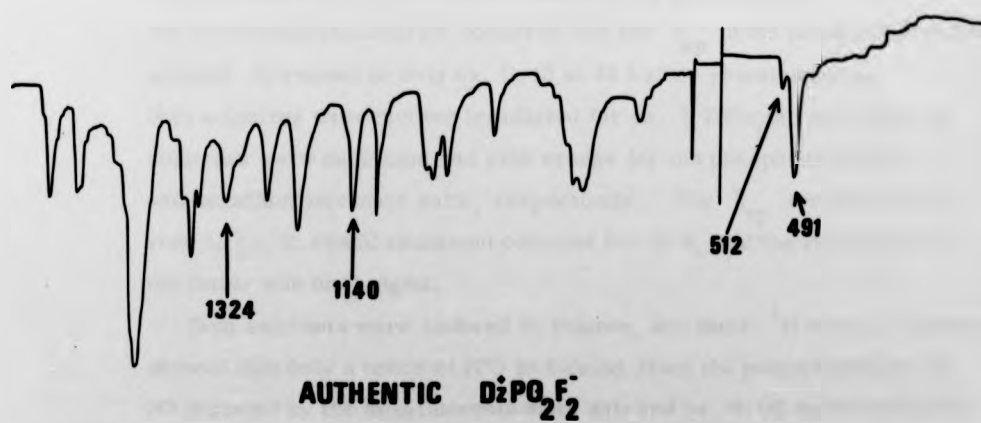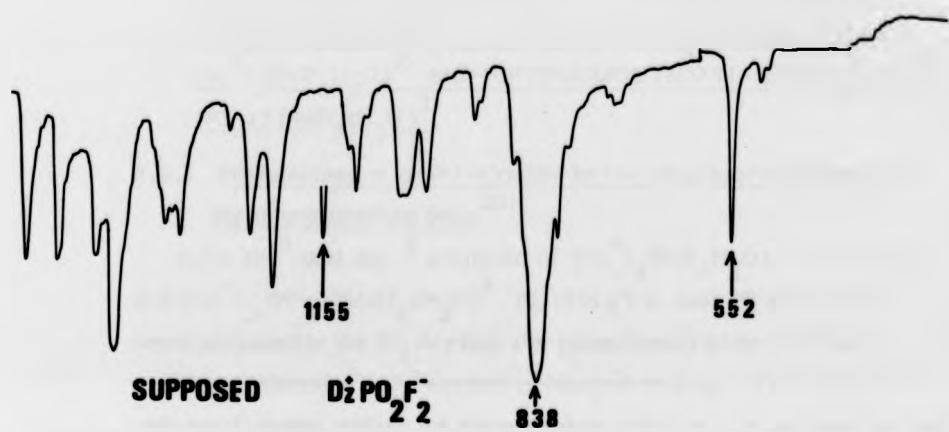
Figure (25)

Infra-red spectra of arenediazonium salts

Upper: $Dz^+PO_2F_2^-$ (I)

Lower: $Dz^+PO_2F_2^-$ (II)

3.3 PHOTOPOLYMERISATION OF 1,2-EPOXIDES INITIATED BY 2,5-DIETHOXY-4-TOLYLTHIOBENZENEDIAZONIUM TETRA-FLUOROBORATE CALLED $Dz^+BF_4^-$, TETRACHLOROZINCATE CALLED $Dz^+_{\frac{1}{2}}(ZnCl_4^{2-})$, HEXAFLUOROSTANNATE CALLED $(Dz^+)_2(SnF_6H_2O)^{2-}$ AND PHOSPHOMOLYBDATE CALLED $(Dz^+)_3-(PO_4 12 MoO_3 xH_2O)^{3-}$

3.3.1 Polymerisation of PO initiated by the Hexafluorostannate and Phosphomolybdate Salts[201]

2.0×10^{-3} mol dm^{-3} solutions of $(Dz^+)_2(SnF_6H_2O)^{2-}$ (0.0441 g) and $(Dz^+)_3 (PO_4 12MoO_3 xH_2O)^{3-}$ (0.1384 g) in neat PO (25.0 cm^3) were prepared in the N_2 dry box; the phosphomolybdate salt was difficult to dissolve and required prolonged shaking. The resulting solutions, green-yellow for the phosphomolybdate salt and deep orange for the hexafluorostannate salt, were irradiated in optical-cell viscometers for 240 and 720 s, respectively; the former solution turned dark green and the latter remained unchanged. (Note - the usual irradiation time for the solution of $Dz^+PF_6^-$ in neat PO is ca. 90 s). The resulting mixtures were placed in a constant-temperature water bath at 298 K and the change in their viscosity was monitored. No detectable change in the flow-time of the fluorostannate solution occurred and the η_{sp} of the phosphomolybdate solution increased to only ca. 0.13 at 24 h after photoinitiation Both mixtures were further irradiated for ca. 7,200 s, and the resulting solutions were dark blue and pale orange for the phosphomolybdate and hexafluorostannate salts, respectively. The η_{sp} for the former rose to ca. 0.16 and remained constant for 16 h, and the flow time of the latter was unchanged.

Both solutions were reduced in volume, and their ^1H n.m.r. spectra showed that only a trace of PPO is formed from the polymerisation of PO initiated by the hexafluorostannate salt and ca. 9.0% by the phospho-molybdate salt. Polymerisation of PO initiated by the phosphomolybdate salt in ^1H n.m.r. tubes shows ca. 5-8% conversion to PPO. The polymer samples isolated from the above reaction mixtures were not

characterised because these viscous liquids contain large amounts
of decomposed initiator and it was thought that the inorganic
components might damage the GPC columns. The hexafluorostannate
and phosphomolybdate initiators were not studied further because
(i) they yield very low percent conversion to polymer and (ii) the
difficulty encountered in determining whether photodecomposition
of the initiator has occurred or not.

3.3.ii Polymerisation of PO initiated by the Tetrafluoroborate and Tetrachlorozincate Salts

2.0×10^{-3} mol dm^{-3} solutions of Dz$^+$BF$_4^-$ (0.0160 g) and
Dz$^+_\frac{1}{2}$(ZnCl$_4^{2-}$) (0.0158 g) in neat PO (20.0 cm^3) were prepared in
the N$_2$ dry box and irradiated at 298K in the optical-cell with internal
cooling (10 cm^3 pathlength). Complete decolouration of the solutions
occurs within ca. 150 s. The polymerising mixtures were allowed to
stand in the optical-cell for 1,800 s and then in 100 cm^3 round bottom
flasks overnight. The resultant mixtures were reduced in volume
using a Buchi rotary evaporator, weighed and their ^{1}H n.m.r.
spectra recorded. The tetrachlorozincate salt gave no isolable polymer;
however, the ^{1}H n.m.r. spectrum shows the presence of trace
amounts of PPO. The tetrafluoroborate salt gives ca. 0.4 g of polymer
compared with 4.0 to 4.5 g usually obtained from the hexafluorophosphate
salt.

A 2.0×10^{-2} mol dm^{-3} solution of Dz$^+$BF$_4^-$ (0.8005 g) in neat PO
(100.0 cm^3) was prepared in the N$_2$ dry box, and photolysed in a
250.0 cm^3 round bottom flask for ca. 7,200 s. The resulting mixture
is an intense orange-brown colour and therefore it was not possible to
determine whether the complete photodecomposition of the arene-
diazonium salt had occurred. The solution was allowed to stand over-
night, and its ^{1}H n.m.r. spectrum showed ca. 15% conversion to
polymer. The polymerisation reactions carried out in ^{1}H n.m.r.
tubes gave ca. 15-18% conversion to PPO. The GPC traces of the
polymer samples isolated from the above mixtures show two large
peaks at low $\bar{M}$ end [namely $\bar{M}_p$ of ca. 140-148 (large peak) and

175-185 (small peak)] with a very long tail to high $\bar{M}$, ca. 100,000. However, the values of $\bar{M}$ obtained by GPC are not the actual molecular weight values of the PPO samples, section (2.7).

3.3.iii Distillation of Polymerised Reaction mixture of PO obtained from the $Dz^+BF_4^-$

A polymerised reaction mixture of PO distilled at atmospheric pressure and tap water pump pressure (2.0×10^3 N m^{-2}) gave a PO fraction only. A distillation carried out at much lower pressure, using a rotary oil pump, gave the PPO fractions listed in Table (16).

Table (16)

Fraction	Bath oil temp/K	Distil head temp/K	Pressure N m^{-3}	% Yield	Colour
A	up to 353	ca.337 (334-338)*	2.7-4.0 (9.3)*	50.2 (40.4)*	Colourless
B	358-383	343	2.7-4.0	8.4	Colourless
C	383-398	Up to 358	ca. 8.0	6.0	Colourless
D	398-437	358-365	ca. 8.0	6.9	Slightly purple
Residue				28.5	Yellow-Black

* A distillation, by Kern,[65] of polymerised mixture obtained from the polymerisation of PO using $(EtO)_3^+BF_4^-$ salt. This fraction was shown to be a cyclic $(PO)_4$.

Note - at bath oil temperature of ca. 400 K, the polymerised residue turns a very dark yellow-black colour.

The C and H elemental analysis, Table (17), for the major fraction, A, are in very good agreement with (i) those expected for a cyclic oligomer (all of which share the same C, H and O analyses) and (ii) the results obtained by Kern[65] for a cyclic tetramer.

Table (17)

Elemental analyses of the major fraction of polymerised mixture of PO obtained using $Dz^+BF_4^-$

Element	% Expected[*]	% Found	
		T.S. Bal	R.J. Kern
Carbon	62.04	61.67	62.4
Hydrogen	10.41	10.55	10.5

[*] for a cyclic oligomer of PO.

The IR spectrum of the fraction A, recorded as a film of neat liquid using the Perkin-Elmer 621 instrument, shows (i) that there is no terminal hydroxyl or carbonyl groups present, and (ii) the C-O stretching band of the polymer is resolved into four strong overlapping bands at 1,067, 1,086, 1,110 and 1,143 cm^{-1} (again in agreement with Kern's work). By contrast, the IR spectra of the fractions B, C and D show (i) fairly strong absorption in the hydroxyl region, ca. 3,530 cm^{-1}. (ii) a weaker but significant absorption band in C=O region, ca. 1,725 cm^{-1} and (iii) the C-O stretching absorption band is unresolved. The IR spectrum of the residue of distillation shows absorption bands which are the same as those in spectra of fractions B, C and D, but is further complicated by the presence of large amounts of decomposed initiator ; for example, there are three bands in the benzene absorption region at ca. 1,495, 1.575 and 1,600 cm^{-1} due to aryl-H vibration frequencies.

The ^{1}H n.m.r. spectra of the fractions A, B and C were virtually identical and showed resonance peaks in the polymeric region only (section 2.6.v). However, the spectrum of fraction D gave additional peaks in olefinic and allylic regions at ca. τ = 4.90 and 8.02 respectively. These may be due to either a slight contamination of this fraction with the decomposition products of initiator [note the slightly purple colour this fraction, Table (16)] or the presence of these groups in the polymer chains.

The mass spectra of fractions A, B, C and D were obtained using a VG micromass model 12 instrument operating at an ionising potential of 70 eV, and a range of source temperatures up to 423 K. The

fraction A gave major peaks at values of m/e of 45, 59, 73, 87, 103, 115, 116, 117, 129, 130, 131, 143, 145, 159, 161, 175, 217 and a parent-ion peak at 232 (4 x 58) and parent-ion plus one peak at 233. The parent-ion minus 18 peak, at a m/e value of 214 (which is usually present in the mass spectra of alcohols, aldehydes and ketones due to the loss of H_2O) is absent.

The above data obtained by infra-red and mass spectroscopy and elemental analysis shows an excellent agreement with the results (i) expected for a cyclic oligomer, $(PO)_4$ and (ii) those published by Kern,[65] and Katnik and Schaefer.[64] Therefore we conclude that the major product of polymerisation of PO initiated by $Dz^+BF_4^-$ is a cyclic tetramer. The mass spectra of fractions B, C and D gave parent-ion and parent-ion plus one peaks at values of m/e of 290 (5 x 58) and 291 respectively.[65] However, these samples are likely to be a mixture of compounds (as shown by the O-H and C=O absorption bands in their IR spectra and the presence of olefinic and allylic protons in fraction D determined by ^1H n.m.r. spectroscopy) which may include a cyclic pentamer $(PO)_5$.

