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STUDIES ON POLYENE CONTAINING HIGH POLYMERS

A Thesis

presented for the degree of

MASTER OF SCIENCE

in the Faculty of Science of the

University of St. Andrews

by

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April 1981

United College of St. Salvator
and St. Leonard, St. Andrews

SUMMARY

High polymers containing sequences of conjugated double bonds have been synthesised, both by polymerisation of alkyne monomers and by degradation of saturated polymers. The emission spectroscopic behaviour of these molecules is investigated, and found to be broadly similar for each of the systems used.

Correlation of emission spectroscopy results to reaction mechanism for degradation of Poly(Vinyl Acetate) is attempted.

Poly(Phenylacetylene) and Poly(3-Methylpentyne) have been reacted with I_2 , and the reaction followed by spectroscopic and conductivity measurements. Evidence for an efficient Charge Transfer reaction in the case of Poly(Phenylacetylene) is presented. Possible causes of the differences between the behaviour of the two polymers are discussed.

Degraded Poly(Vinyl Acetate) has been exposed to HCl, and a novel HCl catalysed deacetylation reaction found. Evidence for this, and a possible mechanism are given.

(i)

DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record was carried out by me, and that it has not been submitted in any previous application for a Higher Degree.

This thesis describes results of research carried out at the Department of Chemistry, under the supervision of Dr. J.R. MacCallum since the 1st of October 1977.

Stuart P. Fairgrieve

(ii)

CERTIFICATE

I hereby certify that Stuart P. Fairgrieve has spent eleven terms of research work under my supervision, has fulfilled the conditions of the Resolution of the University Court 1974 No. 2, and is qualified to submit the accompanying thesis in application for the degree of Master of Science.

J.R. MacCallum
Director of Research

ACKNOWLEDGEMENTS

I would like to record my thanks to Dr. James R. MacCallum for his help and encouragement in all aspects of this work.

I am indebted to the University of St. Andrews for a Research Studentship from 1977 to 1980, and to Professor Lord Tedder and Professor P.A.H. Wyatt for research facilities during this period.

I would like to thank the technical staff and others of the Chemistry Department for their help, especially Mrs. S. Johnson, librarian, for putting up with my endless requests for obscure journals, and Mr. M. Zochowski for translations from Russian and Polish.

I would finally like to record my grateful thanks to Mrs. W. Pogorzelec for typing this thesis under the severe handicap of my handwriting.

"That which I report herein I have seen with
mine own eyes, and do not repeat from the heresay
of others"

Thucydides "The Pelepponesian War"

(v)

To

H.P.F.

A.F.F.

and

A.R.

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SUMMARY

High polymers containing sequences of conjugated double bonds have been synthesised, both by polymerisation of alkyne monomers and by degradation of saturated polymers. The emission spectroscopic behaviour of these molecules is investigated, and found to be broadly similar for each of the systems used.

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SECTION A - BACKGROUND

The chemical and theoretical study of polyene systems was a neglected field for almost thirty years between 1940 and the beginning of the 1970's; the bulk of spectroscopic and concurrent Quantum Mechanical (QM) work being devoted to aromatic systems during this time. The reasons for this state of affairs were:-

a) During the 1930's extensive work by Kuhn, Hausser and co-workers¹ had comprehensively investigated the synthesis, characterisation, and spectroscopic study of the polyenes of various homologous series.

b) The initial theoretical calculations of the LCAO-MO theory of polyenes by Mulliken² explained the state ordering perfectly well, in fact this was one of the early successes of semi-empirical QM and was held up as proof of the correctness of the assumptions made.

Anomalies had been noted however in the results obtained, particularly the large differences between the experimental and calculated fluorescence lifetimes, and energy gaps between the fluorescence and absorption O-O transitions. These had been explained in terms of Frank-Condon effects by Mulliken, but one vital fact which remained unexplained was that shifts in energy of spectral bands, brought about by changes in solvent refractive index, were totally different for the absorption and emission spectra.

In 1972, with the arrival of more sophisticated spectroscopic techniques, and faster methods of calculating QM parameters, two papers appeared which challenged the above conclusions, and brought

about a fundamental reappraisal of the excited state ordering of the polyenes, and of the SCF-MO basis sets required for QM calculations on such compounds.

In the last decade, the renewed study of polyene systems has increased rapidly, splitting into two main fields; the investigation of the spectroscopic, and hence excited state properties, of short polyene sequences, and the investigation of the electrical properties of long sequences.

As noted above, the starting point for the extensive work done on polyene spectroscopy came in 1972 with the publication of papers by Hudson and Kohler³, and Schulten and Karplus⁴. Hudson and Kohler presented evidence from high resolution spectroscopy of α,ω -Diphenyloctatetra-1,3,5,7-ene (DPO) that the first excited state is not the ^1Bu state associated with the first strong $^1\text{Ag}-^1\text{Bu}$ absorption, but is a $^1\text{Ag}^-$ state associated with a symmetry forbidden $^1\text{Ag}-^1\text{Ag}$ transition. Since the emission photon must return to the ground state from the lowest excited state, this new state ordering explains all the anomalies noted; since the absorption and emission are due to two different excited states, not the same one, as assumed up till then. This result however is in direct contradiction to the state ordering obtained from simple LCAO-MO theory.

Schulten and Karplus obtained theoretically the same state ordering as Hudson and Kohler by the inclusion of doubly excited configurations used in the Pariser-Parr-Pople (PPP) calculations. The $^1\text{Ag}^-$ state, which is one of a pair of nearly degenerate states,

has a valence-like charge distribution and appears to consist of predominantly double excitations relative to the ground-state Hartree-Fock configuration⁵. This state is therefore significantly lowered in energy by the inclusion of double-excited configurations; on the other hand, the ^1Bu state is a diffuse Rydberg state, and is only slightly affected by the inclusion of higher excitation levels. Further work by Tavan and Schulten⁶, using triply and quadruply excited configurations, has refined this model until it now gives reasonable explanations for almost all the spectroscopic behaviour of polyenes.

Extensive work carried out by various authors since 1972⁷⁻¹⁴ has established that this state ordering applies in most polyene systems, although some anomalies remain for very short sequences¹⁵, and for *s-cis* conformers¹⁶.

Graphically, the differences between the Mulliken, and the Hudson-Kohler models can be shown as in Fig. A-1.

Polyenes have proved a fruitful area of research in the field of organic conductors and semi-conductors, the possibility of large conducting films as opposed to single crystals as found for systems such as TTF-TCNQ has particularly attracted attention.

Each CH fragment in a polyene chain has an odd number of electrons, ie. a polyene should behave as a metal, however, QM calculations have shown that, in the ground state, bond alternation should persist even for long polyenes, resulting in a filled valence band, and an unfilled conductance band with a band gap between

therefore these materials behave as semi-conductors¹⁷. The persistence of bond alternation has been confirmed by X-Ray analysis¹⁸.

Recent studies¹⁷ have concluded that the band gap present in long chain polyenes is not entirely due to bond alternation, but includes a large contribution from electron-electron interactions. Theoretical calculations predict effects at long length that point towards significant contributions from doubly excited modes for the transition from valence to conductance band, which ties in well with the results noted already for large contributions by doubly excited configurations in the First Excited $^1\text{Ag}-^1\text{Ag}$ transition.

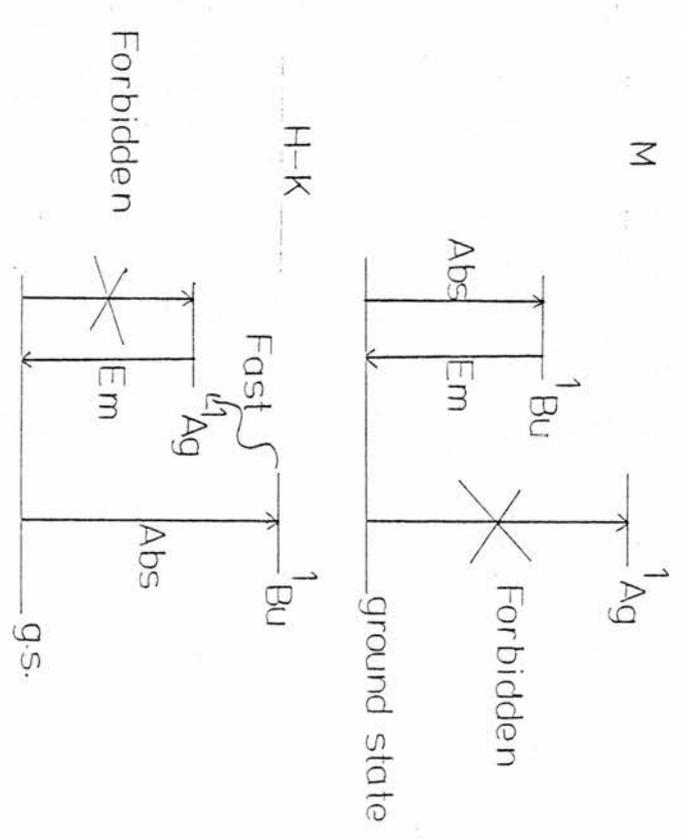
Polyacetylene has long been the main subject of investigation into polyene electronic properties since it is the simplest possible polyene with a structure which may be represented as $(\text{CH})_x$. However, workers before 1970 were either unable to produce polyenes of any great length, or found that their products were black refractory powders which made investigation difficult¹⁹⁻²⁵.

In 1971, Shirakawa and co-workers²⁶ succeeded in producing high MW flexible films of polyacetylene $(\text{CH})_x$. These films were made by introducing acetylene gas into a reaction vessel containing an unstirred concentrated solution of $\text{Ti}(\text{OC}_4\text{H}_9)_4/\text{Al}(\text{C}_2\text{H}_5)_3$, sample thickness being controlled by evacuating the reaction vessel. Samples varied from black-metallic to copper-like lustre, depending on the trans-cis content²⁷.

Doping $(\text{CH})_x$ with electron acceptor and donor species²⁸ results in the production of p or n type conductive materials respectively. Addition of AsF_5 or I_2 results in a massive increase in conductivity, Far IR spectra showing no observable transmission, which implies a continuous excitation spectrum, hence metallic behaviour. By careful control of conditions, these polyenes can be doped with I_2 , AsF_5 etc, to produce specific conductances varying over 11 orders of magnitude.

Raman studies of I_2 doped $(\text{CH})_x$ have identified the presence of I_3^- and I_5^- . Based on this observation, the demonstration of stoichiometric compensation of Na doped films with I_2 , the fact that I_2 can be removed by hard vacuum pumping or suitable solvent, and the analogy with graphite intercalation, brings about the conclusion that the doping on $(\text{CH})_x$ results from a charge-transfer process. The mechanism of conductance has been shown to be electronic rather than ionic.

As can be noted from this brief outline, the spectroscopic, electronic, and chemical investigation of polyenes is a rapidly expanding field. The purpose of this programme of research is to investigate the mixtures of polyenes produced both by polymerisation of alkyne monomers ("Direct" synthesis) and by degradation of high MW saturated polyenes ("Indirect" synthesis). This has been carried out by observation of absorption and emission spectra, and by reaction of the produced polyenes with "dopants" such as I_2 and HX.



SECTION B - INTRODUCTION

Part 1 - Direct Synthesis

The polymerisation of alkyne monomers to produce long chain, high molecular weight (mw), products has been attempted in a variety of ways and, until recently, with little success. The problems associated with a typical monomer, such as phenylacetylene (PA) can be summarised as follows:-

- I. MW is usually low (<3000)
- II. Products contain a high percentage of methanol soluble oligomer, and/or a benzene insoluble fraction.
- III. A cyclic trimer (1, 3, 5-triphenylbenzene) is formed as a by-product.
- IV. Reaction requires long time, and/or high temperature.

The methods used in attempts to polymerise alkyne monomers can be roughly divided into three sections; Radical, Cationic and Coordination.

a) Radical Methods

Many organic reactions take place through intermediates which contain an odd number of electrons, and hence an unpaired electron. Such intermediates are known as free radicals. In the alkyne polymerisations under consideration, these species can be generated in a number of ways. Berlin et al²⁹ utilised both thermal initiation of the reaction in the presence of hydroperoxide, and also a free-radical generating system of $\text{Et}_3\text{Al}/\text{TiCl}_4/\text{TiCl}_3$. Okamoto et al³⁰

utilised direct thermal creation of radicals without a peroxide initiator, both on the neat monomer, and on solutions in various solvents. Both these authors failed to produce a polymer of over 1000 MW. A third method of radical generation is the use of high energy electron beams³¹, however the products were of low MW, and in low yield compared to the amount of energy expended. Recent work using Electron Spin Resonance (ESR)³² has confirmed that the thermal polymerisation of PA to produce linear oligomers is a radical process, and identified the types of radicals involved in this and in the cyclisation side reaction.

b) Cationic Methods

Typical catalysts for cationic polymerisation are Lewis Acids and Friedel-Crafts catalysts such as AlCl_3 , BF_3 , SnCl_4 , H_2SO_4 , and other strong acids. All these are strong electron acceptors. Most of them, except possibly the strong protonic acids, require a co-catalyst to initiate polymerisation, usually a Lewis base, which is presumed to be the effective initiator.

Luttinger and Calthup³³ carried out a series of experiments using compounds of Group VIII transition metals in conjunction with a hydritic reducing agent (NaBH_4). They found that compounds of all the metals, except Fe, acted as effective catalysts in the system, and that non-hydritic reducing agents, even very powerful ones such as hydrazine, show little or no catalytic action. These processes were, however, unsuccessful in producing large MW polymers, the products being restricted to di-, tri- and tetra-mers. Powerful

acids such as $\text{CF}_3\text{CO}_2\text{H}$ or BF_3EtO ³⁴ succeeded in producing polymers with MW's of only 600-700.

The most probable reason for the low MW of this type of polymerisation is that, as the chain grows, the conjugation effect tends to deactivate the propagating site³⁵, i.e. the stability of the propagating end towards further reaction increases rapidly with chain length.

c) Coordination Methods

The coordination catalyst, developed by Natta³⁶ since the mid-1950's was a major development in the polymer industry. The name "coordination polymerisation" is used to suggest the essential feature of the catalyst system, in that they are formed as coordination complexes by the interaction of alkyls of groups I-III in the periodic table with halides and other derivatives of transition metals of groups IV-VIII. A typical coordination catalyst could be a complex between an aluminium alkyl, and a titanium halide.

These Ziegler-Natta catalysts (ZN) have the remarkable property of polymerising a wide variety of monomers to linear and stereoregular polymers, exerting a directing force which controls the orientation with which a monomer approaches the growing chain end. Two mechanisms have been proposed³⁷ for the catalytic action; one involving both metals, and one essentially non-metallic.

Although this type of system ($\text{R}_3\text{Al}/\text{MX}_4$) achieved good results with alkene monomers, only limited success was found on reactions with alkyne monomers.

Later work³⁸ using chelate compounds of transition metals in conjunction with aluminium alkyls provided much better results. Catalysts synthesised from R_3Al in conjunction with transition metal compounds of either dimethylglyoximate ($M(dmg)_2$), or acetoacetone ($M(acac)_3$), readily gave high MW products at low T ($\sim 30^\circ C$).

The catalytic effect of such systems appears to be mainly dependent on the transition metal species of the catalyst, and to a lesser extent on the ligand structure. The production of high MW polymer by this method may be explained by a resonance stabilisation of the propagating polymer. This coordination of the propagating species to the catalyst ligands can explain the higher MW found compared to the products of cationic or radical catalysis, since in these cases the species will be in a "free" state, and susceptible to cyclisation and self-termination. A large increase in viscosity of the reaction mixture, too large to be explained by the MW of the product, which was noted during the reaction, was explained as an additional interaction between the propagating species and the catalyst, i.e. a π -complexation between the propagating species and the zero-valent metal ion of the complex. Further ligand species³⁹ have been complexed with the transition metal in the $M(Lig)_n/R_3Al$ system, with varying degrees of success.

Since the pioneering work on coordination polymerisation of alkynes was carried out, many new combinations have been tried, and a variety of single compound catalysts discovered:-

a) Kern⁴⁰ compared the catalytic action of $Fe(acac)_3(iBu)_2ALH$ against that of $RhCl[(C_6H_5)_3P]_3$, finding that different crystallinities and

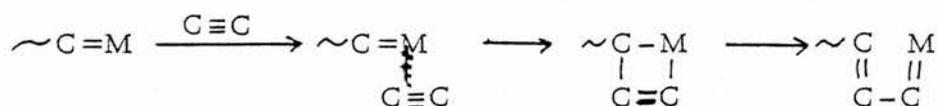
cis-trans ratios were produced. Since the Rh phosphine did not produce a polymer with styrene, it is tempting to consider PA as a bifunctional molecule, the two functional groups being $C\equiv C$ and C-H. C-H could add to the Rh coordination sphere producing R-H and σ bonded $Rh-C\equiv C-C_6H_5$. These two species can be imagined then to react with still another π -bonded acetylenic group in the same coordination sphere.

b) Metallocenes, and carbonyl metallocenes have been used to good effect in polymerising alkynes. Dicyclopentadienyl titanium⁴¹ gave good yield in Poly(Acetylene) in a highly crystalline form. MW's in excess of 10,000 were obtained for Poly(PA) using catalysts of the $ArM(CO)_3$ ⁴² type (where Ar = Arene and M = Cr, Mo, or W).

The use of the latter class of compound eliminates the need for high reaction temperatures, and formation of linear polymers is promoted due to the catalysts inability to coordinate more than two monomer molecules, thus making formation of the cyclic trimer extremely difficult. The reaction proceeds through an intermediate "ladder" compound consisting of fused cyclobutane rings, which, in the case of the PA polymerisation, can be isolated, and has an MW of 2000. Addition of catalyst to a solution of this intermediate causes rapid formation of Poly(PA).

c) Masuda et al⁴³, in a study of Lewis acid catalysts, found that the metal halides WCl_6 and $MoCl_5$ were extremely effective in producing high MW Poly (PA) (~ 15000) in good yield. Although WCl_6 is well known as a cationic catalyst in the polymerisation of

styrene, certain results obtained by the authors seemed to point to a different mechanism for the polymerisation of PA; eg. addition of H_2O enhanced the reaction time and yield, whereas addition of CCl_3CO_2H inhibited the reaction, and the polymerisation rate dropped drastically in polar solvents - behaviour opposite to that expected of a cationic mechanism. Further work, on the substituent effects of the reaction⁴⁴, showed that the Hammett σ relationships did not conform to a cationic mechanism, and pointed to a novel coordination mechanism. The propagating species suggested for the reaction is as follows:-⁴⁵

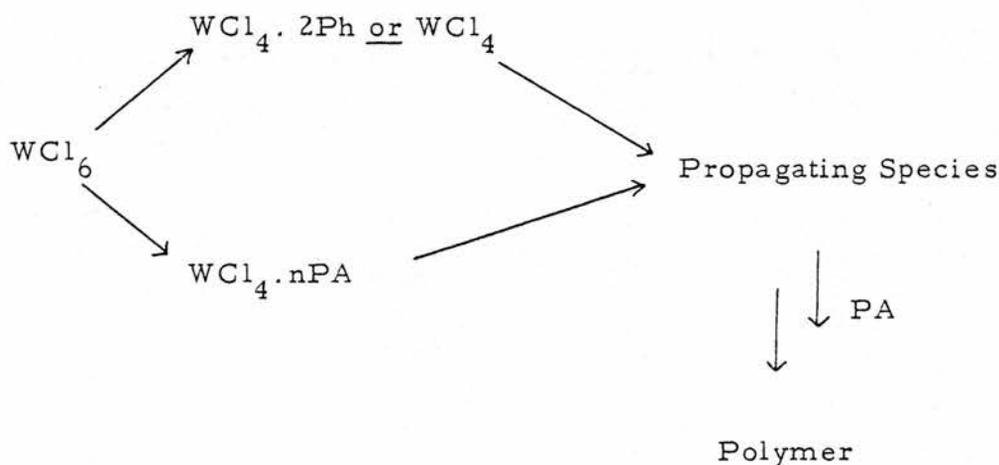


Since WCl_6 is used in conjunction with organometallics in the polymerisation of styrene, the effect of including such compounds in the PA polymerisation was investigated⁴⁶. During this investigation, the authors found that Ph_4Sn not only increased the final yield, but also increased the initial rate. (Other organometallics such as Et_3Al , Et_2AlCl and $BuLi$ inhibited the reaction; nBu_4Sn slightly accelerated polymerisation.) Polymers produced by this catalyst mixture were of a similar type to those produced by WCl_6 alone. "Aging" of the catalyst system, in the amount of time it is allowed to mix at reaction temperature before adding monomer, is very important, and this may be because of the formation of a complex in the initial stages.

This polymerisation can now be confirmed as a novel coordination reaction by the following points:-⁴⁶

- I. Non-polar solvents favour the polymerisation.
- II. The Hammett σ relationship denies a cationic species as propagating end.
- III. Reducing agents such as Ph_4Sn accelerate the polymerisation.
- IV. O_2 depresses the polymerisation.

The reaction scheme of the polymerisation can be tentatively described as follows:-



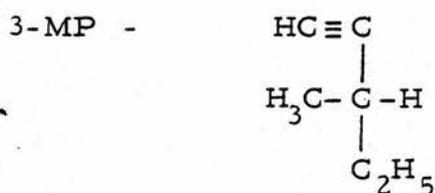
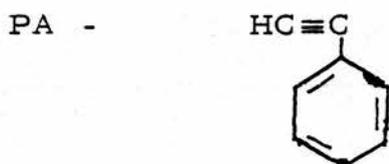
Using the same catalyst system a number of other di- and mono-substituted alkyne monomers have been successfully polymerised to high MW products⁴⁷⁻⁴⁹.

Recently other workers⁵⁰ have confirmed the efficiency of WCl_6 and MoCl_5 as catalysts for the polymerisation of monosubstituted acetylenes, and have also shown that OMoCl_4 is an effective catalyst.

d) Metal carbenes⁵¹ have been shown to be slow, but extremely efficient, catalysts for the polymerisation of alkyne monomers, giving vastly increased yields over other methods in most cases.

PA has recently also been polymerised to MW's of around 3000 by electroinitiation⁵².

In the present investigation two alkyne monomers were selected; phenylacetylene (PA), and 3-methylpentyne (3-MP). These have the structures shown below:-



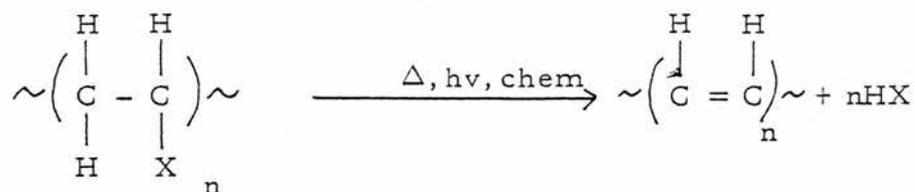
PA was polymerised by the method of Masuda et al⁴³ using $\text{WCl}_6/\text{H}_2\text{O}$, and 3-MP was polymerised using $\text{Fe}(\text{acac})_3/\text{AlR}_3$, according to the method of Ciardelli et al⁵³.

Part 2 - Indirect Synthesis

Under the influence of heat, radiation, or chemical attack polymer molecules tend to behave in two general ways; either they break down to yield products similar to themselves, ie. oligomers of various sizes or, in extreme cases the monomer, or they yield products which are different, by the splitting off of side groups attached to the main chain of the polymer molecule. We are here interested in the second category, in particular with polymers which undergo degradation to produce a polyene product by the elimination of a single volatile molecule.

The class of polymer which generally undergoes this type of reaction has the structure $\sim(\text{CH}_2-\text{CHX})\sim$ (polymers of the structure $\sim(\text{CH}_2-\text{CXY})\sim$ tend to undergo the first reaction, called depolymerisation, but this does depend on the nature of X and Y.)

A simplified scheme for the reaction under consideration is as shown below:-

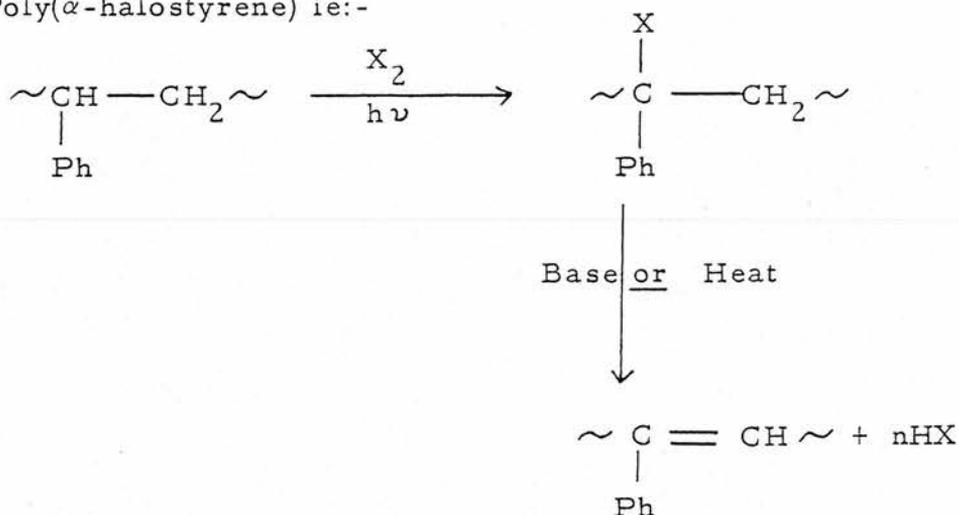


Three polymers were chosen for this investigation. These were Poly(Styrene) (PS), Poly(Vinyl Chloride) (PVC), and Poly(Vinyl Acetate) (PVAc)

1) Poly(Styrene)

A seemingly useful method of obtaining a conjugated polymer from PS is to attach a halogen atom to the α -carbon of the saturated polymer backbone, and then dehydrohalogenate the resultant

Poly(α -halostyrene) ie:-



Use of Cl_2 in the above reaction tends to be non-selective, and Cl adds to the β -carbon and to the ring during the halogenation⁵⁴. Using Br_2 , the halogen will attach to the α -position only, but the % of Br present in the final product is disappointing. Results obtained by Jones⁵⁵, and Kaeriyama et al⁵⁶ using Br_2 and UV irradiation show a maximum of 2-5 wt % bromine in final products. Work done in this department⁵⁷ has shown that a greater % of Br addition can be achieved by long exposure of the reaction mixture to normal indoor daylight than with the use of UV lamps. Experiments have shown that this treatment can result in products with up to 23% Br content.

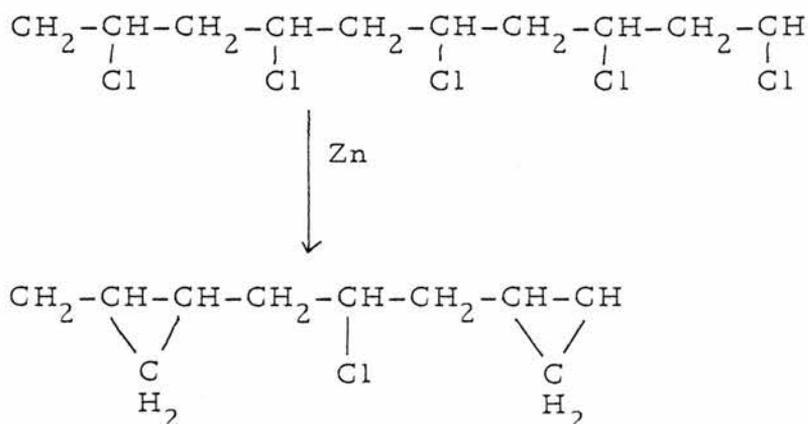
Since the C-Br bond is much weaker than C-C or C-H, it is to be expected that it can be homolytically broken, and HBr eliminated, by simply heating the brominated PS under vacuum. This was the technique used in this investigation.

2) Poly(Vinyl Chloride)

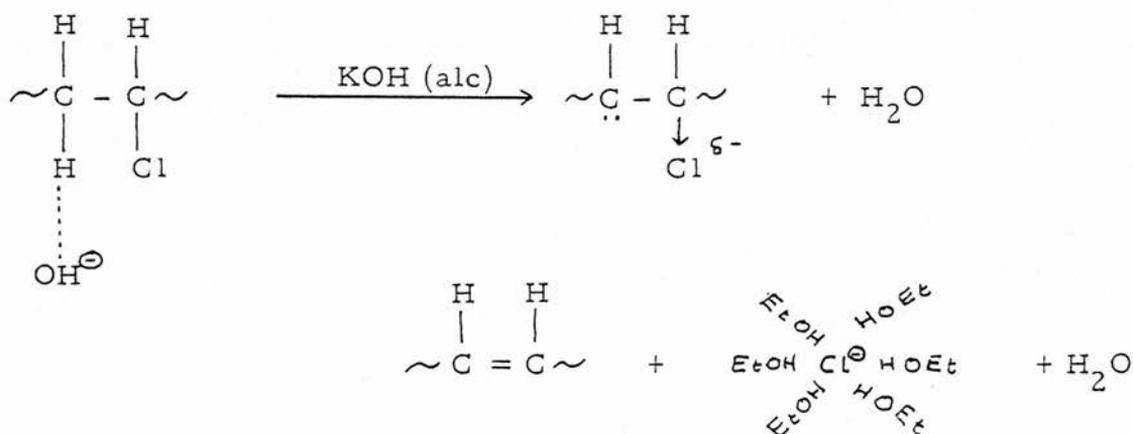
a) Chemical Degradation

It has been found that polyhalogen containing polymers, in which halogen atoms are attached directly to the carbon atoms of the main chain, can be dehydrohalogenated easily if they are treated with appropriate nucleophilic reagents.

Early work⁵⁸ on the treatment of PVC and Poly(Vinyl Bromide) with Na and Zn resulted in large degrees of dehydrohalogenation. However, the structure assumed - that of a 1,2-dihalide - was wrong, and therefore the conclusions made must be called into question. Marvel et al⁵⁹ carried out reactions between PVC in dilute dioxan solution and Zn dust, and subsequent investigation showed PVC to have a 1,3-dihalide structure. The authors noted that the product of the Zn reaction was not in fact a polyene, but consisted of cyclopropane units with occasional isolated $-\text{CH}_2\text{CHCl}-$ units:-



An additional experiment carried out by the same authors used KOH to treat a solution of PVC, and produced an insoluble red-brown polymer which was tentatively identified as a long chain polyene, $(CH)_n$. Work carried out by Shindo and co-workers^{60, 61} has extensively investigated the reaction between THF solutions of PVC and alcoholic KOH. The mechanism proposed is similar to that for reactions between model alkyl halides and basic reagents in solution:-



The initial reaction will take place at an "activated" site, i.e. a branched site causing the creation of a tertiary C-H bond, a head to head structure, or an adjacent double bond. Propagation of the reaction will then progress through allylic activation of subsequent C-H bonds. Östensson and Flodin⁶² have recently examined the kinetics of this reaction, and reacted the product with dienophile reagents, Cl_2 , and Br_2 .

Due to solubility problems with KOH, Perichand et al⁶³ used KO^tBu which is soluble in THF. This has a number of advantages as a dehydrochlorination reagent over KOH:-

- I. Higher basicity
- II. Large size anion precludes substitution reactions

III. Spectroscopic problems with mixed solvents, and the tendency of KOH to produce precipitating side products, are eliminated.

Tokarzewski⁶⁴ has used a series of sodium alcoholates, and appears to have achieved a degree of controlability in eliminating HCl from PVC, by manipulation of reaction temperatures, and ratios of reactants.

Tsuchida et al^{65, 66} reacted solutions of PVC with mixtures of alkali metal amides in polar solvents such as NH_3 , THF, and DMF. The resultant degraded polymer exhibited reactions typical of an organic unsaturated material which is considered to have resulted, for the most part, from a dehydrochlorination reaction. The authors considered that the reaction occurs at first at several random sites in a long polyene chain to form unsaturated bonds. When these are formed, the α -hydrogen (relative to the double bond) becomes activated, and succeeding double bonds are formed more easily. The mechanism suggested is that when nucleophilic reagents approach the chain, they act as a key does in unzipping a fastener. Assuming this to be the case, it would appear that the limiting factor on polyene length would be anomalies in the chain structure of the PVC, preventing the conjugation from continuing.

Roth et al^{67, 68} reacted solutions of lithium salts in DMF with solutions of PVC in THF to produce conjugated products. Earlier work on the dehydrobromination of selectively brominated steroids⁶⁹, has suggested two possible mechanisms for this reaction:-

I. In the steroid reaction, the Br atom is in a cis position, and as the removal of HBr entails a trans elimination it has been

come to this conclusion. However, due to the flexible nature of the PVC chain it is difficult to state this with certainty.

During the course of this work, methods based on those of Shindo et al⁶⁰, and Roth et al⁶⁷ were utilised to chemically degrade PVC.

b) Photochemical Degradation

While photo-oxidation of PVC has been extensively studied, due to its importance to the weathering of commercial plastics, the photodegradation reaction under inert atmosphere, or under vacuum, has not received as much attention. Investigation of the photodegradation of PVC films under vacuum⁷², and under N₂ atmosphere⁷³⁻⁷⁸ have established the following facts relevant to polyene formation in the degraded product:-

1) The formation of a surface layer of degraded material during UV irradiation of PVC films, and hence the inhomogeneity of the reaction, was first noted by Sobue et al⁷⁹ and later under more rigorous conditions by Reinisch et al⁷² and by Gibb and MacCallum⁷³. The latter authors found that sample films irradiated under N₂ degraded only on a thin surface layer; once this had been formed, it protected the bulk of the sample from further degradation.

Experiments have shown⁷⁴ that this surface layer formation markedly affects the dependence of the reaction on irradiation intensity. During the first hour of the reaction, the rate of dehydrochlorination is dependent on intensity of radiation, and temperature; after an hour, this changes markedly and it would

appear that the photodegradation becomes dependent on the "availability" of HCl. One can consider two extreme cases:-

- a. Most Intense Radiation - A lot more damaging light is absorbed, but 35% of the HCl has already been evolved in the first hour.
- b. Least Intense Radiation - Less quanta of damaging light absorbed, but only 8% of HCl lost in the first hour.

If the reaction investigated lies between these extremes then the rate of reaction will be independent of intensity. Because this "availability" will be unaffected by temperature (T), the dehydrochlorination will also be independent of T.

II) As has been noted previously, the primary reaction of PVC under degradation is the evolution of HCl. Various methods have been used to detect this evolution - changes in absorption spectrum of the film⁸⁰, analysis of products for HCl acidity⁷³, and mass spectrometry⁷². The latter method, used in a modified, very sensitive, form confirmed that HCl is the only volatile product of PVC degradation under vacuum.

III) Films containing varying amounts of tetrahydrofuran (THF) solvent⁷⁶ showed that the amount of HCl evolved under irradiation was unaffected, but the UV spectrum changed. As the amount of THF increased, the optical density dropped. A possible explanation involves THF acting as a plasticiser, enabling long sequences of double bonds formed in the sample to rotate about single bonds to create two or more short sequences of conjugated double bonds. This decrease in long polyenes, and increase in short sequences was observed by the authors.

IV) Comparison of low (LP) and medium (MP) pressure Hg lamps⁷⁷ shows that the LP lamp (monochromatic; 253.7 nm) produces a slower decomposition. Analysis of relative concentrations of polyenes shows that in the early part of the decomposition by the MP (polychromatic) lamp, the distribution of polyenes remains almost constant. On the other hand, irradiation using the LP lamp does show a trend towards the production of longer polyene sequences at higher conversion.

For both lamps, the absorption by dienes and trienes is necessary for the reaction to proceed, and yet the relative concentrations of such species remain fairly constant. It is proposed that a significant proportion of the high energy absorbed by these polyenes causes reaction in non-absorbing parts of the polymer as a result of Energy Transfer (ET) processes.

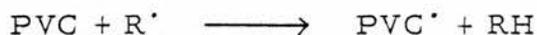
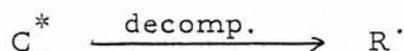
Kinetics and Mechanism - Because the initial absorption sites are constantly reacting to form different lengths of polyene, which absorb at differing wavelengths, the nature of the reaction is constantly changing, and therefore kinetic analysis of the reaction is virtually impossible. Also, since the film thickness, and hence the weight of material under a given area has no effect on degradation, the term "percentage degradation" is meaningless.

The three stages of the mechanism of photodegradation can be briefly described as follows:-

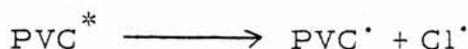
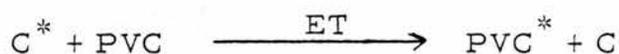
a) Initiation:- The initiation of photodegradation of PVC, under the conditions considered, requires the presence of a chromophoric

group with the ability to absorb light in the range 250-300 nm. While Braun⁸¹ favoured single double bonds randomly spread throughout the polymer, Gibb⁸² has shown that the most likely causes are small series of conjugated double bonds, residual initiator moieties or residual solvent. These chromophores can act in one of two ways:-

I. Decomposition to produce radicals, which then abstract to form a macroradical.



II. Photosensitisation; ET from the chromophore to PVC which then splits homolytically



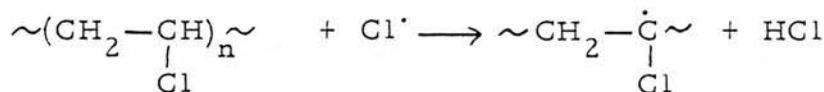
It may be noted that conjugated systems as low as dienes and trienes are quite capable of absorbing light in the damaging region; also a very low concentration of initiation is required, since once a few polyenes are formed, they will act as chromophores for further degradation.

b) Propagation:- Two basic mechanisms have been proposed.