3.3.iv Polymerisation of Epikote 828 initiated by the Tetrafluoro-borate and Tetrachlorozincate Salts

A 2.0×10^{-3} mol dm^{-3} solution of $Dz^+BF_4^-$ and $Dz^+\frac{1}{2}(ZnCl_4^{2-})$ in Epikote 828 (10.0 g) and 1,2-dichloroethane (25.0 cm^3) were prepared, and 20.0 cm^3 of each solution were irradiated for ca. 420 s in the optical-cell viscometers. The plots of η_{sp} versus time, Fig. (26), show that $Dz^+BF_4^-$ gives only a small amount of polymer-isation compared with $Dz^+PF_6^-$ and $Dz^+SbF_6^-$, and that there is virtually no increase in the η_{sp} of the mixture initiated by $Dz^+\frac{1}{2}(ZnCl_4^{2-})$. Molecular weights of the resultant mixtures were determined by GPC and the traces obtained, Fig. (27), show that there is a very small amount of high $\bar{M}$ polymer formed in the polymerisation reactions initiated by $Dz^+BF_4^-$ and $Dz^+\frac{1}{2}(ZnCl_4^{2-})$.

Figure (26)

Polymerisation of Epikote 828 (10.0 g) in 1, 2- dichloroethane (total volume 25 cm^3) initiated by the various arenediazonium salts $(2.0 \times 10^{-3}$ mol dm$^{-3})$

Plots of η_{sp} versus time

A : $Dz^+\frac{1}{2}(ZnCl_4^{2-})$

B : $Dz^+BF_4^-$

C and D : $Dz^+PO_2F_2^-$ (I) This is actually 1.8×10^{-3} mol dm^{-3} solution of $Dz^+PF_6^-$, see section (3.2).

E : $Dz^+PF_6^-$, section (3.1).

F : $Dz^+SbF_6^-$, section (3.4).

oethane (total volume 25 cm^3)

(10^{-3} mol dm^{-3})

$^{-3}$ mol dm^{-3}

section (3.2).
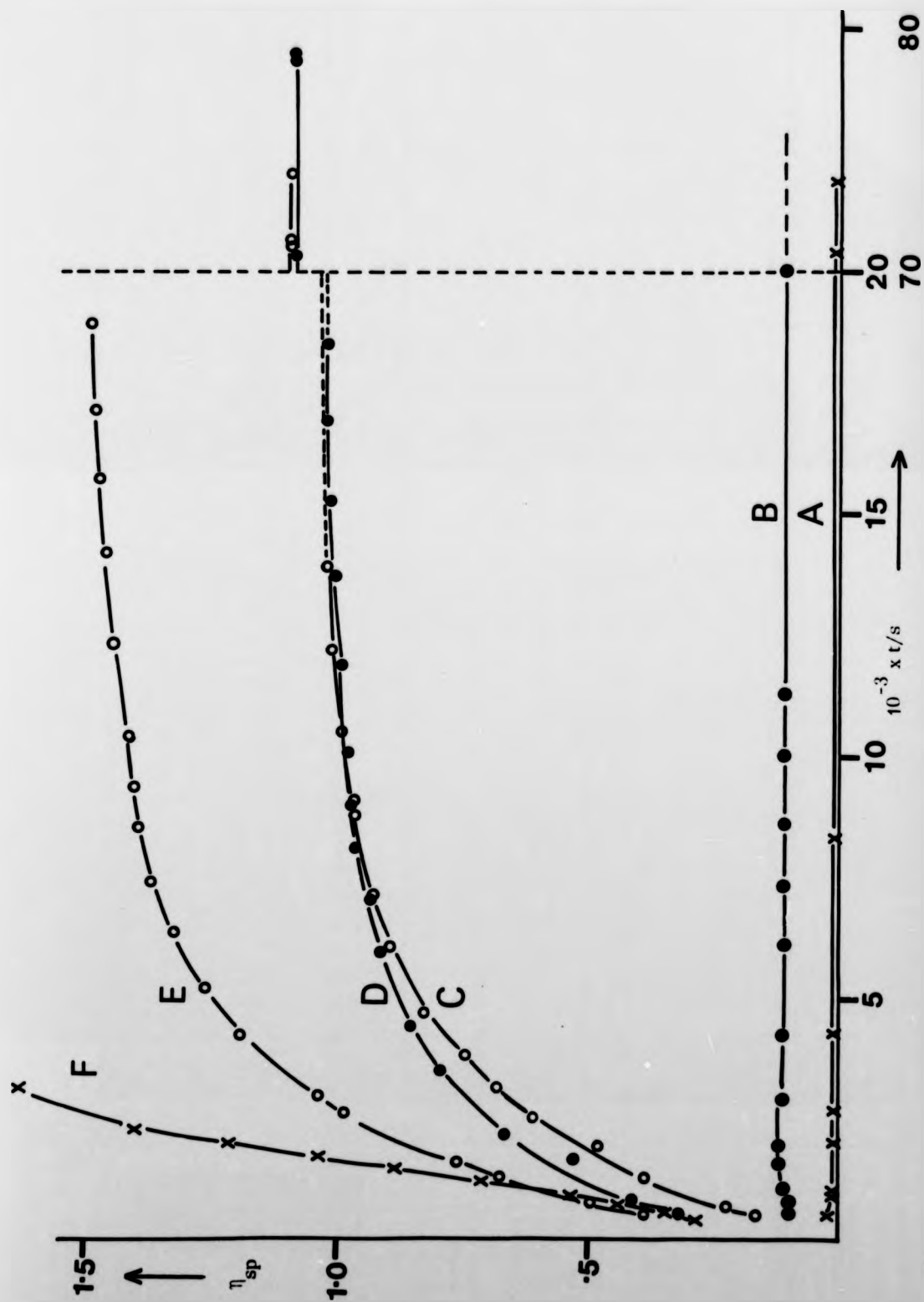
Figure (27)

GPC traces of polymerised reaction mixtures of Epikote 828 initiated by the various arenediazonium salts

			$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A :	$Dz^+PF_6^-$		3,436	25,540	7.43
B :	$Dz^+BF_4^-$	B1	1,029	3,916	3.81
		B2	291	295	1.01
C :	$Dz^+\frac{1}{2}(ZnCl_4^{2-})$		8,795	14,100	1.60

Epikote 828 initiated

$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
540	7.43
916	3.81
295	1.01
100	1.60

C

B1

B2

A

80

90

100

110

120

Elution Volume (EV)
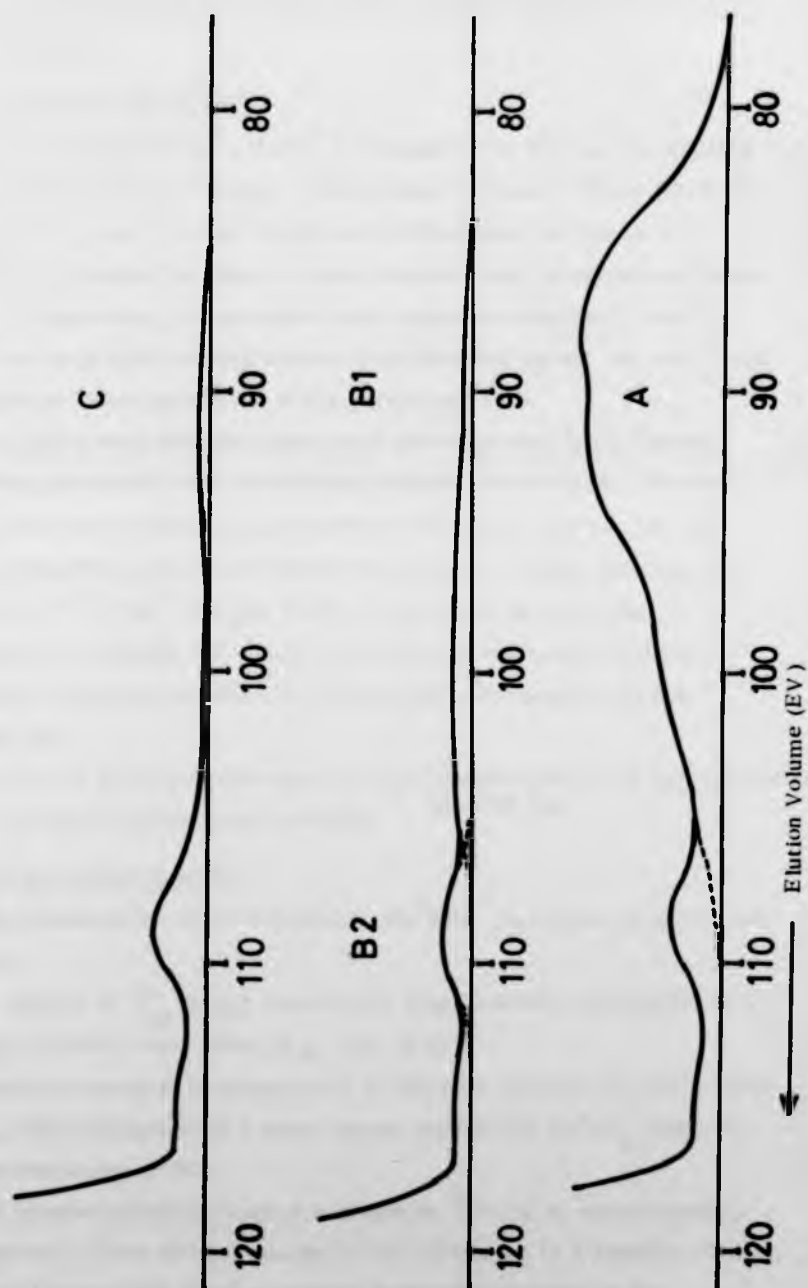
3.4 PHOTOPOLYMERISATION OF PO, BuO AND EPIKOTE 828 INITIATED BY $Dz^+SbF_6^-$

3.4.i Preparation of $Dz^+SbF_6^-$

5.0 g (0.012 mol) of $Dz^+\frac{1}{2}(ZnCl_4^{2-})$ is dissolved in 400 cm^3 of distilled water and filtered through celite. The filtrate is cooled to below 273 K in an ice/salt bath, and 5.0 cm^3 (0.026 mol) of hexafluoroantimonic acid $(HSbF_6.6H_2O$ supplied by Alfa) is added dropwise with continuous stirring. There is an immediate precipitation of the arenediazonium salt which is filtered and thoroughly washed with ice-cold distilled water, and then dried in an evacuated desiccator over silica gel for ca. 12 h.

The bright yellow arenediazonium salt was dissolved in a minimum amount of acetone (AR) and the resulting solution was filtered. The salt was precipitated by adding a large excess of Et_2O and filtered, and then washed thoroughly with ice-cold ether and dried by vacuum pumping on a line at 6.7×10^{-1} N m^{-3} for ca. 1.5 h. A further fraction of salt is precipitated by reducing the volume of the filtrate and adding more Et_2O. The yield of combined fractions is 81% relative to the starting arene-diazonium salt.

The anion of the arenediazonium salt was identified by its IR spectrum which shows a strong absorption peak at 658 cm^{-1}. [234, 239, 241]

3.4.ii Polymerisation of PO

The polymerisation of PO initiated by $Dz^+SbF_6^-$ is characterised by the following:-

(i)　The shapes of η_{sp} versus time curves [Fig. (28)] are very similar to η_{sp} versus concentration plots [e.g. Fig. (6)A].

(ii)　There is a gradual increase in $\bar{M}$ of PPO as a function of time, Table (18), which occurs over a much longer period than $Dz^+PF_6^-$-initiated polymerisation of PO.

(iii)　The course of polymerisation followed by ^1H n.m.r. spectroscopy, Table (19), shows that the amount of PPO increases as a function of time.

These observations indicate that the increased viscosity of the polymerising mixture is due to increases both in amount and $\bar{M}$ of polymer.