I. Stepwise dehydrochlorination⁸³, in this case a radical pair is formed, and subsequently the polyene lengthens one double bond at a time.

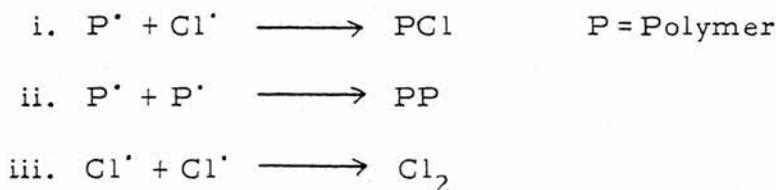
c) Termination; this can be achieved in a variety of ways⁸².

I. Abstraction of a tertiary hydrogen to produce an unreactive macroradical



II. Many polyenyl radicals exhibit long lifetimes because of their high resonance stability. This is probably what happens to the macroradical left behind when transfer occurs.

III. The combination of two radicals will cause termination, and there are three possibilities.

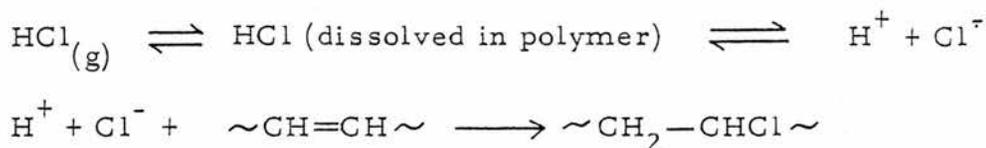


Reaction i. may occur, but ii. is probably commonest, and gives rise to a cross link. Molecular chlorine has never been found experimentally, presumably because, as soon as a $\text{Cl}\cdot$ radical is formed, it will immediately abstract an H atom. The chance of another chlorine being nearby is remote, and even if Cl_2 did form, it would immediately be broken up by the UV light.

We must now consider the possibility of HCl adding back onto the polyene system in the sample. Gibb and MacCallum⁷⁴ irradiated a sample of PVC in their apparatus under different HCl containing conditions:-

- i. Continuous N_2 purge
- ii. Starting with pure N_2 and retaining evolved HCl
- iii. Filling cell with an atmosphere of HCl.

In going from i. \rightarrow iii. it was found that there was a sharp decrease in the change in optical density, i.e. as the presence of HCl increased, the rate of polyene formation decreased. Mechanism postulated for this inhibition is as follows:-



Owen and Williams⁸⁵ found that the reaction rate of HCl with degraded PVC depends on the HCl pressure, increasing with increasing HCl, and appears to reach a limiting value. This suggests that the process may be reversible and may occur in two ways, depending on whether HCl attack takes place on end groups, or at random in the polymer molecule.

Braun⁸¹, and Schlimperer⁸⁶ have suggested that HCl forms complexes with polyene or polyenyl ions.

The hypothesis of HCl trapped in the film and available for reaction is further supported by the work of Lawton and Balwitt⁸⁷ who used high energy methods to degrade PVC at liquid N₂ T (77 K). The authors found that no discolouration occurred until the samples were allowed to warm up to room T, under an N₂ atmosphere. Colour ranged from clear \rightarrow straw yellow over a period of five minutes, and after 360 hours had reached a reddish-brown shade.

As may be realised from the above, the degradation of PVC to polyenes under non-oxidising conditions is much more complex than it at first appears, and all the factors noted must be taken into consideration in our subsequent photodegradation study of PVC.

3) Poly(Vinyl Acetate)

The thermal degradation of PVAc, unlike that of PVC, has not been extensively investigated, and a great deal of controversy still surrounds various aspects of the reaction.

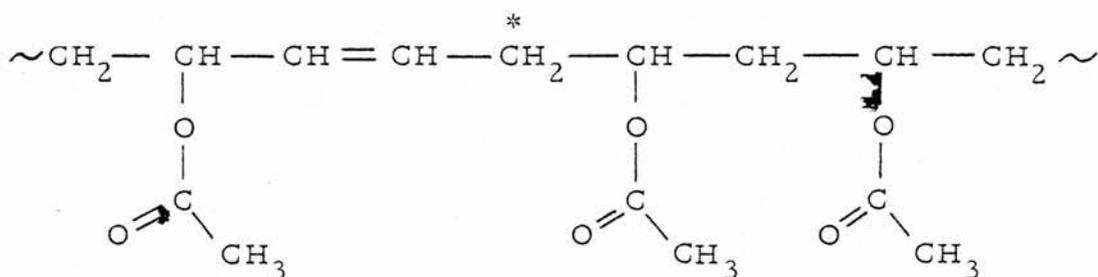
It was established in 1948⁸⁸ that the primary degradation reaction of PVAc was similar to that of PVC, i.e. the elimination of acid molecules and the creation of a conjugated polyene system. The first detailed study of the thermal behaviour of PVAc was made by Grassie^{89, 90}, in this he found that the onset of thermal degradation came at about 210°C, and confirmed acetic acid as the only volatile product in the temperature range 210-300°C. The technique used was a vacuum system, with the sample chamber in a controlled oven, and side arms which could be cooled down to trap out volatile products. In this way the acetic acid was collected and titrated to obtain percentage degradation measurements. The solid residue left in the reaction chamber became progressively darker, indicating the presence of an acetylenic residue. It was also noted that the residue became insoluble in organic solvents after only a small percentage degradation. The original technique employed by this author to separate volatiles out during thermal degradation has since been improved and modified into the method of Thermal Volatilisation Analysis (TVA)⁹¹ whereby several traps at different temperatures are employed to study the evolution of volatiles from degrading polymers⁹².

TVA has been used in conjunction with other techniques in the investigation of PVAc degradation. Bataille and Van⁹³ used TVA



It has definitely been established⁹⁹ that the reaction does not involve radical species.

b) Propagation:- It is generally accepted^{89, 95, 97} that the propagation reaction results from allylic activation of an α methylene group adjacent to the initial double bond, the reaction of elimination involving the same six-membered intermediate as the initiation.



Khokhlova et al⁹⁷ refer to allylic activation of the C-OAc bond, but this would not assist the elimination reaction.

Servotte and Desreux⁹⁵ suggest that, in the early stages of the reaction, deacylation reactions occur intermolecularly to produce cross-linking. It is also proposed that cross-linking may occur by Diels-Alder type reactions between ethene and diene structures on adjacent molecules.

c) Termination:- According to Grassie's^{89, 90} reaction scheme, the creation of conjugated double bonds along a polymer chain should only cease when the end of that chain is reached. This is obviously not so,

as PVAc tends to form shorter polyene sequences than PVC, and the propagation reaction scheme cited requires that each successive double bond be conjugated to the growing polyene chains.

Servotte and Desreux⁹⁶ made a more extensive investigation of possible termination reactions and proposed three possibilities:-

i. "Head to Head" structures would affectively terminate a deacetylation chain reaction. The amount of these structures increases with increasing polymerisation T, but it is always a small percentage.

ii. The radical $\sim\text{CH}_2-\dot{\text{C}}\text{H}$, which can be stabilised by

$$\begin{array}{c} | \\ \text{O} \\ | \\ \text{C} \\ // \quad \backslash \\ \text{O} \quad \text{CH}_3 \end{array}$$

resonance, can take part in transfer reactions to produce branched structures during polymerisation of vinyl acetate.

iii. Chain end structures can be very diverse, but as evidence seems to be in favour of a random initiation of reaction, this may not be an important factor.

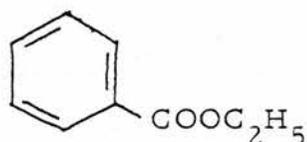
Kholchlova et al⁹⁷ cite stereochemical factors as the cause of termination. Since a number of atoms must be lined up precisely to make the postulated intermediate, the presence of rigid polyene sequences, and possible cross-links, may prevent the reaction taking place.

The autocatalytic character of PVAc degradation is also a matter of some dispute. Grassie's⁸⁹ results showed that thermal degradation of PVAc (with constant elimination of volatiles) exhibited autocatalytic behaviour, while those of Servotte and Desreux⁹⁵ did not.

Work by Razuvaev et al⁹⁹ suggests that the latter workers were correct, and also that the reaction does show autocatalytic behaviour in the presence of acetic acid and other organic acids. Results seem to indicate that a definite part is played by polar species in the transition complex.

Varma and Sadhir¹⁰⁰ have carried out a series of experiments in which they thermally degraded PVAc in solution. The solvents were as follows:-

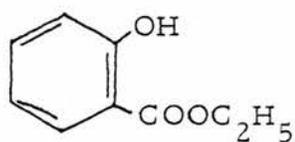
Ethyl Benzoate



Benzyl Benzoate

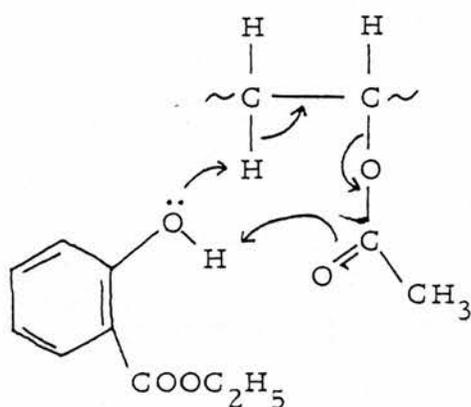


Ethyl Salicylate



Both the rate of reaction, and the type of product formed, were influenced by the solvent used. In the case of ethyl and benzyl benzoate, absorption spectra of the degraded solutions showed a mixture of short polyenes being formed, with no character being shown. In the case of ethyl salicylate however, absorption continued into the visible region as far as 500 nm, and a series of discrete peaks were observed between 380 and 460 nm.

The participation of the solvent in the reaction mechanism is proposed by the authors in the case of ethyl salicylate, the phenyl group influencing the α methylene group as shown below:-



Chemically assisted degradation of PVAc¹⁰¹ has been carried out using p-toluenesulphonic acid at 110°C in toluene solution. The authors obtained highly coloured, soluble, products containing polyene sequences of between 2 and 12 double bonds. No mechanism was put forward for the reaction.

In this investigation, the thermal degradation of PVAc in the form of thin films and in solution, and behaviour of degraded products, was investigated by absorption and emission spectroscopy.

SECTION C - SYNTHESIS

I. Direct Synthesisa) Poly(Phenylacetylene)

The PPA used in this work was synthesised by the original method of Masuda et al⁴³; ie. WCl_6 catalyst system, polymerisation carried out under vacuum in benzene.

Benzene was dried from AR material in the usual manner, and then stored over sodium wire. The phenylacetylene (BDH) was purified by distillation over CaH_2 . Tungsten hexachloride (Alfa) was supplied resublimed and stored in an ampoule equipped with a break-seal, and so was used without any further preparation. H_2O used was normal laboratory distilled water. Apparatus used was as shown in Fig. C1.

10.2 g (0.1 mole) monomer was dissolved in 100 ml benzene and placed in vessel (a); 0.1 g (2.5×10^{-4} moles) WCl_6 and 0.0033 g (1.75×10^{-4} moles) H_2O were dissolved in 25 ml benzene and placed in vessel (b). These solutions were then degassed on a vacuum line by five repeats of a freeze-pump-thaw cycle. Vessel (b) was attached to (a) by the side arm, stop-cock (2) was released.

Stop-cock (3) was then slowly opened, and the WCl_6/H_2O solution added to the monomer solution with constant stirring. After all had been added, the mixture was left stirring under vacuum at room temperature.

It was noted that the solution turned green on addition of the catalyst mixture, but after approx. five minutes had turned deep red.

The mixture was left to polymerise for 5 hrs. The reaction was terminated by releasing the vacuum, and pouring the solution into a massive excess of cold methanol under a Vibromix stirrer. The mixture was then filtered through a No. 3 sintered glass funnel, and the dark red polymer obtained dried in a vacuum oven at RT for 5 days.

The crude polymer was purified by dissolving in Analar methylene chloride and reprecipitating from excess cold methanol. The procedure was repeated three times.

Characterisation

i. Microanalysis:-	Results		Literature ⁴³	
(C = 3.9% error H = 8.1% error)	C	H	C	H
	89.31%	5.60%	92.95%	6.15%

ii. Absorption spectrum:- The UV/Visible absorption spectrum was taken on a Unicam SP-800 spectrophotometer, and was the same as indicated in the literature⁴⁵.

iii. Infra-red spectrum:- The infrared spectrum of the product was taken using the KBr disc method, using a Perkin-Elmer 257 IR spectrometer. The spectrum showed absorption between 1700 and 1500 cm^{-1} characteristic of the stretching vibration of polyconjugated double bonds, and between 800 and 625 cm^{-1} characteristic of C-H out of plane deformation of monosubstituted benzene. Two peaks at 870 cm^{-1} and 910 cm^{-1} are characteristic of cis and trans structures respectively. The ratio of these peaks is 0.733 which is

close to the literature value of 0.746⁴⁵, ie. the structure of the product is similar to that of the polymer obtained by Masuda et al.

iv. Nuclear magnetic resonance:- ¹³C nmr spectrum of the product was obtained and agrees with theory; ie. only olefinic and aromatic signals noted. Broadening of the olefinic peak denotes both cis and trans structures present, confirming IR data.

v. Molecular weight:- Molecular weight was measured by Gel Permeation Chromatography (RAPRA).

$$\overline{M}_n = 16400, \quad \overline{M}_w = 36120$$

$$\text{Polydispersity} = 2.20$$

From the above characterisation data, it would appear that the product of this synthesis is very similar in all respects to the polymer obtained by Masuda et al.

b) Poly(3-Methylpentyne)

In 1974, Ciardelli et al⁵³ synthesised a number of conjugated polymers containing chiral side groups. It was decided to synthesise one of this series, Poly(3-methylpentyne) (PMP).

Heptane (BDH), 3-methylpentyne (ICN Pharmaceuticals), and Al(nC₄H₉)₃ (Alfa; 25% solution in hexane), were used as supplied. Ferric acetoacetate (Fe(acac)₃) was synthesised by the method of Charles and Paulikowski¹⁰². Reaction set-up was as shown in Fig. C2.

A solution of 0.441 g Fe(acac)₃ (1.25 mmol) in 10 ml heptane was stirred under N₂ for 15 mins at room temperature, and then

25 ml of the hexane solution of $\text{Al}(\text{nC}_4\text{H}_9)_3$ (3.75 mmol) was added by glass syringe through the Suba-seal. The mixture was heated at 60°C with vigorous stirring for 15 mins, then allowed to cool. The Suba-seal was carefully replaced with a 50 ml dropping funnel containing 2.5 g (26 mmol) 3-methylpentyne in 25 ml heptane. This was added carefully to the mixture with stirring.

The mixture was then heated mildly ($30\text{-}40^\circ\text{C}$) and stirred for two hours, and then allowed to cool for 22 hrs. The polymerisation was then terminated by the addition of 20 ml 0.5M HCl to destroy the catalyst, and 50 ml diethyl ether to dissolve the polymer. The ether layer was treated with saturated NaHCO_3 solution and washed with water.

The mixture was poured into a massive excess of MeOH and an amorphous rubbery yellow polymer obtained. On carrying out this procedure, it was noted that there was a methanol soluble product. The non MeOH soluble portion was found to be inhomogeneous in texture and colour, and was redissolved, with some difficulty, in benzene. A small benzene insoluble fraction was noted, and this was filtered off before reprecipitating the solution from methanol. A pale yellow powder was obtained.

The yellow colour of this polymer, compared with the deep red of PPA shows that the conjugation between the backbone double bonds is less pronounced in this case. This can be explained by the bulky nature of the chiral side group and its inability to "stack" like the phenyl rings of the PPA, or to participate in any way in the conjugation.

Characterisation

i. Microanalysis:-	Results	Theory
Carbon	85.59%	87.73%
Hydrogen	12.30%	12.27%

ii. Absorption spectrum:- Measurements taken both in heptane, and in methylene chloride, gave spectra similar to that in the literature, with a broad absorption centering on c. 300 nm with no fine structure visible.

iii. Infrared spectrum:- Spectrum showed broad band at 1600 cm^{-1} indicating conjugated double bonds. Other bands also matched the literature spectrum¹⁰³.

iv. Nuclear magnetic resonance: ^1H nmr spectrum was similar in all essentials to that of 3-methylpentene, and showed series similarity to Poly(4-methylhexyne)⁵³. ^{13}C nmr spectrum was also similar to that of 3-methylpentene, ie. (numbering peaks from right to left from TMS):-

Peak	Literature ¹⁰⁴	Results
1	11.62 ppm	12.19 ppm
2	19.81 ppm	20.80 ppm
3	29.65 ppm	29.40 ppm
4	39.72 ppm	36.40 ppm
5	112.51 ppm	126.75 ppm
6	144.74 ppm	143.57 ppm

v. Molecular weight:- MW was again measured using Gel Permeation Chromatography (RAPRA)

$$\overline{M}_n = 5958, \quad \overline{M}_w = 14380$$

$$\text{Polydispersity} = 2.41$$

II. Indirect Synthesis

a) Halogenation/Dehydrohalogenation of Poly(styrene)

The degradation of Poly(styrene) (PS) has been extensively investigated, and the initial step is understood to be abstraction of hydrogen from the α -carbon of the styrene unit, and the subsequent formation of free-radicals. If we can add a halogen to this site instead of the proton, then it should be relatively easy to remove HX from the polymer, and generate unsaturated moieties. In this series of experiments, two halogens were used - iodine and bromine.

(1) Iodine

PS used had an \overline{M}_n of approx. 2.5×10^5 , and was purified by dissolving in CH_2Cl_2 and precipitating from cold MeOH; this being repeated twice. The material was then dried in a vacuum oven at RT for 7 days, and subsequently stored in a brown glass bottle. Iodine (Fisons SLR) was used as supplied, as was CH_2Cl_2 (BDH, Analar).

Solutions containing 0.5% w/v PS in CH_2Cl_2 were used, one being retained as a control sample, and others having I_2 added. A small crystal of I_2 was added to a solution, and the flask allowed to stand in normal laboratory daylight. After 1 hr, a comparison UV/Visible spectrum of the treated sample against the control showed only the appearance of the strong I_2 absorption between 600 and 400 nm, but no change in the characteristic absorption of PS between 250 and 275 nm. No change in absorption was noted between these two regions.

After 3 days, the spectrum was repeated; it was found that there was a substantial increase in the PS characteristic absorption pattern, and a noticeable increase in absorption between 350 and 375 nm. Tests to ascertain if this slight reaction was due to a photolytic or dark reaction showed that what little reaction occurred was due to light. A sample treated under a filtered medium pressure (MP) Hg lamp at 313 nm showed similar characteristics.

The sunlight treated "I₂PS" sample was reprecipitated from MeOH, and a white powder obtained, which showed some pale pink patches which disappeared after drying in the vacuum oven at RT. This material was essentially the same as PS in appearance and UV characteristics. Heating the sample gently (50°C) under vacuum modified the absorption properties slightly, making the "I₂PS" sample indistinguishable from PS.

A possible explanation of the increase in absorption between 350 and 300 nm, and the increase in intensity of the PS characteristic pattern may be the formation of a small percentage of charge-transfer complex.

(2) Bromine

The PS and methylene chloride used in this series of experiments was the same as that used in the iodine experiments; bromine was a standard laboratory reagent (Fisons) used as supplied.

i. Preliminary:- Again a 0.5% w/v solution of PS was used. A drop of Br₂ was added to a test solution and it was found that the yellow/brown colour which immediately developed faded rapidly in daylight. Comparison of UV/Visible absorption spectra (Unicam SP800)

of the bromine treated sample (BrPS) and of PS showed a large increase in the characteristic pattern of PS, and a distinct increase in absorption between 275 and 325 nm. On reprecipitating the test sample, heavy white fumes were given off which quickly turned moist blue litmus paper red; this is evidently HBr formed during a rapid reaction between PS and Br₂. The material recovered from the precipitation was pure white, which shows that the product does not contain any long sequence polyenes to act as chromophores in the visible region. The product was recovered as a fine powder, unlike the usual fibrous appearance of PS, which suggests that some reduction in MW by chain scission may have occurred.

In order to test whether the Br₂ was in fact escaping from the reaction vessel and not attacking the PS, a portion of Br₂ dissolved in CH₂Cl₂ was left on the window ledge for 48 hrs with no visible loss of colour. After adding a sample of PS the mixture discoloured, and when the sample vessel was opened after 72 hrs it gave off dense white fumes. On reprecipitation, the usual large amounts of white fumes were given off, and an off-white solid product obtained.

A sample of conc. PS/CH₂Cl₂ solution was treated with excess Br₂ and left in daylight. Another vessel of the same mixture was placed alongside in an opaque container as a control. After 4 days, the test sample was reprecipitated and an off-white powder obtained. On reprecipitating the control batch, a fibrous mat of PS was obtained, which shows that the reaction does not occur to any great extent in the dark.

A solution of PS which was saturated with a large excess of Br₂ was left in daylight for 7 days, and then reprecipitated. Comparison

of this against a solution of PS showed a massive absorption stretching from 400 to 220 nm.

A portion of the above product was placed in the vacuum oven, and a controlled heating test carried out. The original sample was pale yellow in colour.

Sample	T (°C)	t	Comments
α	100	2 hrs	No change
β	110	24 hrs	"
γ	120	10 mins	Turned bright yellow
δ	120	6 hrs	Orange/yellow with some fused particles

UV/Visible spectra of all samples showed a slight increase in absorption over the range 400-220 nm. Samples γ and δ , after reprecipitation, were noted to have changed colour back to the original pale yellow, showing none of the glassiness noted after heat treatment. It would therefore appear that this colouration is a surface effect, brought about by heating the samples over their glass transition temperature (T_g).

Proton NMR spectra (100 MHz) of PS, BrPS, and Oven Test (OT) β were taken, and compared in an attempt to ascertain whether there had been any appreciable formation of olefinic H to replace the backbone proton signal. Peaks obtained were as shown below:-

	Signal (δ)			
	Aromatic		Backbone	
PS	7.00	6.50	1.42	1.80
BrPS	7.00	6.50	1.43	1.80
OT β	7.01	6.50	1.43	1.80

If any β substitution of the PS by bromine was occurring, we would expect a peak in the NMR at $\delta \sim 4.1$ due to CHBr (chain)¹⁰⁶; as this did not occur, it may be concluded that no such substitution took place. Also, no splitting of the aromatic peaks was observed, which would be expected with Br attached to the ring, therefore this did not occur either. Since the aromatic protons appear to remain constant, any change in the ratio of aromatic to backbone protons should reflect the degree of unsaturation obtained; however, difficulties with the intensities of these spectra prevented any conclusive data being obtained.

ii. Series A:- 0.1 g portions of PS were dissolved in 25 ml CH_2Cl_2 , and varying amounts of bromine added-

Sample	PS (g)	PS (M)	Br_2 (ml)	Br_2 (M)
A ₁	0.1	9.6×10^{-4}	0.05	9.7×10^{-4}
A ₂	0.1	9.6×10^{-4}	0.1	1.9×10^{-3}
A ₃	0.1	9.6×10^{-4}	0.2	3.9×10^{-3}
A ₄	0.1	9.6×10^{-4}	0.5	9.7×10^{-3}

As can be seen, the lowest concentration of Br_2 used provides one bromine molecule per styrene unit.

These samples were then placed, alongside a PS control, on the window-ledge for 24 hrs of daylight, and then precipitated from cold MeOH. A portion of each sample was placed in the vacuum oven at 120°C for 24 hrs. The eight test samples were then investigated by various means as follows:-

a) UV/Visible spectroscopy:- Spectra were taken in 1 cm quartz cells on the Unicam SP800, using a solution of PS as reference.

Conc. = 0.4 gl^{-1}

In both the BrPS and OT samples there is a vast increase in absorption between 400 and 250 nm over that of PS. The trend of this increase over the four samples of each type is the same in both groups but does not follow the increase in bromine concentration. These trends, and the differences between the two groups can be seen by noting the absorbances at various wavelengths.

λ (nm)	BrPS				OT			
	A ₁	A ₂	A ₃	A ₄	A ₁	A ₂	A ₃	A ₄
400	0.09	0.09	0.11	0.11	0.10	0.10	0.12	0.12
350	0.24	0.19	0.36	0.37	0.28	0.23	0.38	0.38
325	0.48	0.36	0.75	0.66	0.52	0.40	0.74	0.70
300	0.69	0.54	1.09	0.96	0.77	0.60	1.10	1.03
275	0.98	0.72	1.70	1.78	1.15	0.79	1.72	1.90

Again there appears to be fairly small differences between respective BrPS and OT samples.

The reason for the mixed up trend in absorption strength is not clear.

b) NMR:- The NMR spectrum of PS itself shows peaks due to the CH₂ group ($\delta = 1.4$), chain CH group ($\delta = 1.8$) and aromatic ring ($\delta = 6.5, 7.0$)¹⁰⁷. Again, great difficulty was found in obtaining high intensity spectra. Peak positions both in the case of the BrPS and OT samples were the same as in PS, and again no trace of β or ring substitution was found. The intensities were such that no information

could be obtained concerning the ratio of aromatic to backbone protons. The use of more concentrated solutions, and of ^{13}C NMR was borne in mind for further work.

c) Microanalysis:-

Sample	%C	%H	Total
PS	92.80	7.20	100.00
A ₁	86.14	7.78	93.92
A ₂	91.19	7.81	99.00
A ₃	83.33	7.06	90.39
A ₄	68.47	5.29	73.76

iii. Series B:- 0.5 g portions of PS were dissolved in 50 ml CH_2Cl_2 ; and varying amounts of Br_2 added.

Sample	PS (g)	PS(m)	Br_2 (ml)	Br_2 (m)
STD	0.5	4.8×10^{-3}		
B ₁	0.5	4.8×10^{-3}	0.1	1.94×10^{-3}
B ₂	0.5	4.8×10^{-3}	0.5	9.70×10^{-3}
B ₃	0.5	4.8×10^{-3}	1.0	1.94×10^{-2}

The above samples were treated in the same way as those in Series A, and their properties investigated by various spectroscopic and analytical means.

a) UV/Visible absorption:- 0.08 gl^{-1} samples of the reprecipitated polymers were made up in CH_2Cl_2 , and their spectra taken in comparison with CH_2Cl_2 on a Unicam SP800 spectrophotometer.

Between 400 and 250 nm, the absorbance strength increases in the ratio B₃, B₂, B₁. However, above 250 nm, the absorbance of B₃ increases rapidly and overtakes that of B₂, and eventually that of B₁.

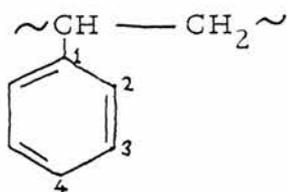
B_2 also increases rapidly in absorbance at lower wavelengths, and overtakes B_1 at 237 nm. Both B_3 and B_2 display a strong absorbance peak centering on c. 233-236 nm which is absent in B_1 . The OT samples showed the same general trends as the BrPS solutions, with slight overall increase in absorbance in the 400-250 nm region.

b) NMR:- 0.1 M samples of PS and the test samples were dissolved in carbon tetrachloride along with TMS standard. These were then placed in 5 mm tubes for proton NMR analysis (100 MHz).

Sample	Peaks (δ)			
	Aromatic		Backbone	
PS	6.52	7.00	1.43	1.79
B_1	6.52	7.00	1.45	1.79
* B_2	6.56	7.08	1.42	1.79
* B_3	6.40	7.12	1.38	1.64
OTPS	6.50	6.99	1.43	1.80
OTB ₁	6.52	7.00	1.45	1.82
OTB ₂	6.50	7.06	1.48	1.85
OTB ₃	6.50	7.12	1.50	

* Samples B_2 and B_3 show an asymmetry, or shoulder, on the 6.50 peak which may denote the presence of an olefinic proton signal, since the structure $\begin{array}{c} -C=C-C=C- \\ | \\ H \end{array}$ resonates at 6.2¹⁰⁸.

Again, as in series A, the proton NMR spectra do not impart a great deal of useful information, and it was therefore decided to try using ¹³C NMR, which has numerous advantages over ¹H NMR¹⁰⁹. Taking the styrene unit as shown below, the various carbons have the following resonance signals:-



Styrenic C = 40.44

$$C_1 = 145.45$$

$$C_1 + C_3 = 128.68$$

$$C_4 = 126.46$$

1.0 M Solutions of the OT samples were prepared in a solvent mixture of carbon tetrachloride, deuterated chloroform, and tetramethylsilane ($\text{CCl}_4/\text{CDCl}_3/\text{TMS}$), and placed in 12 mm tubes for ^{13}C NMR analysis.

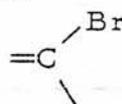
Sample	Styr. C	C_1	$C_2 + C_3$	C_4
OTB ₁	40.71	145.53	128.69	125.78
* OTB ₂	41.16	144.39	128.11, 129.33 130.69	126.38
* OTB ₃	40.26	143.90	131.50, 129.17 128.19, 127.41	126.14
PS	40.44	145.45	128.68	126.46

* OTB₂ and OTB₃ both show the appearance of a weak resonance at ~ 119.5 (slightly stronger in the case of OTB₃ than for OTB₂) as well as the "multiplication" of peaks around the $C_2 + C_3$ resonance region.

Comparing the PS spectrum with that of Poly(butadiene)¹¹⁰ it was noted that the latter features resonances at 130-131 δ which are assigned to olefinic carbons. This makes it reasonable to suggest that the extra peaks appearing around the $C_2 + C_3$ resonance can be attributed to double bond structures, and their effects on the environments of the other carbons. The peak pattern attributable to

C_1 carbon resonance changes in going from PS to the test samples, showing an increase in atacticity in going from $OTB_1 \longrightarrow OTB_3$, which is consistent with the disruptive effects of the bromination/dehydrobromination reaction on the predominantly isotactic starting material.

The weak resonance formed at $\sim 119.5\delta$ can be regarded as a modified olefinic resonance. As it has been shifted downfield with respect to the other peaks, a plausible assignment is as a



environment.

c) Microanalysis:-

Sample	%C	%H	%Br	Total (%)
PS	91.11	7.25		98.36
B_1	83.35	6.38	9.44	99.17
B_2	67.60	5.09	25.75	99.44
B_3	58.51	4.27	35.60	98.38
OTPS	90.98	7.34		98.32
OTB_1	74.69	5.68	10.10	90.47
OTB_2	67.61	4.22	27.76	99.59
OTB_3	42.68	2.95	37.12	82.75

b) Poly(Vinyl Chloride)

1. Photochemical Degradation

Materials

i. PVC:- PVC sample was supplied by BP Ltd (JLB 948) and had \bar{M}_n of 48800. Films of c. 0.10 mm thickness were cast from THF

solution, and dried. UV/Visible spectroscopic investigation showed there to be no appreciable residual impurities.

ii. Sources:- Irradiation sources used were -

a) Low Pressure Lamp. This was a 125 watt Hg lamp (GEC Model No. MVW/U) giving approximately monochromatic irradiation at 253.7 nm.

b) Medium Pressure Lamp - this was a 500 watt Hg lamp (Engelhard Hanovia, Type 509/10) emitting radiation over a wide range of wavelength in the UV and visible regions. Relative intensities of lines are given

below (Manufacturer's Data):-

(nm)	Intensity (W per 100 W loading)
235	0.12
238	0.23
240	0.21
246	0.09
248	0.53
254	0.68
258	0.08
260	0.11
264	0.14
265	0.98
270	0.23
275	0.17
280	0.55
289	0.26
292	0.11
297	0.74
302	1.42
313	2.72
334	0.37
366/	

(nm)	Intensity (W per 100W loading)
366	4.30
391	0.06
405	1.14
406	0.24
436	2.10

iii. Instrumentation:- UV/Visible absorption spectra of the films were taken using a Unicam SP800 spectrophotometer, IR spectra using a Perkin-Elmer 257 Grating spectrometer, and Emission and Excitation spectra using a Perkin-Elmer MPF-2A spectrofluorimeter.

The irradiation cell used was as shown in Fig. C3.

Procedure

20 mm square samples were cut from the PVC film and placed in the irradiation apparatus, and the apparatus pumped out using a Rotary oil pump. This pumping was continued for 15 mins, and then the tap closed for experiments under static vacuum; or continued throughout for experiments under dynamic vacuum.

The irradiation apparatus was placed under the lamp at a constant distance (sample distance from source was c. 200 nm), and the reaction followed by UV/Visible spectroscopy.

Four reactions were carried out with differing conditions of volatile product removal and irradiation, ie.

- | | |
|-----------------------------|---------|
| I. Static vacuum, MP Lamp | Fig. C4 |
| II. Dynamic vacuum, MP Lamp | |
| III. Static vacuum, LP Lamp | Fig. C5 |
| IV. Dynamic vacuum, LP Lamp | |

Results

All samples showed essentially the same characteristics in their UV/Visible spectra. A broad shoulder appeared at 225-250 nm, a broad, featureless, band between 260 and 300 nm, and peaks at c. 312 nm, 325 nm, 360 nm, 395 nm, and 420 nm.

Removal of volatile products, in this case HCl, during the dynamic vacuum experiments appears to initially enhance the production of polyenes, but after 30 mins in the case of the MP lamp, and 2-3 hrs in the case of the LP lamp, this enhancement ceases, and the reaction appears to be proceeding at the same, or a slower rate, than the static vacuum experiments.

Emission and Excitation spectroscopy of these samples will be discussed in the next chapter.

2. Chemical Degradation

Materials

- i. PVC :- PVC used was supplied by BP Ltd (JLB 748) and was used without further purification.
- ii. Solvents:- Tetrahydrofuran (THF, Fisons), was purified in the usual manner¹¹¹, dimethylformamide (DMF, Fisons) was used as supplied. Ethanol used was laboratory grade solvent .
- iii. Chemicals:- Potassium hydroxide and all lithium halide salts were SLR grade, used as supplied.

In this investigation of the chemical degradation of PVC, two types of reaction were compared; the lithium halide/DMF catalysed dehydrochlorination of Sadron et al⁶⁷, and the alcoholic KOH reaction

reported by Shindo and Hirai⁶¹.

a) LiX

Sadron et al have reported good results for the dehydrochlorination reaction between a THF solution of PVC, and a DMF solution of anhydrous LiCl, and this procedure was carried out as an initial investigation into this type of reaction.

3 g PVC was dissolved in 150 ml THF and 150 ml DMF. 12.75 g anhydrous LiCl was added, and the reaction mixture and vessel saturated with N₂. The reaction vessel consisted of a three-necked flask (1 litre), fitted with a screw adaptor with thermometer, condenser, and a right-angled connector to the N₂ supply. The vessel was placed on a stirrer hot-plate and heated rapidly to 80°C with constant stirring. Colour changes noted during the reaction were as follows:-

t (hrs)	Colour
0	Clear
2	Red
3	Deep Wine
4	Purple
5	Black/Purple

The heat source was removed after five hours, and the solution allowed to cool for 10 hrs under N₂. The product was obtained by pouring the reaction mixture into a large excess of hexane under a "Vibromix" stirrer. On filtering, a purple/violet rubbery product was obtained, which exuded a clear liquid, shown on IR investigation to be DMF.

In order to remove the DMF from the polymer, it was refluxed in distilled water for 2 hrs, filtered, washed with acetone, and dried in a vacuum oven at RT for 15 days. The violet powder obtained was

then stored in a brown glass bottle. (The polymers produced by this method should be stable towards O_2 as long as they are kept away from light.)

A reaction was now set up using a molar equivalent of LiBr in place of LiCl, and carrying out the reaction under the same conditions as before. The reaction proceeded similarly to that using LiCl, the colour changes noted being as follows:-

t (hrs)	Colour
0	Clear
0.5	Pale Lemon
1	Red
2	Deep Red
4	Purple
5	Black/Purple

As the reaction now appeared to be at a similar stage to the LiCl procedure, the heat was removed, the sample allowed to cool, and the product worked up in the manner described above.

Similar procedures were carried out using molar equivalents of LiF and LiI, but no observable reaction occurred. Some difficulty was encountered in obtaining UV/Visible spectra of the degraded polymers since they were found to be soluble only in a 1:1 mixture of DMF and THF which cuts off light transmittance at c. 290 nm, making observations on any polyenes absorbing below this wavelength impossible. Spectra (Figs. C6, C7), however, did show the presence of two strong peaks at 321 and 334 nm, and a broad weak band between 400 and 600 nm. Both the LiCl and the LiBr catalysed samples showed similar spectra.

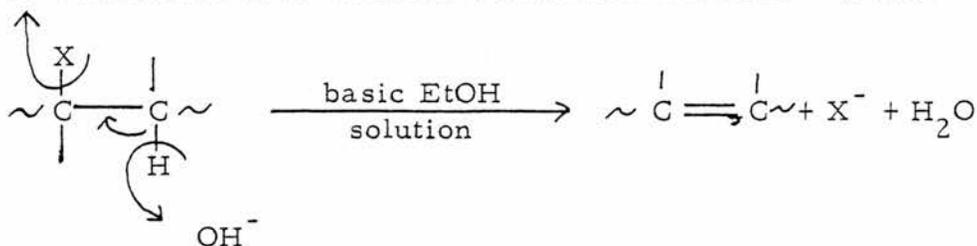
IR spectrum was taken using the KBr disc method. The resultant spectrum was not very clear, but showed a strong absorbance between 1600 and 1700 cm^{-1} indicating the presence of conjugated double bond structures.

Microanalysis results (Elemental Micro-Analysis Ltd, Kingston-upon-Thames) appeared to show that little reaction had taken place, although the strong colour of the products denies this. Results were as shown in the table below:-

Element	PVC (%)	LiCl Product (%)	LiBr Product (%)
C	38.44	37.38	36.13
H	4.84	4.83	4.67
Cl	56.72	54.78	52.67
Total	100.00	96.99	93.47

b) KOH

It has been reported by Shindo and Hirai that PVC can be effectively dehydrochlorinated using alcoholic KOH at low T (high T would tend to cause chain scission and gel formation). The mechanism of dehydrohalogenation of alkyl halides with basic reagents has been well studied and is considered to be an ionic elimination reaction¹¹², ie.



Removal of halogen is made easier by the formation of ion-dipole bonds between X^- and the polar ethanol molecules.

In this experiment, the procedure used by Shindo and Hirai was followed, as far as possible.

5 g PVC was dissolved in 200 ml THF and refluxed for two hours. 4.5 g KOH was dissolved in 50 ml ethanol, the solution then being made up to 100 ml with THF. The PVC solution was cooled in an ice bath, with constant stirring, for 0.5 hrs, then the KOH solution added with vigorous stirring. At hourly intervals 50 ml samples of the mixture were removed and poured into 500 ml portions of deionised water; these samples were left for 24 hrs to dissolve as much base as possible. The products were then filtered, washed with water, and dried in vacuo at RT for 5 days.

Appearance

t (hrs)	On precipitation	dry	T (°C)
1	Salmon Pink	Salmon Pink	1
2	Salmon Pink	Salmon Pink	1
3	Slightly darker	Salmon Pink	1.5
5	Pale Orange	Pale Orange	6
20	Black	Black	19

It would appear that this reaction is an efficient method of dehydrochlorinating PVC, but it was noted that the T is an overriding critical factor in the reaction of equal importance to the reaction time. The 20 hr sample particularly shows a very high degree of dehydrochlorination.

In order to investigate the UV/Visible spectroscopic properties of these materials, solutions of the 1, 2, 3 and 5 hrs samples were made up to 10^{-2} M in THF and examined on the SP800 spectrophotometer (20 hrs sample was insoluble in all organic solvents). As expected,

the spectra (Figs. C8, 9) show a gradual overall increase in absorbance going from the 1 hr to the 5 hr samples. After 5 hrs discrete maxima can be located (approximately) at 265-300 nm, 275, 307, 320, 335, 360, 385 and 410 nm, 433, 455 corresponding to polyene segments with up to ~ 10 conjugated double bonds.

On re-examining the samples after 24 hrs it was found that all had faded slightly, especially the 5 hr sample in which the peaks at 335, 352, 380, and 408 nm had all but disappeared. This loss of higher polyenes is most likely due to a "reshuffling" of the distribution of conjugated sequences brought about by the increased ease of rotation about single bonds in dilute solution and/or to the action of light on the solutions.

c) Poly(Vinyl Acetate)

1. Thermal Degradation

Materials

i. PVAc - The Poly(Vinyl Acetate) samples used (BDH Ltd) had molecular weights of 160000 and 45000. These were purified by dissolving in toluene, then precipitating from large excess of hexane under a "Vibromix" stirrer. The product was then dried in a vacuum oven at RT for 7 days. The white, fibrous polymer was then dissolved in methylene chloride (CH_2Cl_2), reprecipitated from hexane, and dried in a vacuum oven at RT for 3 days.

- ii. Monomers - Vinyl acetate, styrene, acrylonitrile, methyl acrylate, and methyl methacrylate (BDH Ltd) were redistilled and stored at 0°C before use; 2-vinyl naphthalene (Koch-Light) was used as supplied.
- iii. Solvents - Methylene chloride and toluene were purified by the usual methods, hexane, methanol, pet. ether and acetone were normal laboratory grade solvents.
- iv. Films - Films of the polymer were cast from 20 gl⁻¹ solutions in CH₂Cl₂ (acetone solution with case of the poly(vinyl acetate-co-acrylonitrile)) onto 25 mm quartz discs. These were dried in air in the dark for 24 hrs, then placed in a vacuum oven at RT for 3 days. Resultant films were 0.02-0.05 mm thick.
- v. Apparatus - The set-up used for thermal degradation of sample films was as shown in Fig. C10. The reaction vessel was pumped out on a standard vacuum line to C. 10⁻⁵ Torr. The oven used was a Perkin-Elmer F-11 Precision oven.
- vi. Instruments - UV/Visible spectra were taken using the Unicam SP800 spectrophotometer. Emission and Excitation spectra were taken using the Perkin-Elmer MPF-2A spectrofluorimeter.

Copolymerisation

Copolymers of vinyl acetate with various monomers were prepared in order to investigate their degradation behaviour in comparison with that of the two homopolymer samples. Copolymerisations were carried out using the methods of Mayo et al¹¹³, but using azobisisobutyronitrile

(AIBN) in place of benzoyl peroxide as initiator. The ratios used and results are reported for each individual copolymer below:-

I. Poly(Vinyl Acetate-co-Styrene)

Moles Vinyl Acetate	= 0.06270
Moles Styrene	= 0.01086
Moles AIBN	= 0.01 M%

The three starting materials were mixed and weighed in a weighing bottle on a balance accurate to 4 decimal places, and then placed in a sealable tube. This tube was attached to a vacuum line and dissolved gases removed by five repetitions of a freeze-pump-thaw cycle. The sealed tube was then placed in the F-11 precision oven at $60 \pm 1^\circ\text{C}$.

After 6 days, it was noted that the reaction mixture was now an opaque viscous liquid. The tube was cut open and the polymer dissolved in 200 ml of CH_2Cl_2 , then precipitated from a large excess of MeOH. On leaving to stand for 48 hrs it was found that a colloid had formed, the polymer not settling out from the non-solvent. As filtering proved ineffective, the solvent and non-solvent were removed on a Buchi rotavapour.

Microanalysis:-	% C	% H	% O
Sample	64.46	7.73	28.18
PVAc	55.81	7.02	37.17
PS	92.26	7.75	0

Films cast of this copolymer showed it to be extremely opaque. The UV/Visible spectrum showed a steadily increasing absorbance between 450 and 230 nm, with the characteristic peak pattern of PS faintly visible between 250 and 275 nm.

II. Poly(Vinyl Acetate-co-Methyl methacrylate)

Moles Vinyl Acetate	= 0.0529
Moles Methyl methacrylate	= 0.01378
Moles AIBN	= 0.01 M %

The mixture of the above components was treated as before on the vacuum line and then the sealed tube transferred to a water bath set at $60 \pm 0.5^{\circ}\text{C}$, and allowed to polymerise for 5.5 hrs.

On cooling, the reaction mixture was poured into excess of MeOH, filtered, dried, then dissolved in 200 ml CH_2Cl_2 . This was then reprecipitated from excess MeOH, filtered, and dried in a vacuum oven at RT for 5 days. The product was a hard, clear polymer.

Microanalysis	% C	% H	%O
Sample	58.26	7.78	33.53
PVAc	55.81	7.02	37.17
PMMA	60.13	8.05	31.82

Films cast of this copolymer were very clear, clean films; UV/Visible spectra showed only a small absorbance between 240 and 200 nm.

III. Poly(Vinyl Acetate-co-Acrylonitrile)

Moles Vinyl Acetate	= 0.06389
Moles Acrylonitrile	= 0.01645
Moles AIBN	= 0.01 M %

The above mixture was degassed in the usual manner and polymerised at 60°C for 15 hrs. The result was a hard, yellowish

polymer, indicating that even at this low T some oligomerisation at the nitrile side groups may have occurred. The product was partially dissolved, with great difficulty, in acetone, filtered, and then precipitated from petroleum ether. A highly viscous pale yellow polymer was obtained, which was then dried in a vacuum oven at 40°C for 5 days.

Microanalysis:	% C	% H	% N	% O
Sample	56.58	7.36	2.71	33.35
PVAc	55.81	7.02	0	37.17
PAN	67.91	5.70	26.40	0

Films cast from this polymer showed the product to be inhomogenous, the film having the appearance of a PVAc film with discrete domains of PAN intersperced. The UV/Visible spectra showed a steady absorbance of c. 0.2-0.3 from 450 to 250 nm with a broad absorption band between 245 and 200 nm.

IV. Poly(Vinyl Acetate-co-Methyl Acrylate)

Moles Vinyl Acetate	= 0.06389
Moles Methyl Acrylate	= 0.01736
Moles AIBN	= 0.01 M %

The time allowed for this polymerisation by Mayo et al is only 15 mins. During the 5 freeze/pump/thaw cycles, it was noted that bubbles of gas, presumably N₂ from the AIBN, were increasing in intensity with each cycle, and that the viscosity had drastically increased by cycle 5. It would thus appear that the polymerisation reaction proceeds rapidly even with the heat of the air blower

used during the "thaw" part of the degassing process.

On allowing the sample to stand for 1 hr, it was found that it was now above RT and appeared quite solid, it was therefore not subjected to further heating, but worked up at this point. The polymer was dissolved in CH_2Cl_2 , precipitated from MeOH, filtered, and dried in a vacuum oven at RT for 5 days. The product was a rubbery polymer.

Since vinyl acetate and methyl acrylate have the same molecular formulae, microanalysis could not be used to determine the ratios present in the copolymer. Instead the ratio of vinyl acetate was estimated by analysis for acetic acid, using the method developed by Mayo et al.¹¹³

	% Acetic Acid
Sample	18.35
PVAc	68.58
PMA	0

Films cast using this polymer were clear, and the UV/Visible spectra show practically no absorption up to 250 nm, with a strong absorption band between 245 and 200 nm.

V. Poly(Vinyl Acetate-co-2-Vinylnaphthalene)

Moles Vinyl Acetate	= 0.01
Moles 2-Vinylnaphthalene	= 0.05
Moles AIBN	= 0.01

The proportions of monomer were taken as being within the range used by Mayo et al. The modified quantity of AIBN, and the

raised polymerisation T (70°C) were assumed from the work of Anderson et al¹¹⁴ on copolymerisation of methyl acrylate and 1-vinylnaphthalene.

The reason for this particular copolymerisation is the possibility of interesting effects on the absorption and emission characteristics of vinyl naphthalene by gradual introduction of polyenic units connecting the naphthyl bearing carbons, and conversely, their effect on the polyene spectroscopy.

The solid 2-VN was dissolved with no difficulty, along with AIBN, in the VAc, and the resultant yellow solution was degassed in the usual manner. After 120 hrs polymerisation, the product was poured into an excess of hexane, and a pale yellow product obtained, which retained the characteristic "Thyme" odour of the monomer. A UV spectrum of a CH_2Cl_2 solution of the polymer was compared to a literature spectrum¹¹⁵ to ascertain if any residual monomer was present. Only a small amount was detected, and this was removed by dissolving the polymer in CH_2Cl_2 and reprecipitating from hexane. The product was dried in a vacuum oven at 40°C for 5 days.

Microanalysis:-	%C	%H	%O
Sample	88.76	7.45	8.58
PVAc	55.81	7.02	37.17
PVN	93.46	6.54	0

Films cast from this polymer were clear, pale, yellow. UV/Visible spectra show the characteristic strong series of peaks of PVN between 300 and 265 nm. Absorbance goes off scale at 245 nm.

1st Series Thermal Degradations

Samples of PVAc, blends of PVAc with PMMA and PS, and copolymers of PVAc with various monomers were cast as thin films onto quartz discs from CH_2Cl_2 solutions. These were dried in a vacuum oven at RT for 48 hrs, the resultant films being 0.02-0.03 mm thick. The samples were placed in the degradation apparatus, which was attached to a vacuum line and pumped out to c. 10^{-5} Torr. The apparatus was then placed with the sample arm in a modified F-11 precision oven, and the trap in liquid N_2 in order to remove evolved acetic acid from the reaction area, for varying lengths of time at 220°C . The development of polyene structures in the samples was followed by UV/Visible spectroscopy.

a) High MW PVAc:- Films cast using the 160000 MW polymer were very clear, and showed no absorption above 260 nm, and only a low, broad, absorption between 225 and 200 nm.

Very thin films (0.02 mm) degraded under these conditions showed a steady overall increase in absorption above 450 nm. Bands attributable to monoene (< 200 nm) and diene (broad, centering on 225 nm) can be seen, while at higher wavelengths very shallow maxima at (approx) 260, 272, 283, 305 and 322 nm can just be made out after 22 hrs corresponding to short polyenes with up to 5 double bonds¹¹⁶.

Plotting peak height vs time for the maxima at 225 and 272 nm, we obtain a graph showing a short initiation period of high rate of formation for both peaks, although the 225 rate is faster. The plots all have a generally sigmoid curve shape and this will be discussed later. It was noted that, even after 40 hrs degradation, little or no absorption was seen above 400 nm, suggesting that long polyene

sequences (> 8) have not been formed.

b) Low MW PVAc:- Films of low MW PVAc show the presence of small amounts of monoene and short polyene sequences even after purification. This is probably due to the higher proportion of double-bonded end groups in the sample. Degradation followed the same pattern as for the high MW material, but with the maxima between 250 and 400 nm being extremely weak even after 15 hrs degradation.

c) Blends:- Blends of high MW PVAc with PS, PMMA and low MW PVAc were made up in the ratio 1:1 in CH_2Cl_2 solution and cast into films in the manner described previously.

The PVAc-PS blend was inhomogenous and no useful results were obtained from the thermal degradation.

The PVAc-PMMA blend exhibited similar behaviour to the high MW PVAc sample, showing the maxima noted for that film after 34hrs degradation.

The high MW-low MW PVAc blend exhibited behaviour similar to that of low MW PVAc.

d) Copolymers:- The purpose of preparing copolymers of VAc with the various monomers was to restrict the polyene sequence length of the degraded PVAc, and to investigate the properties of polyene-vinyl monomer copolymers of various types. However, the UV/Visible spectroscopy results for the copolymers were disappointing. VAc is an inefficient co-monomer and this is reflected in the microanalysis results, and in the non-appearance of any discrete maxima in the UV/Visible spectra of the degraded copolymers. This, coupled with the "self-restriction" on polyene sequence length by PVAc led to the abandonment of all the copolymers except Poly(Vinyl Acetate-co-Acrylonitrile) and Poly(Vinyl Acetate-co-Methyl Acrylate) at this stage of the investigation.

2nd Series Thermal Degradations

In order to speed up the creation of polyene sequences and, if possible, clarify the exact positions of the maxima noted tentatively for PVAc degraded under 1st Series conditions, it was decided to utilise films of 0.04-0.06 mm thickness and to increase the degradation temperature to 250°C. This set-up gave good results within a moderate time scale.

a) High MW PVAc:- Fig. C11. The initial spectrum of the 0.05 mm thick sample film showed no absorbance above 250 nm, and a broad band between 240 and 200 nm. After 60 min the peak at 200 nm, the broad peak centering on 225 nm, and the maxima at 262, 272, 283, 306, and 321 nm had developed. The degradation was continued for 360 min with UV/Visible spectra being taken at 30 min intervals. These spectra showed the development of very distinct maxima at the wavelengths noted above, while other maxima at 334 (very shallow), 354, and 385 nm had developed by 300 min. No significant absorption was noted above 400 nm, even after 360 min, confirming that, with the time scale used, polyenes created in PVAc samples are limited to sequences of about 8 double bonds.

Plots of the peak heights of the maxima at 272, 321, and 354 nm vs time show no high initial rate of polyene creation like those of the 1st Series samples, but they again have a sigmoidal appearance.

b) Low MW PVAc:- Fig. C12. As before, the initial undegraded samples showed the presence of traces of polyene sequences. Degradation carried out over a 10 hr period, with UV/Visible spectra

being taken at intervals, showed the maxima corresponding to sequence lengths of 3-8 double bonds to be much less distinct than those for the High MW sample. Again the sample showed little inclination to form sequences of greater than 8 double bonds within the 10 hrs reaction time.

Plots of peak height vs time for the 272 and 321 nm maxima showed similar shapes to that encountered for the high MW PVAc sample.

c) Copolymers:- Only two of the five copolymers synthesised were used at this stage of the polyene synthesis. Poly(Vinyl Acetate-co-Methyl Acrylate) Fig. C13 showed a general increase in absorption after 2 hrs. degradation under the conditions described above, but no indication of forming discrete maxima at any wavelength corresponding to polyene sequences; indeed, little or no formation of mono- or di-ene structures was detected.

After 1 hr degradation Poly(Vinyl Acetate-co-Acrylonitrile) Fig.C14 showed formation of polyene maxima similar to that of PVAc, however, the sample was inhomogeneous, suggesting that the two monomers had separately homopolymerised. The opaque nature of the sample would prevent clear emission spectra being obtained.

It was now decided to abandon further work on copolymer systems, and to concentrate on the chemical and fluorescence properties of the polyene systems created in the degraded PVAc samples.

2. Solution Phase Thermal Degradation

Materials

i. PVAc:- The polymer sample used in this investigation was of

$\overline{M}_n = 160000$, and was purified by the methods already described.

ii. Solvents:- Ethyl salicylate (Hopkin and Williams Ltd, BP=231-232°C) was used as supplied. Hexane was laboratory grade solvent. CH_2Cl_2 was purified by the usual methods.

iii. Equipment:- Thermal degradation was carried out using a heating mantle, with the T monitored by a thermocouple (See Fig. C15).

iv. Instruments:- UV/Visible spectra were taken using the Unicam SP800 spectrophotometer. Emission spectra were taken using the Perkin-Elmer MPF-2A spectrofluorimeter.

Procedure

Ethyl salicylate was used as a solvent here, due to the clear UV/Visible maxima obtained by Varma and Sadhin using this particular system.

A solution of 0.5 g PVAc in 50 ml ethyl salicylate was made up, and 10 ml samples were placed in the reaction tube for each experimental run. These samples were then degassed on the vacuum line with 3 repeats of a freeze/pump/thaw cycle, and then placed in the heating mantle, which had been pre-heated to the required T, under dynamic N_2 atmosphere. After the specified degradation time, the sample tube was removed from the heating mantle and allowed to cool to RT under N_2 atmosphere. The product was recovered by precipitation from large excess of hexane, filtered, washed with hexane, and dried at RT in vacuo.

Expt. 1:- Two samples were degraded after 1 hr at 184°C and 205°C respectively. Spectra of the cooled solutions, in comparison

with ethyl salicylate, showed that T has a large effect on the products. The 205°C spectra being much more intense overall, as is evidenced by the comparison of the absorbances of the discrete maxima noted below:- (Fig. C16)

λ max	Absorbance	
	205°C	184°C
357	1.58	0.36
389	1.56	0.31
413	1.32	0.28
437	1.10	0.26
460	0.96	0.25
480	0.85	0.25

Maxima at λ less than 350 nm could not be noted, as the machine cut-off came at 340-350 nm.

Expt. 2:- A sample was degraded at 184°C for 5 hrs, with spectra being taken of the cooled solution in comparison with ethyl salicylate at hourly intervals. It was found that the spectra were similar for readings taken at 2, 3, 4, and 5 hrs, and it was further noted that there was an increasing amount of insoluble polymer attached to the sides of the reaction tube.

Expt. 3:- A sample was degraded at 205°C for 1 hr, and the product worked up in the way described above. A dilute solution of the dried product was made up in CH_2Cl_2 and the UV/Visible spectrum taken immediately, 5 mins after preparation, and 24 hrs after preparation, Fig. C17. After 5 mins a noticeable drop in absorbance was noted for the solution, and after 24 hrs a large drop

had occurred, and no discrete maxima could be discerned above the cut-off point at 340 nm.

Products obtained from the above experiments were pink, rubbery, materials which appear to be stable in air. Further purification by dissolving in CH_2Cl_2 and reprecipitating from hexane appeared to cause no change in the spectral properties.

3. Chemical Degradation

One of the few references in the literature to chemical degradation of PVAc, is to the procedure involving p-toluenesulphonic acid (p-TSA) discovered by Braun and Agha-Ebrahim¹⁰¹. It was decided to test this reaction, and the reaction of PVAc with similar acids, as a method of producing polyene sequences in PVAc.

Materials

- i. PVAc:- As section 2.
- ii. Solvents:- Toluene was used as supplied (Fisons). Hexane was laboratory grade solvent.
- iii. Chemicals:- p-TSA, p-cresol, p-toluic acid, p-chlorobenzoic acid, pentachlorophenol, and phosphoric acid (98%) were all used as supplied.
- iv. Apparatus:- Quickfit reflux set-up.
- v. Instruments:- As section 2.

Procedure

A master solution of 5 g PVAc ($\overline{M}_n = 160000$) in 150 ml toluene was made up. Each experimental run consisted of 50 ml of this solution, plus 50 ml toluene, and 0.05 g of catalyst (3% by weight of PVAc). Degradation was carried out by refluxing the above solution

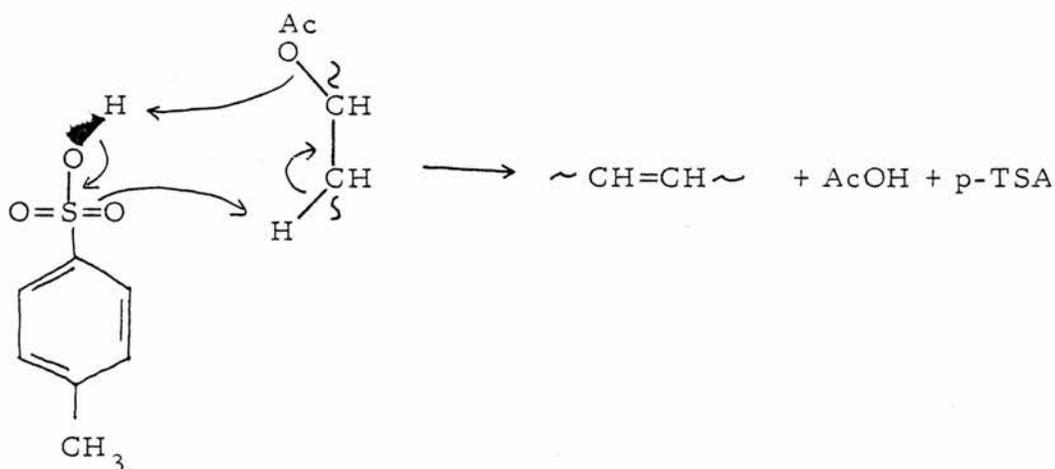
under dynamic N_2 atmosphere.

The preliminary experiment was carried out using p-TSA as catalyst. Five minutes after the commencement of boiling, the solution turned yellow; after 15 mins, orange; and after 30 mins, red. After 75 mins the solution was dark red, and the heat was removed. N_2 flow was maintained until the reaction mixture cooled to RT. The product was precipitated by pouring the reaction mixture into a large excess of hexane; filtered, and dried at RT in vacuo for 48 hrs. A pink elastic material was obtained.

The degraded polymer was purified by dissolving in CH_2Cl_2 and reprecipitating from hexane. The rubbery brown product was then dried in a vacuum oven for 10 days at RT.

UV/Visible spectrum of a dilute solution of the above product showed the presence of a small amount of polyene absorption, but faded rapidly (Fig. C18).

Since only catalytic amounts of p-TSA are required for this reaction, a possible mechanism is that shown below: -



If the above mechanism holds, then requirements for a successful catalyst are ; a) A highly acidic proton

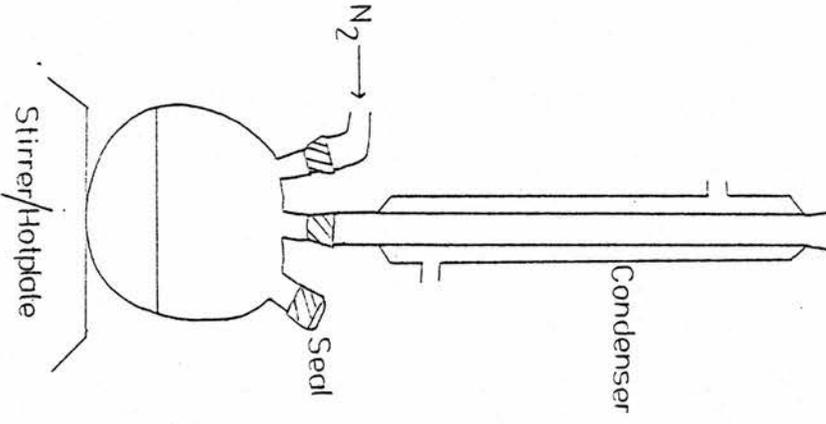
b) A nearby proton receiving group

Both these conditions must be filled for a successful catalyst, therefore strongly acidic phenols should not cause this reaction, while carboxylic, sulphonic or phosphonic acids might. To test this theory two phenols (p-cresol and pentachlorophenol) and three acids (p-toluene, p-chlorobenzoic, and phosphoric) were used as catalysts, in the same proportion as p-TSA.

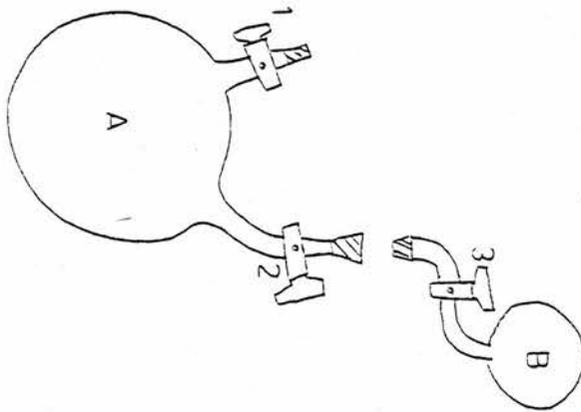
Of the above, only phosphoric acid gave a slight deacetylation reaction.

Of the methods noted in this chapter for the production of polyene systems in saturated polymers, it has been shown that thermal and photochemical treatment of polymer films gives the best results. Chemical degradation can produce a greater variety of double bond sequence lengths, but solutions of these products fade rapidly and in many instances the products are insoluble in any organic solvent and are therefore useless for spectroscopic investigations.

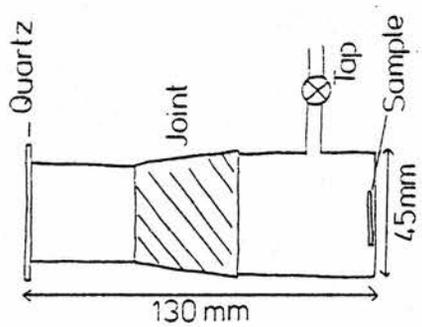
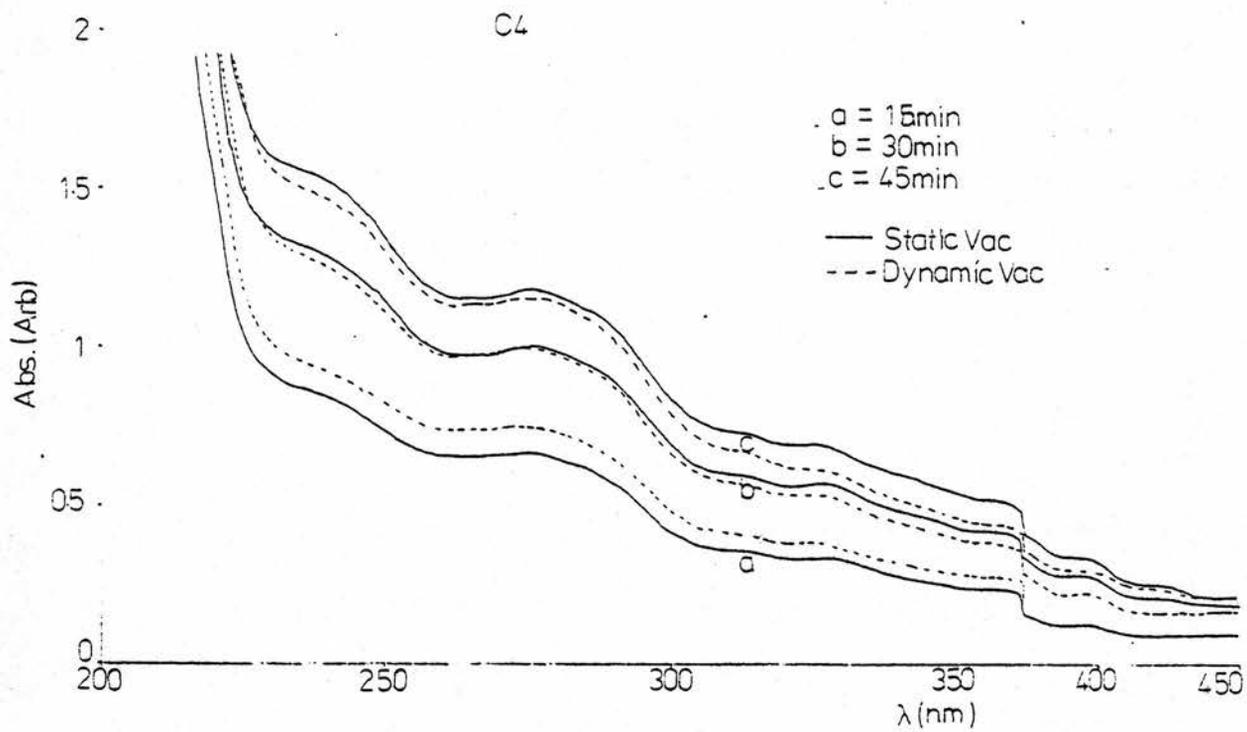
In the next chapter we shall investigate the emission spectroscopic properties of the systems synthesised by the methods described above.

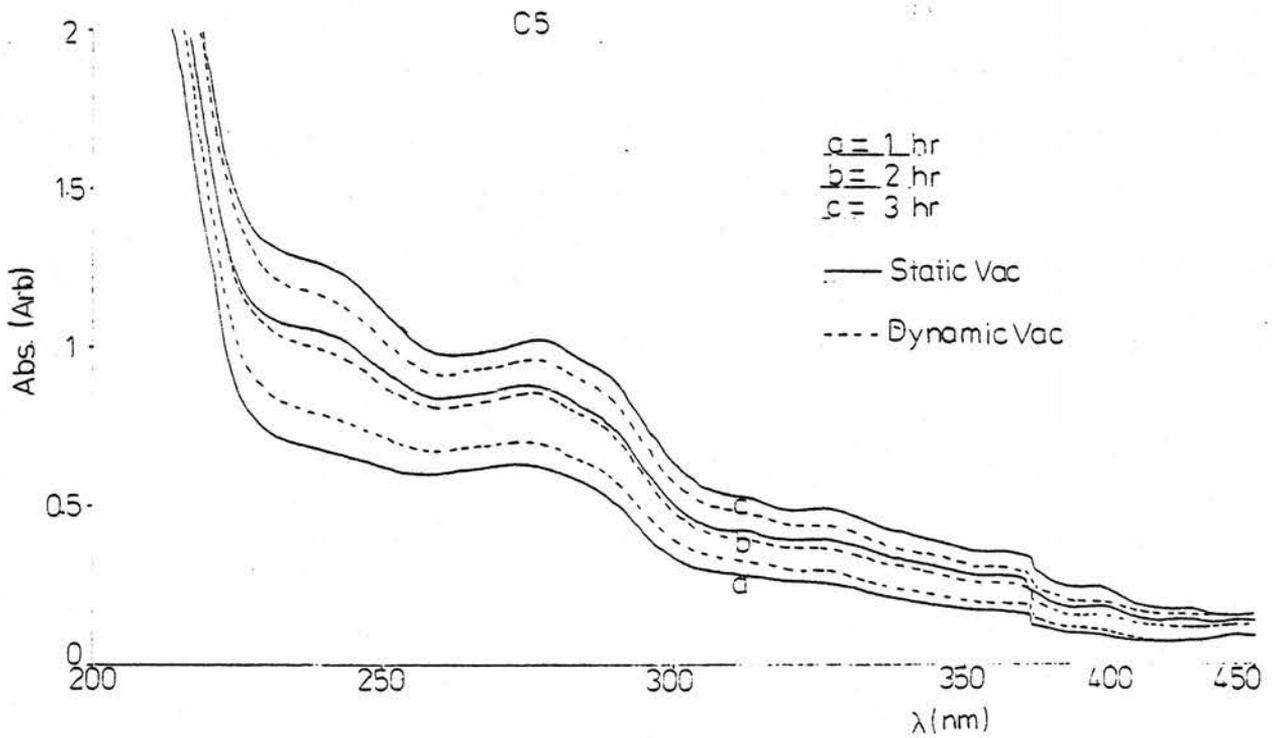
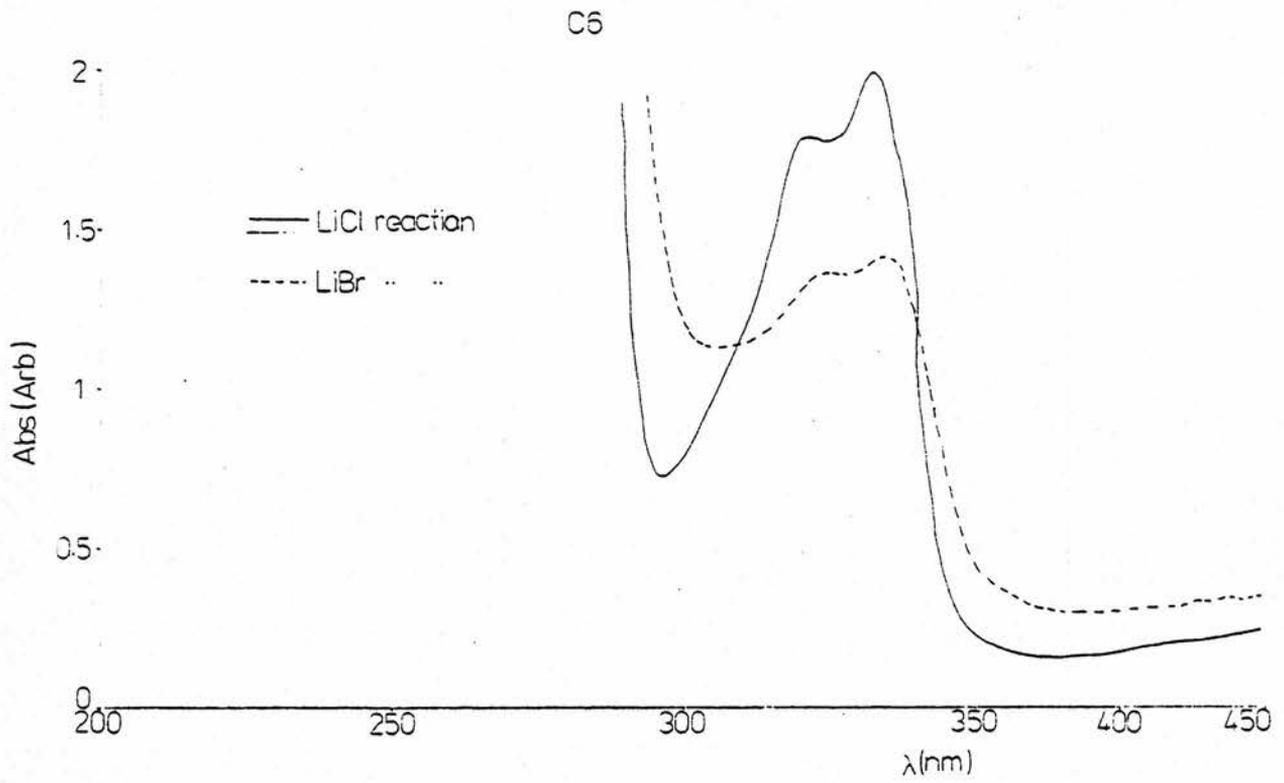