Figure (28)

Viscometric runs for the polymerisation of PO
initiated by $Dz^+SbF_6^-$

Sample	$[Dz^+SbF_6^-]$ mol dm^{-3}	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A:	2.0×10^{-3}	-	-	-
B:	2.0×10^{-3}	2,631	6,277	2.39
C:	7.5×10^{-4}	2,811	7,671	2.73
D:	7.5×10^{-4}	-	-	-
E:	2.0×10^{-4}	9,823	28,830	2.94
F:	2.0×10^{-3} $Dz^+PF_6^-$ (control)	-	-	-
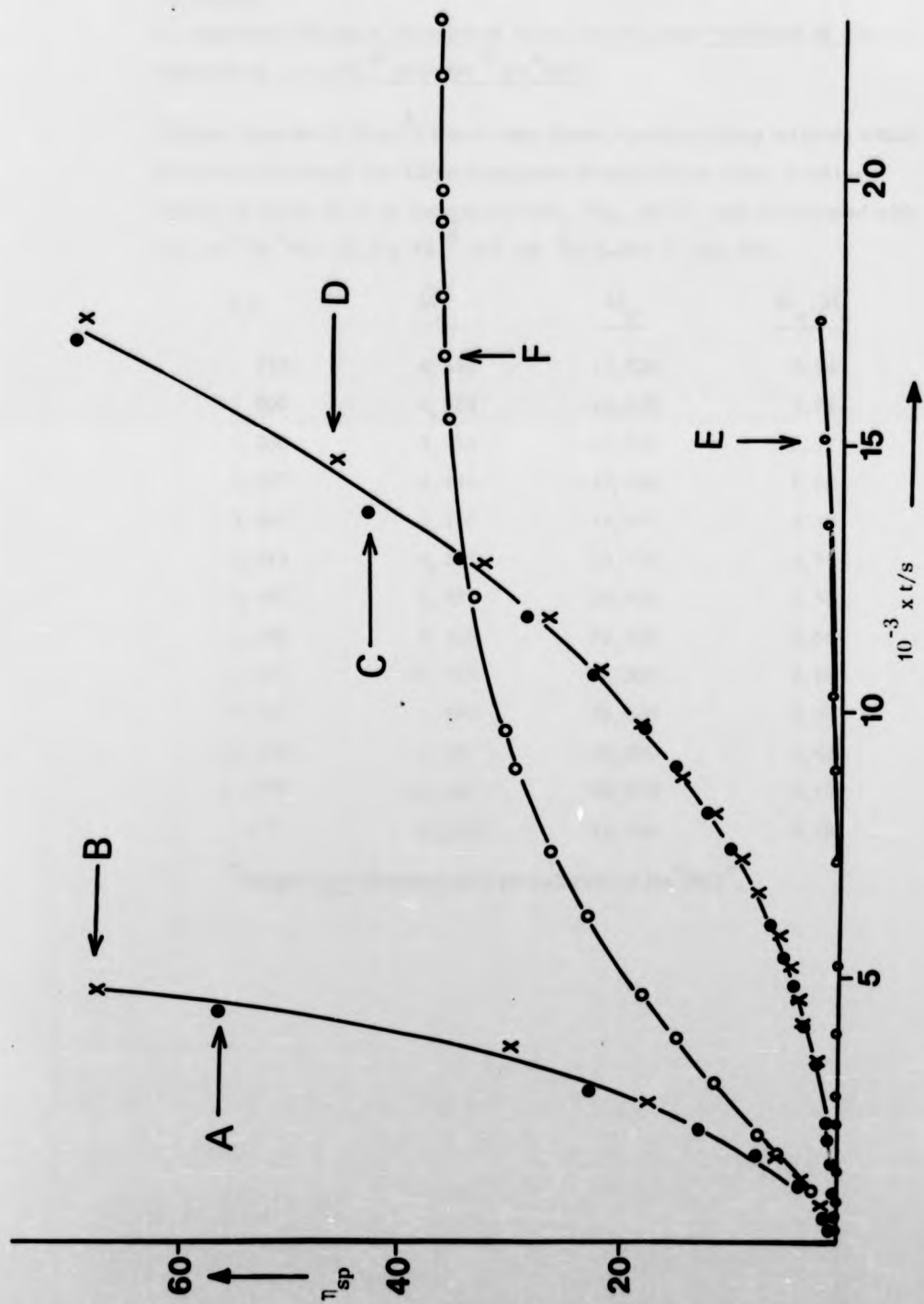
ion of PO

w	$\bar{M}_w/\bar{M}_n$
	-
277	2.39
671	2.73
	-
830	2.94
	-

B

A

D

C

F

E

η_{sp}

60

40

20

$10^{-3} \times t/s$

5

10

15

20

Table (18)

$\bar{M}$ values of PPO as a function of time for the polymerisation of neat PO initiated by 7.5×10^{-4} mol dm^{-3} Dz^{+}SbF$_{6}^{-}$

Aliquot samples (1.0cm^{3}) were taken from a polymerising mixture which had been irradiated for 120 s (complete decolouration of the solution occurred within 90 s) in an optical-cell, Fig. (9) D, and terminated with 1.0 cm^{3} Na^{+}PhO^{-} (5.0×10^{-3} mol dm^{-3}) solution in neat PO.

t/s	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
210	4,336	11,020	2.54
605	3,589	14,020	3.91
1,260	3,254	12,930	3.97
1,835	4,441	15,820	3.56
2,467	3,386	14,890	4.40
3,915	4,839	22,170	4.58
5,405	8,490	29,980	3.53
6,310	8,865	32,480	3.66
7,210	16,730	35,300	2.11
9,725	8,890	36,060	4.05
10,805	5,830	38,950	6.68
12,075	12,660	39,570	3.13
∞ *	5,0760	14,160	2.79

*Sample not terminated with solution of Na^{+}PhO^{-}.

Table (19) Per cent conversion to PPO, determined by ^{1}H n.m.r. spectroscopy as a function of time for the polymerisation of neat PO initiated by $Dz^+ SbF_6^-$

2.0×10^{-4} mol dm^{-3} $Dz^+ SbF_6^-$		5.0×10^{-4} mol dm^{-3} $Dz^+ SbF_6^-$		1.0×10^{-3} mol dm^{-3} $Dz^+ SbF_6^-$	
t/s	%PO(monomer)	t/s	%PO(monomer)	t/s	%PO(monomer)
1,620	96.2	1,100	90.7	565	85.8
2,550	93.1	2,230	84.7	1,572	54.2
4,560	89.7	3,060	81.9	2,645	49.1
7,020	82.2	3,915	78.9	3,480	45.9
10,620	78.8	4,785	77.1	4,350	42.9
13,740	74.1	5,640	74.6	5,232	39.8
16,260	72.6	7,210	70.4	6,060	38.5
19,980	68.7	9,300	67.2	6,800	37.2
22,680	66.6	10,480	65.1	7,620	36.3
25,500	64.4	11,640	64.4	8,870	35.3
83,250	47.6	13,180	62.1	9,745	33.9
98,880	46.2	15,250	59.7	11,140	32.0
106,140	45.3	16,635	58.5	12,025	31.3
199,800	36.1	18,150	56.4	12,785	31.0
5 days	26.4	58,080	38.1	14,830	28.5
16 days	17.2	90,141	30.2	15,970	27.8
		173,940	23.1	57,480	11.7
				173,520	9.5

However, the amount of PPO may increase either by an addition of PO to the existing PPO chains or by formation of further polymer units. The data given in Tables (18) and (19) (i.e. referring to a small increase in $\bar{M}$ and a very large increase in per cent conversion) indicates that both a growth in length of propagating species and chain-transfer to form further polymer units must occur concurrently. Furthermore, the $\bar{M}$ value of the unterminated fraction, Table (18) * , is much lower than those of samples which are terminated in the later stages of polymerisation by reaction with Na^+PhO^-. This indicates that the chain-transfer process must continue until the most probable (thermodynamic) distribution of $\bar{M}$ is achieved.

At the most probable $\bar{M}$ distribution,[16, 242] the ratio $\bar{M}_w/\bar{M}_n = 2$. In this work, however, the $\bar{M}$ values, Table (18), show a broader distribution due to adsorption of PPO on GPC (styragel) columns, section (2.7). The samples which have been terminated with Na^+PhO^- give higher $\bar{M}_w/\bar{M}_n$ values than those left unterminated because of the presence of a range of growing chains in the former which are not present in the latter, since it represents an overall equilibrium distribution of molecular weights.

3.4.iii The Effect of Na^+PhO^- upon Polymerisation of PO

The results obtained by adding $1.0 cm^3$ Na^+PhO^- (1.0×10^{-2} mol dm^{-3}) solution in neat PO to a polymerising reaction mixture initiated by 2.0×10^{-4} mol dm^{-3} $Dz^+SbF_6^-$ are summarised as follows:-

(i) There is no further increase in viscosity of the solution.

(ii) A lower per cent conversion to PPO is obtained (i.e. 24 h after photo-initiation, ca. 22% of polymer is detected by ^1H n.m.r. spectroscopy compared with 37% for the control).

(iii) The terminated sample shows higher $\bar{M}$ values than the control because the unterminated sample will yield a 'most probable' $\bar{M}$ distribution, section (3.4.ii).

From the above data we conclude that Na^+PhO^- is an effective terminator of post-irradiation polymerisation of PO initiated by $Dz^+SbF_6^-$, and therefore the overall mechanism of polymerisation must be cationic.

3.4.iv Effect of H_2O upon Polymerisation of PO

To a polymerisation mixture [1.0×10^{-3} mol dm^{-3} Dz$^+$SbF$_6^-$ in neat PO (20.0 cm^3)], 0.02 cm^{-3} (5.6×10^{-2} mol dm^{-3}) H_2O was added prior to photoinitiation and the following results, Table (20), were obtained:

(i) The increase in η_{sp} of the solution is greatly diminished.

(ii) A smaller conversion to PPO is achieved.

(iii) $\bar{M}$ of the resultant PPO is greatly reduced.

Table (20)

Effect of H_2O (5.6×10^{-2} mol dm^{-3}) added prior to Photoinitiation

	η_{sp}	% PPO after 3 days	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
H_2O	3.9 at 12,329 s	88	4,419	9,596	2.17
Control	74.3 at 12,453 s	93	5,515	20,400	3.70

Addition of large amounts of H_2O (2.65 mol dm^{-3}) similarly leads to greatly diminished η_{sp} and $\bar{M}$ values; however, in this case, conversion to PPO increases to virtually 100%. The low $\bar{M}$ of isolated PPO is attributed to H_2O acting as a transfer agent, and the increase in per cent conversion to polymer is discussed in section (3.4.vi).

Table (21)

Effect of a large amount of H_2O (2.65 mol dm^{-3}) added to 6.4×10^{-4} mol dm^{-3} Dz$^+$SbF$_6^-$ solution in neat PO prior to photoinitiation

	η_{sp}	% PPO after 24 h	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
H_2O	0.2 at 13,938 s	ca. 100	276	294	1.07
Control	24.1 at 14,320 s	65	4,523	9,796	2.17

3.4.v Polymerisation of BuO

The kinetic data, Tables (19) and (22), show that the rate of polymer-isation of BuO initiated by 2.0×10^{-4} mol dm^{-3} Dz$^+$SbF$_6^-$ is much greater than that of PO. Consequently a smaller concentration of Dz$^+$SbF$_6^-$ ($2.0 \times$

10^{-4} mol dm^{-3}) is required for the viscometric runs of BuO, Fig. (29)B, to produce the same viscosity change as in PO (7.5 x 10^{-4} mol dm^{-3} $Dz^+SbF_6^-$), Fig. (29) C. If the concentration of $Dz^+SbF_6^-$ is increased to that used for PO (7.5 x 10^{-4} mol dm^{-3}), an uncontrolled polymerisation reaction occurs which results in loss of some of the polymerising mixture, Fig. (29) A.

A ten-fold decrease in the concentration of $Dz^+SbF_6^-$ led to only a small increase in the $\bar{M}$, Table (23), of the resultant PPO, indicating the importance of the chain-transfer process.

Table (23)

Effect of $Dz^+SbF_6^-$ concentration on $\bar{M}$ of the resultant PBuO

$[Dz^+SbF_6^-]$ mol dm^{-3}	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1.0 x 10^{-3}	4,772	12,310	2.58
5.0 x 10^{-4}	5,862	14,630	2.50
1.0 x 10^{-4}	7,600	19,640	2.58

3.4.vi   Kinetics of Polymerisation of PO and BuO (neat liquids) initiated by $Dz^+SbF_6^-$

The data, Table (19) and (22), concerning per cent conversion to polymer as a function of time, determined by ^{1}H n.m.r. spectroscopy, can be analysed to obtain fourth- and seventh-orders of reaction for the polymerisation of PO and BuO, respectively.   However, these very high values for the order of reaction are probably due to (i) a very large increase in viscosity of the polymerising mixtures which restricts the availability of monomer for further reaction, and (ii) the large heat of polymerisation which causes an increase in temperature of the polymerising solutions especially during the early part of the process (for example, the polymerisation of neat BuO initiated by 8.0 x 10^{-4} mol dm^{-3} $Dz^+SbF_6^-$ in an n.m.r. tube shows an increase in temperature of 12, 3 and 1.5 K after 400, 3,900 and 10,700 s , respectively, from start of photoinitiation).