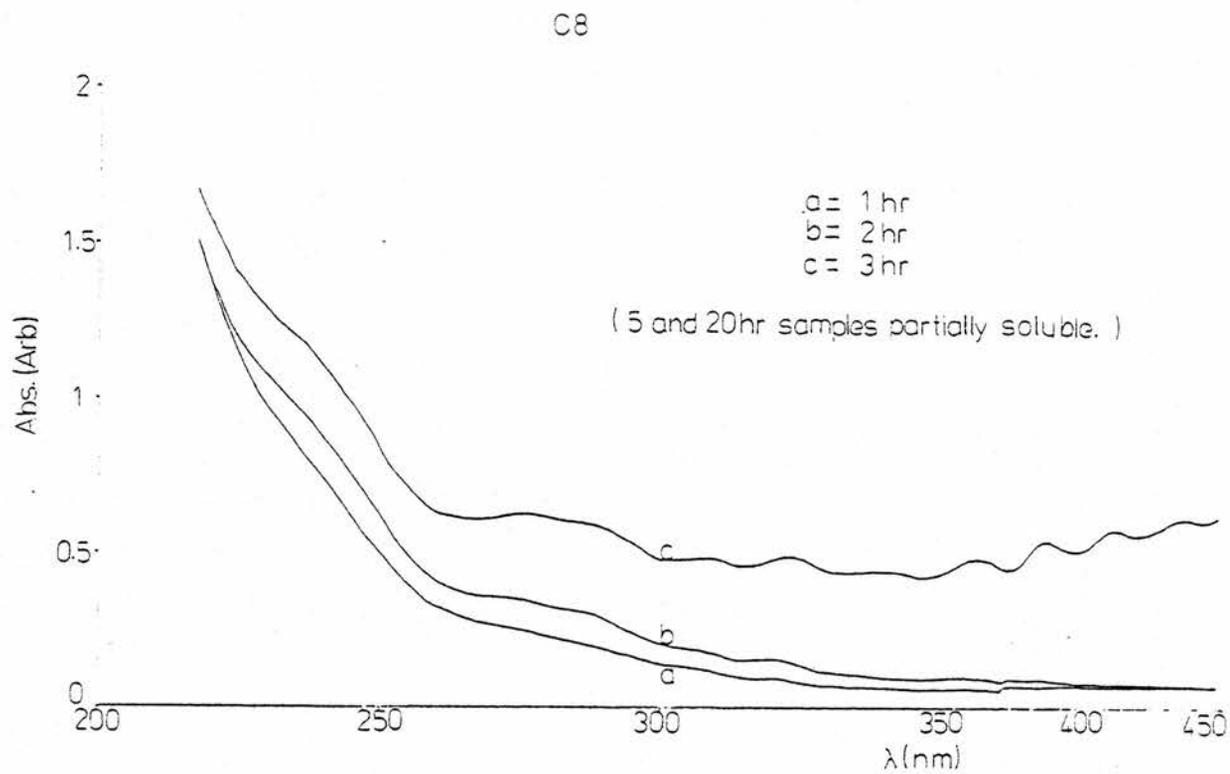
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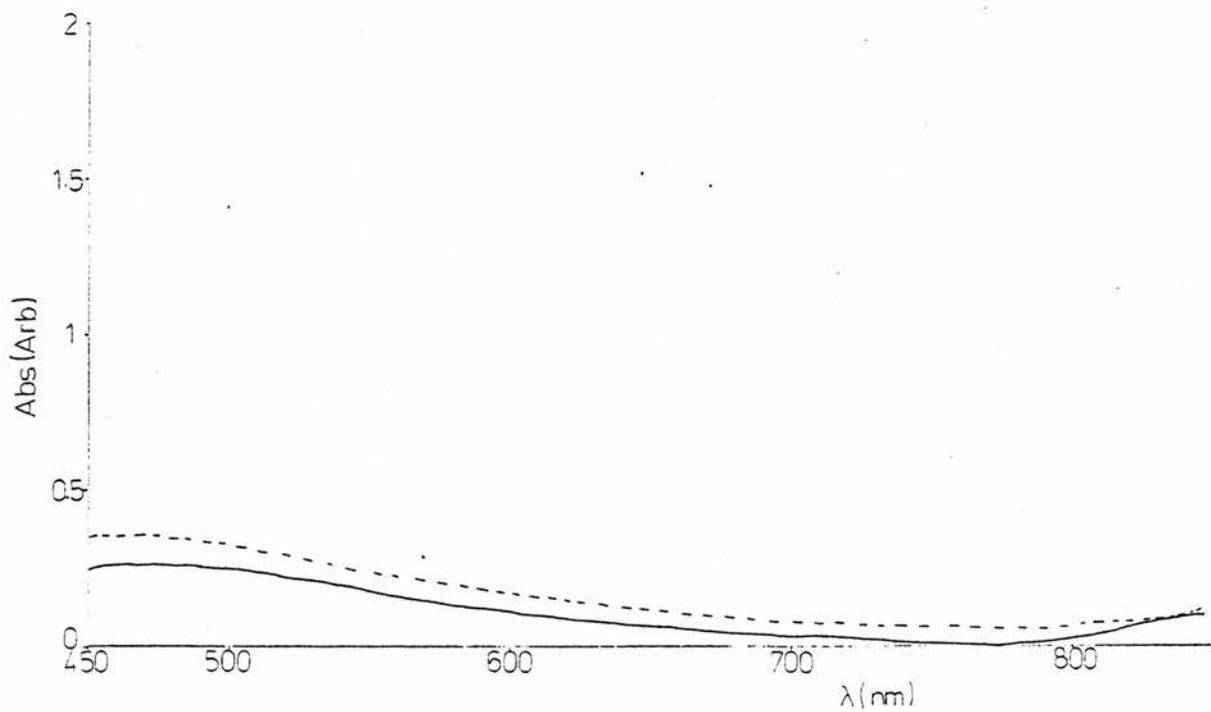
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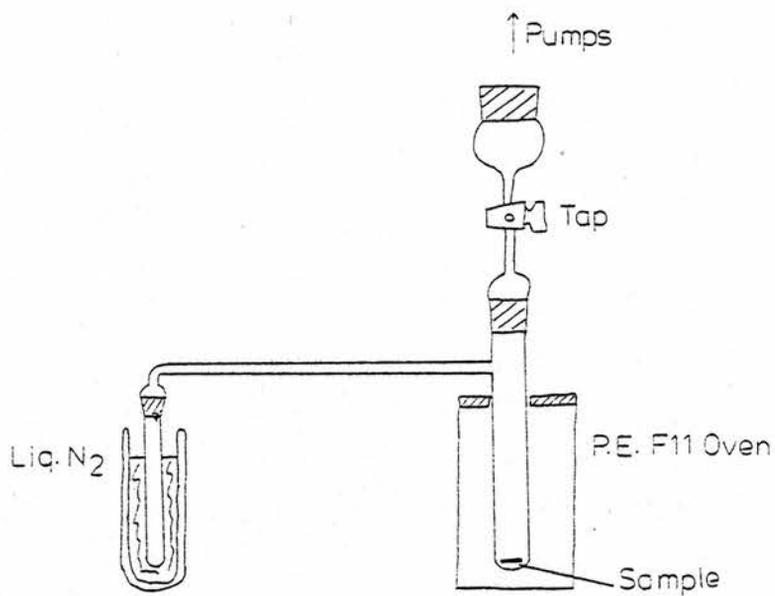




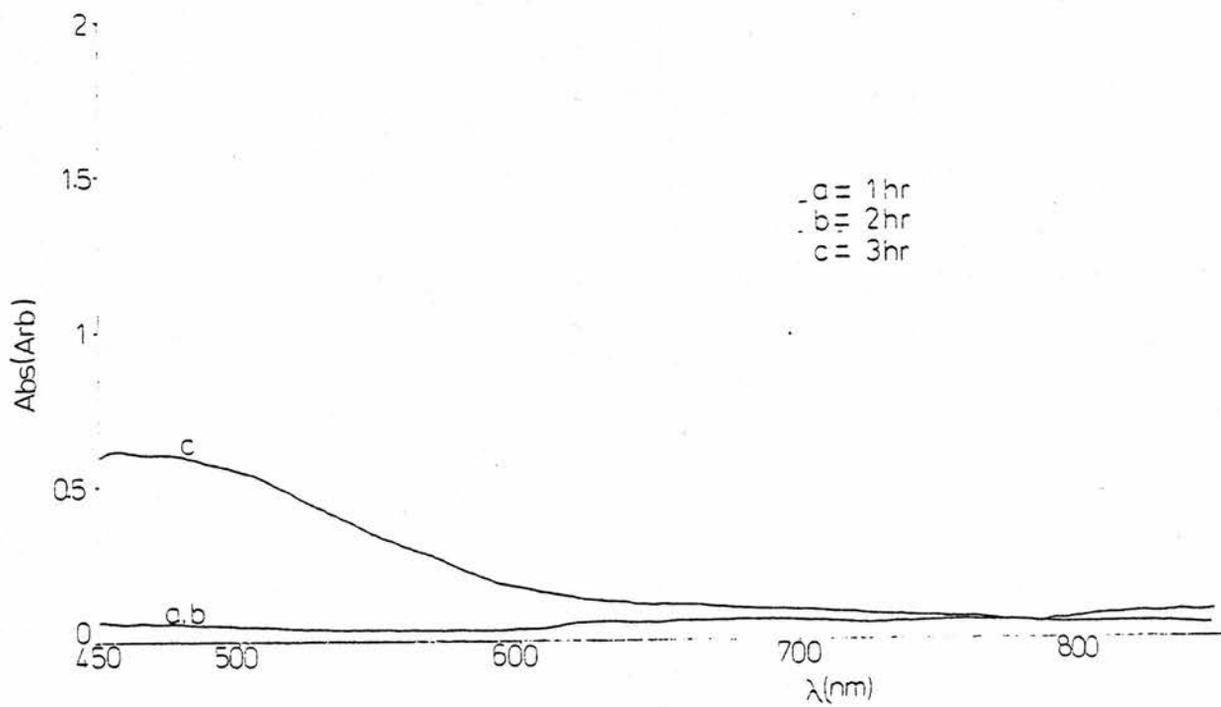
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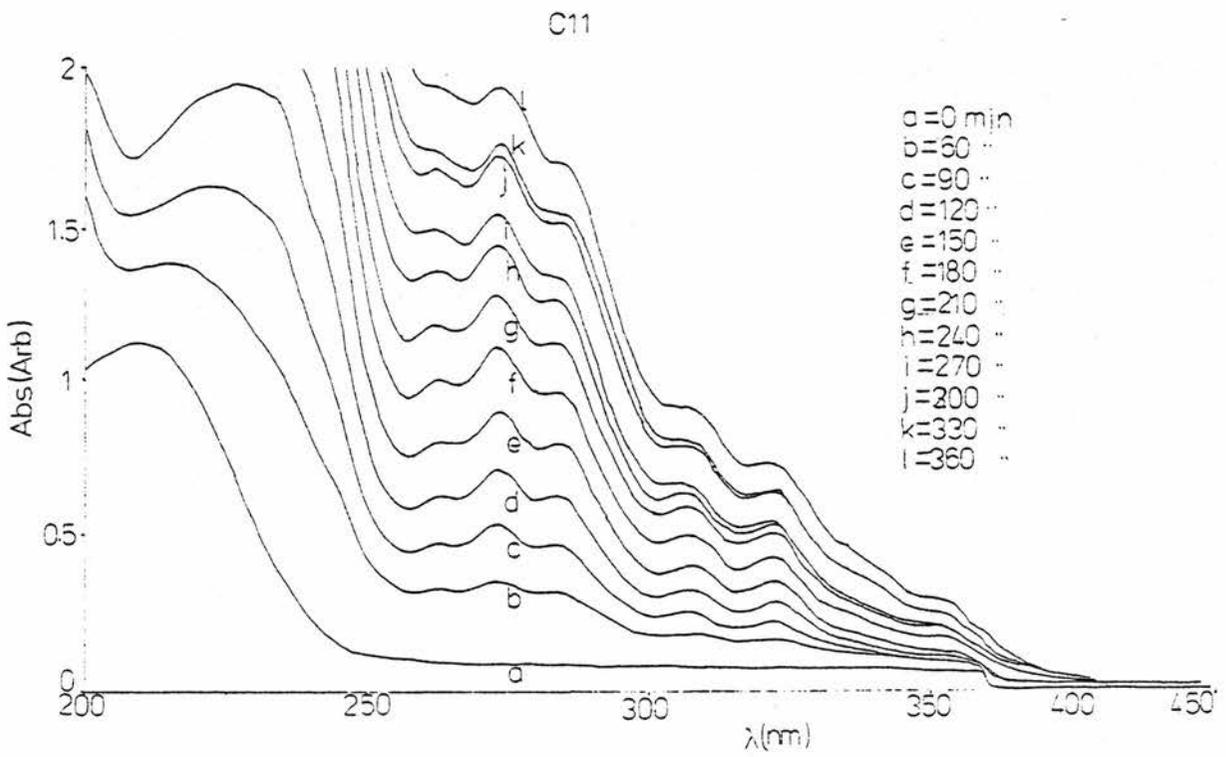
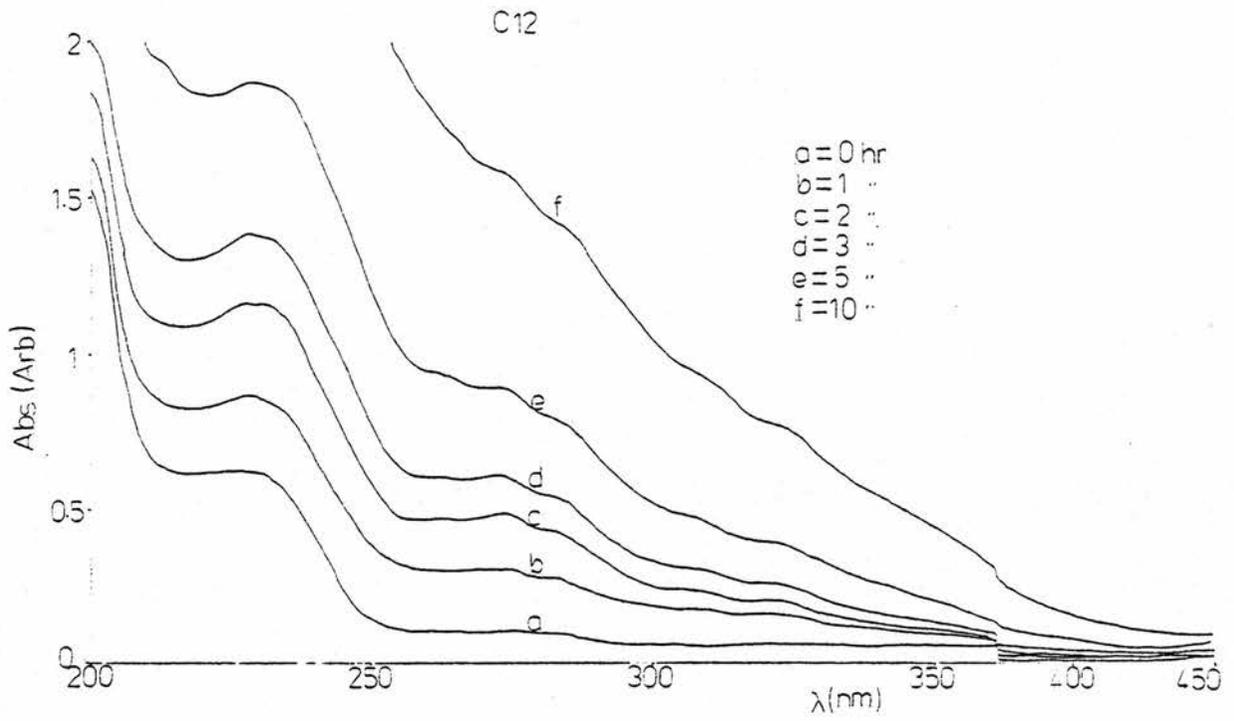


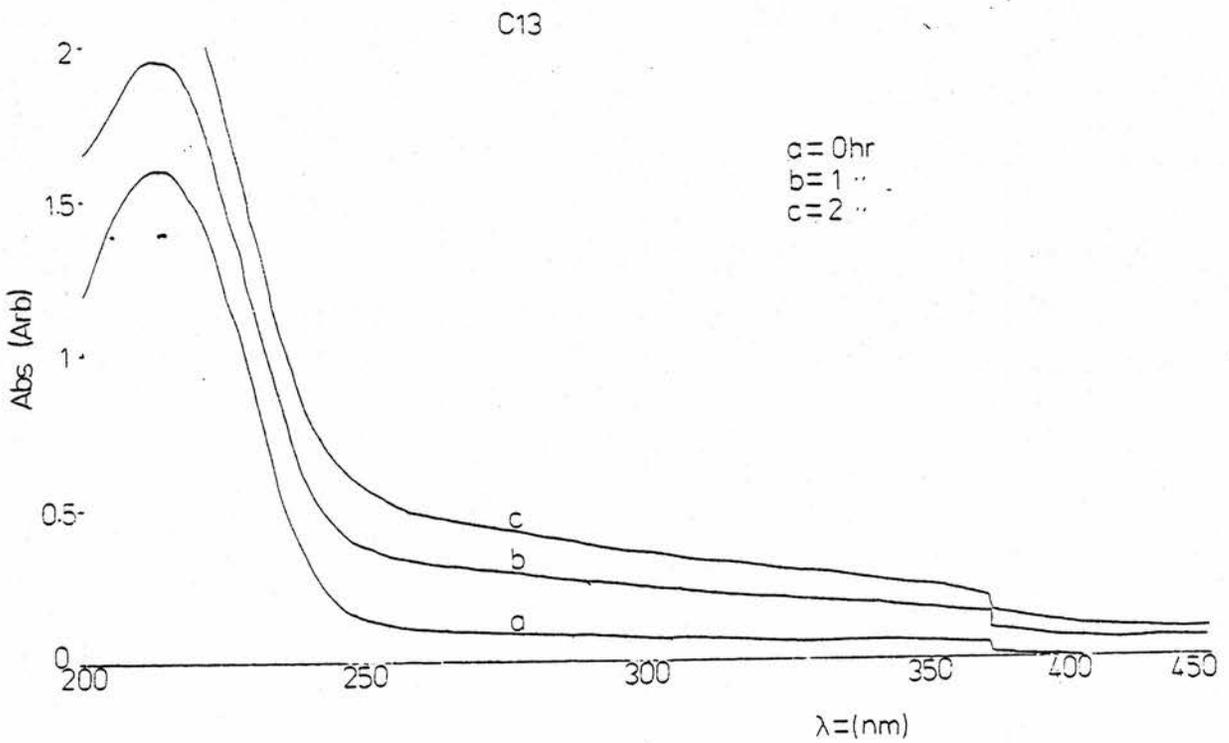
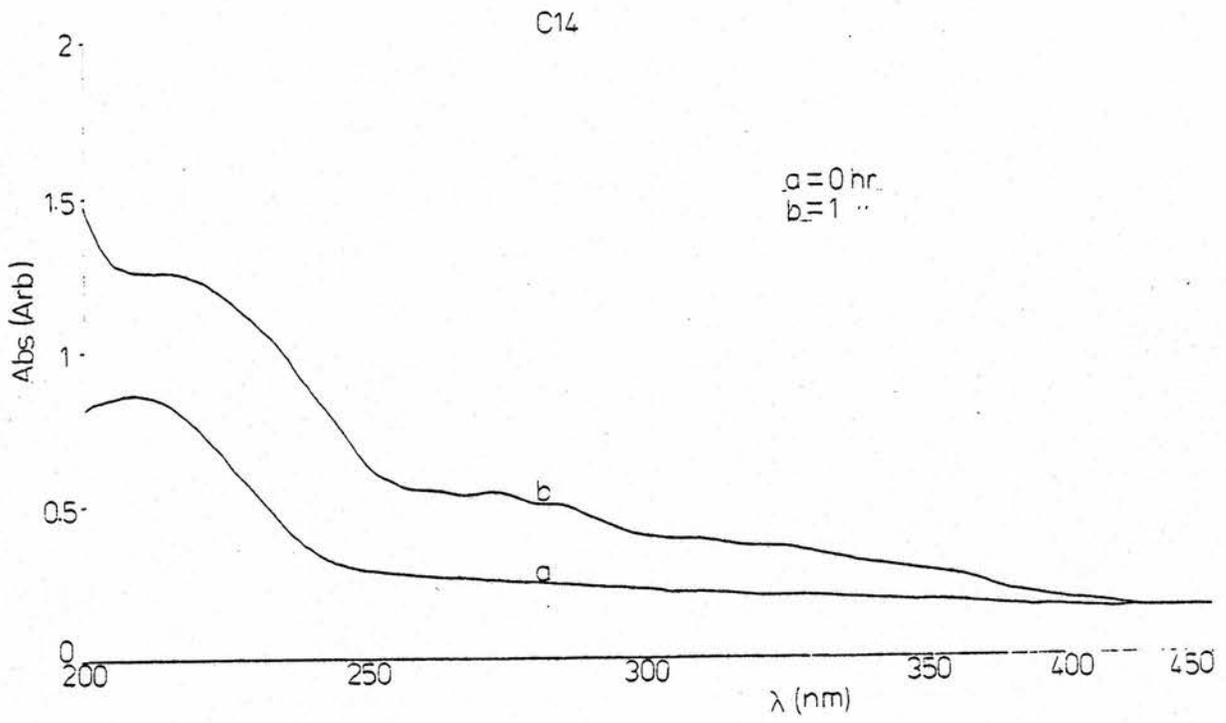
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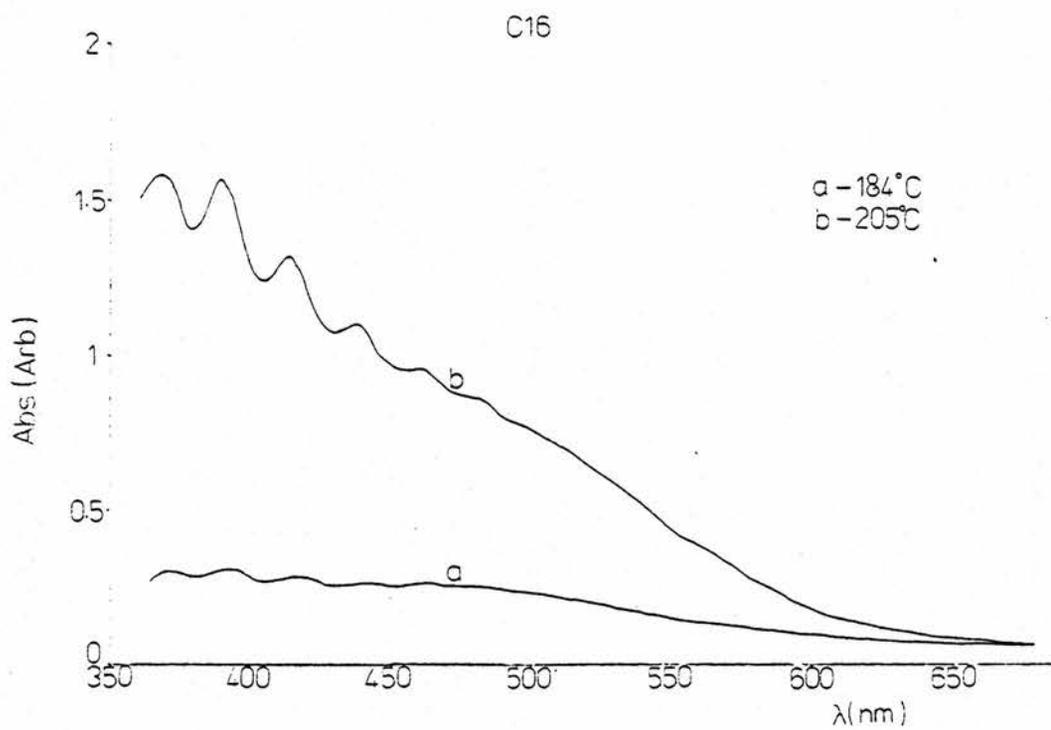


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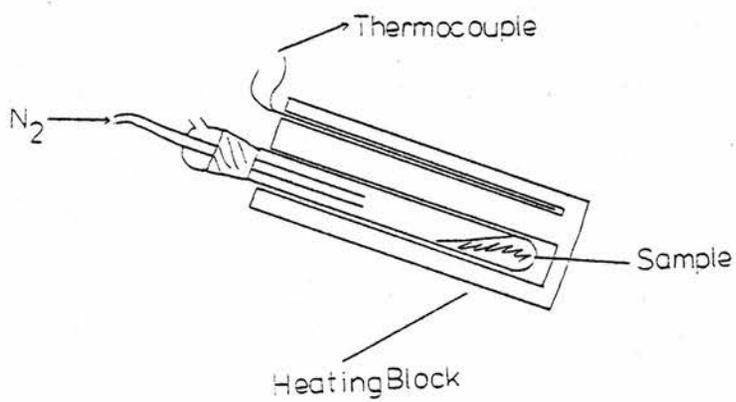


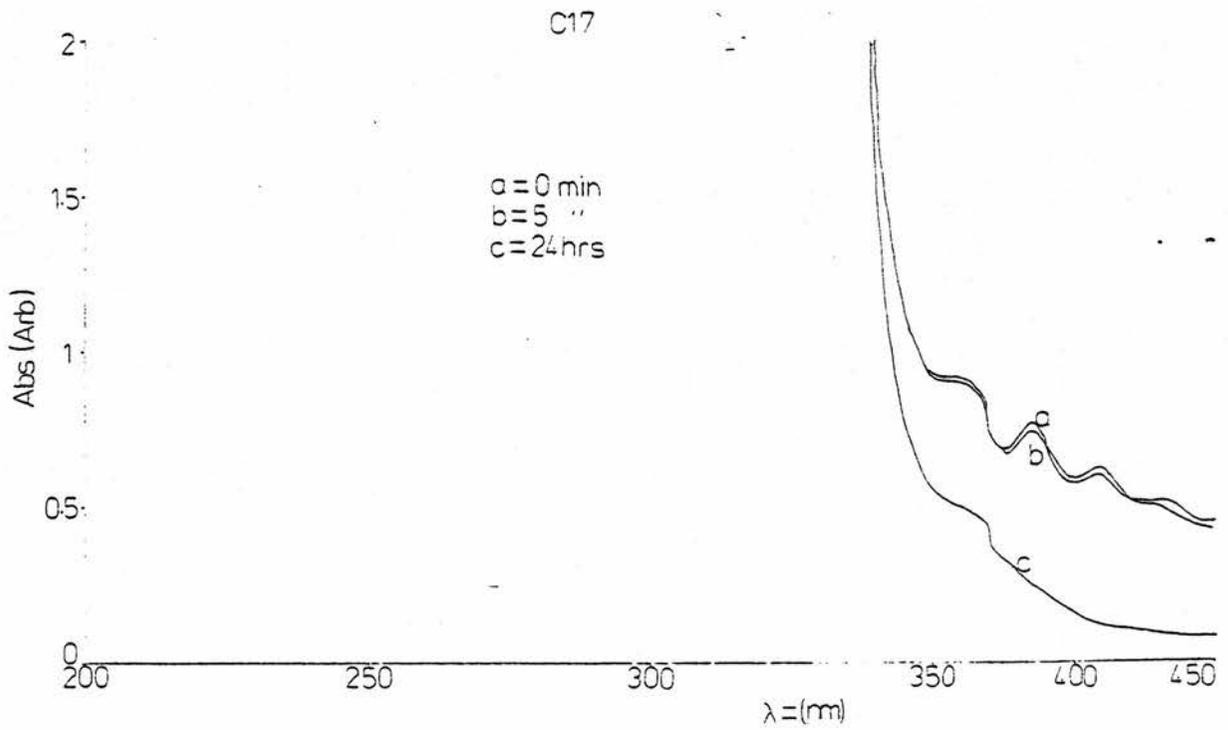
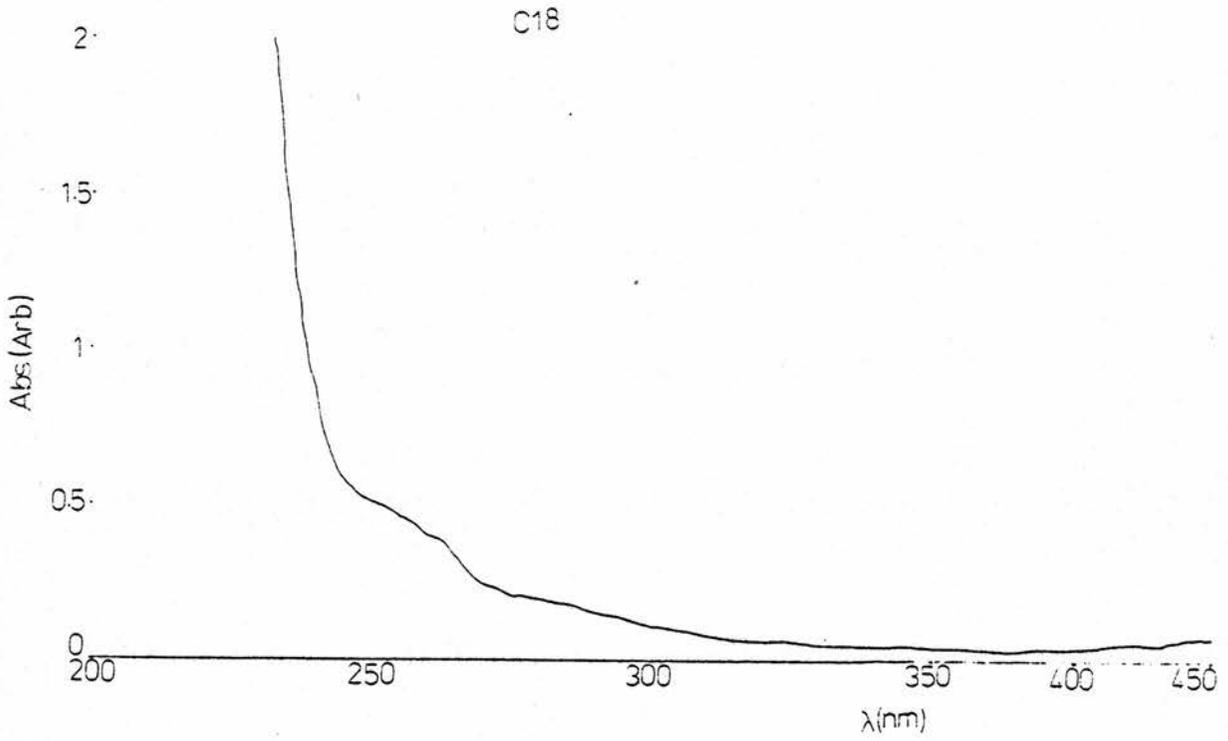






C15





SECTION D - EMISSION SPECTROSCOPY

Introduction

Fluorescence spectroscopy has been used to investigate the photo-physical properties of polyene containing polymers such as Poly(Phenylacetylene)¹¹⁷, and Poly(Phenyl Acetylene-co-Styrene)^{118,119}, with varying degrees of success. Until recently¹²⁰, however, the use of fluorescence spectroscopy to investigate the properties of polyenes formed during "Indirect" synthesis, i.e. to follow the degradation of saturated polymers, had not been reported. In this section we report on the various attempts made to investigate the fluorescence properties of the polyene systems synthesised as described in the previous section.

Emission and excitation spectra were taken using either the Perkin-Elmer MPF-44 or MPF-2A spectrofluorimeters, spectra shown are uncorrected. Film sample spectra were taken by mounting the free-standing, or quartz disc supported films in the solid sample holder assembly (Fig. D1) and front viewing of the emission. Solution spectra were obtained using 1 cm fluorescence cuvettes (Thermal Syndicate Ltd, Spectrosil FRS1/S).

1. Materials

a) Solvents:- CH_2Cl_2 (laboratory grade) was purified by the method of Perrin, Armarego and Perrin¹²¹, but still retained an emission spectrum on excitation in the range 250-300 nm. Emission and excitation spectra are shown in Figs. D2-4.

THF was purified in the usual manner, and showed no emission spectrum on excitation in the range 250-400 nm.

b) Polymers:- PVAc films showed a weak emission on excitation at 250 and 275 nm (Figs. D5 and D6).

PVC films showed no discernible emission on exciting in the range 250-400 nm.

2. Directly Synthesised Polymers

Emission spectra of the two directly synthesised polymers, Poly(3-Methylpentyne) (PMP) and Poly(Phenylacetylene) (PPA) were taken in CH_2Cl_2 solution, and in polymer matrix. Attempts were made to obtain spectra at Room Temperature ($\sim 22^\circ\text{C}$), 77 K, and under vacuum.

a) Poly(3-Methylpentyne)

I. Solution:- 10^{-3} M solution of PMP (benzene soluble fraction) was made up in purified CH_2Cl_2 and its emission spectrum investigated in the range of excitation from 350 to 380 nm. The spectrum obtained (Fig. D7) was weak and showed two maxima at approximately 395 and 420 nm. Using excitation wavelengths greater than 380 nm resulted in no discernible emission. It was noted that the colour of the polymer solution faded over a period of 24 hrs.

II. Polymer matrix:- In order to evaluate the fluorescence properties of PMP in a polymer matrix, a variety of polymers were selected as possible matrices:-

Polymer	Comments
Poly(Vinyl Acetate)	Poor quality films
Poly(Methyl methacrylate)	No detectable emission.
Poly(Acrylonitrile)	No suitable solvent
Poly(Styrene)	Only suitable matrix

A solution of 0.01 Moles PS in 50 ml CH_2Cl_2 was made up and 10^{-4} Moles PMP added; this provides films of PS 10^{-1} in PMP.

These films were prepared by coating the solution onto 25 mm quartz discs. The films were left in a closed dessicator for 12 hrs, peeled off the disc, and dried in vacuo at RT for 5 days. Resultant films were 0.10-0.15 mm thick.

Spectra were taken under vacuum at RT using the apparatus shown in Fig. D8. Since no obvious maxima were present in the absorption spectrum, the sample was excited between 300 and 380 nm at 10 nm intervals. The spectra, shown in Figs. D9-10, were weak, and showed two maxima at 390 and 420 nm, with possible shoulder at 440 and 470 nm. As can be seen, in going from $\lambda_{\text{Ex}} = 300$ to $\lambda_{\text{Ex}} = 380$ nm the ratio of the 390 nm to the 420 nm peak varied.

Excitation spectra taken with $\lambda_{\text{Em}} = 390$ and 420 nm showed no discrete peaks, and were broadly similar to the absorption spectrum.

Due to the weak nature of the emission, and the increased scatter caused by the quartz dewar, spectra at 77 K could not be obtained.

b) Poly(Phenylacetylene)

Emission spectra of 10^{-4} M solutions of PPA in CH_2Cl_2 and in $\text{C}_2\text{H}_4\text{Cl}_2$ were taken. No discernible spectrum

could be obtained from either solution at excitation wavelengths below 350 nm or about 400 nm. Spectra obtained for $\lambda_{\text{Ex}} = 350, 375$ and 400 nm showed very broad, weak, bands centring on approx. 470 nm (Fig. D11). An excitation spectrum taken at $\lambda_{\text{Em}} = 470$ nm shows a similar character to the absorption spectrum, except for the more pronounced maxima at 410 and 435 nm (Fig. D12).

Attempts to obtain spectra of PPA in polymer matrix were all unsuccessful.

As may be noted from the above, the emission spectra of the directly synthesised polyenes proved extremely difficult to obtain, particularly in the case of PPA. The reasons for this lie in two facts:-

I. The extreme sensitivity of the solutions to air and light, as put forward by Masuda et al to explain the difficulties they encountered with obtaining reproducible spectra in $\text{C}_2\text{H}_4\text{Cl}_2$ solution. This has been noted with the PPA sample used here and with the PMP sample; solutions of both rapidly fading in sunlight.

II. It has been noted that increasing the MW of PPA severely reduces the intensity of emission spectra, as shown by the

table below¹²² :-

MW	I/I_0
800	92
1060	65
1310	87
1340	100
1510	45
2160	10

Since the sample used here has a $\overline{M}_n = 16400$ it is to be expected that the intensity of emission will be very low indeed.

The length of conjugation present in a long chain polyene is a critical factor in the intensity of emission obtained therefore it was now decided to produce shorter conjugated units for emission spectroscopic investigation by indirect methods as explained in the next part of this section.

3. Indirectly Synthesised Polyenes

a) Brominated/Dehydrobrominated Poly(Styrene)

I. Series A Samples

Solutions of the PSBr and OT samples, plus a PS control, were made up to 8×10^{-4} M in CH_2Cl_2 , and their emission characteristics

investigated on the MPF-44 spectrofluorimeter using the techniques already described. Machine conditions were as noted below:-

Excitation Slit	2
Emission Slit	3
Sensitivity	100
Range	10 mV

i. PSBr Samples:- The spectra obtained from these samples were very broad and showed similar maxima, although changing intensity as shown in the table below ($\lambda_{Ex} = 350 \text{ nm}$):-

Polymer	λ_{max} (nm)	Intensity of highest peak
PS	c. 330	v. weak
1	380, 395, 415	84
2	380, 395, 415	44
3	410	48
4	410	28

ii. OT Samples:- These were investigated under the same conditions as the PSBr samples above, and gave spectra generally the same shape as those.

Polymer	λ_{max} (nm)	Intensity of highest peak
OT 1	395	100
OT 2	382, 395, 415	35
OT 3	408	50
OT 4	410	32

As can be seen from the above table, both the peak positions and the intensity trend at the OT samples are very similar to those of the PSBr samples.

iii. Irradiation of Sample 2 at Various Wavelengths:- Irradiation of this sample in the range 300-350 nm showed two peaks at 378 and 395 nm respectively, which varied in intensity, the 378 peak being stronger at 300 nm, and the 395 peak at 350 nm. The 415 nm peak appeared only as a shoulder at $\lambda_{\text{Ex}} = 330, 340$ and 350 nm.

iv. Irradiation of Sample OT 2 at Various Wavelengths:- Emission spectra of this sample showed similar results to that above in the range 300-350 nm, although the trend in intensity between the 380 and 395 emission peaks was not so clear.

Investigation of the Series A emission properties would seem to suggest that there is little or no difference between the PSBr and OT samples.

II. Series B Samples

Emission spectra of solutions of the Series B samples were taken under the same conditions as those noted above for the Series A spectra.

It must be noted that the emission bands are, as usual, broad and diffuse, with a large amount of pen stutter caused by machine noise at such a high sensitivity therefore λ_{max} values are approximate ($\lambda_{\text{Ex}} = 350$ nm).

i.	Polymer	λ_{\max}	Intensity
	PS	/	/
	1	410	59
	2	410-415	27
	3	415	18
	OTPS	/	/
	OT 1	410	45
	OT 2	410	19
	OT 3	410	10

As may be seen from the above preliminary investigation, there is little difference between the emission properties of the six test samples.

ii. Comparison of emission properties of PSBr 1 and OT 1 at various excitation wavelengths gives the results shown in the table below:-

λ_{Ex} (nm)	λ_{Em} (max)	
	PSBr 1	OT 1
300	400	405
310	402	405
320	400, 412(shoulder)	405
330	400, 412(shoulder)	405
340	410	405
350	410	410
360	415	420
380	435	400
400	450	455

The emission intensity reaches a maximum for $\lambda_{Ex} = 340-350$ nm in both cases. Due to the machine scatter, the differences noted between the two samples are not significant and again we can say that there is little or no difference between them.

iii. Comparison of the emission properties of all three PSBr samples gave the following results:-

λ_{Ex} (nm)	Sample Emission		
	1	2	3
300	400	405	405
310	402	405	/
320	405	410	405
330	400	410	/
340	400	405	410
350	410	410	/
360	415	410	415
370	/	415	/
380	435	/	440
400	450	/	/

The spectra are weak, and the gaps result from cases in which the machine scatter makes identification of λ_{max} impossible. These results indicate that there is very little difference in emission properties between the three PSBr samples.

iv. Emission Spectra of Test Samples in Polymer Matrix:- Films of PS and PMMA containing low concentrations (10^{-3} M) of the test samples were cast from CH_2Cl_2 solution onto quartz discs, and dried in vacuo at RT for 7 days. These were then mounted on the solid sample accessory (Hitachi Japan 018-0051 Solid Sample Holder),

and set up for emission spectroscopy (front viewing), on the Perkin-Elmer MPF-44 spectrofluorimeter. Unfortunately, continuing problems with scatter from this machine meant that only one set of approximate results could be obtained for the OT samples. The following table gives approximate λ_{\max} values for these samples in PMMA matrix.

λ_{Ex} (nm)	Sample Emission		
	OT 1	OT 2	OT 3
300	400	405	405
310	400	405	400
320	400	400	405
330	402	410	410
340	400	405	410
350	405	410	405
360	415	415	420
370	435	440	440

Maximum intensity again lies between $\lambda_{\text{Ex}} = 340$ and $\lambda_{\text{Ex}} = 350$ nm.

From the above results it is difficult to note any significant difference in the emission behaviour of the PSBr and OT samples. The emission is weak, and because of this the machine noise from the MPF-44, which encroaches at high sensitivity, has prevented accurate readings of the emission wavelength. This would seem to lie in the region 400-410 nm, except at high λ_{Ex} . This "movement" of emission will be discussed later, in the context of all the emission results from indirectly synthesised polyenes.

b) Poly(Vinyl Chloride)

I. Photochemical Degradation

Samples of PVC film were degraded as described in the previous section, and their emission spectroscopic properties investigated on the MPF-2A spectrofluorimeter. Degraded films were placed in the solid sample accessory with the degraded face towards the analysing beam, and examined by front viewing. Measurements were taken at maximum machine sensitivity with λ_{Ex} set at various wavelengths corresponding to maxima in the UV/Visible spectra.

a. Medium Pressure Lamp

Emission spectra at $\lambda_{Ex} = 250, 275, 300, 325$ and 360 nm were taken after the sample had been degraded for 15 mins (Figs. D13-17) while the spectra taken with $\lambda_{Ex} = 395$ nm was taken after 30 mins degradation (Fig. D18). At higher degrees of degradation the 310 nm emission maximum was lost, and a general decrease in emission intensity was noted.

Excitation spectra at $\lambda_{Em} = 310, 385$ and 410 nm were taken after 15 mins degradation (Figs. D19-21). In addition, maxima were noted at 470 and 490 nm, after 30 mins degradation, to be stronger than the slight shoulder at these wavelengths exhibited by the 15 min sample, and so the excitation spectra of these emission wavelengths were taken at this point (Figs. D22-23). Comparing the excitation and absorption spectra, it was noted that, contrary to results above, the excitation spectra in this case do not correspond well with the absorption spectra.

b. Low Pressure Lamp

Spectra shown are from the sample degraded for 1 hr under static vacuum (Figs. D24-28), and the emission maxima appear to be very similar to those obtained for the MP Lamp experiments. Again, the emission intensity decreased with increasing degradation time.

In both the above cases, the spectra of the samples degraded under dynamic vacuum corresponded closely to those shown, except that the intensity was diminished. In this instance, and in the case of the more highly degraded samples, this decrease in emission intensity can be attributed to reabsorption by the sample, due to greater extent of dehydrochlorination.

II. Chemical Degradation

a) LiX

Samples of PVC degraded using LiX were soluble only in mixed solvents involving DMF and THF. No emission spectra could be detected from these solutions.

b) KOH

Samples of PVC degraded by KOH for 1, 2, 3 and 5 hrs were made up to 10^{-2} M in THF. The 5 hr sample did not completely dissolve therefore comparisons of emission intensity between it and the other samples could not be made. Spectra show a greater contribution from emissions at 440 and 470 nm (Figs. D29-32) than those taken of the photochemically degraded samples, suggesting the presence of longer polyenes. This is in accordance with both the absorption and excitation spectra (Figs. D33-36).

c) Poly(Vinyl Acetate)I. Thermal Degradation

Samples c. 0.05 mm thick of the two PVAc samples, and selected co-polymers, were cast onto quartz discs and degraded under the conditions noted in Section C. Emission spectra of the samples were taken at regular intervals during the degradation procedure by placing the samples in the Solid Sample Holder in the analyser compartment of the MPF-2A spectrofluorimeter, and front-viewing the emission.

1. High MW PVAc

Emission spectra of the degraded samples were taken at wavelengths corresponding to maxima in the absorption spectrum. Two sets of results are shown, with the degradation time equal to 120 mins (Figs. D37-44) and 330 mins (Figs. D45-50).

Spectra taken at $\lambda_{\text{Ex}} = 250, 262, \text{ and } 272 \text{ nm}$ show emissions at 310-320 nm, and 380-400 nm; at $\lambda_{\text{Ex}} = 283, 306 \text{ and } 321 \text{ nm}$, the 310 nm emission has been lost, and only the 385 and 400 nm emissions are present. Emission spectra taken at 306 and 321 nm are of much greater intensity than those taken at lower wavelengths. At $\lambda_{\text{Ex}} = 350 \text{ nm}$, the 385 and 400 nm emissions have coalesced into a single shoulder and strong emissions at 415 and 440 nm are noted. Spectra taken at $\lambda_{\text{Ex}} > 350 \text{ nm}$ showed no measureable emission spectra. From the spectra shown, it can be seen that the position of the emission for each excitation wavelength does not differ markedly with degradation time.

Excitation spectra are shown, for 120 mins degradation, in Figs. D51-56. These show that the emission at 310-320 nm comes from excitation in the region 260-270 nm, while those at 385, 400, and 415 nm are predominantly from 306 and 321 nm excitations. In going from $\lambda_{Em} = 385$ nm to $\lambda_{Em} = 440$ nm, it may be seen that excitations at 334 and 354 nm play an increasingly important role. An excitation spectrum taken with $\lambda_{Em} = 500$ nm is also included to show that this trend continues, with the lower wavelength emissions playing a decreasingly important role at λ_{Em} increases. It may also be seen from this spectrum that new peaks at 395, and 400-410 nm are playing a weak role in this high wavelength emission. The peak positions look very similar to PPA.

Plots of corrected emission intensity vs degradation time for emission peaks at selected excitation wavelengths (Fig. D57) show that the intensity of emission reaches a maximum after 90-120 mins, then decreases rapidly to low values at 150-180 mins. A second intensity maximum, lower than the first, is also noted between 210 and 240 mins.

A sample of high MW PVAc was cast onto a 13 mm glass disc, and degraded under the usual conditions for 2 hrs. This was then placed in the apparatus shown in Fig. D58, and its emission spectrum taken by front viewing, under vacuum at 77 K. Due to the increased scattering created by the quartz dewar and liquid N_2 present, it was found to be difficult to obtain good spectra and only those taken at $\lambda_{Ex} = 306$ and 321 nm are shown in Fig. D59. The 385 and 400 nm bands noted in the RT spectra are clearly present, along with a 415 nm emission. A possible emission at c. 360 nm is difficult to resolve

from the very large scatter peak, but may be a contribution due to the weak 283 nm absorption. Slight shoulders at this wavelength were noted in a few cases in RT spectra of degraded PVAc. A possible shoulder at 440 nm is also noted, this is in keeping with the long degradation time used for this sample.

2. Low MW PVAc

Spectra taken after 2 hrs degradation show similar characteristics to those of high MW PVAc, however after 10 hrs degradation a marked shift in emission wavelength to higher wavelengths is noted at all excitation wavelengths, the emission peaks at 415, 440 and 470 nm appearing even in spectra taken at $\lambda_{\text{Ex}} = 250$ nm. Nowhere in the 10 hr degraded sample spectra is the 310 nm emission in evidence, but the low intensity of spectra taken between 250 and 306 nm may mask this. 2 hrs Degradation Figs. D60-66, 10 hrs Figs. D67-69.

Excitation spectra show that the 306 and 321 excitations contribute to all the emission bands, but the 334 and 354 nm contributions become increasingly significant as λ_{Em} increases. Emissions at 440 and 470 nm contain contributions from excitations at c. 370, 395, and 408 nm (Figs. D70-72).

Plots of corrected emission intensity vs degradation time for selected emission peaks at specific excitation wavelength show a single maximum at 2-3 hrs, with intensity rapidly dropping off to 10 hrs (Fig. D73). A second maximum may be present but was not detected due to the large time gap between the 5 hr and 10 hr spectra.

Low temperature studies of low MW PVAc produced no interpretable emission spectra.

3. Copolymers

The emission spectra of two copolymers, Poly(Vinyl Acetate-co-Methyl Methacrylate) (VA/MMA), and Poly(Vinyl Acetate-co-Methyl Acrylate) (VA/MA) were studied. Samples were degraded for 2 hrs under the usual conditions and the spectra taken by the method described above. Spectra were taken at $\lambda_{Ex} = 280, 300, 320, 340, 360, 380, \text{ and } 400 \text{ nm}$.

I. VA/MMA - The spectra show a general trend to increase intensity with increasing λ_{Ex} , except in the case of $\lambda_{Ex} = 400 \text{ nm}$. Spectra are very broad, featureless, bands centering on $\lambda_{Em} = 460\text{-}480 \text{ nm}$ (Fig. D74).

II. VA/MA - The general shape of these spectra is similar to that of the VA/MMA spectra, but the band appears to centre on c. 415 nm for $\lambda_{Ex} = 280\text{-}340 \text{ nm}$. In going from $\lambda_{Ex} = 340 - \lambda_{Ex} = 400 \text{ nm}$, the emission wavelength varies from 415-460 nm. Intensity again increases with increasing λ_{Ex} , except in the case of $\lambda_{Ex} = 400 \text{ nm}$ (Figs. D75-77).

No other copolymer samples were found to be suitable for investigation of emission properties.

II. Solution Phase Thermal Degradation

A sample of PVAc degraded for 2 hrs at 205°C by the method described in Section C was used as representative of this type of polyene containing material, and the emission characteristics in CH_2Cl_2 solution investigated. In order to evaluate the effect of

concentration of chromophores on the emission behaviour, two solutions were made up of widely differing concentrations - one at 10^{-3} M, the other at 6×10^{-2} M, and then emission spectra investigated and compared.

1. 6×10^{-2} M:- Emission spectra were taken at excitation wavelengths from 300-400 nm using a degassed solution in a 1 cm fluorescence cuvette (Figs. D78-80).

Spectra obtained show that the emission is similar for λ_{Ex} between 300 and 340 nm, showing a very broad emission centering on c. 390 nm, with a shoulder at c. 440 nm. The intensity increases over this range. In going from $\lambda_{Ex} = 340$ - $\lambda_{Ex} = 380$ nm the 390 nm peak decreases, and the 440 nm peak becomes the predominant one; by 400 nm the emission wavelength has shifted to even higher values. Intensity decreases over this range. These weak, characterless spectra are broadly similar to those obtained for the thermally degraded PVAc films.

The excitation spectrum taken for $\lambda_{Em} = 390$ nm is a broad structureless band between 300 and 350 nm, while the 450 nm emission originates mainly from the 354 nm excitation, with small contributions from excitations at 321, 334, 370, and 395 nm (Fig. D81).

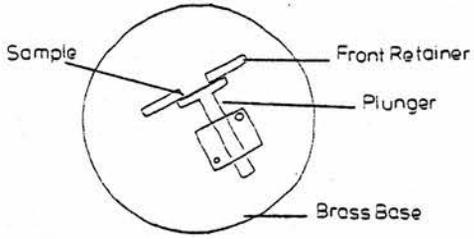
It has already been noted that substantial changes occur in the absorption spectrum of solution degraded material when solutions are exposed to light. The possibility of a similar effect on the emission spectra was investigated. The spectra (Fig. D82) show that, over a short period of time, the intensity of emission decreases noticeably; a slight shift in the emission wavelength may also be noted.

2. 10^{-3} M :- No polyene emission could be obtained from this solution, only emissions at low excitation wavelength due to solvent.

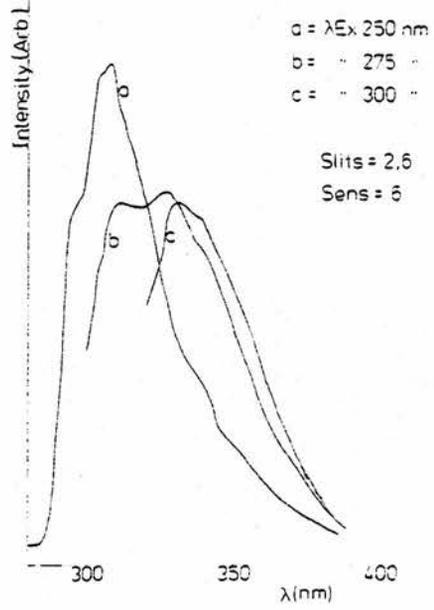
III. Chemical Degradation

Attempts to redissolve the solid polymers obtained from degradation of PVAc by p-toluenesulphonic acid resulted in the formation of gel s which rapidly decolourised therefore no reproducible emission spectra were obtained.

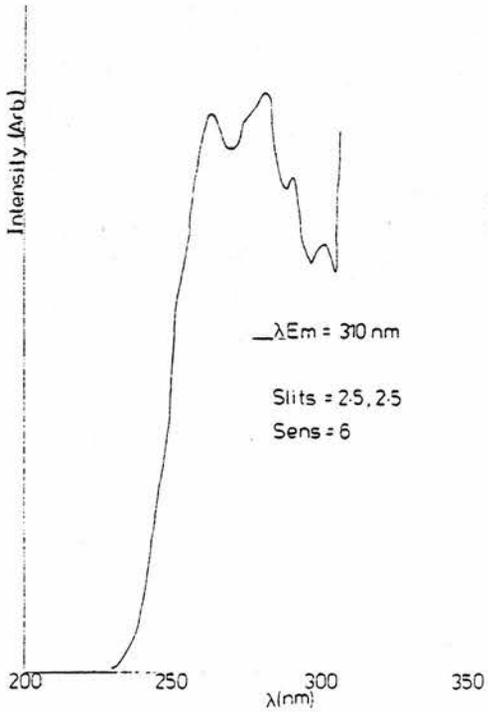
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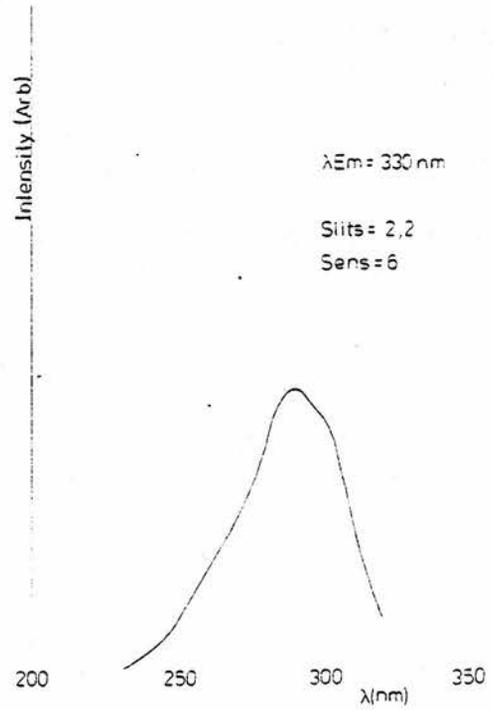
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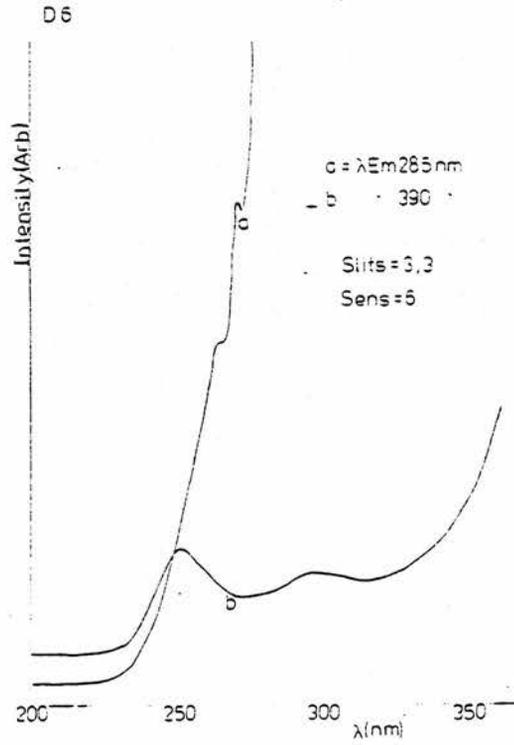
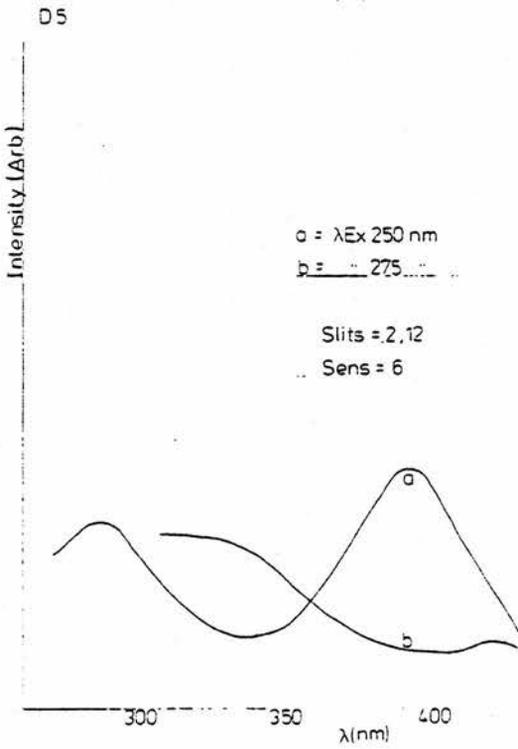
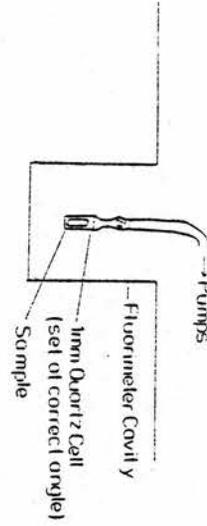
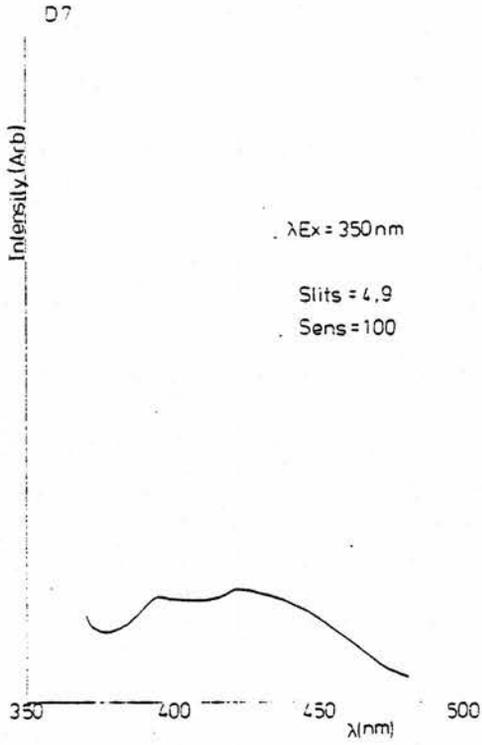


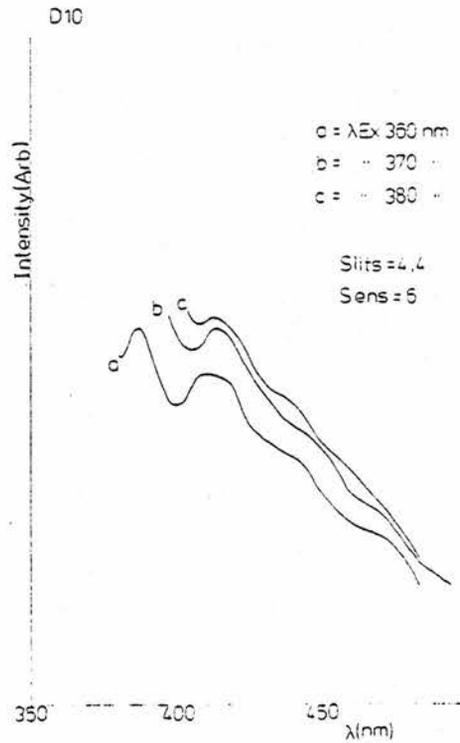
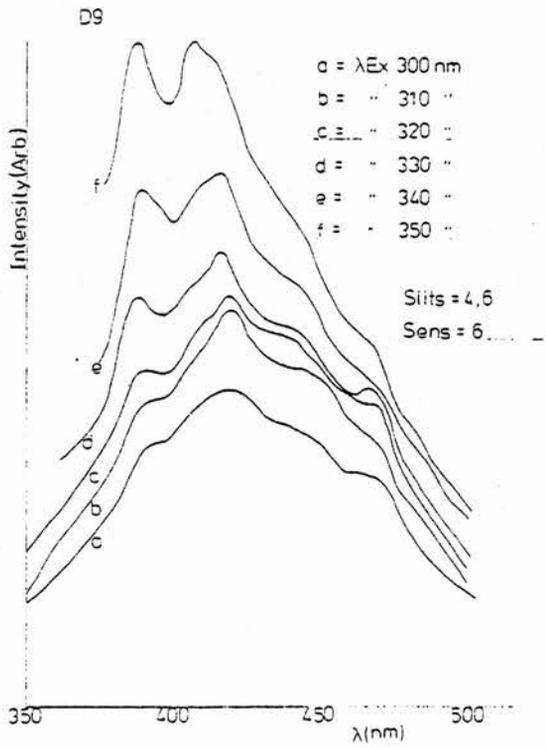
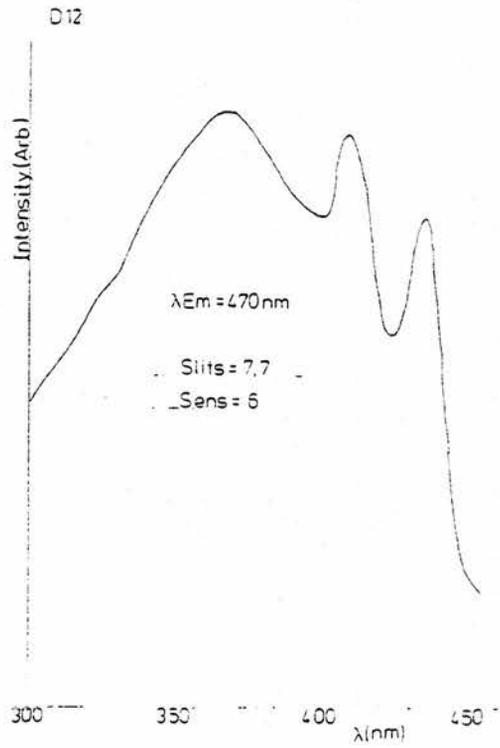
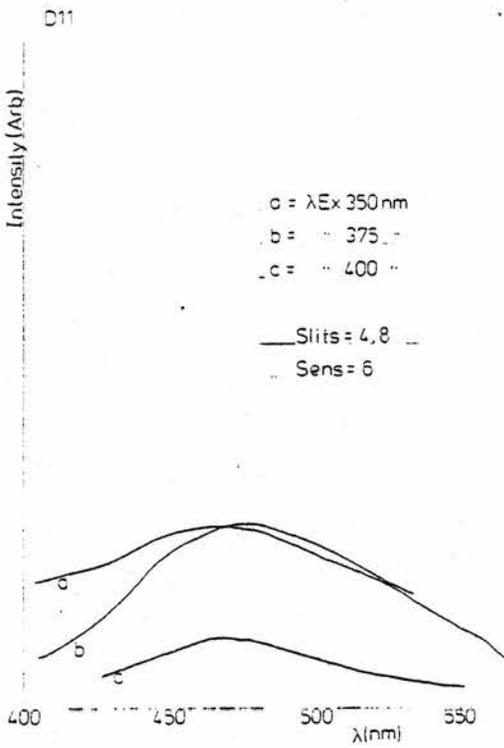
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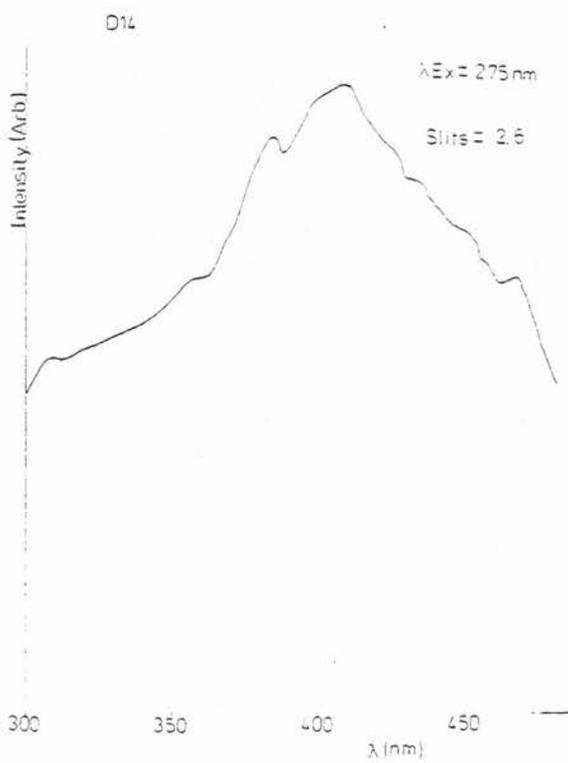
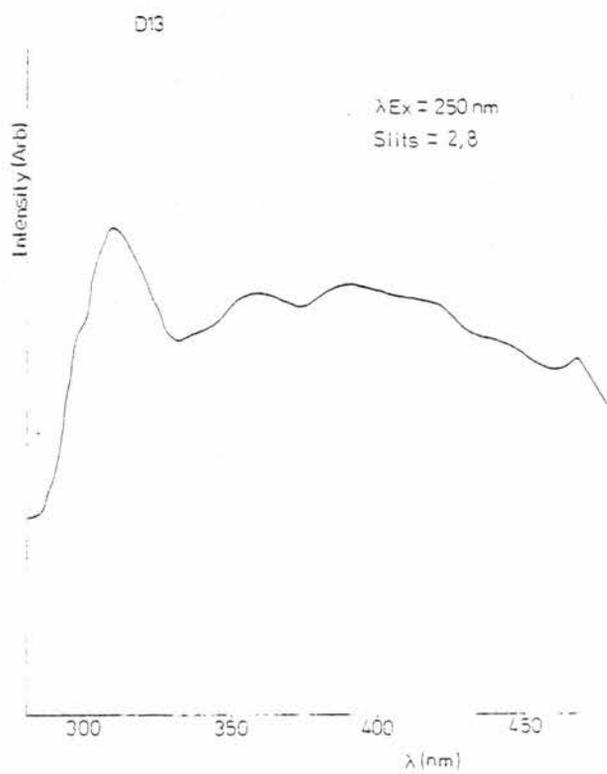
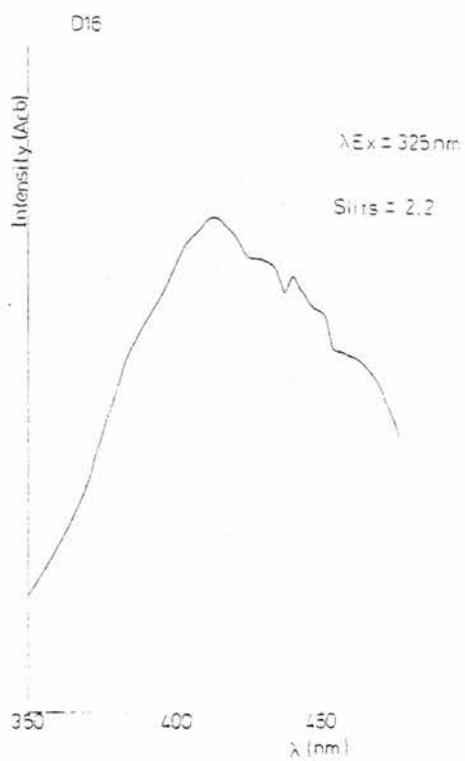
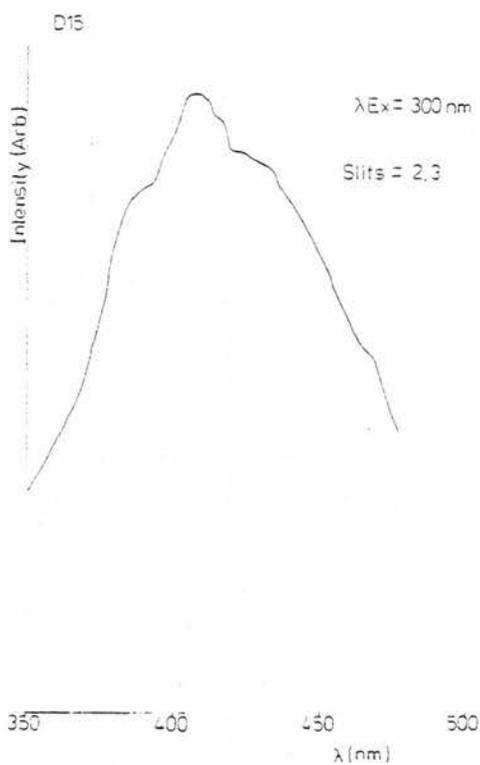


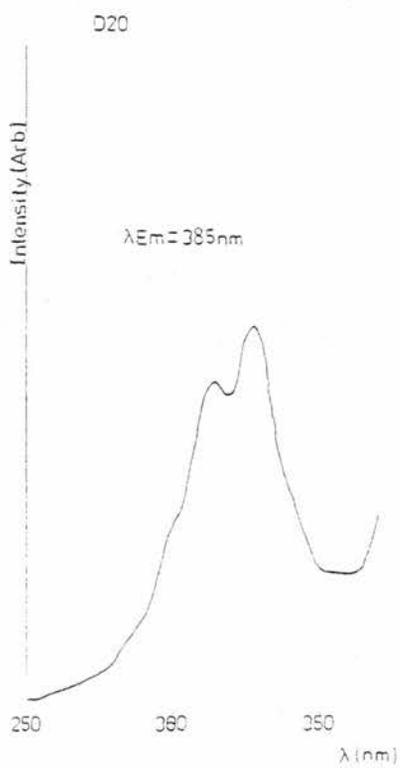
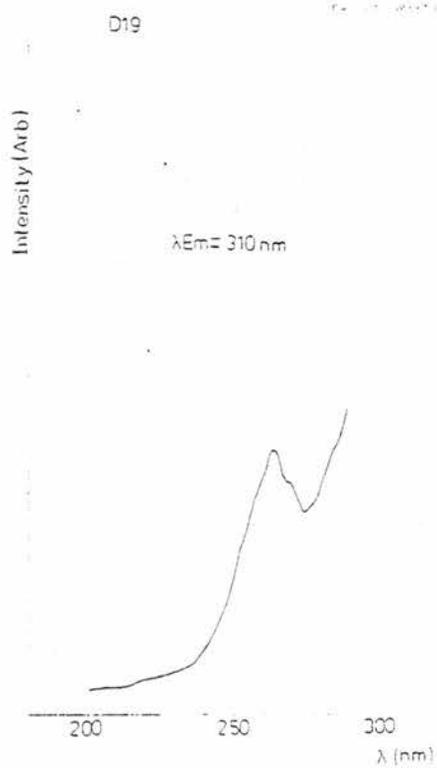
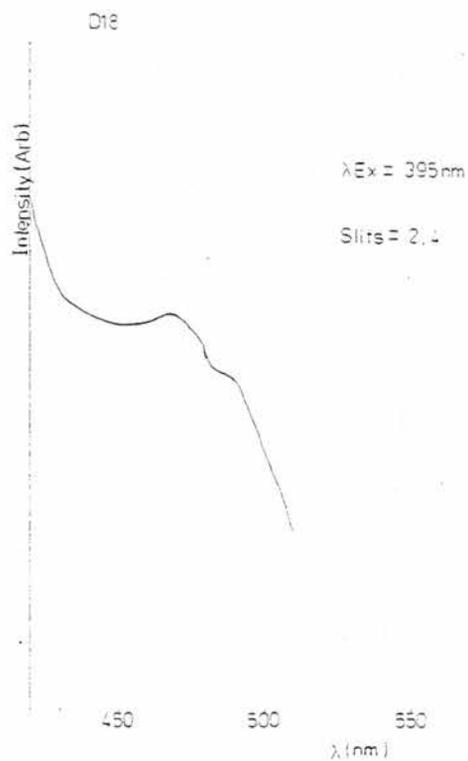
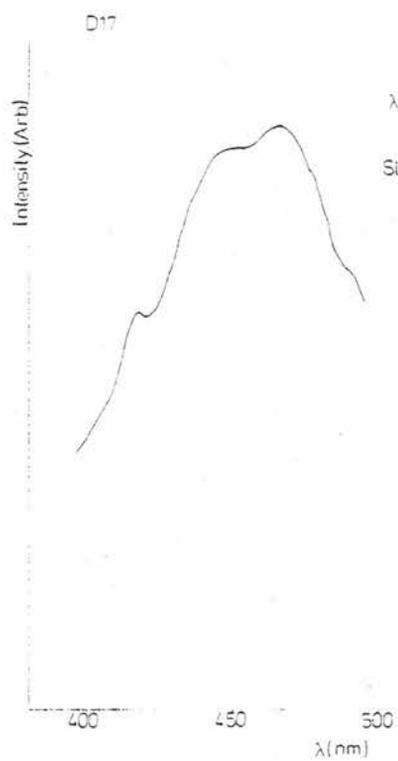
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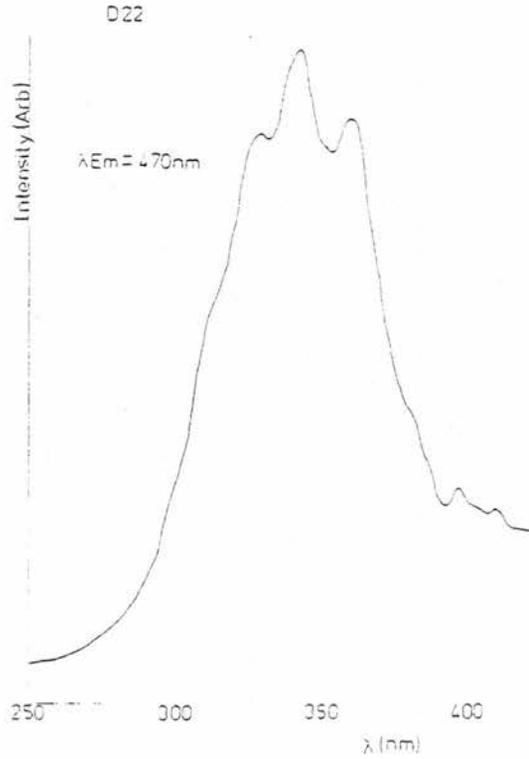
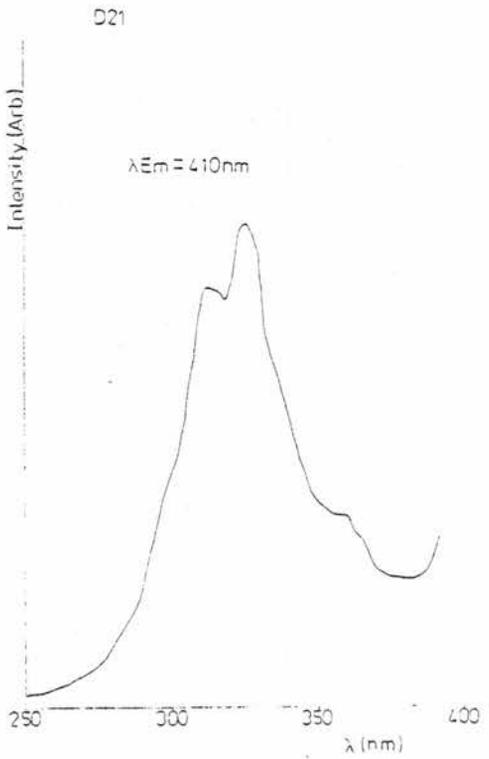
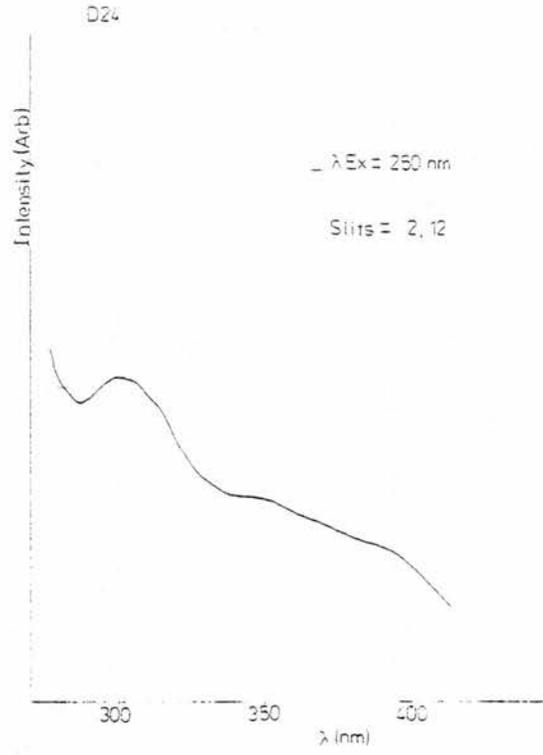
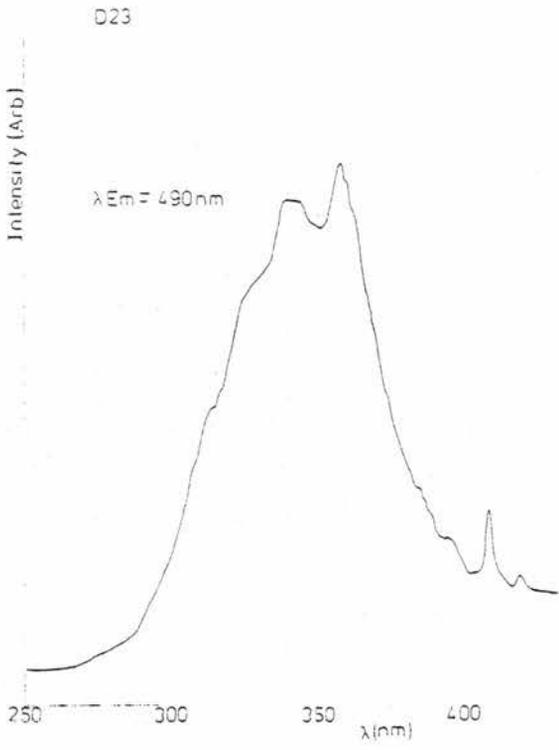