Table (22)   Per cent conversion to PhO, determined by ^{1}H n.m.r. spectroscopy, as a function of time for the polymerisation of neat BuO initiated by $Dz^+ SbF_6^-$

2.0×10^{-4} mol dm^{-3} $Dz^+SbF_6^-$		1.0×10^{-3} mol dm^{-4} $Dz^+SbF_6^-$		1.0×10^{-4} mol dm^{-3} $Dz^+SbF_6^-$	
t/s	%BuO(monomer)	t/s	%BuO (monomer)	t/s	%BuO(monomer)
540	83.0	145	93.5	107	95.8
620	79.9	170	93.9	245	94.6
705	75.4	265	94.0	307	94.1
790	62.7	375	95.7	377	93.2
855	61.4	510	94.2	468	91.9
930	60.1	612	91.2	550	90.8
995	60.0	672	89.9	737	89.5
1,355	59.2	783	90.4	830	88.9
1,425	58.8	933	88.5	910	88.2
1,505	58.2	1,465	85.9	995	87.8
1,595	58.7	1,695	85.5	1,132	86.8
1,680	58.5	2,435	82.4	1,510	85.3
1,810	58.6	3,307	79.7	1,945	83.1
1,903	58.9	4,815	72.9	2,307	81.6
1,977	58.9	6,700	69.6	2,827	80.0
2,054	58.9	8,515	64.0	3,392	77.3
2,125	58.8	9,951	62.6	3,955	76.3
2,202	58.8	70,090	38.6	66,967	44.0
		ca. 5 days	34.0	ca. 5 days	40.7
		ca. 7 days	34.4	ca. 7 days	41.1

Figure (29)

Viscometric runs for the polymerisation of BuO initiated by $Dz^+SbF_6^-$

Sample	$[Dz^+SbF_6^-]$ mol dm^{-3}	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A:	7.5×10^{-4}	4,879	12,790	2.62
B:	2.0×10^{-4}	10,270	18,490	1.80
C:	7.5×10^{-4} PO (control)	2,811	7,671	2.73

X - approximately 300 s after start of photo-initiation, violent ebullition occurs, which results in loss of some of the polymerising reaction mixture.
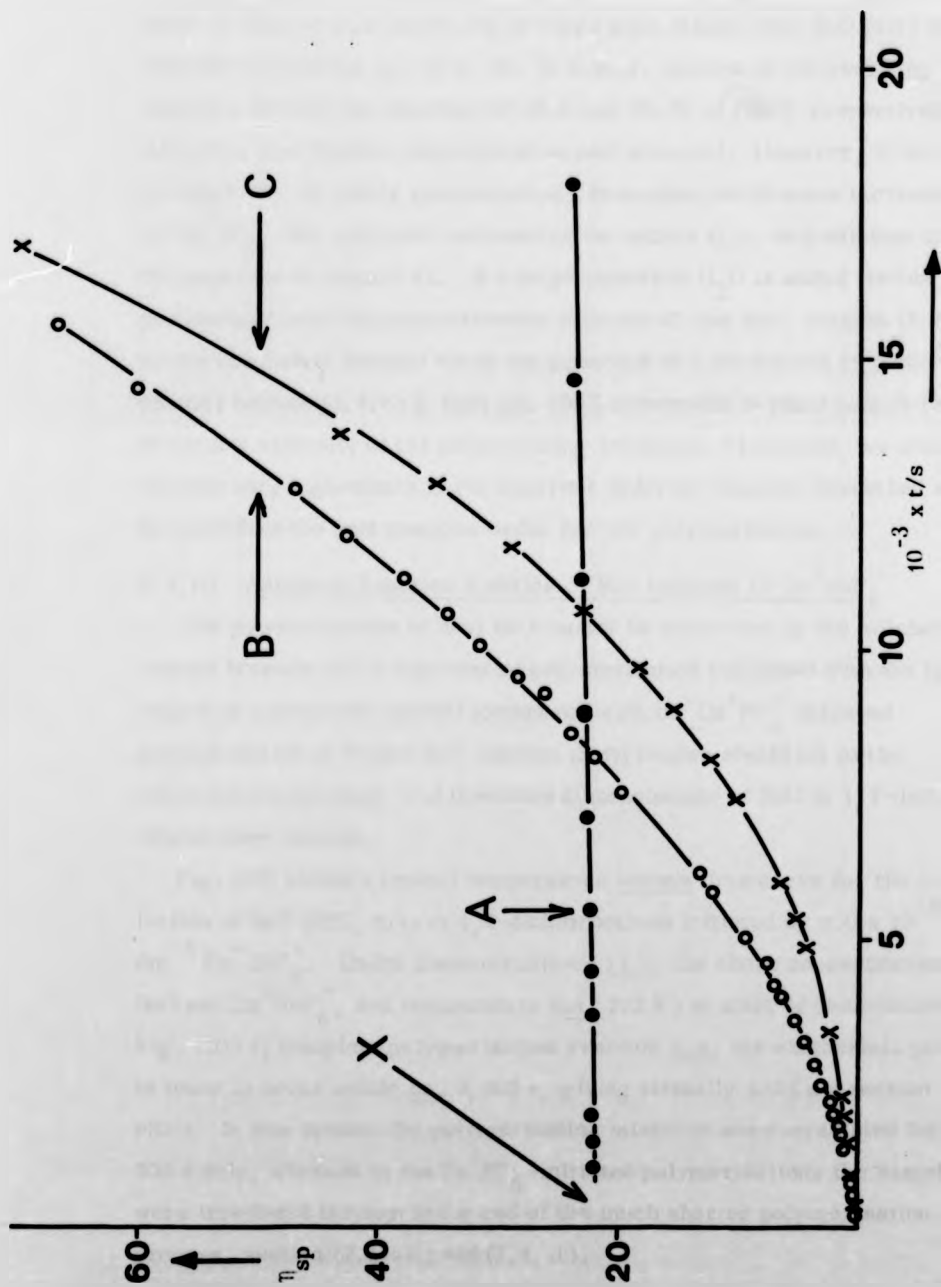
initiated by $Dz^+SbF_6^-$

$\bar{M}_w/\bar{M}_n$

790   2.62

490   1.80

671   2.73

itiation, violent

of the polymerising

C

B

A

X

η_{sp}

60

40

20

$10^{-3} \times t/s$

5   10   15   20

The effect of viscosity is demonstrated by the further polymerisation of prepolymerised mixtures by adding monomer. Polymerised mixtures which contained 48.0 and 59.0% of PBuO were diluted with BuO (1:1) and allowed to stand for ca. 24 h; the ^{1}H n.m.r. spectra of the resulting solutions showed the presence of 42.0 and 57.3% of PBuO, respectively, indicating that further polymerisation had occurred. However, if BuO is added (ca. 48 h after photoinitation) to samples which were initiated by $Dz^+PF_6^-$ then no further polymerisation occurs (i.e. only dilution of the mixtures is observed). If a large amount of H_2O is added (before photoinitiation) to the polymerisation mixture of neat BuO, section (3.4.iv), or the reaction is carried out in the presence of a co-solvent (1,2-dichloro- ethane) section (3.4.vii), then ca. 100% conversion to PBuO occurs because of the low viscosity of the polymerising solutions. Therefore, we conclude that the very high values of the apparent order of reaction described above do not reflect the true reaction order for the polymerisation.

3.4.vii Adiabatic Reaction Kinetics of BuO initiated by $Dz^+SbF_6^-$

The polymerisation of neat BuO cannot be monitored by the adiabatic method because of the high heat of polymerisation combined with the large degree of conversion to PBuO [compared with the $Dz^+PF_6^-$-initiated polymerisation of PO and BuO, section (3.1)] causes ebullition of the polymerising mixture, and therefore dilute solutions of BuO in 1,2-dichloro- ethane were studied.

Fig. (30) shows a typical temperature versus time curve for the polymer- isation of BuO (20%, v/v) in 1,2-dichloroethane initiated by 1.0×10^{-3} mol dm^{-3} $Dz^+SbF_6^-$. Under these conditions [i.e. the above concentrations of BuO and $Dz^+SbF_6^-$, and temperature (ca. 272 K) at start of photoinitiation, Fig. (30) I] complete polymerisation reaction (i.e. the exothermic process) is found to occur within ca. 3,000 s, giving virtually 100% conversion to PBuO. In this system the polymerisation mixtures were irradiated for ca. 300 s only, whereas in the $Dz^+PF_6^-$-initiated polymerisations the samples were irradiated through to the end of the much shorter polymerisation process, sections(2.6.vii) and (3.1.xi).

The temperature versus time curve, Fig. (30), can be divided into two parts (M and N). In part M it is possible that (i) further initiating species are formed by thermal decomposition of $Dz^+SbF_6^-$ and, (ii) the initiation step may be exothermic; both of these processes can contribute to a rapid initial increase in temperature which will diminish as they are completed. Analyses of part N of the curves, where these contributions are likely to be absent, give straight lines for first-order plots, Fig. (31). By contrast the plots for orders of reaction greater than one (particularly two) are non-linear (Fig. 32).

The values obtained for the activation energy, E_p (BuO), the first-order rate constant for the propagation step at 298 K, k_p (BuO) and the pre-exponential frequency factor, A (BuO), are given in Table (24). Although the use of a co-solvent allows E_p (BuO), A (BuO) and order of reaction to be determined, it must be noted that the polymerisations carried out in 1, 2-dichloroethane give much lower $\bar{M}$, Fig. (31), than neat BuO, Table (23).

Table (24)

The results* obtained from adiabatic reaction kinetics of the polymerisation of BuO in 1, 2-dichloroethane initiated by $Dz^+SbF_6^-$

Sample	k_p(BuO)/s^{-1} (at 298 K)	E_p (BuO) /kJ mol^{-1}	A (BuO)/s^{-1}
A	3.6×10^{-4}	75.7 ± 1.0	$(6.9 \pm 1.6) \times 10^9$
B	5.6×10^{-4}	66.9 ± 0.6	$(3.0 \pm 0.6) \times 10^8$
C	6.5×10^{-4}	64.0 ± 1.0	$(1.1 \pm 0.3) \times 10^8$
D	6.7×10^{-4}	58.5 ± 0.4	$(1.2 \pm 0.1) \times 10^7$
Average †	5.6×10^{-4}	66.9	3.0×10^8

* Slope and intercept values are obtained using a weighted linear least squares analysis (WLLSA) computer program for the points in part N of the plots given in Fig. (31).

† All data points in part N treated as a single run.

<u>Figure (30)</u>

<u>Adiabatic reaction kinetics of polymerisation of BuO (20%) in</u>
<u>1. 2-dichloroethane initiated by 1.0×10^{-3} mol dm^{-3} Dz$^+$SbF$_6^-$</u>

I - Start of irradiation

TI - Termination of irradiation

T_f - Final temperature

of BuO (20%) in
dm^{-3} Dz^{+}SbF$_6$$^{-}$

Figure (31)

Linearised temperature versus time curves for the polymerisation
of BuO initiated by $Dz^+SbF_6^-$

Sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A:	563	1,216	2.16
B:	862	1,918	2.22
C:	616	1,141	1.85
D:	576	1,127	1.96

for the polymerisation

$\bar{M}_w/\bar{M}_n$
2.16
2.22
1.85
1.96

Figure (32)

First-, second- and fourth-order of reaction plots for the adiabatic reaction kinetics of polymerisation of BuO

A: First-order plot of $\log_{10} P$ versus $1/T$

B: Second-order plot of $\log_{10} [P(T_f-T)]$ versus $1/T$

C: Fourth-order plot of $\log_{10} [P(T_f-T)^3]$ versus $1/T$

plots for the adiabatic

us 1/T

rsus 1/T

3.4.viii Polymerisation of Epikote 828

Since small concentrations of $Dz^+SbF_6^-$ led to a large viscosity increase in the polymerisation of PO, Fig. (28), and BuO, Fig.(29), then it was anticipated that ca. 7.5×10^{-4} mol dm^{-3} $Dz^+SbF_6^-$ would produce similarly acceptable η_{sp} versus time curves. However, it was found that the $Dz^+SbF_6^-$ concentration has to be greater than some threshold value (probably because of impurities that may be present in the epoxy resin) which lies between 1.0×10^{-3} and 2.0×10^{-3} mol dm^{-3}, for successful post-irradiation polymerisation to occur. This is demonstrated by the η_{sp} versus time curves, Fig. (33), and the $\bar{M}$ of the resultant pooymer, Table (25).