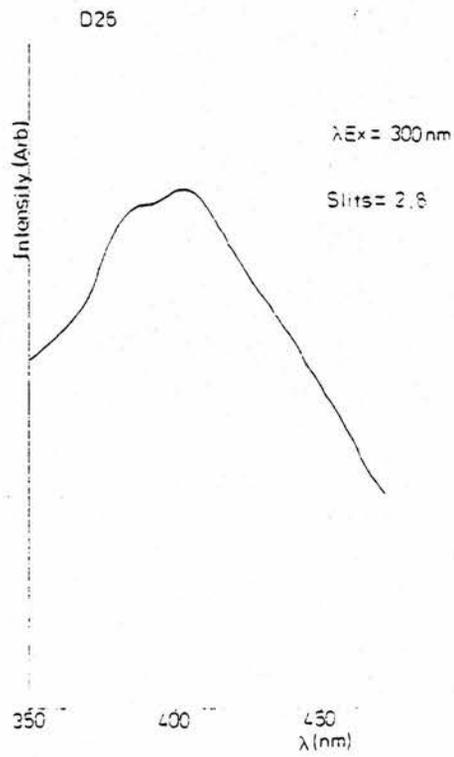
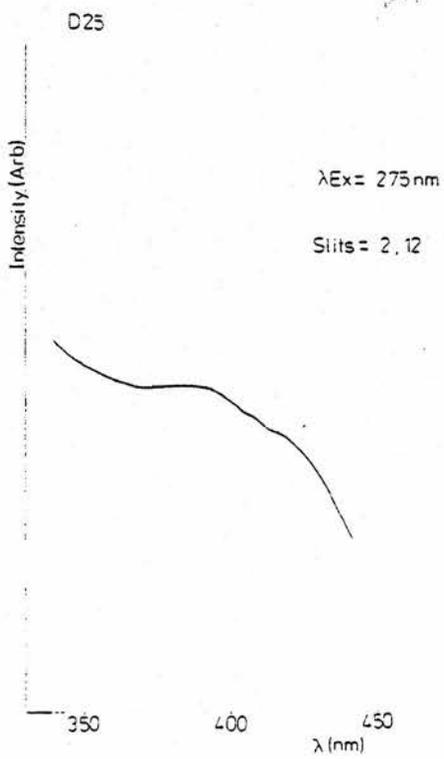
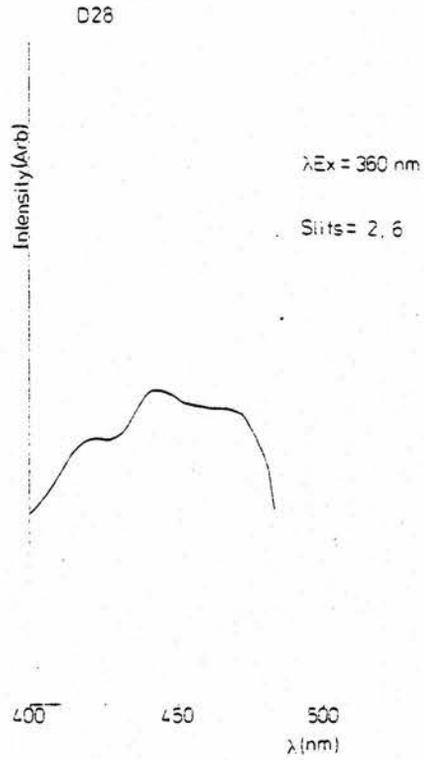
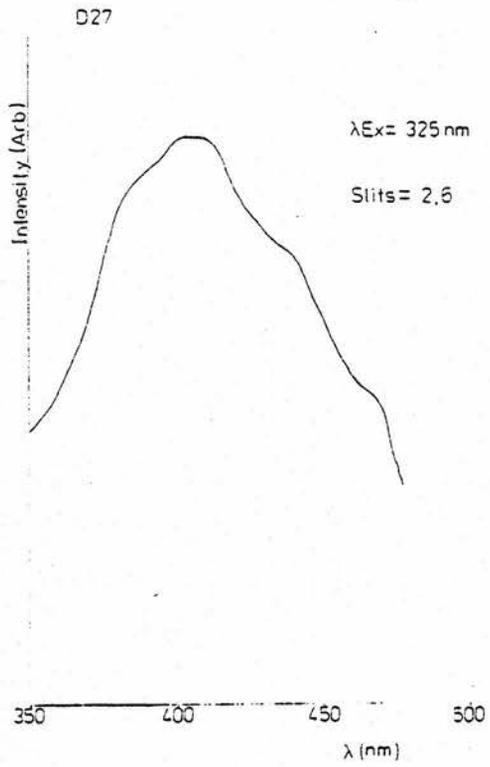


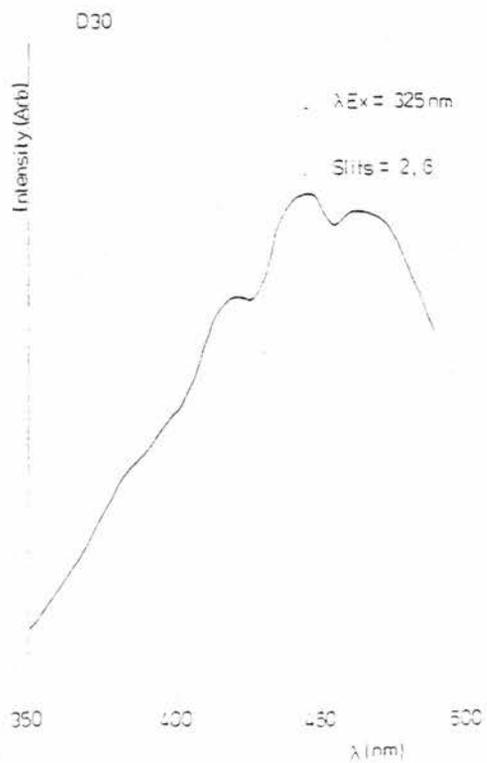
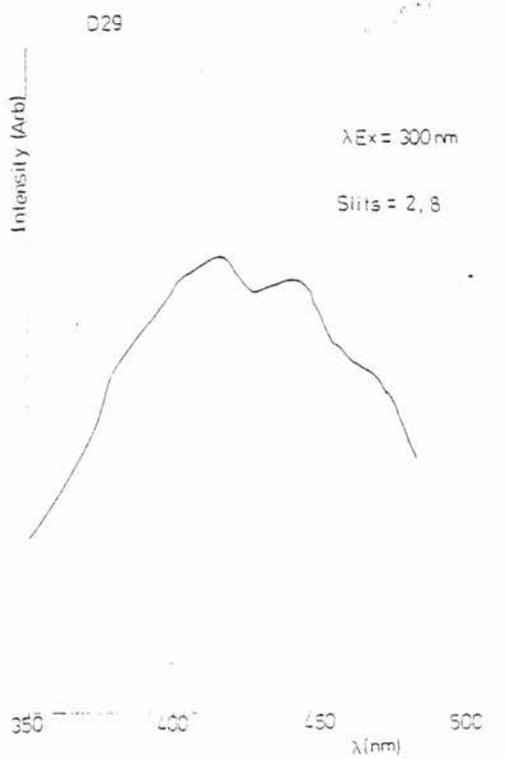
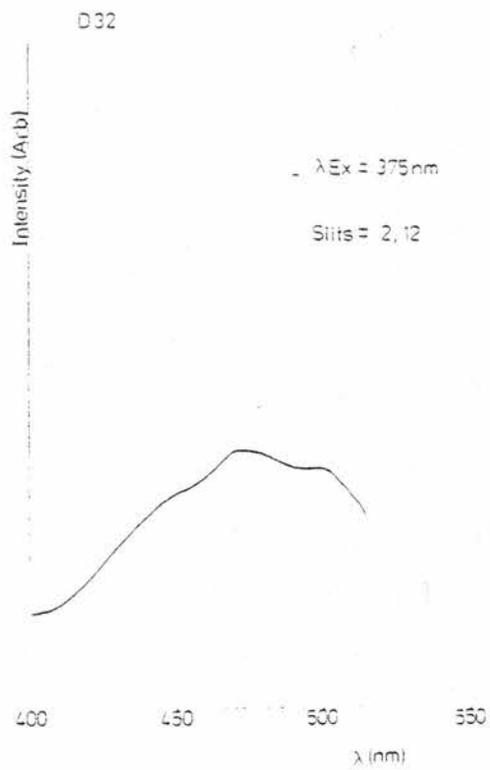
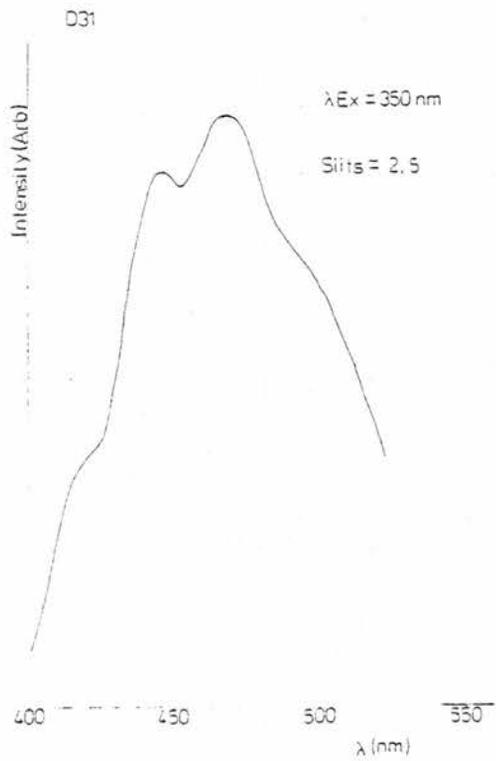


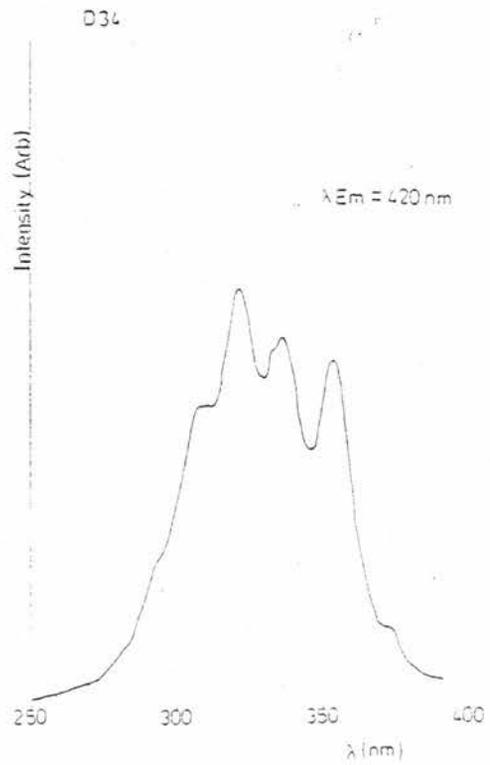
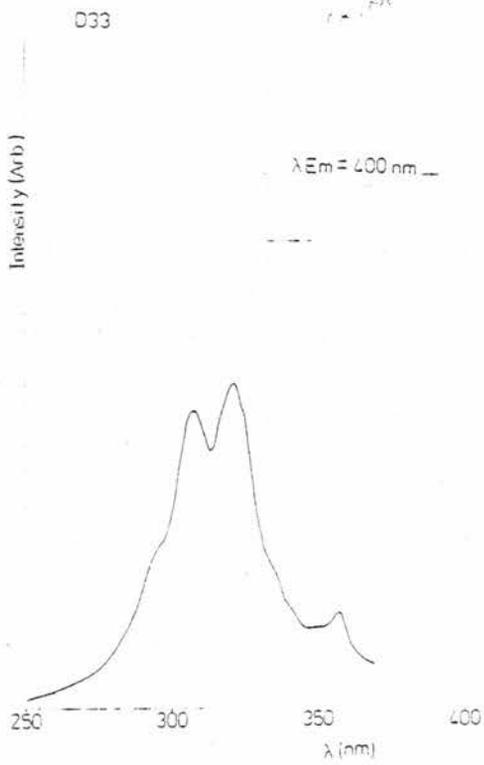
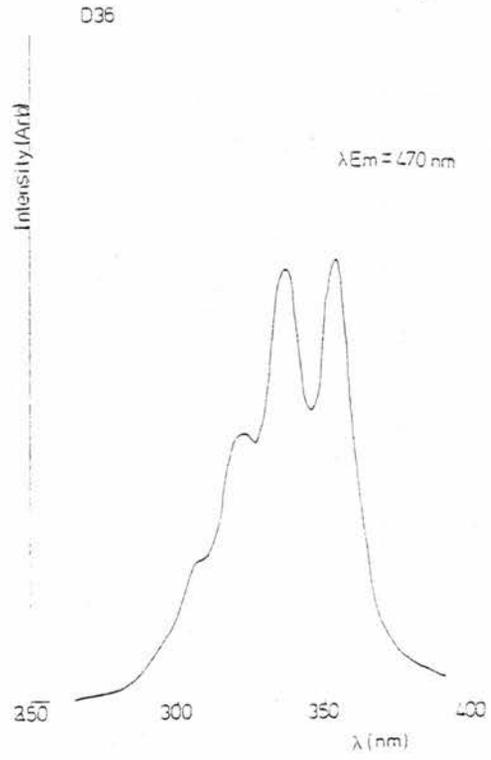
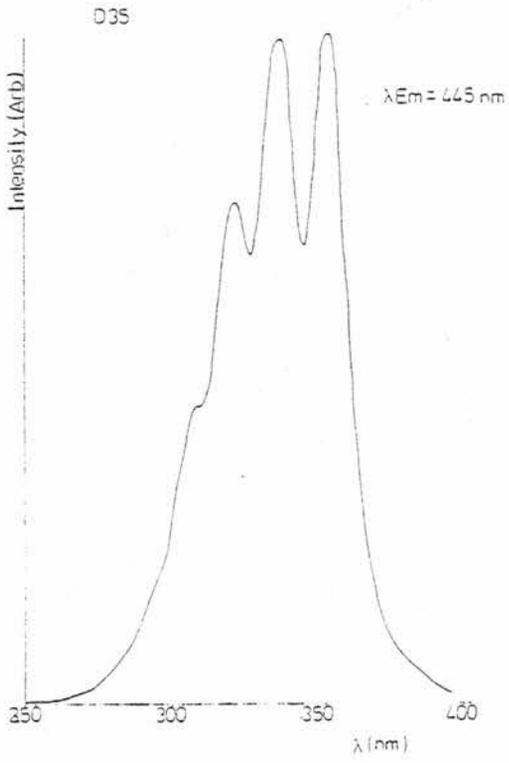


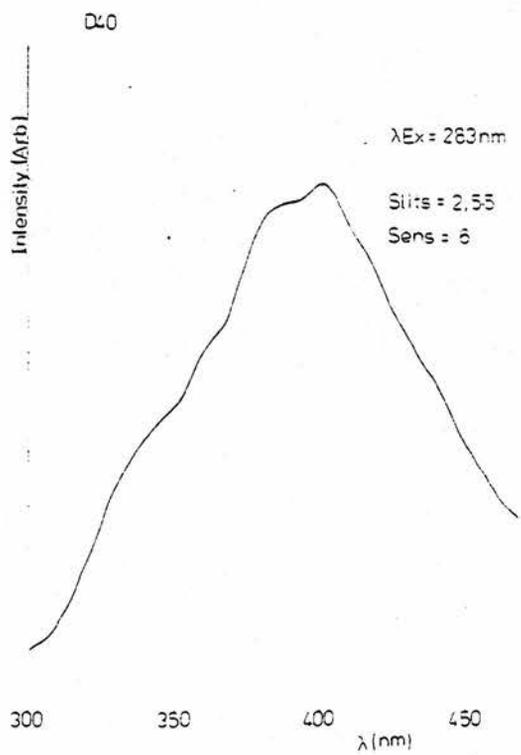
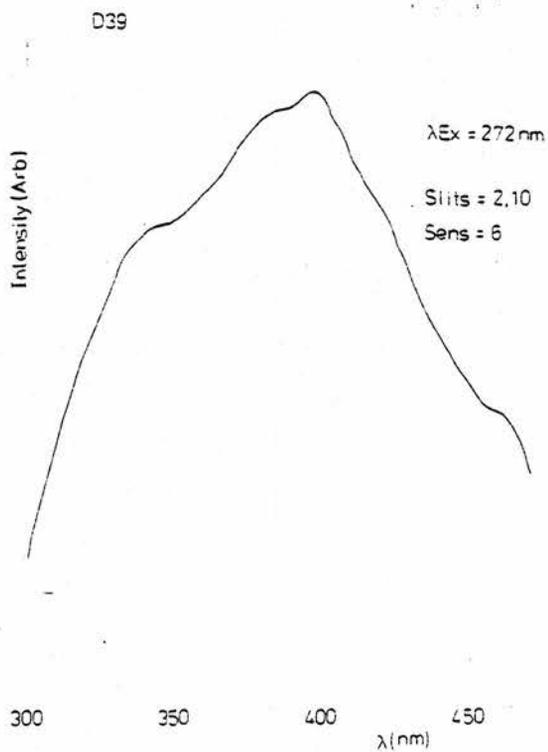
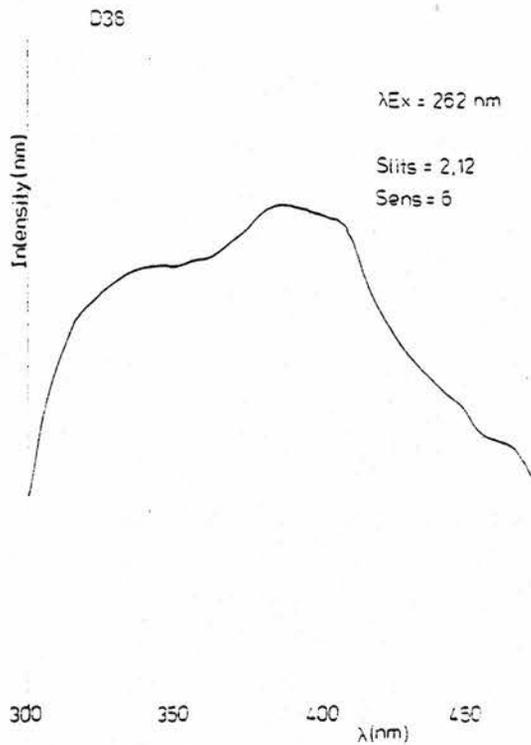
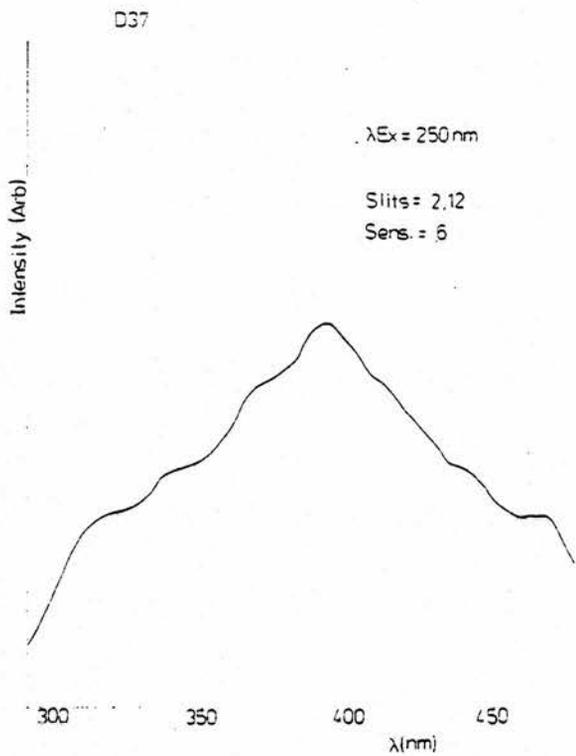


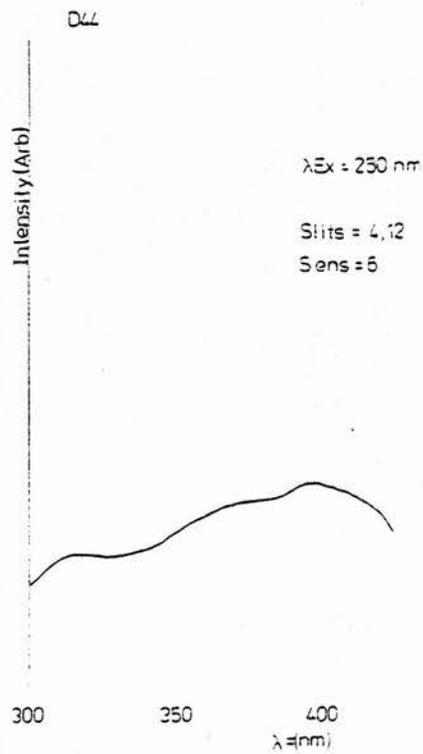
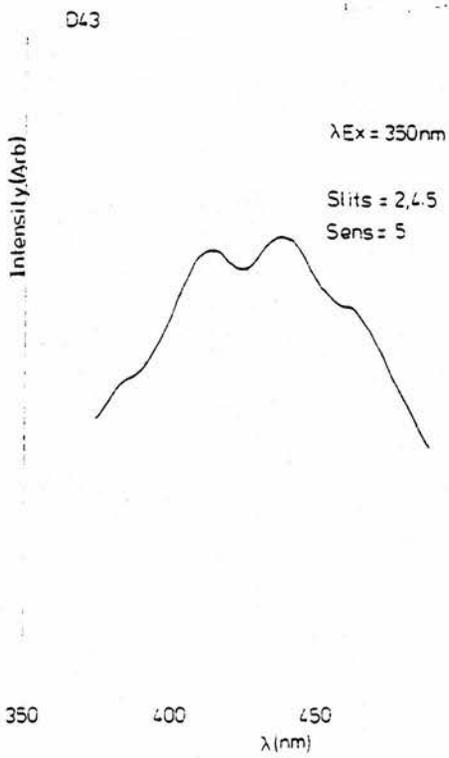
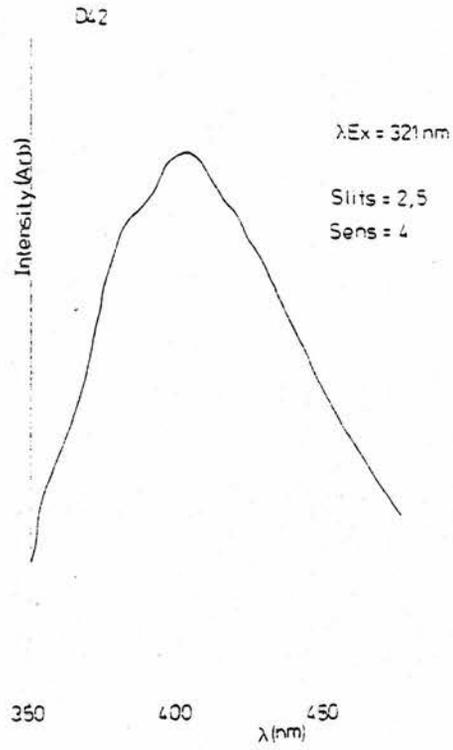
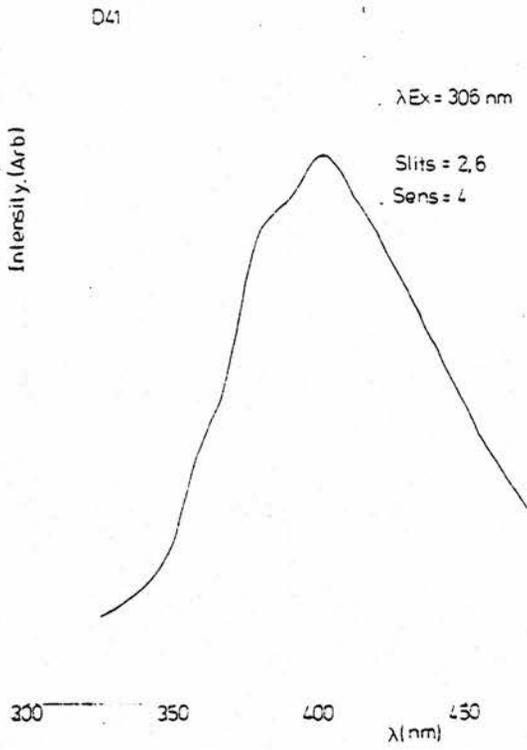


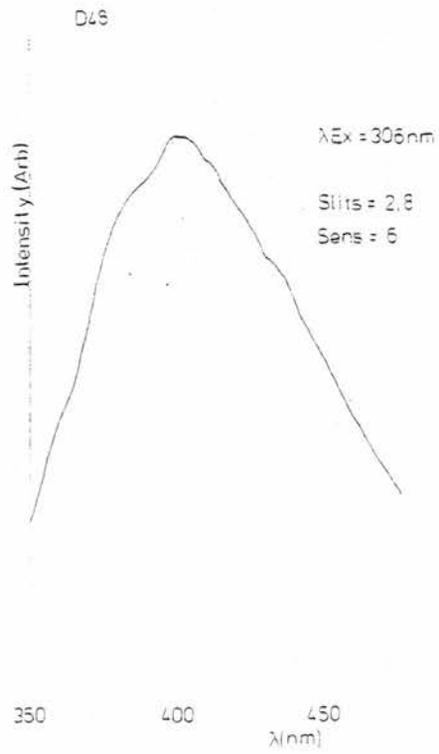
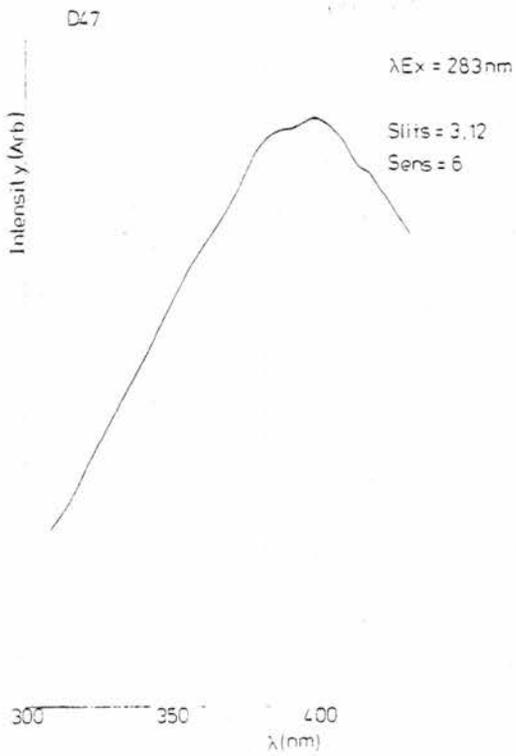
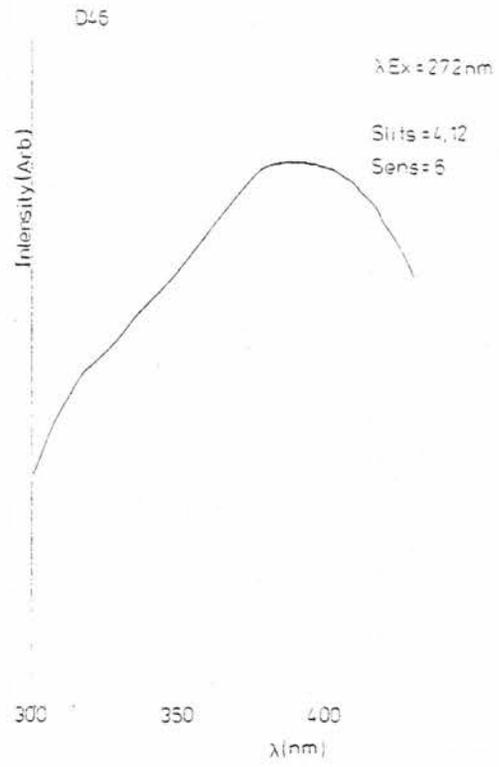
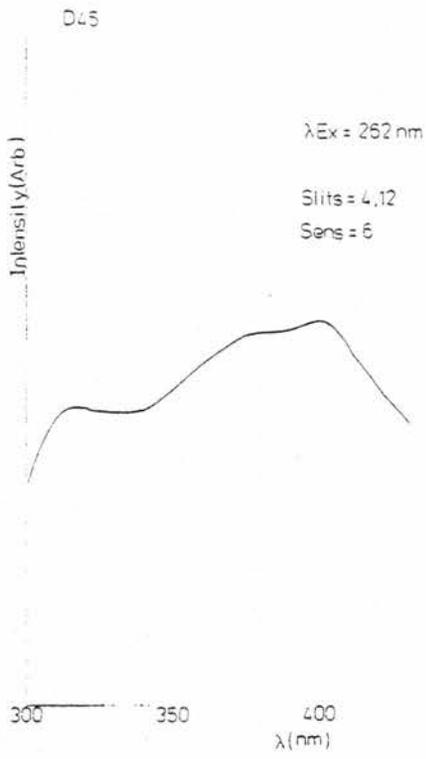


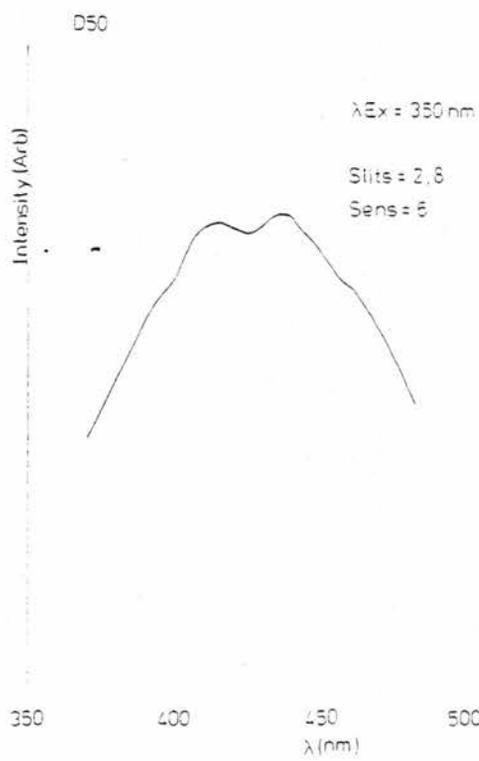
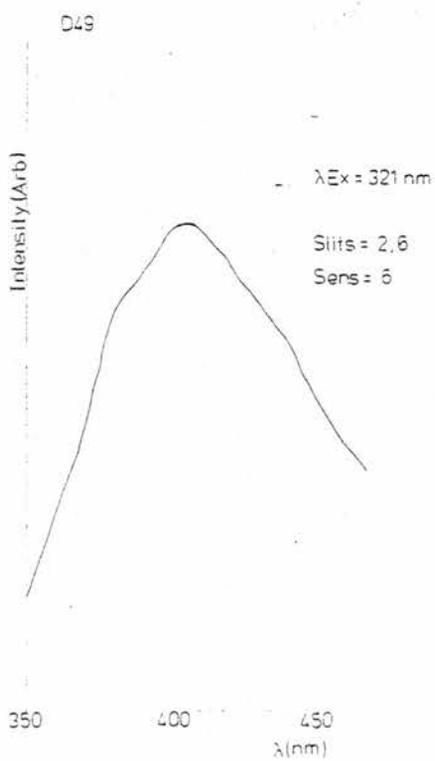
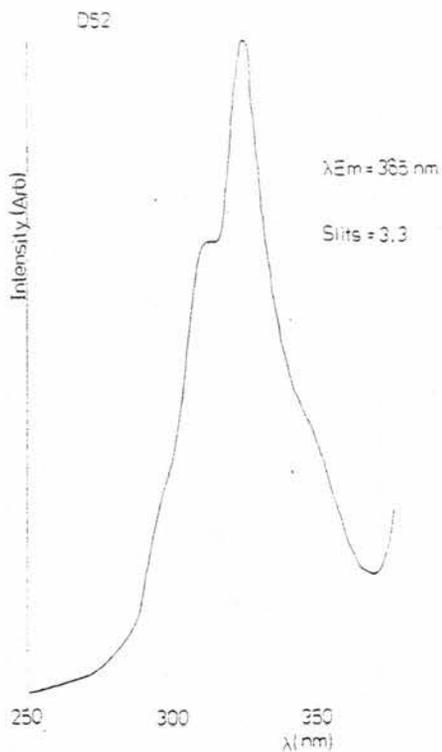
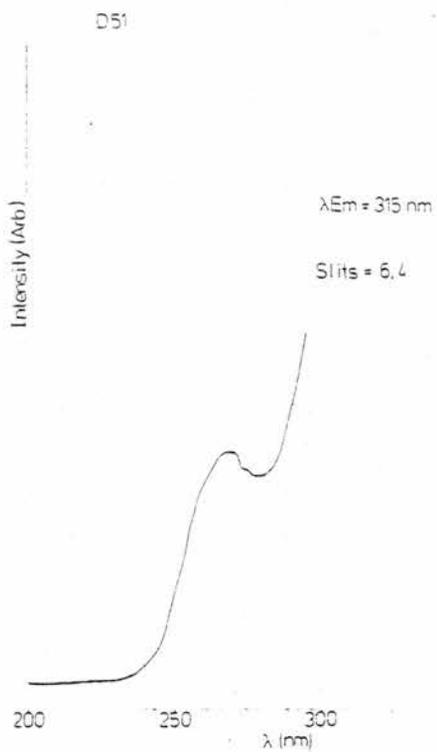


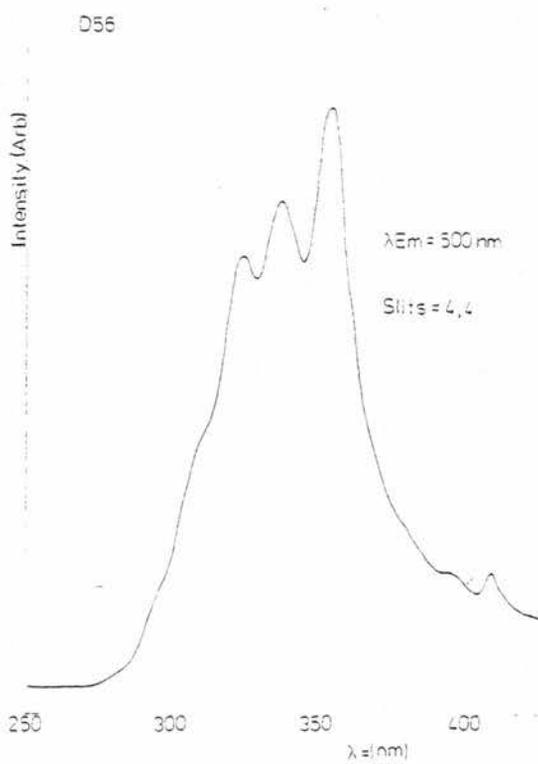
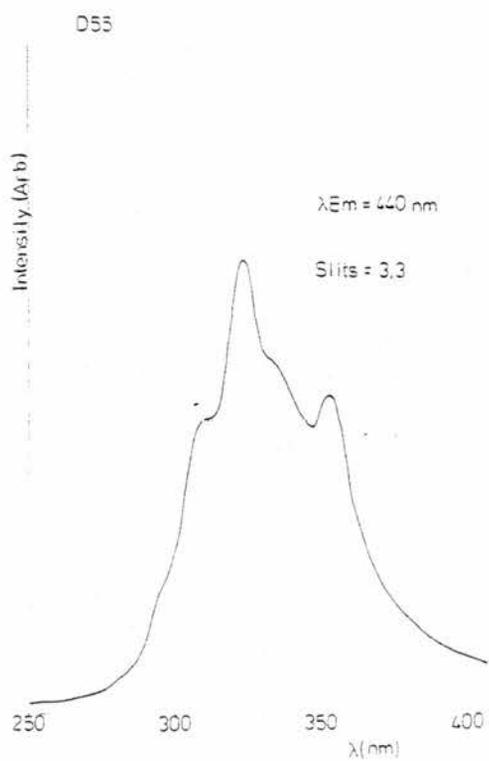
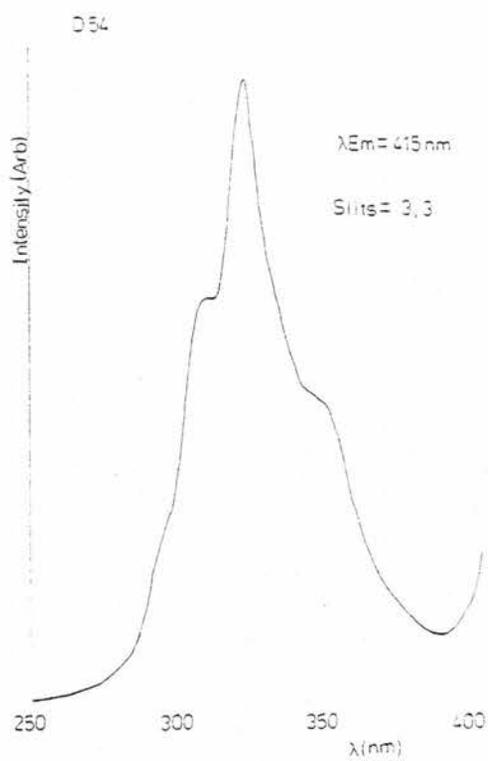
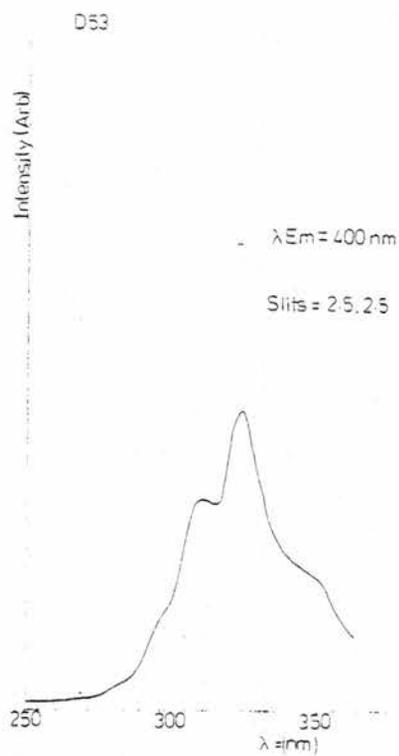