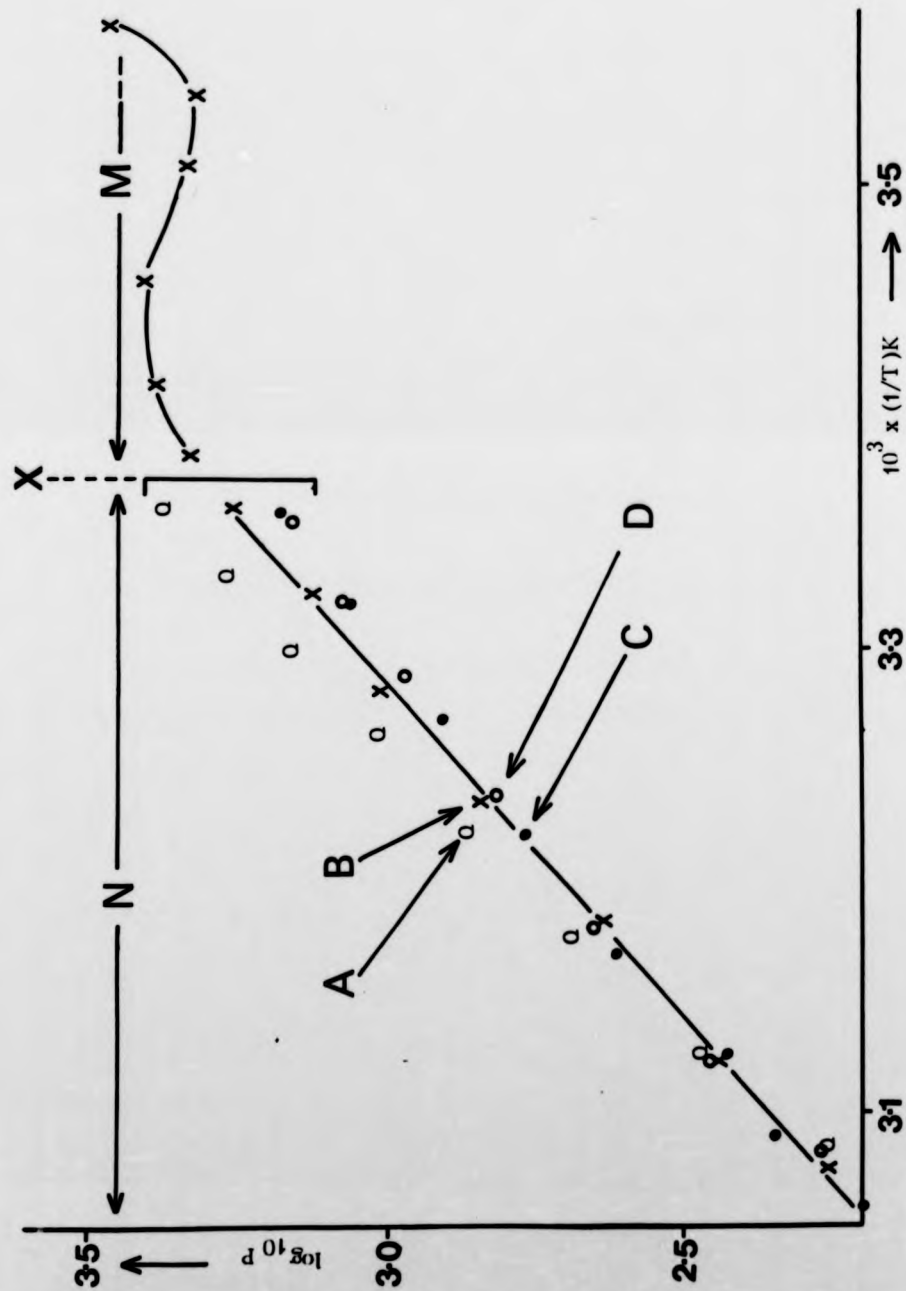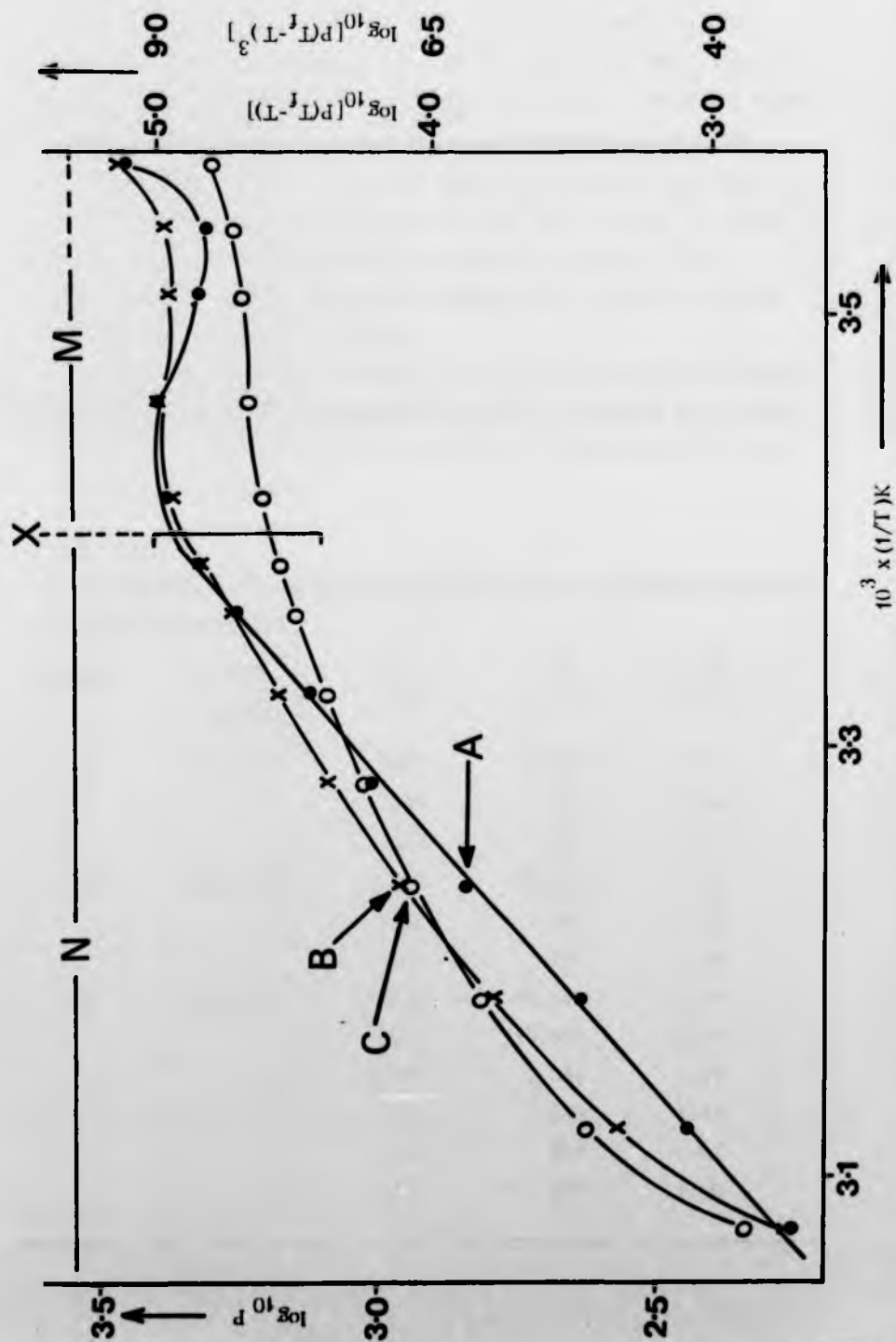At 2.0×10^{-3} mol dm^{-3} $Dz^+SbF_6^-$, the $\bar{M}$ of the resultant polyepikote 828 is very similar to that obtained from $Dz^+PF_6^-$ initiation (i.e. these results are consistent with the $\bar{M}$ data for PPO and PBuO which are also alike for both initiators).

Table (25)

$\bar{M}$ of Polyepikote 828 samples obtained from the polymerisation of Epikote 828 initiated by $Dz^+SbF_6^-$

Sample	$[Dz^+SbF_6^-]$ mol dm^{-3}	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
A	7.5×10^{-4}	965	2,484	2.57
		490	406	1.04
		233	235	1.01
B	1.0×10^{-3}	3,741	6,432	1.72
		379	387	1.02
		236	237	1.01
C	2.0×10^{-3}	24,550	54,150	2.21
		7,694	15,610	2.03
		1,834	2,034	1.11
		754	840	1.11
		432	442	1.02
		255	257	1.00

Figure (33)

Viscometric runs for the polymerisation of Epikote 828 (10.0 g) in 1, 2-dichloroethane (total volume 25.0 cm^3) initiated by Dz$^+$SbF$_6^-$

A: 7.5 x 10^{-4} mol dm^{-3} Dz$^+$SbF$_6^-$

B: 1.0 x 10^{-3} mol dm^{-3} Dz$^+$SbF$_6^-$

C: 2.0 x 10^{-3} mol dm^{-3} Dz$^+$SbF$_6^-$

9-

$\uparrow$

η_{sp}

7-

5-

3-

1-

ikote 828 (10.0 g)
initiated by $Dz^{+}SbF_6^{-}$

η_{sp}

9

7

5

3

1

C

B

A

5   10   15

$10^{-3} \times t/s$

3.5 POLYMERISATION OF PO INITIATED BY $SbCl_5$, $K^+SbF_6^-$, $NH_4^+PF_6^-$ AND $K^+PF_6^-$

3.5.i $SbCl_5$

A 'solution' of $SbCl_5$ in neat PO was prepared in the N_2 dry box as follows:-

(i)   The bottle containing $SbCl_5$ (Hopkins and Williams) when opened had a crust of oxidised material which was removed using a small screwdriver (the liquid gives off white fumes when exposed to the N_2 atmosphere).

(ii) A 2.0×10^{-2} mol dm^{-3} 'solution' was obtained by transferring 1.28×10^{-2} cm^3 of $SbCl_5$ into neat PO (25.0 cm^3) with a syringe. The resulting mixture was transferred into an optical-cell viscometer, and subsequently placed in a water bath at 298 K.

The flow-time of this mixture was 11.9 s (measured at 660 s from moment of addition of $SbCl_5$) compared with 11.3 s for neat PO, indicating that a little polymerisation had occurred. No further increase in viscosity was observed after 24 h, and an ^{1}H n.m.r. spectrum of the mixture showed only a trace of PPO. However, addition of four drops of $SbCl_5$ to 5.0 cm^3 of neat PO (0.23 mol dm^{-3}) caused an immediate violent reaction resulting in a dark green/brown mixture. An ^{1}H n.m.r. spectrum of this mixture recorded at 2 h showed ca. 24% conversion to PPO, which increases to ca. 45% after 24 h.

3.5.ii $K^+SbF_6^-$

A saturated solution of $K^+SbF_6^-$ (supplied by Alfa Products) in neat PO which had been allowed to stand at room temperature for ca. 20 h showed ca. 2% conversion to PPO. This mixture becomes very viscous ca. 2 weeks indicating extensive conversion to polymer.

3.5.iii $NH_4^+PF_6^-$ and $K^+PF_6^-$

Addition of a small quantity of $NH_4^+PF_6^-$ (Ralph N. Emanuel, Ltd., Wembley, England) to neat PO causes violent effervescence and loss of monomer, and the resulting mixture is very viscous, indicating the presence of large amount of polymer. By contrast, a saturated solution of $K^+PF_6^-$ (K and K Laboratories Inc., Plainview N.Y. Hollywood, Calif., U.S.A.) in neat PO shows no detectable (by ^{1}H n.m.r. spectroscopy) PPO after ca. 2 weeks.

DISCUSSION AND CONCLUSIONS

4.1 POLYMERISATION OF PO INITIATED (THERMALLY) BY SbCl$_5$, K$^+$SbF$_6^-$ AND NH$_4^+$PF$_6^-$

In this work we have shown that the polymerisation of PO can be initiated by the following:

(i) K$^+$SbF$_6^-$,

(ii) NH$_4^+$PF$_6^-$,

(iii) SbCl$_5$ and

(iv) photodecomposition products of Dz$^+$X$^-$ where X$^-$ = BF$_4^-$, PF$_6^-$, SbF$_6^-$.

In the absence of a cocatalyst such as H$_2$O, the initiation reaction due to SbCl$_5$ may be represented by eqns. (103) and (104) which are analogous to the initiation of polymerisation of THF by SbCl$_5$[111, 112] [eqn. (32)] and PF$_5$[107, 153] [eqn.(34)] respectively.

$$2\left[SbCl_5 \cdot O \overset{R}{\triangleleft}\right] \longrightarrow Cl_4SbOCH_2\overset{R}{\underset{SbCl_6^-}{C}}H - \overset{+}{O}\overset{R}{\triangleleft} \tag{103}$$

where R = CH$_3$

$$PF_5 \cdot O \overset{R}{\triangleleft} \longrightarrow \ldots \longrightarrow F_4P(OCH_2\overset{R}{CH})_2 \overset{PF_6^-}{\overset{+}{O}}\overset{R}{\triangleleft} \tag{104}$$

The possibility that two molecules of Lewis Acid (e.g. AsF$_5$) might self-ionise to initiate polymerisation has also been suggested,[67] as follows:

$$2As\,F_5 \longrightarrow AsF_6^- + AsF_4^+ \tag{105}$$

$$AsF_6^- + AsF_4^+ + M \longrightarrow AsF_4\underset{AsF_6^-}{M^+} \tag{106}$$

where M = monomer.