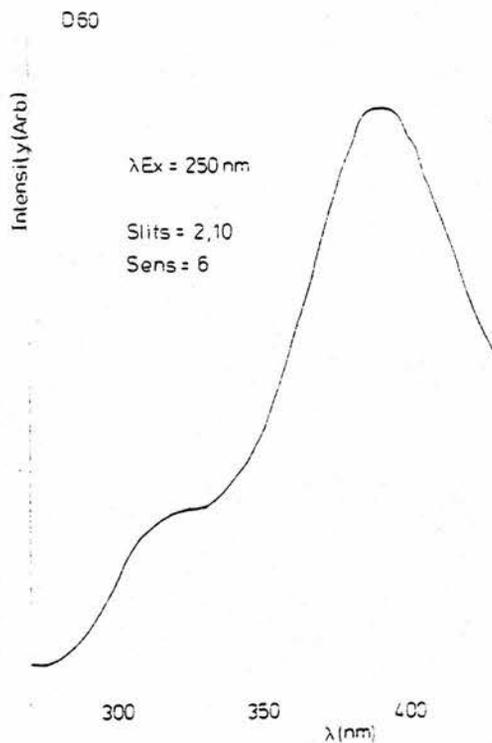
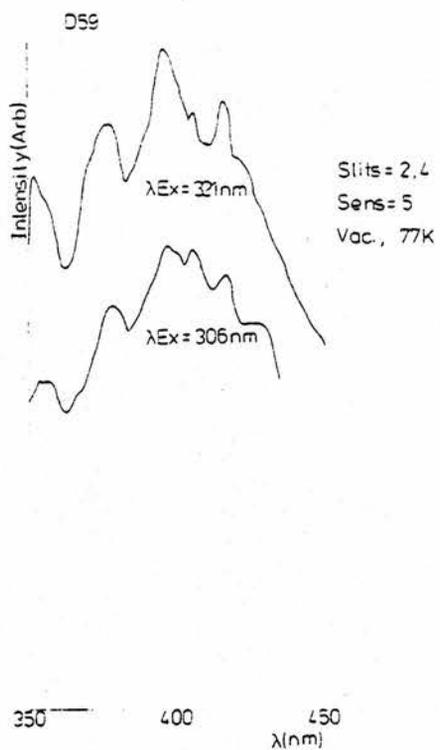




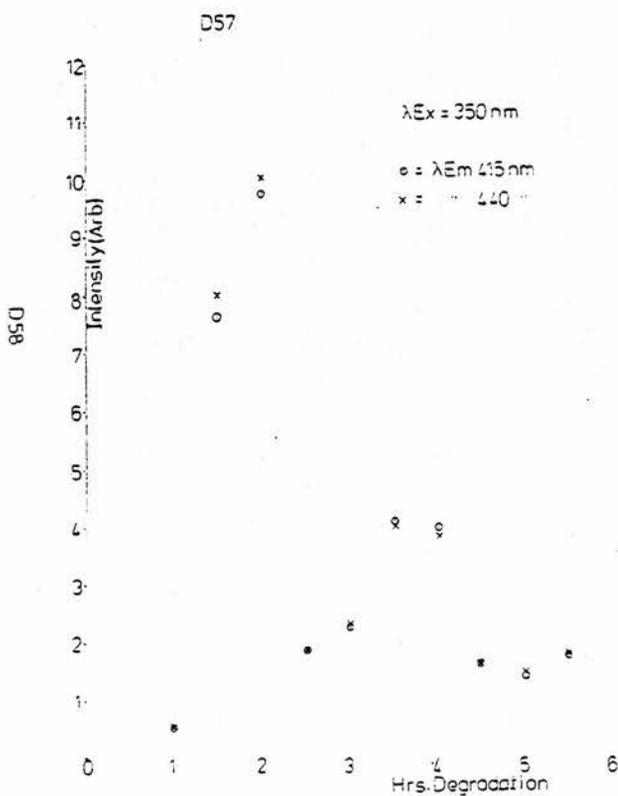
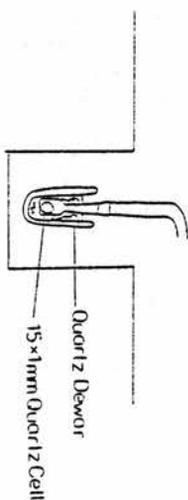


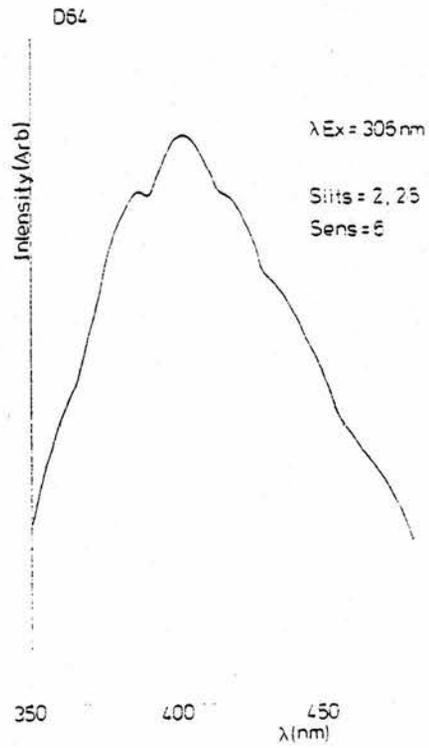
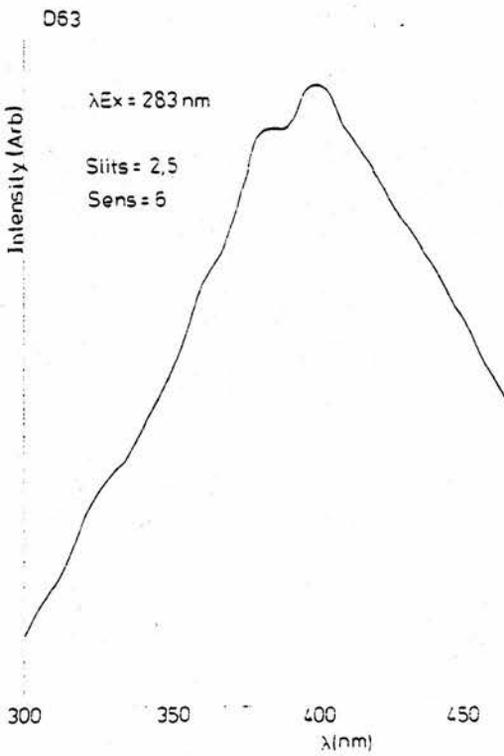
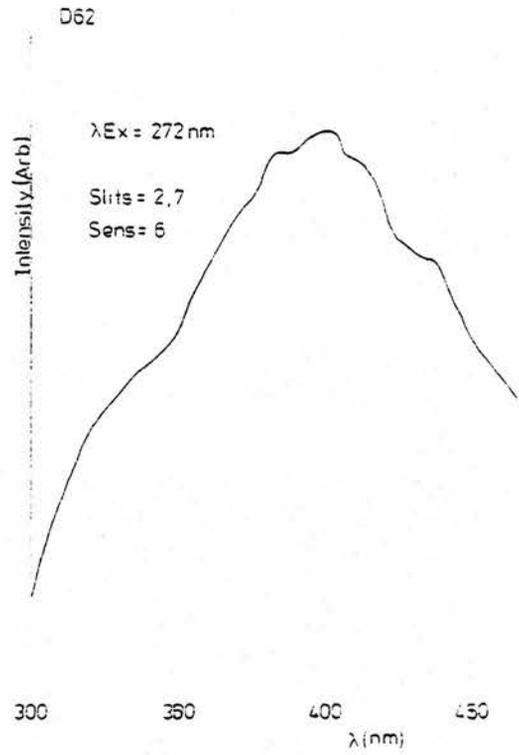
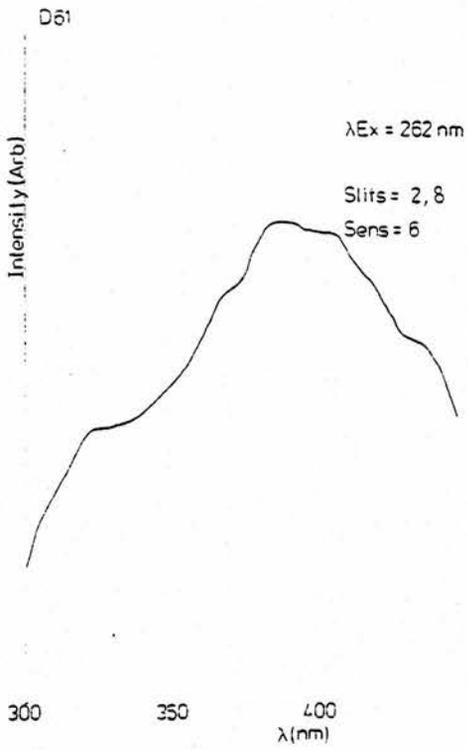


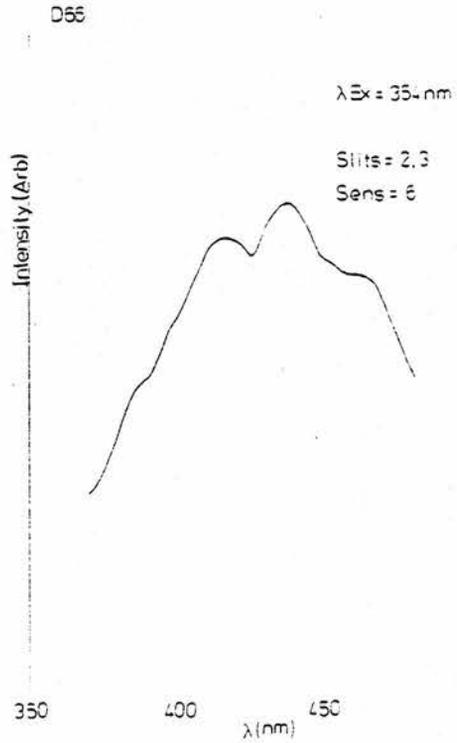
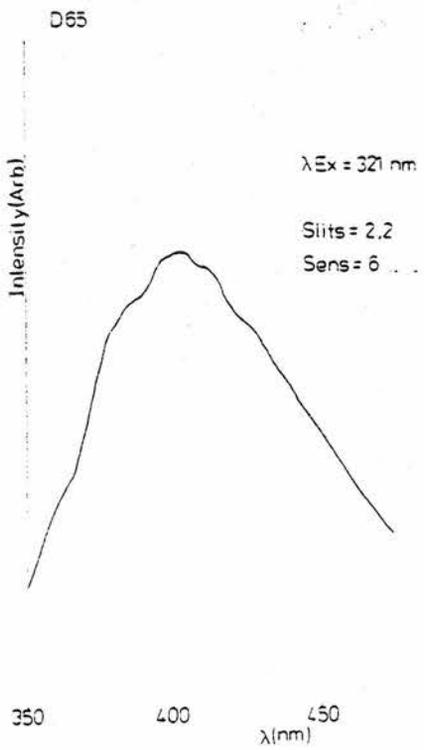
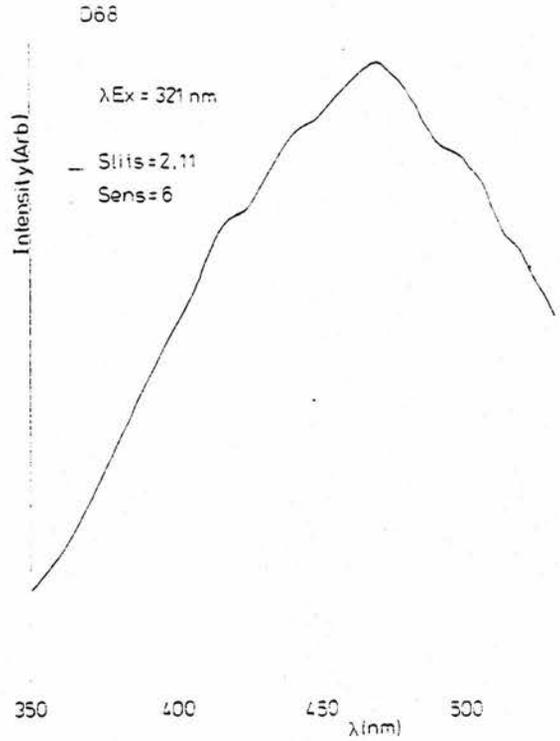
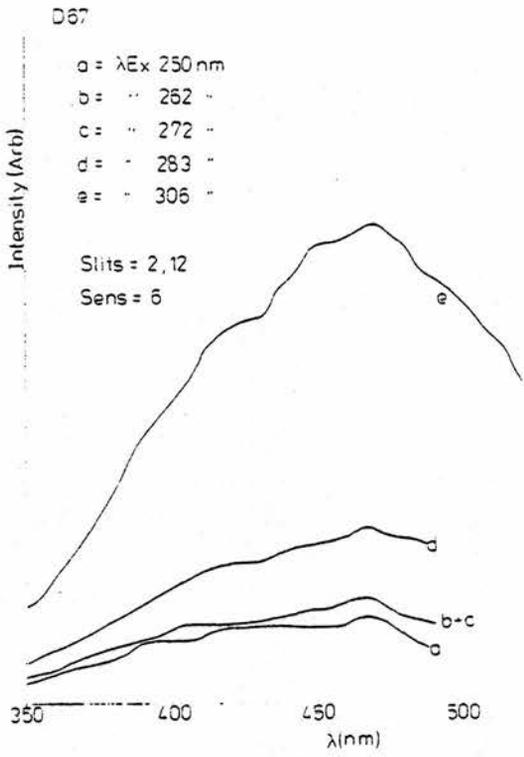


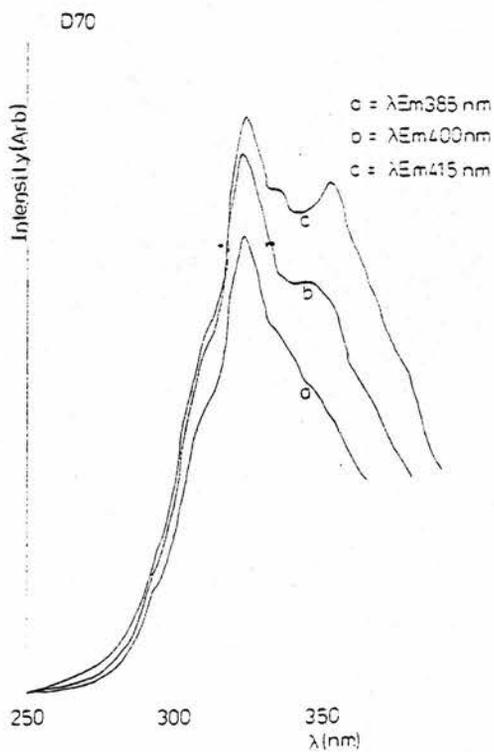
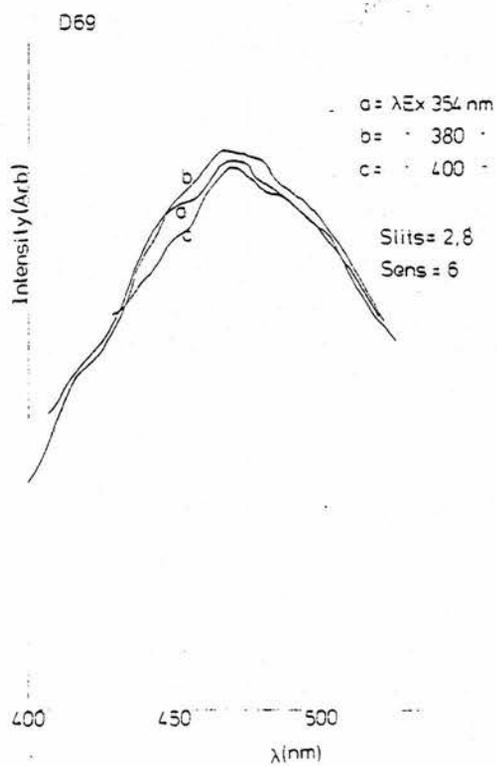
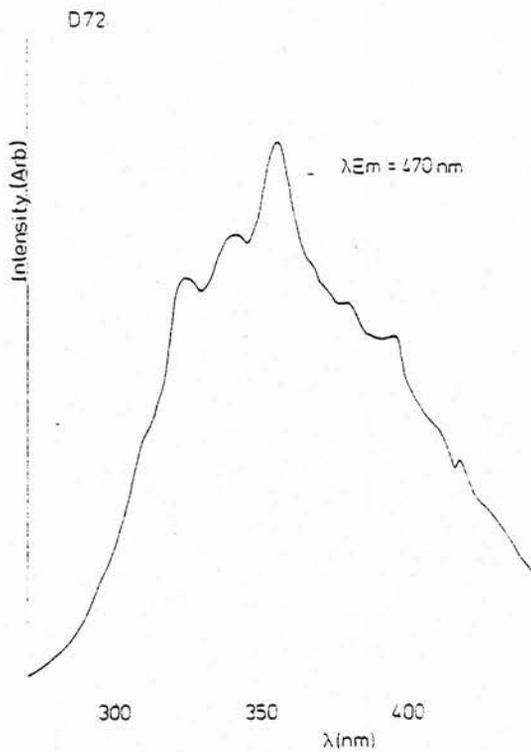
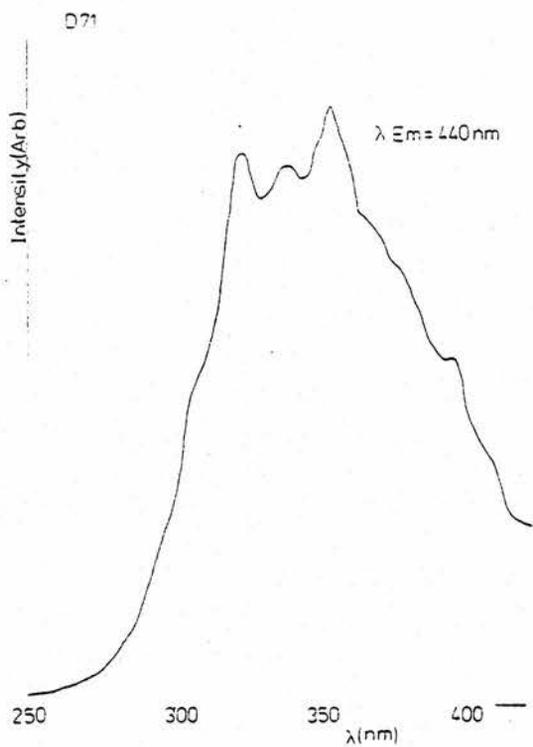


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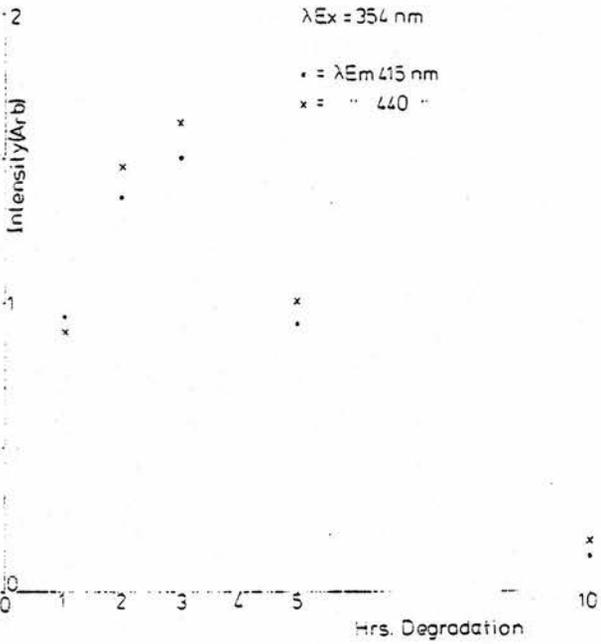




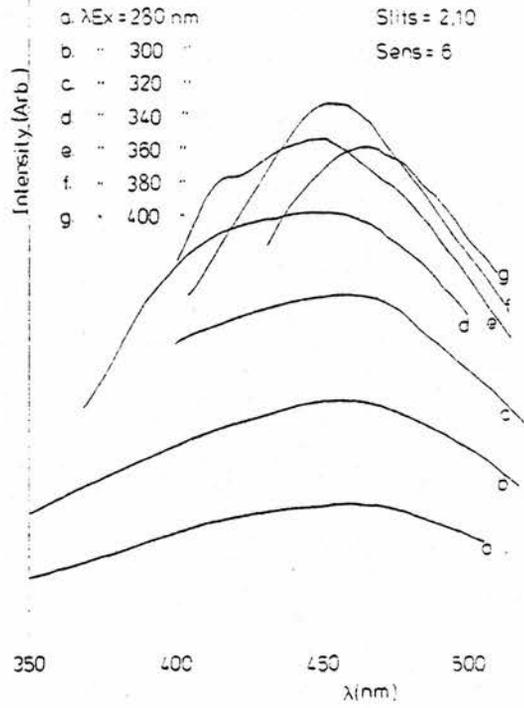




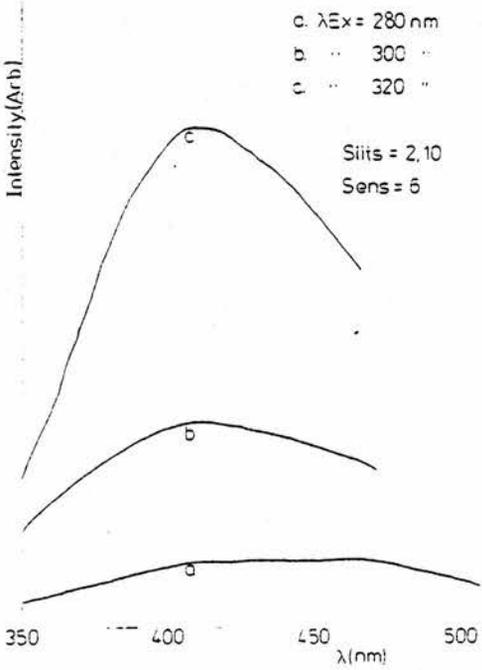
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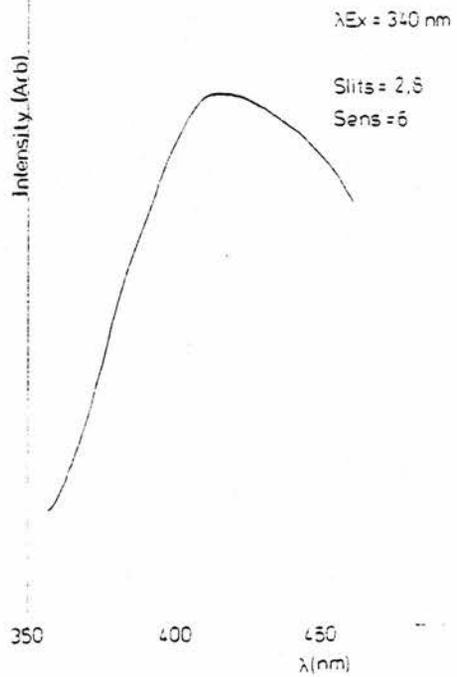
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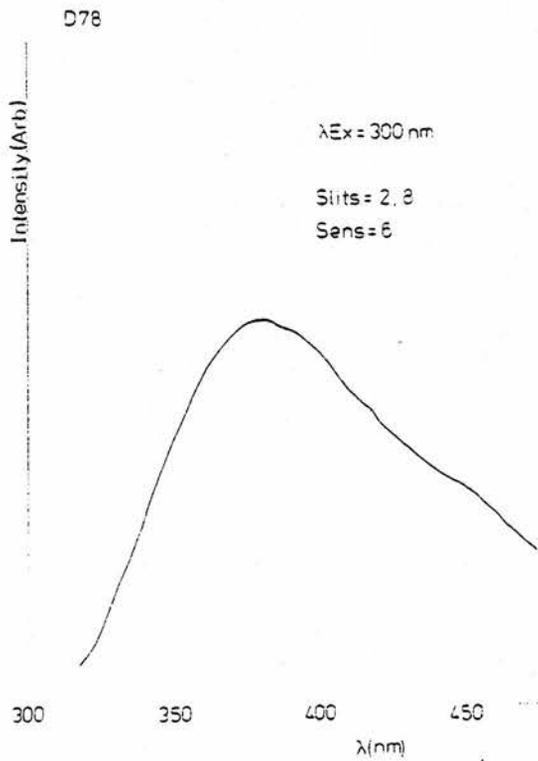
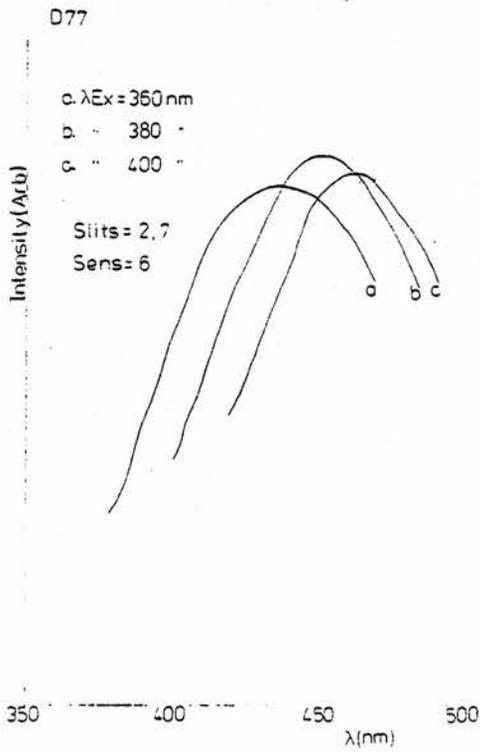
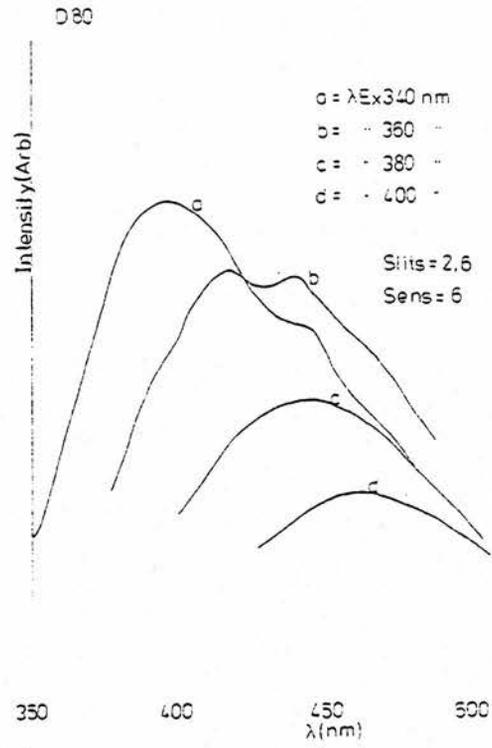
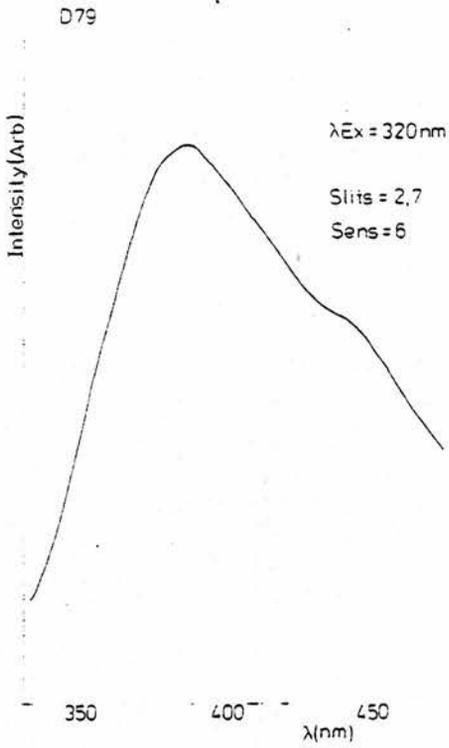


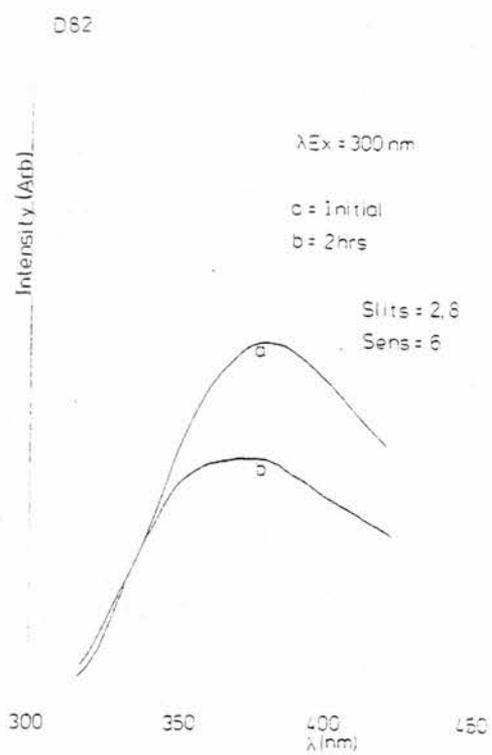
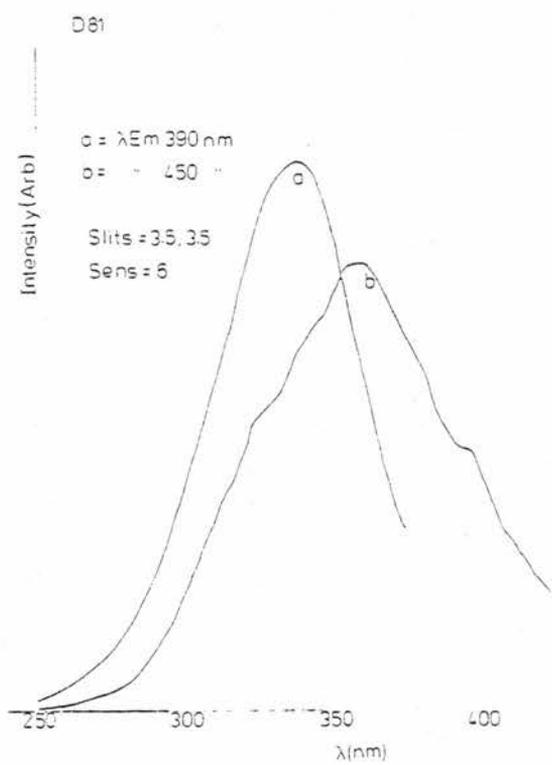
D75



D76







SECTION E - CHEMICAL EFFECTS

1. Effect of I₂ on Directly Synthesised Polyenesa) Introduction

As noted in Section A²⁸, exposing Poly(Acetylene) to controlled amounts of iodine, either in a solid/vapour reaction or in solution, results in an increase in conductivity of the polymer over as much as 11 orders of magnitude. Poly(Phenylacetylene), due to its conjugated double bond system, also exhibits conductivity, and Holub and Ehrlich¹²³ have noted that complexes formed between this polymer and iodine have greatly enhanced conductivity.

It was decided to expose the two polymers produced by direct means (PPA, PMP) to I₂ and to investigate the effects on the spectroscopic properties of these materials.

b) Poly(Phenylacetylene)

A sample of finely powdered PPA was placed in a ceramic boat, and exposed to I₂ vapour (Fisons, resublimed, MP 112-114°C) in the apparatus shown in Fig. E1 at 80°C. The sample was carefully weighed before and after exposure, and the molar ratio of iodine to PPA calculated:-

Wt of PP originally = 0.0693 g

Wt of PPA exposed to I₂ for 8 days = 0.1052 g

∴ Wt of Iodine = 0.0359 g

From the above data it may be deduced that the formula of the product is approximately (C₈H₆I_{0.42})_n. The sample was pumped out in a vacuum oven for 24 hrs before further use; no weight loss occurred. The product was a dark green lustrous powder.

Absorption spectra of 10^{-4} M solutions of PPA and IPPA were taken and compared in Fig. E2. As can be seen, the I_2 doping has reduced drastically the absorption above 300 nm, while increasing that below 300 nm, indicating a possible reshuffling of long polyenes to shorter length species.

Investigation into the emission spectrum of a 10^{-4} M solution of $(C_8H_6I_{0.42})_n$ in CH_2Cl_2 , by the methods described in Section D, produced the spectra shown in Fig. E3. Surprisingly, these spectra show a fairly broad, strong, emission centering on 460-470 nm on excitation between 350 and 425 nm. The emission intensity decreases steadily with increasing λ_{Ex} .

An excitation spectrum taken at $\lambda_{Em} = 460$ nm (Fig. E4) shows a similar shape and position to that of the PPA excitation spectrum at $\lambda_{Em} = 470$ nm (Fig. D12), but with the sharp peaks on the long wavelength side of the band excitation envelope reduced to shoulders.

A solution of PPA in CH_2Cl_2 was treated with excess I_2 for a period of 8 days. The product, a black-green powder, was recovered by stripping off the solvent on a Buchi Rotavapor, and finally drying in vacuum oven at RT for 48 hrs. The amount of I_2 present in the sample was not calculated, but it was in excess, as evidenced by the discolouration of sample tube stoppers over a period of time. Emission spectra for excitations in the range 300-425 nm were strong and broad, the centre of emission varying from 440-470 nm with increasing λ_{Ex} (Figs. E5-7). Again emission intensity generally increases with increasing λ_{Ex} .

Electrical properties of the polymer/iodine complexes were investigated on a Wayne Kerr Universal Bridge, model B221 using 5 mm or 13 mm pressed discs. The sample prepared by solid/vapour interface reaction showed a conductivity of $(5.78 \pm 0.5) \times 10^{-8} \text{ Scm}^{-1}$, while that of the solution prepared sample had a conductivity of $(6.0 \pm 0.5) \times 10^{-7} \text{ Scm}^{-1}$ (cf. PPA conductivity of $3.8 \times 10^{-15} \text{ Scm}^{-1}$).

Infrared spectra (Perkin Elmer 257 Grating Spectrometer; KBr discs) showed no significant differences between PPA and IPPA.

Carrying out two similar reactions in solution under light and dark conditions respectively, showed that light did not interfere with, or enhance, the reaction.

c) Poly(3-Methylpentyne)

A sample of PMP was treated in the same way as shown for PPA in Fig. E1:-

$$\text{Wt of PMP} = 0.1085 \text{ g}$$

$$\text{Wt of PMP after } I_2 \text{ exposure for 8 days} = 0.2550 \text{ g}$$

$$\therefore \text{Wt of Iodine absorbed} = 0.1465 \text{ g}$$

$$\text{Formula} = (C_6H_{10}I_{0.87})_n$$

The product was worked up as noted for the IPPA samples, but in this case was a bituminous black/green mass which gave off I_2 over a period of weeks. No conductivity measurements could be carried out, as the material would not form a pellet.

Comparison of the absorption spectra of PMP and IPMP (Figs. E8-9) shows that iodine affects PMP very differently to PPA. A

large overall increase in absorption is noted, with two previously unnoted large absorptions centering on 292 and 363 nm, and a series of smaller maxima between 450 and 500 nm.