It must be noted, however, that under completely dry conditions BF$_3$ does not initiate the polymerisation of oxetane,[119] and THF[110] can be polymerised only at very high BF$_3$ concentration (i.e. in excess of 5 mole per cent).

Since there is no initiation of polymerisation by $K^+PF_6^-$, then NH_4^+ and SbF_6^- must be the active species of $NH_4^+PF_6^-$ and $K^+SbF_6^-$, respectively. The initiation reaction due to $NH_4^+PF_6^-$ may be represented as in eqn. (107).

$$NH_4^+PF_6^- + PO \longrightarrow \quad + NH_3 \longrightarrow \quad HOCHCH_2-O \qquad (10\ )$$

where $R = CH_3$

The very slow polymerisation due to $K^+SbF_6^-$ may be explained as follows:

(i) Unlike PF_6^-, SbF_6^- ions are readily hydrolysed by water,[244] and SbF_6^- is more likely to react with PO.

(ii) Fluoro complexes such as $Li^+SbF_6^-$ partially dissociate[243] to Li^+F^-; $K^+SbF_6^-$ is relatively less dissociated but some small degree of dissociation to form K^+F^- and SbF_5 may occur. Both of the above

processes may possibly lead to initiation of polymerisation: however, as we have noted these effects in passing and have made no detailed mechanistic studies, the above suggestions should be regarded only as speculation.

4.2 PHOTO-INITIATION OF POLYMERISATION BY ARENEDIAZONIUM SALTS

The polymerisation of THF initiated by $Ph_3C^+X^-$ and $p\text{-}ClC_6H_4N_2^+PF_6^-$ (thermal dediazoniation) involves an overall hydride ion abstraction to form Ph_3CH[99, 101] and chlorobenzene,[61] respectively. By contrast, the polymerisation of PuO initiated by $Ph_3C^+AsF_6^-$ occurs by the direct addition of a carbenium ion to the epoxide ring to form an ether similar to a model compound $Ph_3COC_2H_5$.[67]

The dediazoniation of arenediazonium salts induced by heat or light occurs via two pathways, eqns. (81) and (82), depending both on the type of substituent present on the benzene ring, and the nature of the solvent. The polymerisation of 1,2-epoxides may be initiated by either (i) the aryl cation on its direct addition to the epoxide ring or (ii) an abstraction of a hydrogen atom by Ar· radical as represented in eqns. (108) and (109) respectively. A third mechanism, discussed below, involves photoproduction of the free Lewis acid, which then acts as the initiator. Considering the aryl intermediates:

$$Ar^+ + PF_6^- + \underset{R}{\triangle^O} \longrightarrow Ar - \overset{+}{\underset{PF_6^-}{O}}\underset{R}{\triangle} \qquad (108)$$

$$Ar^\cdot + PF_6^\cdot + \underset{R}{\triangle^O} \xrightarrow[(a)]{} ArH + PF_6^\cdot + \underset{R}{\triangle^O}{}^\cdot \qquad (109)$$

$$\downarrow (b)$$

$$ArH + PF_6^- + \underset{R}{\triangle^{+O}}$$

where R = CH_3

$$\underset{R}{\overset{PF_6^-}{\underset{\triangle}{+O}}} \xrightarrow[(c)]{PO} \underset{PF_6^-}{R\overset{O}{C}CH_2 - \overset{+}{O}}\underset{R}{\triangle} \quad or \quad \underset{PF_6^-}{H\overset{O}{C}CHR - {}^+O}\underset{R}{\triangle}$$

Since the homolytic dediazoniation is favoured by the specific nucleophilic solvation, eqn. (83), then it is anticipated that addition of PhOH prior to photo-initiation would lead to modification of polymerisation of PO. However, the presence of 5.0×10^{-2} mol dm^{-3} PhOH in a polymerisation reaction mixture, 1.8×10^{-3} mol dm^{-3} $Dz^+PF_6^-$ in neat PO, before irradiation has no effect upon the η_{sp} versus time curve. Similarly, addition of further 1.06 mol dm^{-3} PhOH during the polymerisation process causes no observable change.[202]

In preliminary experiments (not presented here) we showed that the hexa-fluorophosphate salt of 2,5-diethoxy-4-tolylthiobenzenediazonium is a more effective initiator than that of 2,5-diethoxy-4-benzamidobenzenediazonium ion, and the 2,5-diethoxy-4-morpholinobenzenediazonium salt photo-induces no polymerisation of PO. Clearly, the efficiency of polymerisation of 1,2-epoxides by arenediazonium salts depend on (i) the substituents present on the benzene ring and (ii) the anion.

The arenediazonium salts listed in Table (26) show ground triplet states in their E.S.R. spectra on irradiation at 77 K; therefore, if these compounds decompose by the heterolytic pathway in the present system, then initiation of polymerisation by all of these salts is expected. However, the hexafluoro-phosphate analogue of salt C, Table (26), does not initiate polymerisation of PO, and we are inclined, therefore, to rule out Ar^+ as the active species, favouring instead the Lewis acid (see later).
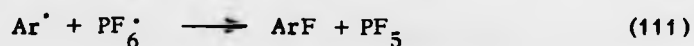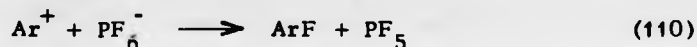
Table (26)

Arenediazonium salts[245] which show triplet states of Ar^+ in their E.S.R. spectrum following irradiation

A: 2,5-diethoxy-4-n-butylthiobenzenediazonium hexafluorophosphate

B: 2,5-diethoxy-4-benzamidobenzenediazonium tetrafluoroborate

C: 2,5-diethoxy-4-morpholinobenzenediazonium tetrafluoroborate

The formation of Lewis acids, which are known to initiate polymerisation [as in eqns. (103) to (106)] has been suggested by Licari,[182] eqn. (78). If $ArN_2^+X^-$ is in a form of tight ion-pairs in PO, then Lewis acids may be formed both by the heterolytic and homolytic pathways as in eqns. (110) and (111), respectively.

$$Ar^+ + PF_6^- \longrightarrow ArF + PF_5 \qquad (110)$$

$$Ar^\cdot + PF_6^\cdot \longrightarrow ArF + PF_5 \qquad (111)$$

If the initiation reaction is due to the Lewis acids, then the polymerisation will depend on (i) the strength of the Lewis acids (and therefore the anions) and (ii) the substituents on the benzene ring of decomposed diazonium salt (which may complex with Lewis acids). In this case, the added PhOH should have no effect.

If the initiation is by the aryl cation or the free radical, then the poly- merisation process is dependent not only upon the substituents on the benzene ring but also the nature of the anion (which may react with these species). From our present knowledge, it is impossible to define precisely the process of initiation ; however, the involvement of Lewis acids is favoured, particularly as known radical scavengers such as phenol are without effect on the extent and rate of polymerisation.

4.3 PHOTOPOLYMERISATIONS OF 1,2-EPOXIDES INITIATED BY $Dz^+PF_6^-$

The polymerisation of PO initiated by $Dz^+PF_6^-$ occurs in two stages; (i) Stage I is characterised by a very rapid polymerisation which gives ca. 14% PPO at 2.0×10^{-3} mol dm^{-3} $Dz^+PF_6^-$ and (ii) Stage II which leads to only a small further conversion to polymer over a longer period (15,000 - 20,000 s) without significant change in $\bar{M}$. By contrast, the polymerisation of BuO occurs as a single stage process which shows the characteristics of Stage I of that of

PO. The kinetic scheme proposed by Goethals[73] for the polymerisation of thietanes initiated by triethyloxonium tetrafluoroborate can be applied to the $Dz^+PF_6^-$/BuO system and this shows that (i) $k_p/k_t \approx 79.0$ and (ii) the termination reaction occurs between the oxygen atoms of dead polymer and the propagating species.

For the polymerisation of PO, it is likely that in Stage I the termination reaction is the same as in the case of BuO with subsequent further initiation by (i) a transfer reaction to a monomer, eqn. (112) and (iii) a termination-transfer reaction involving the non-strained tertiary oxonium ion of the polymer and the counter-ion which will generate a Lewis acid, eqn. (113).

$$R^1\!-\!\overset{\overset{\displaystyle R^2}{|}}{\underset{\underset{\displaystyle R^3}{|}}{O^+}}PF_6^- \xrightarrow[\text{transfer}]{\text{slow}}^{PO} \quad R^1\!-\!O\!-\!R^2 \;+\; R^3\!-\!\overset{+}{O}\!\!\underset{PF_6^-}{\overset{R}{\triangle}} \tag{112}$$

(112.I)   (112.II)

$$R^1\!-\!\overset{\overset{\displaystyle R^2}{|}}{\underset{\underset{\displaystyle R^3}{|}}{O^+}}PF_6^- \xrightarrow[\substack{\text{transfer-}\\\text{termination}}]{\text{slow}} \quad R^1\!-\!O\!-\!R^2 \;+\; R^3F \;+\; PF_5 \tag{113}$$

where R^1, R^2 and R^3 are polymer chains, and $R = CH_3$.

The absence of Stage II in the polymerisation of BuO is explained as follows:

(i) The ethyl group (CH_3CH_2-) is more electron donating than the methyl group (CH_3-) as shown by their pK_a values (viz. $CH_3CH_2COOH = 4.87$ and $CH_3COOH = 4.75$)[246] and, therefore, the tertiary oxonium ion (of the polymer oxygen atoms) formed at end of Stage I may be more adequately stabilised by BuO than PO.

(ii) The presence of bulkier side groups (CH_3CH_2-) in the polymer may prevent an attack on the oxonium ion by monomer, eqn. (112).

Both of these processes will inhibit further polymerisation.

The polymerisation of Epikote 828 [Fig. (34), in which the epoxide ring has large side groups] is like that of PO rather than BuO and, therefore, the steric effect mentioned above must be relatively unimportant. However, the presence of electronegative oxygen atoms (*) will provide a strong inductive

effect and therefore cause its polymerisation process to be more like that of PO rather than BuO (i.e. favour the initiation of Stage II). It must be noted that the viscosity of the polymerising mixture of Epikote 828 may be affected by (i) the presence of the solvent 1, 2-dichloroethane and (ii) cross-linking of the epoxy-resin, and therefore the linearisation of η_{sp} versus time curve may be fortuitous, Fig. (23.1). Nonetheless, the existence of Stage II of its polymerisation is clearly demonstrated in Fig. (23).

Figure (34) Epikote 828

4.4 PHOTOPOLYMERISATION OF 1, 2-EPOXIDES INITIATED BY $Dz^+SbF_6^-$

In the polymerisation of 1, 2-epoxides initiated by $Dz^+SbF_6^-$ there is a small amount of thermal initiation, which is shown by the presence of PPO in unirradiated solutions which have been allowed to stand for several days in the dark at 277 K. However, the extent of reaction is very small, as shown by the minute increase in viscosity (flowtime increases to 11.6 s from 11.3 s for neat PO) of the unirradiated polymerisation mixture after 1, 800 s at 298 K.

The polymerisation of PO and BuO initiated by $Dz^+SbF_6^-$ differs from that by other arenediazonium salts in that (i) a much smaller $Dz^+SbF_6^-$ concentration results in a greater extent of polymerisation[70] and (ii) pre-polymerised mixtures can be further polymerised by adding more monomer; both of these processes indicate a lack of overall termination of polymerisation.

The order of reaction, equal to one, obtained for the process of polymer-isation (by the method of adiabatic reaction kinetics) is difficult to explain in terms of the generally accepted scheme, eqn. (114), for the propagation of four- and five-membered cyclic ethers.[6, 53, 54, 61, 106]

$$M_n\!-\!\overset{+}{O}\!\!\!\overbrace{}\atop X^- \quad \overset{M}{\longrightarrow} \quad M_{(n+1)}\!\!=\!\!\overset{+}{O}\!\!\!\overbrace{}\atop X^- \tag{114}$$

where M = monomer and X = counter-ion.

Since the oxygen atom of the epoxide ring is the least nucleophilic of those of all cyclic ethers (the electron donor ability of the oxygen atom in the cyclic ethers decreases in order $4 > 5 > 6 > 3$)[117] then it is possible that the propagation process may not be a simple S_N2[54] process as represented in eqn. (29); in fact, propagation via a carbenium ion, eqn. (80), has been suggested by Schlesinger.[183] In the polymerisation of BuO initiated by $Dz^+SbF_6^-$, the rate-determining step may be the opening of the epoxide ring, eqn. (115).

$$(BuO)_n - \overset{+}{O}\!\!\underset{SbF_6^-}{\diagup\!\!\triangle\!\!\diagdown}\!\!-R \quad \xrightarrow{slow} \quad (BuO)_n - O - CH_2 - \overset{R}{\underset{H}{\overset{|}{\underset{|}{C}}}}{}^+ SbF_6^- \tag{115}$$

where $R = C_2H_5$

$$(BuO)_{n+1} - \overset{+}{O}\!\!\underset{SbF_6^-}{\diagup\!\!\triangle\!\!\diagdown}\!\!-R \quad \xleftarrow[\text{fast}]{BuO}$$

It must be noted that the ring-opening (thermal) polymerisation of 1,2-epoxides initiated by anionic, co-ordination and cationic catalysts occurs almost entirely with inversion of configuration at the carbon atom.[148-151] However, this is not inconsistent with a cationic mechanism of polymerisation of mainly S_N1 character because the counter-ion, which is adjacent to the oxygen atom before ring-opening, will migrate to a new position on that same side of a trigonal carbenium ion and thus favour an attack from the opposite side leading to an inversion of configuration.

The differences in the polymerisation of PO and BuO initiated by $Dz^+SbF_6^-$ may be explained as follows:

(i) The ethyl group is more electron-donating than the methyl group and therefore the oxygen atom of BuO will be more nucleophilic than that in PO and will favour the polymerisation reaction by lowering the activation energy, section (3.4.v). A similar effect operates in the polymerisation of 3,3-bis-(chloromethyl) oxetane where the presence of electrophilic chloromethyl groups reduces the rate significantly by withdrawing electrons from the oxygen atom.[122, 124, 126]

(ii) The viscosity increase in the polymerisation of BuO is likely to be greater (for the same percentage conversion of BuO and PO to PBuO and PPO,

respectively) than PO due to the larger side group of the former. This will retard the polymerisation process more rapidly and yield a higher 'apparent' order of reaction as obtained by ^{1}H n.m.r. spectroscopy, section (3.4.vi).

4.5 THE DIFFERENCES IN THE POLYMERISATION OF 1,2-EPOXIDES INITIATED BY ARENEDIAZONIUM SALTS WITH VARIOUS ANIONS

The extent of polymerisation of PO initiated by arenediazonium salts with various anions decreases in the order $SbF_6^- \gg PF_6^- > PO_4 12MoO_3 xH_2O^{3-} > BF_4^- > SnF_6^- > ZnCl_4^{2-} \approx PO_2F_2^-$. The results $SbF_6^- \gg PF_6^-$ and $PF_6^- > BF_4^-$ are consistent with the polymerisation of oxetane initiated by $Et_3O^+ SbF_6^-$ and PF_6^-,[70] and the curing of epoxy resins photo-initiated by $Dz^+ PF_6^-$ and BF_4^-,[185] respectively.

The polymerisation of PO initiated by $Dz^+ BF_4^-$ gives a cyclic tetramer as the major product, a result which parallels the polymerisation of PO using $Et_3O^+ BF_4^-$;[65] the possible mechanisms for this process have been discussed in section (1.6.iv). The products of the polymerisations initiated by arene-diazonium salts with $PO_4 12MoO_3 xH_2O^{3-}$ and SnF_6^- anions were not characterised.

The polymerisation of 1,2-epoxides initiated by $Dz^+ SbF_6^-$ proceeds without termination; by contrast the $Dz^+ PF_6^-$-initiated polymerisation ceases at limited conversion. This is demonstrated as follows:-

(i) Further polymerisation of pre-polymerised mixture (which had been initiated by $Dz^+ SbF_6^-$) can be achieved, section (3.4.vi).

(ii) Polymerisation of BuO (20% v/v) in 1,2-dichloroethane initiated by $Dz^+ SbF_6^-$ gives virtually 100% conversion to PBuO [i.e. greater conversion than in neat liquid, section (3.4.vi)]

(iii) Polymerisation of PO in the presence of cosolvent (50:50) initiated by $Dz^+ PF_6^-$ gives smaller conversion to PPO, section (3.1.iv).

The kinetic schemes applied to the polymerisation of PO and BuO initiated by $Dz^+ PF_6^-$, section (3.1.x), indicate that the termination process of Stage I is likely to be formation of non-strained tertiary oxonium ions of the type shown in (40.III) and (112.I). Since the $\overline{M}$ values of resultant polymers obtained from the polymerisations initiated by $Dz^+ SbF_6^-$ and $Dz^+ PF_6^-$ are similar, then the chain-transfer process must be equally important in both of

these systems. The following types of transfer reactions may be postulated:-

(i)   A process analogous to that represented in eqn. (30) [for THF]which requires the formation of a tertiary cyclic oxonium ion. However, this is unlikely because the opening of a four-membered ring such as oxetane is an irreversible process,[247] and therefore cyclisation to form a three-membered (more strained) ring would be even less (thermodynamically) favourable.

(ii) The reaction represented in eqn. (116) involves the formation of a carbenium ion. However, this is unfavourable because the tertiary oxonium ion (non-strained form) is thermodynamically more stable than the carbenium ion; in fact, the usual 'active' centre in the cationic polymerisation of 1, 2-epoxides is not a carbenium ion but rather an oxonium ion:[54, 248]

$$R^1OCH_2CHR \overset{+}{\underset{\underset{R^2}{|}}{-O}} - CH_2CHROR^3 \rightleftharpoons R^1OCH_2\overset{\overset{H}{|}}{\underset{\underset{R}{|}}{C}}X^- + R_2OCH_2CHROR^3 \quad (116)$$
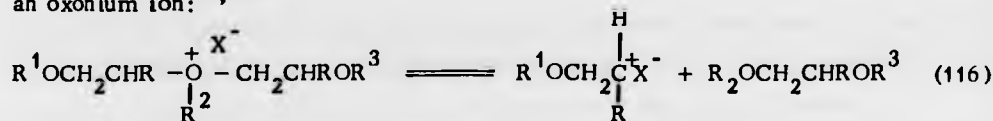
(iii)   The most likely transfer reaction is that given in eqn. (112), where the monomer attacks the non-cyclic tertiary oxonium ion to form 'dead' polymer and an 'active' cyclic oxonium ion (112. II) which can either propagate by reaction with monomer or cause further chain-transfer with polymer.

The larger extent of polymerisation of oxetane initiated by $Et_3O^+SbF_6^-$ (compared with $Et_3O^+PF_6^-$ and BF_4^-) is attributed to the longer effective lifetime of the active species[70] (however, no details of the termination reaction are given). In the present work it is likely that the termination-transfer reaction represented in eqn. (113) is more important in $Dz^+PF_6^-$-initiated polymerisation than for $Dz^+SbF_6^-$. Evidence for the transfer of fluorine atoms to the polymer chains was obtained by ^{19}F n.m.r. spectroscopy. The results of the preliminary ^{19}F n.m.r. experiments are summarised as follows:-

(i)(a)   A polymerised reaction mixture obtained from the polymerisation of PO initiated by 0.1 mol dm^{-3} $Dz^+PF_6^-$ shows a doublet peak centred at $\delta = -67.2$ (relative to CCl_3F which is used as a reference standard) due to PF_6^-,[249] and a broad peak at ca. -175.7 which we have tentatively assigned to a signal due to fluorine atoms attached to the terminal ends of the polymer chain;[250] [cf. poly(vinyl fluoride) which shows chemical shifts in the range $\delta = -174.5$ to -196.7].[251] There are a number of smaller peaks which at present are unassigned.

(b)   The spectrum of 2.0×10^{-3} mol dm^{-3} Dz^{+}PF$_6^{-}$ in neat PO (unirradiated) shows
an absorption peak due to PF$_6^{-}$ and absence of any peaks upfield from C$_6$F$_6$ (ca. -162.9).
However, there are a number of very small peaks (*) (which at present are unassigned)
at ca. -105.9, -108.4, -114.9, -117.7, -119.7, -130.1, -132.3, -133.4 and others.
In the spectrum of the polymerising mixture recorded at 1 h after photoinitiation,
there appear (i) two peaks at -59.8 and -60.7, which are virtually equal in intensity
to the doublet of PF$_6^{-}$, (ii) a broad peak at -177.1, and (iii) a marked increase in
intensity of the smaller peaks listed above (*). The spectrum of the above solution
recorded two weeks later is essentially unchanged, except for a small further increase in
the peak at -177.1.

(c)   The spectra of Dz^{+}PF$_6^{-}$ (2.0×10^{-3} mol dm^{-3}) in neat BuO are very similar to
PO, and at ca. 2 h and 24 h after photoinitiation the peaks listed above are observed.
However, there are three peaks upfield of C$_6$F$_6$ at ca. -176.8, -185.4 and -190.9.

(ii)(a) A polymerised reaction mixture obtained from the polymerisation of PO
initiated by 0.1 mol dm^{-3} Dz^{+}SbF$_6^{-}$ gives the following peaks: δ = -83.1 (very broad -
unassigned), -108.5 (strong singlet due to SbF$_6^{-}$),[249] -114 to -118 and -127 to -133
(collection of small peaks - unassigned), -145.5 (singlet virtually equal in intensity
to SbF$_6^{-}$ peak - unassigned) and -175.5 (broad and relatively weak, attributed to
fluorine atoms incorporated into the terminal end of polymer chain).

(b)   The spectra of 2.0×10^{-3} mol dm^{-3} Dz^{+}SbF$_6^{-}$ in neat PO (unirradiated) feature
two very weak peaks at -59.8 and -60.7, and a collection of peaks in the range -114 to
-132. There is also an intense peak due to SbF$_6^{-}$ at ca. -105.9 but no resonances
upfield from C$_6$F$_6$. At 1 h after photoinitiation, the SbF$_6^{-}$ absorption peak virtually
disappears and there are no resonances upfield of C$_6$F$_6$. 24 h later, a similar spectrum
is obtained.

(c)   The polymerisation of BuO (neat) initiated by Dz^{+}SbF$_6^{-}$ (2.0×10^{-3} mol dm^{-3})
shows no absorption peak due to SbF$_6^{-}$, but there is some resonance at ca. -184.7 due
to the fluorine atoms in the polymer chain.

(iii)   A spectrum of 0.1 mol dm^{-3} Dz^{+}BF$_4^{-}$ shows two absorption peaks (only) at ca.
-47.1[249] and -176.3 due to BF$_4^{-}$ and fluorine atoms in the polymer chains, respectively.

The results summarised above (although very preliminary) indicate that

(1)   The polymerisation of 1,2-epoxides (PO and BuO) initiated by Dz^{+}PF$_6^{-}$ and BF$_6^{-}$
involves incorporation of fluorine atoms into the polymer chains (probably in the
termination step).

(ii)   The propagating species in the $Dz^+PF_6^-$ and BF_4^--initiated polymerisations may carry its attendant counter-ions, namely PF_6^- and BF_4^- respectively.

(iii)   The polymerisation of BuO initiated by $Dz^+SbF_6^-$ involves the transfer of fluorine atoms to the terminal end of polymer chains; however, this does <u>not</u> occur in the polymerisation of PO initiated by 2.0×10^{-3} mol dm^{-3} $Dz^+SbF_6^-$.

(iv)   The polymerisation of both PO and BuO may <u>not</u> involve SbF_6^- as a counter-ion in the propagating species.

The terminating effect of PF_6^- upon the polymerisation of neat PO initiated by 7.5×10^{-4} mol dm^{-3} $Dz^+SbF_6^-$ is shown by the smaller increase in viscosity of the polymerising mixture (compared with the control) after 1.0 cm^3 saturated solution (concentration unknown) of $K^+PF_6^-$ in neat PO is added. However, approximately 70% conversion to PPO is obtained for both of the mixtures; this is explained in terms of insufficient amounts of PF_6^- present in the added sample to give complete termination and the ability of $Dz^+SbF_6^-$ to produce very large conversions to polymer at low concentrations, see Figure (35).

4.6   SUGGESTIONS FOR FURTHER WORK

Further work is necessary to define completely the nature of the photo-polymerisation of 1,2-epoxides initiated by arenediazonium salts and is suggested as follows:-

(i)   Information concerning the initiation process may be obtained by analysing the decomposition products (in propylene oxide) of arenediazonium salts, such as $Dz^+SbF_6^-$, PF_6^-, $PO_2F_2^-$, AsF_6^-, BF_4^-, etc. by ^{19}F n.m.r. and ^{31}P n.m.r. (where applicable) spectroscopy. However, it may be necessary to compare these spectra with those of model compounds, e.g. 2,5-diethoxy-4-tolylthio-1-fluorobenzene.

(ii) ^{19}F n.m.r. spectra of polymerised reaction mixtures of 1,2-epoxides initiated by SbF_3 and SbF_5 may be useful in interpreting the results obtained with $Dz^+SbF_6^-$.

(iii)   Polymerisation of 1,2-epoxides initiated by $Dz^+SbF_4^-$ (provided this compound can be prepared and the reactions carried out) will provide further useful information.

(iv) ^{19}F n.m.r. spectra of model compounds such as $-OCH_2CHRF$ and $-OCHRCH_2F$ (where $R = CH_3$ or C_2H_5) are required for comparison with those listed in this
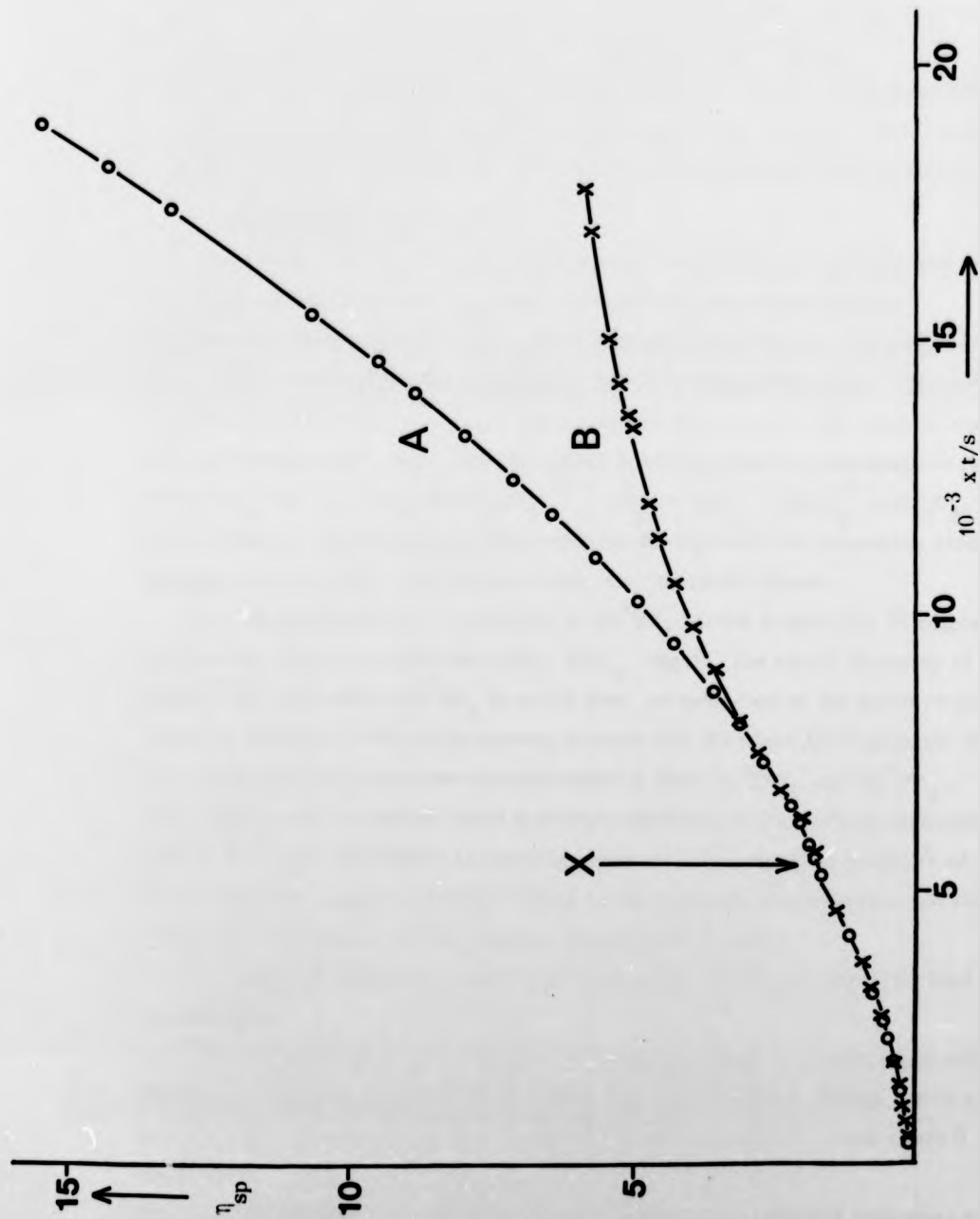
Figure (35)

Terminating effect of PF_6^- upon the polymerisation of neat PO initiated by 7.5×10^{-4} mol dm^{-3} $Dz^+SbF_6^-$

A: Control -1.0 cm^3 of neat PO is added at X

B: PF_6^- -1.0 cm^3 saturated solution (concentration unknown) of $K^+PF_6^-$ in neat PO is added at X.

isation of neat PO

x

entration unknown) of

thesis to confirm the termination process.

(v) To test whether the mechanism of propagation is $S_N 1$, as suggested in this work, or $S_N 2$, it would be useful to know whether the process of ring-opening occurs with inversion of configuration at the carbon atom or not.

(vi) ^{19}F n.m.r. spectra of polymerised reaction mixtures of 1, 2-epoxides initiated by $Ph_3C^+X^-$ (where $X = SbF_6^-$, PF_6^-, AsF_6^-, BF_4^-, $PO_2F_2^-$, etc.) would be useful for comparison with the arenediazonium salt-initiated polymerisations.

4.7 SUMMARISING REMARKS

In this work, we have shown that the polymerisation of 1, 2-epoxides can be photoinitiated with near u.v. light (with virtually no concurrent thermal initiation) by certain arylthio-substituted arenediazonium salts, and the process of the often very highly efficient polymerisation is exclusively ionic. The polymerisation reactions show a large dependence on the nature of the counter-ion of the arenediazonium salts, and the extent of polymerisation decreases in the order $SbF_6^- \gg PF_6^- > PO_4 12MoO_3 xH_2O^{3-} > BF_4^- > SnF_6^- > ZnCl_4^{2-} \approx PO_2F_2^-$. In this respect, the polymerisations contrast strongly with the ostensibly similar thermal initiations by carbenium salts, etc. of cyclic ethers.

The polymerisation of PO initiated by $Dz^+BF_4^-$ yields largely low $\bar{M}$ oligomers of which ca. 50% is a cyclic tetramer, $(PO)_4$. Again, the extent of curing of Epikote 828 initiated by $Dz^+BF_4^-$ is much less, as indicated by the much smaller viscosity increase of the polymerising mixture and the lower $\bar{M}$ of polymer than the analogous polymerisations photoinitiated by both $Dz^+SbF_6^-$ and $Dz^+PF_6^-$. The polymerisations photoinitiated by phosphomolybdate and hexafluorostannate salts of Dz^+ were not studied in detail because the decomposition products of these initiators impart an intense colour to the polymerising solutions and thus complicate the kinetics of the primary photoinitiation stage.

The polymerisation of 1, 2-epoxides initiated by $Dz^+PF_6^-$ is characterised by the following:-

(i) The polymerisation of PO occurs in two stages; Stage I is very rapid and yields ca. 14% conversion to PPO and Stage II is much longer, during which a small amount of further polymer is formed without an increase in the overall value of $\bar{M}$.

(ii) The polymerisation of BuO occurs in a single stage which is analogous to Stage I of that of PO. The termination reaction for this process involves the

pre-formed polymer and probably results in the formation of non-strained tertiary oxonium ions.

(iii) The polymerisations of both PO and BuO involve incorporation of fluorine atoms into the polymer chains (quite possibly as a result of termination of the active species).

(iv) The presence of cosolvents (such as 1,2-dichloroethane, dichloromethane and cyclohexane) in the polymerisation of PO leads to marked decreases in the percentage yields and $\bar{M}$ values of the resultant polymer.

(v) DPPH added during the process of polymerisation shows no observable effect on either the rate, extent or $\bar{M}$-value.

(vi) PhOH ($5.8 \times 10^{-2} : 2.0 \times 10^{-3}$/PhOH:Dz$^+PF_6^-$) added prior to photoinitiation, and during polymerisation ($1.06 : 2.0 \times 10^{-3}$/PhOH:initiator) also shows no observable effects on rate extent or $\bar{M}$-value.

(vii) The $\bar{M}$ of the resultant PPO is markedly decreased by the addition of H_2O, either prior to photoinitiation or during polymerisation.

(viii) There is no significant difference in the $\bar{M}$ values of PPO and PBuO.

(ix) PO is a better model compound for the study of the polymerisation of Epikote 828; this has been demonstrated by the presence of Stage II in the polymerisation of both PO and Epikote 828.

In contrast to other arenediazonium salt initiators, Dz$^+$SbF$_6^-$ leads to "living polymers" of both PO and BuO (i.e. the pre-polymerised reaction mixtures of BuO can be further polymerised by adding neat BuO 2 weeks after the original photoinitiation) and a very small amount of initiator is required to give a large conversion to polymer (e.g. 1.0×10^{-4} mol dm^{-3} Dz$^+$SbF$_6^-$ in neat BuO gives ca. 66% PBuO 7 days after photoinitiation compared with the performance of 2.0×10^{-3} mol dm^{-3} Dz$^+$PF$_6^-$ in neat PO and BuO, which yields final conversions of ca. 25 and 17%, respectively). However, for the polymerisation of Epikote 828, a Dz$^+$SbF$_6^-$ concentration greater than a threshold value of ca. 1.0×10^{-3} mol dm^{-3} is required to react with all the impurities present in the polymerisation mixture prior to initiating polymerisation.

The main features of the polymerisation of 1,2-epoxides initiated by Dz$^+$SbF$_6^-$ are as follows:-

(i)   The polymerisation process is characterised chiefly by an increase in percentage conversion to polymer and only a small change in $\bar{M}$.

(ii)   Addition of a large amount of H_2O leads to a much reduced $\bar{M}$ of resultant polymer (PPO) but no decrease in percentage conversion.

(iii)   A similar effect to (ii) is obtained with 1,2-dichloroethane as cosolvent.

(iv)   The polymerisation reaction can be completely terminated with Na^+PhO^-.

(v)   In the polymerisation of PO at low (2.0×10^{-3} mol dm^{-3}) initiator concentrations, no incorporation of fluorine atoms into the polymer chains is found, and it occurs to only a minor extent with BuO.

(vi) The $\bar{M}$ values obtained with PPO, PBuO and polyepikote 828 are very similar to those obtained with $Dz^+PF_6^-$ as initiator, and it is concluded therefore that chain transfer reactions must play an important role in these polymerisations.

(vii)   A reaction order of one is obtained for the heat liberating step, which is attributed to a unimolecular ring-opening of the highly strained oxonium ion.

(viii) ^{19}F n.m.r. spectra of polymerisation reaction mixtures indicate that SbF_6^- is unlikely to be present as the counter-ion to the propagating species.

From the results presented in this thesis, it is concluded that the photo-polymerisation of 1,2-epoxides initiated by arenediazonium salts are significantly different from those thermally initiated by $Ph_3C^+X^-$ (where $X^- = AsF_6^-$, SbF_6^- and PF_6^-),[66,67] and show a marked dependence on the anion. While this may well indicate the photo-released Lewis acid to be the initiator, the counter-anion may also have a leading role as a terminating agent. We incline against the view that either Ar^+ or $Ar^·$ are active initiators in view (i) of the failure of 4-morpholino salts to be active despite their ready production of Ar^+ and (ii) the failure of large amounts of phenol to inhibit polymerisation, despite the scavenging power of this molecule for primary radicals.

We have also shown that the patent[201] concerning the use of (alleged) 2,5-diethoxy-4-tolylthiobenzenediazonium difluorophosphate as a photoinitiator for the polymerisation of epoxy resins is void because (i) the anion in the above salt is in fact PF_6^-, and (ii) the genuine difluorophosphate salt (which has now been prepared and characterised) is ineffective as a catalyst.

Appendix: Effect of Oxygen upon Polymerisation of PO initiated by $Dz^+PF_6^-$

A 2.0×10^{-3} mol dm^{-3} solution of $Dz^+PF_6^-$ in neat PO was prepared in the N_2 dry box and split into two fractions (A and B). Fraction A was oxygenated by passing O_2 through the solution for ca. 1,500 s and fraction B was allowed to stand in the N_2 atmosphere. Aliquot samples (two from each solution) were transferred to ^1H n.m.r. tubes, and irradiated for ca. 20 s (i.e. to complete photolysis of $Dz^+PF_6^-$). ^1H n.m.r. spectra of the resulting mixtures (recorded at ca. 7,200 s after photoinitiation) gave ca. 19 ± 1 and 25 ± 1% PPO for the control (fraction B) and the oxygenated solution (fraction A), respectively, i.e. the extent of polymerisation is essentially unaffected by the presence of O_2 at saturation levels. This confirms our impression that no radical intermediates are involved in the polymerisation of 1, 2-epoxides photoinitiated by $Dz^+PF_6^-$.

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1