Remembering that the solution phase spectrum of PMP could only be obtained as a very weak spectrum at $\lambda_{\text{Ex}} = 350$ nm (Fig. D7) it is interesting to see (Figs. E10-12) that, for a 10^{-4} M solution in CH_2Cl_2 , strong spectra can be obtained of IPMP in the excitation range 325-500 nm. The emission maximum varies considerably from c. 390-530 nm with increasing λ_{Ex} .

As λ_{Ex} increases, a distinctive pattern emerges in the intensity of the centre of emission, which is quite different from the general downward trend shown in the emission spectra of IPPA. As shown in Fig. E13, the emission intensity, starting from a high point at $\lambda_{\text{Ex}} = 325$, drops rapidly, but then re-increases to a new maximum at $\lambda_{\text{Ex}} = 450$ nm. This second maximum would appear to correspond to the low intensity series of maxima between 450 and 500 nm.

Excitation spectra were taken at $\lambda_{\text{Em}} = 400, 450,$ and 500 nm.

- i. $\lambda_{\text{Em}} = 400$ nm (Fig. E14):- The main contribution to emission at 400 nm appears to come from a broad area between 300 and 360 nm, not corresponding to either of the broad absorption bands in the UV region. Additional contributions appear between 250 and 300 nm, and a shoulder at 360-370 nm.
- ii. $\lambda_{\text{Em}} = 450$ nm (Fig. E15):- This shows a very broad excitation area, with numerous maxima, to be responsible for the 450 nm emission. The smaller contribution between 250 and 300 nm persists, and a strong maximum at c. 395 nm is in evidence.

iii. $\lambda_{Em} = 500 \text{ nm}$ (Figs. E16, 17):- This shows that, while the contributions at 250-300 nm, 300-350 nm, and 395 nm still persist at this very long wavelength emission, the main contribution comes from a series of sharp excitations between 450 and 490 nm, located at 452, 459, 463, 458, 472, 480 and 490 nm.

d) Checks

In order to eliminate the possibility of any effects noted above being due to the spectroscopic properties of iodine itself, absorption and emission spectra of I_2 solutions in CH_2Cl_2 were taken. The absorption spectrum of I_2 (c. 10^{-2} M) in CH_2Cl_2 shows only a broad absorption centering on 504 nm, while emission spectra of solutions of I_2 in CH_2Cl_2 (10^{-3} , 10^{-4} M) show only the CH_2Cl_2 emission at low λ_{Ex} , and no emission above $\lambda_{Ex} = 375 \text{ nm}$.

2. Effect of HX on Degraded Poly(Vinyl Acetate)

a) Introduction

It has been stated by various authors^{81, 86} that HCl forms a highly coloured complex with degraded PVC under certain conditions. It was decided to investigate the possibility of a similar reaction between degraded PVAc and HCl, Starting off with the mildest possible conditions, ie. in the dark at RT ($\sim 25^\circ \text{C}$). As is explained in the following paragraph, it was not found necessary to increase the severity of the conditions in order to produce a reaction.

b) Initial Study

A sample film of 160000 $\overline{\text{Mn}}$ PVAc was cast onto a 25 mm quartz disc, from CH_2Cl_2 solution, to a thickness of c. 0.05 nm, and degraded under the usual conditions at 250°C for 2 hrs. Hydrogen chloride gas (HCl) was generated by the addition of analar NH_4Cl (Fisons) to conc. H_2SO_4 (Fisons, 98%), which produces the reaction:-



The sample film was placed in a sealed, darkened, container, pumped out, and HCl allowed in to 1 atm. pressure. The absorption spectrum of the film was taken at intervals of 1 hr, 5 hrs, and 20 hrs; after each measurement fresh HCl was placed in the container. Figs. E18 and 19 show that the discrete peaks at 262, 272, 283, 306, and 321 nm are lost with increasing exposure time, although the overall absorption does increase.

The most surprising result is the appearance of a large, very broad, absorption between 350 and 650 nm, with the suggestion of a new series of discrete peaks on the low wavelength side. The appearance of this very broad absorption was unexpected from the point of view of a complex similar to that of the degraded PVC/HCl⁸⁶, and degraded PVC/ $\text{CF}_3\text{CO}_2\text{H}$ ¹²⁴ pairs, since a sharper peak would be expected at higher wavelength (c. 650-700 nm).

It was decided to use a thicker sample of PVAc in order to observe the new discrete peaks more clearly. This sample, of c. 0.10 mm thickness, was degraded under the same conditions as the first sample, and then subjected to HCl in the dark at 20°C for 2 hrs, showing the same characteristics as before. The sample was then left in air in the dark for 120 hrs, and the reaction

continued. It was also noted that the lower wavelength discrete peaks now reappeared (Figs. E20, 21). The sample was seen to change in colour from pale yellow to deep purple. The new discrete peaks noted were at 365, 389, 414, 439, 461, and 480 nm.

Similar results to the above were found for samples degraded for 1 hr and for 30 mins.

c) Complex, or Not?

The extreme colour change noted above for samples degraded and then exposed to HCl would, at first glance, be taken to indicate the formation of a highly coloured charge-transfer complex; however, numerous results suggest that this is not so.

I. Due to the reversible nature of a CT complex formation, it should be possible to remove HCl from the sample, and restore its original condition by either high vacuum pumping to remove HCl gas, or by leaching out HCl with a suitable solvent. Attempts to do this failed.

II. Due to its presence in a CT complex as a relatively free species, it should be possible to induce HCl to react with a suitable gaseous base, such as ammonia, and thus destroy the complex. This "compensation" of HCl with NH_3 proved unsuccessful.

III. After removing the sample from an HCl environment and leaving it in the dark in air, the increase in absorption continued at more or less the same rate for some considerable time. In Fig. E22 is shown the plot of Absorption intensity vs time for two peaks in the absorption spectrum, the sample being removed from HCl after 3hrs,

and then left in the dark in air for 20 hrs. The observed behaviour is inconsistent with a CT reaction.

IV. The most convincing evidence against a CT reaction comes from the following experiment. A degraded film of PVAc was placed in a 10 cm IR gas cell, which was then pumped out, and an atmosphere of HCl introduced. The whole apparatus was then placed in a dessicator, in the dark at 20°C.

The IR spectrum of the cell was taken, on a Perkin-Elmer PE257 spectrometer, at various times. As shown in Fig. E23, there appeared, over a period of 16 days, a series of peaks at 1790, 1775, 1725, 1420, 1290, and 1180 cm^{-1} , which correlate with a gas phase spectrum of acetic acid. The vibrational spectrum of HCl between 3060 and 2640 cm^{-1} did not change markedly. The progress of the 1725 cm^{-1} peak with time is recorded in Fig. E24.

As a result of the above data, it may be stated that the reaction observed between HCl and degraded PVAc is not a CT process, but a continuation of the deacetylation reaction involved in thermal degradation, catalysed in some manner by HCl.

d) HCl vs HBr

A comparison study of the reactions between degraded PVAc and HCl, and degraded PVAc and HBr was now carried out. HCl was produced in the manner already described, while HBr was produced by the reaction of Br_2 with dry tetralin (Fisons, bp = 206-209°C):-



The gas evolved was bubbled through a further dreschel bottle of dry tetralin, in order to remove any Br_2 carried over from the initial reaction bottle, before being introduced to the reaction vessel.

Resulting absorption spectra are shown in Figs. E25-28, and reveal that the reaction between degraded PVAc and HBr occurs at a faster rate than the reaction between degraded PVAc and HCl. This difference in reaction times would seem to suggest a connection between reaction rate and H-X bond strength. (It would also be expected that, for a CT reaction, HBr would react more slowly, due to the larger size of the Br atom.)

e) Photolytic Reactions

In order to investigate the effect of light on the reaction, two experiments were carried out, as explained below:-

- I. A sample of PVAc ($\overline{M}_n = 160000$), cast as a 0.05 mm thick film on a quartz disc, was degraded under the usual conditions at 250°C for 2 hrs. The degraded film was then exposed to HCl for 2 hrs in the dark at 20°C , then left in air in the dark for 24 hrs. In Fig. E29 can be seen the effect of irradiating this sample under HCl atmosphere (MP Hg Lamp, pyrex filter cutting out radiation of wavelength < 300 nm). The reaction may be observed to be continuing, apparently at an enhanced rate.
- II. A second sample, degraded in the same manner as the above, was placed in HCl atmosphere and irradiated immediately. From Fig. E30 it can be seen that the subsequent absorption spectroscopic behaviour of the sample is completely different to that observed in the first experiment. Irradiation rapidly diminishes the double bond content

of the sample, lowering the absorption overall above 230 nm, and causing the disappearance of the discrete peaks at 262, 272, 283, 306, and 321 nm.

Storing the sample in the dark at 19°C for 72 hrs in HCl brought about a considerable increase in absorption, but no discrete peaks were noted.

f) Emission Spectra

I. Degraded PVAc/HCl

The absorption spectrum of the sample used in this case is shown in Figs. E18, 19. The initial emission spectra (Figs. E31, 32) are similar to those discussed in Section D, showing the peaks at 385, 400, and 415 nm at excitation wavelengths between 250 and 321 nm, and the 310-320 nm emission at $\lambda_{Ex} = 250$ and 262 nm.

Emission spectra taken after 1 hr exposure to HCl (Figs. E33-37) show a rapid drop in emission intensity for the peaks between 380 and 420 nm, for spectra taken at $\lambda_{Ex} = 250, 262$ and 272 nm. The additional absorption maxima noted at 350, 368 and 392 nm showed emissions with peaks centering on 440, and 470 nm. Additional absorption maxima noted at longer wavelengths gave no emission spectra.

Spectra taken after 5 hrs and 20 hrs exposure were similar, but slightly weaker.

II. Degraded PVAc/HBr

The absorption spectrum of the sample used in this case is shown in Figs. E27, 28. The initial emission spectra (Figs. E38-44) show similar characteristics to those discussed in Section D, with

strong emissions from excitations at $\lambda_{\text{Ex}} = 250, 262, 272, 283, 306, 321$ and 354 nm.

Spectra taken after 30 mins exposure to HBr (Figs. E45-47) show a massive drop in intensity of all emissions. At $\lambda_{\text{Ex}} = 250-272$ nm, the higher λ emissions (385, 400 and 415 nm) are virtually non-existent. Spectra taken at $\lambda_{\text{Ex}} = 283, 306, 321$ and 354 show the HBr reacted material to have similar emission wavelengths to the degraded material. Spectra taken at 370 and 394 nm show weak, broad, spectra centering on c. 470 nm.

III. Photolytic Experiments

The sample from experiment "e)I" showed similar emission behaviour to that noted for the degraded PVAc/HCl experiment.

The sample from experiment "e)II" showed a very weak emission at $\lambda_{\text{Ex}} = 250$ nm with peaks centering on 310 and 390 nm. Excitation at $\lambda_{\text{Ex}} = 262, 272, 283, 306, 321,$ and 354 nm produced no discernable emission.

g) Low_MW_PVAc

Samples of PVAc of $\overline{Mn} = 45000$ were treated in the same way as the high MW samples described above, and gave similar results throughout.

h) Undegraded_PVAc

A sample of powdered, purified, PVAc was placed in a sealed tube in HCl atmosphere, and kept in the dark at 20°C for a long period of time. Its appearance was monitored over a period of days, with the results noted below:-

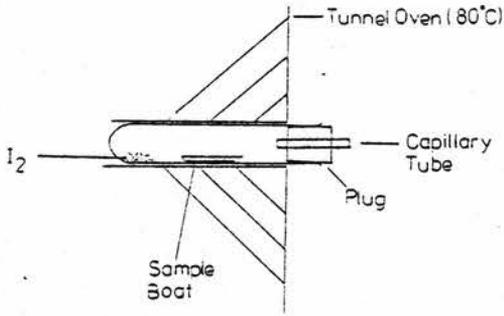
t (days)	Sample Appearance
0	white
2	white
4	white
6	off-white
8	pink
10	reddish brown
14	violet
16	purple
42	dark purple

It would thus appear that purified, undegraded PVAc undergoes a similar reaction to the degraded material, but over a much longer time scale. The probability is that this is due to residual double bonds, left as end groups during the polymerisation, acting as starting points for an HCl catalysed deacetylation.

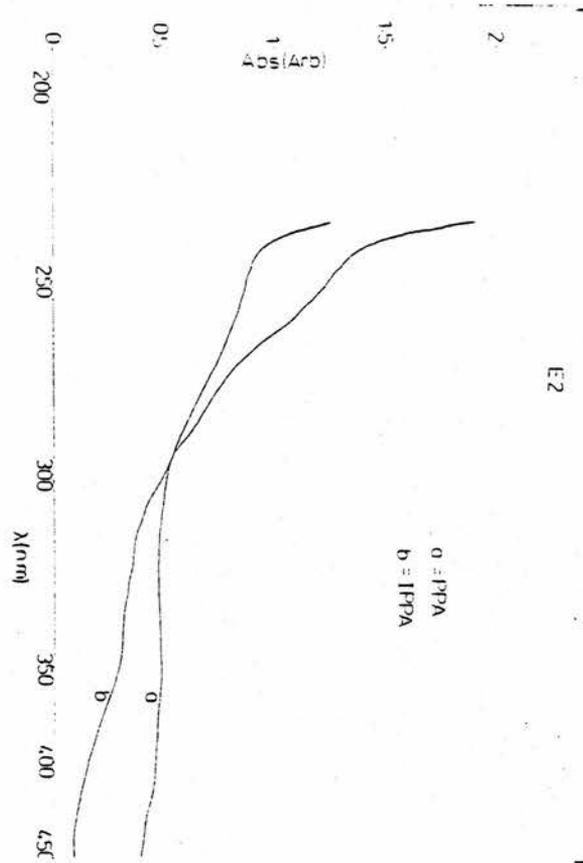
i) PVC

Attempts to react HCl with photochemically degraded samples of PVC, under the conditions used in the above experiments, met with no success.

E1

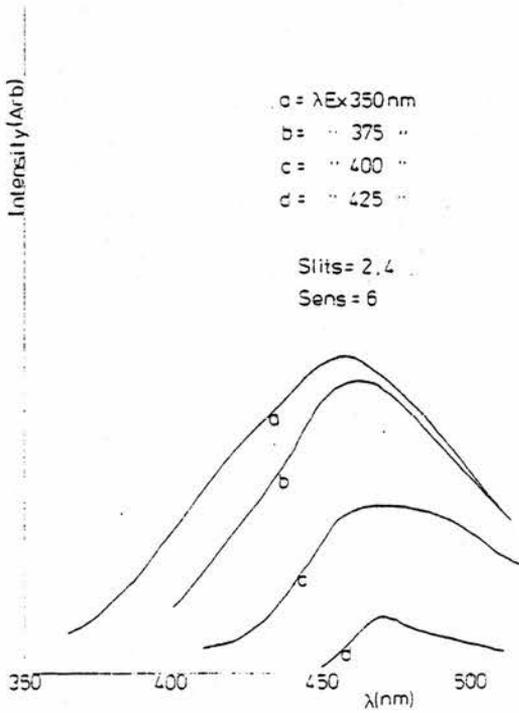


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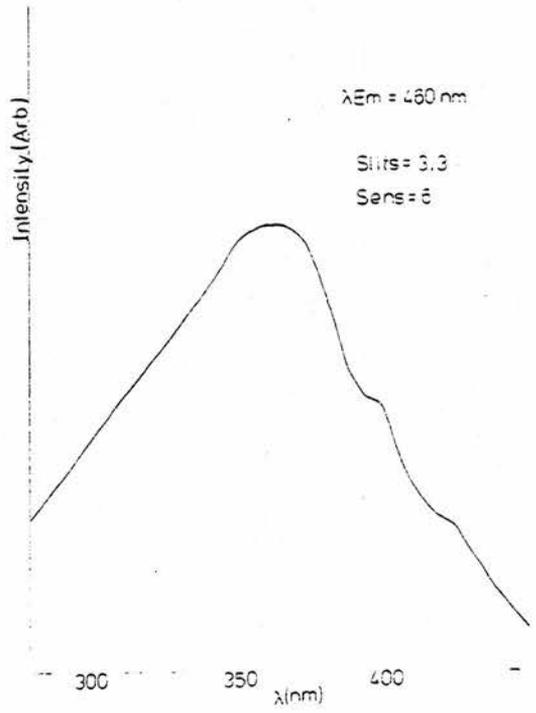


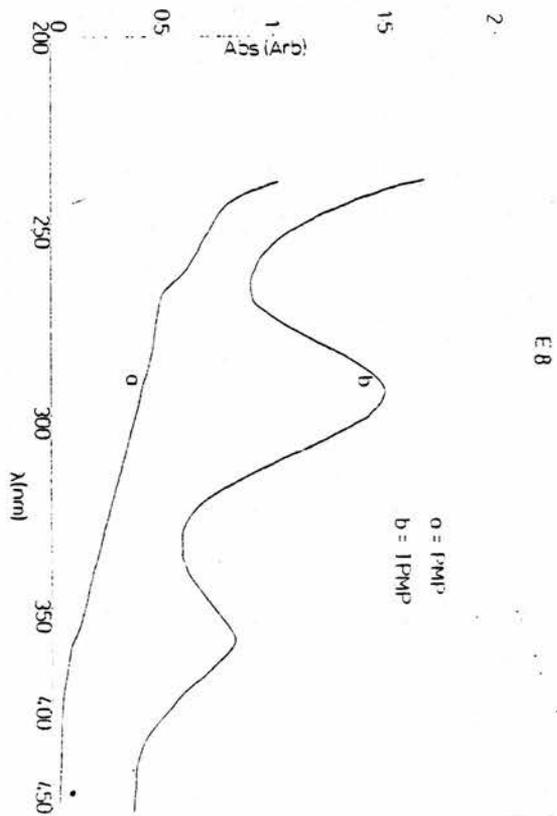
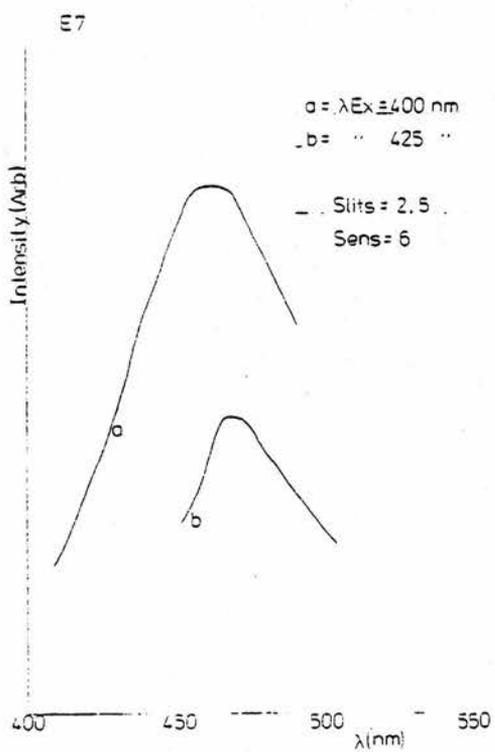
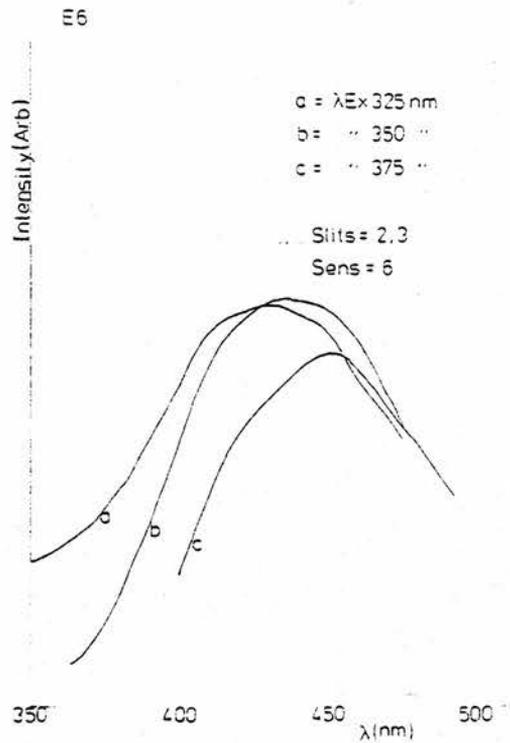
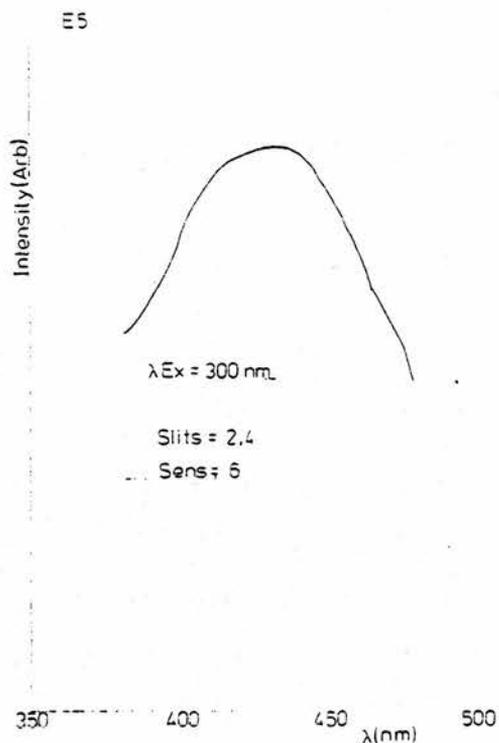
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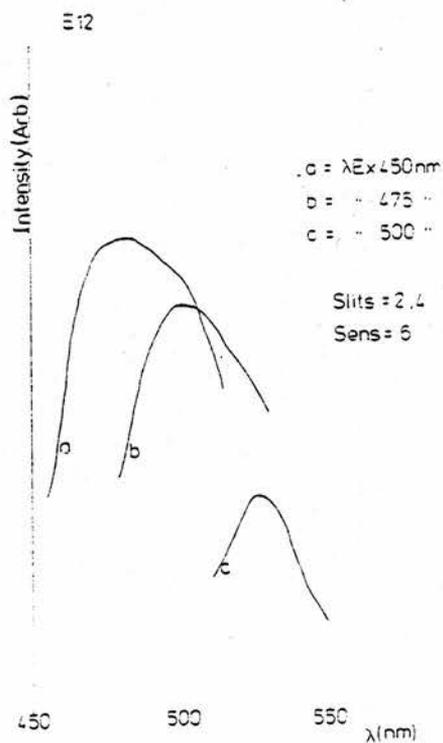
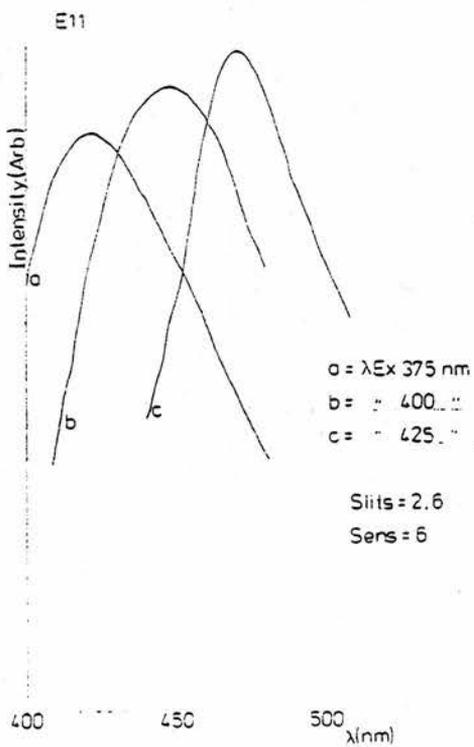
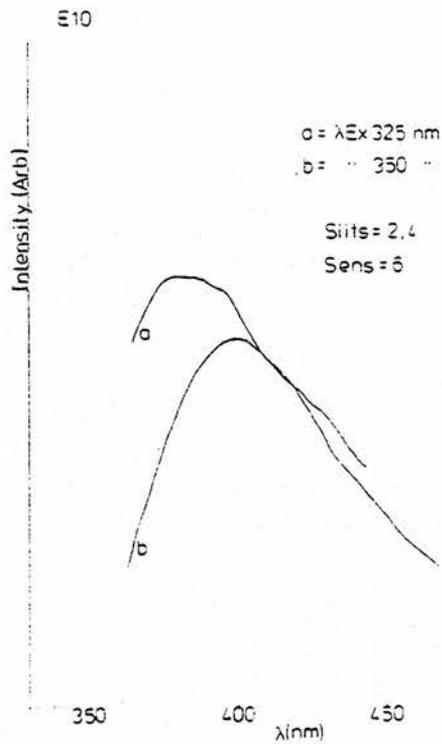
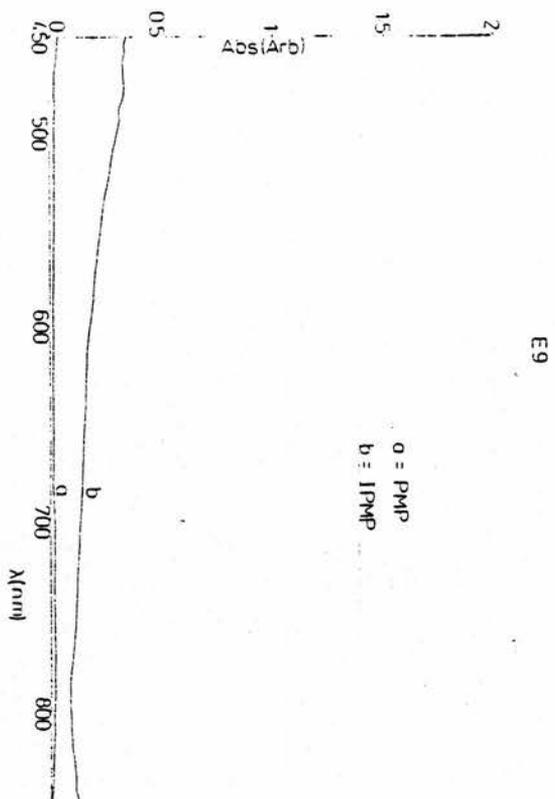
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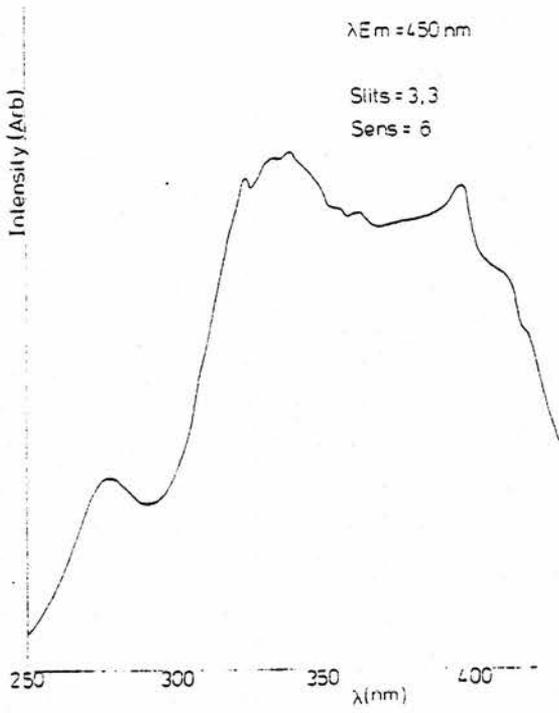
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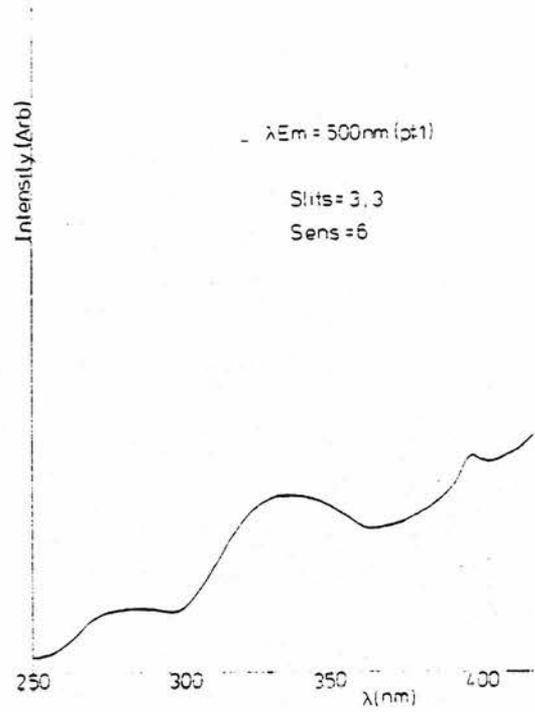




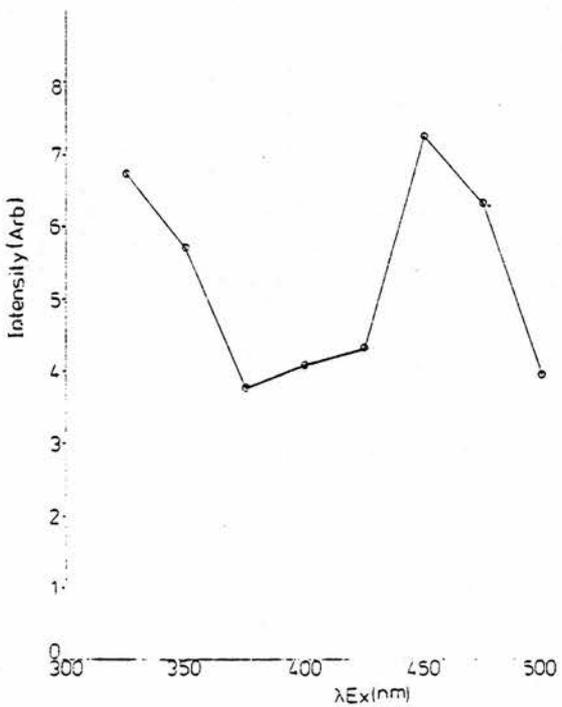
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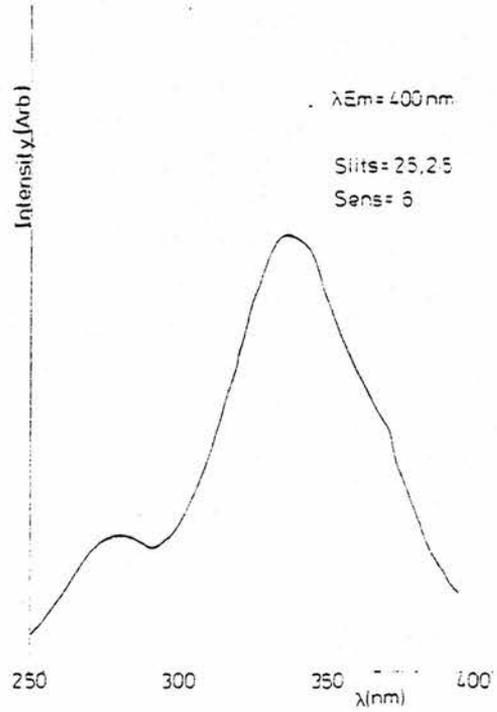
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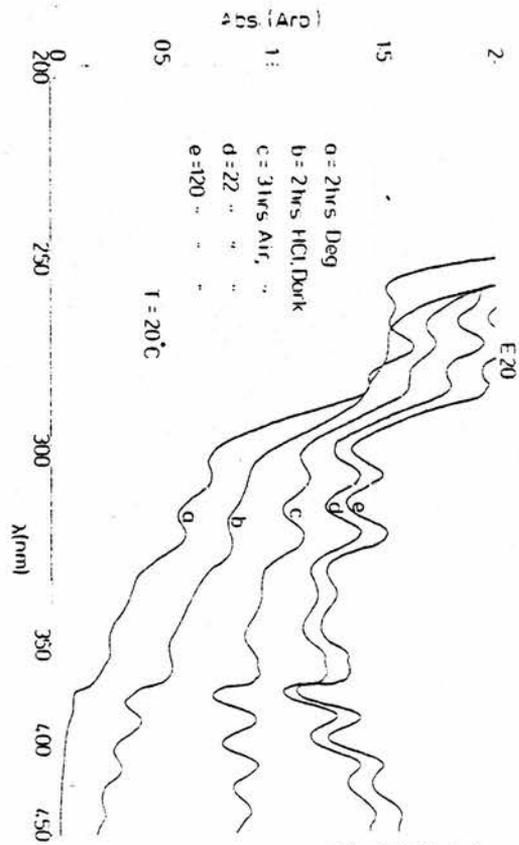
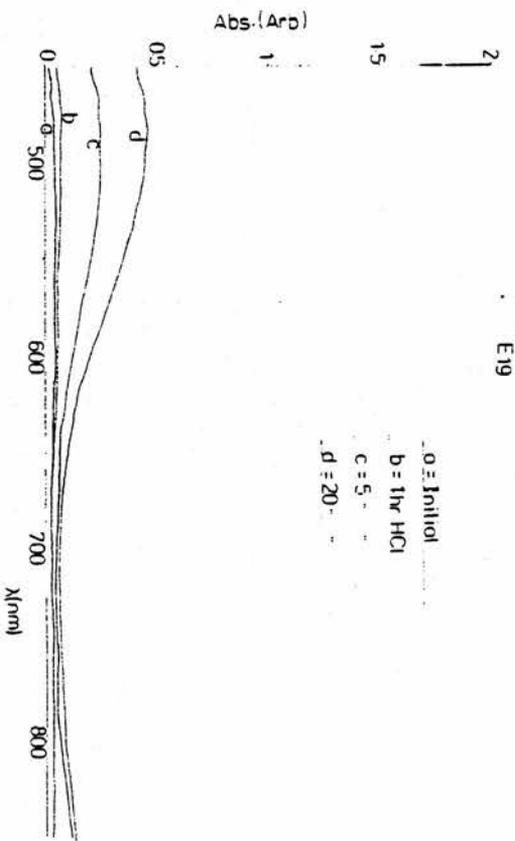
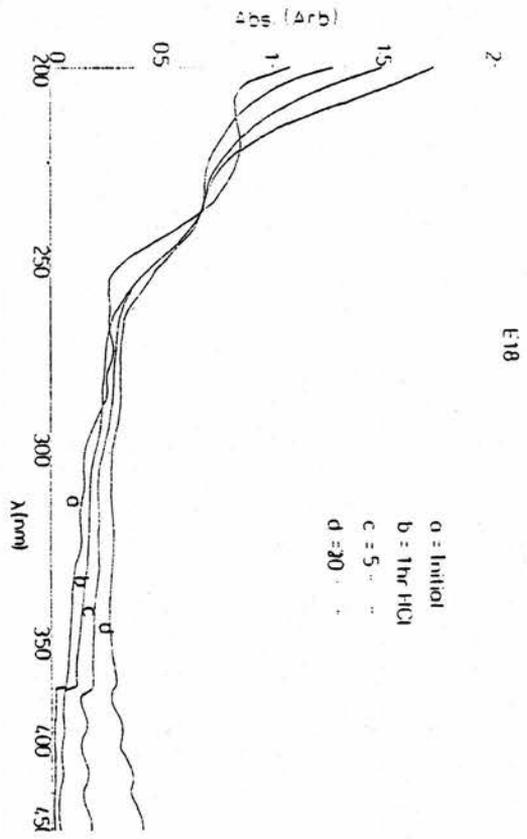
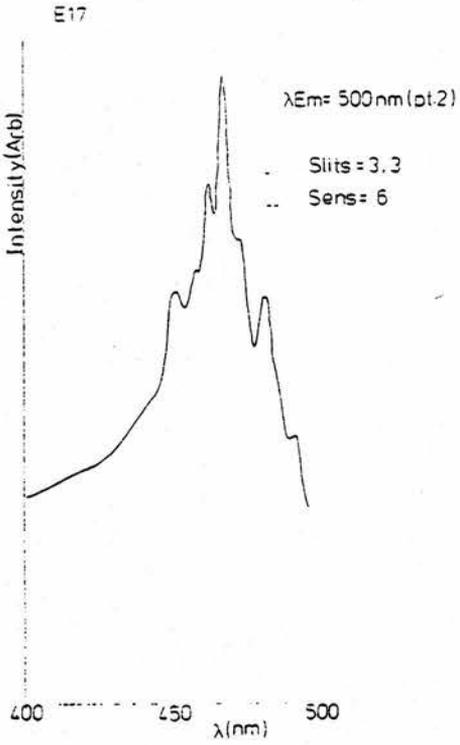


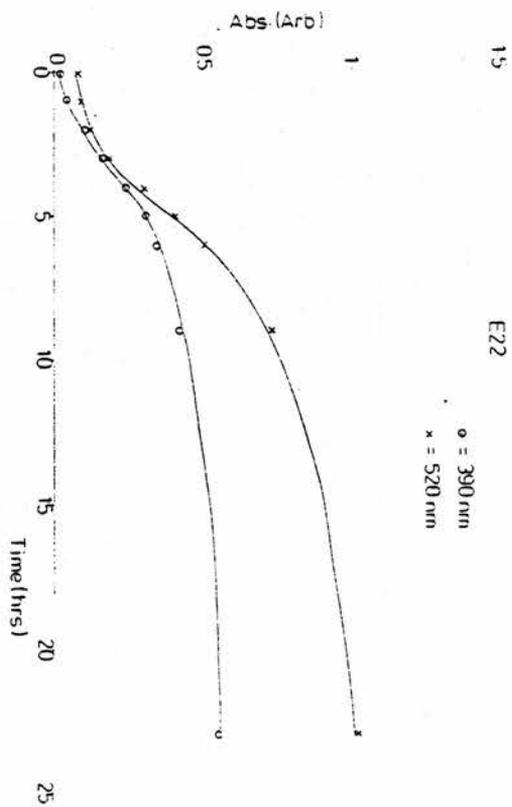
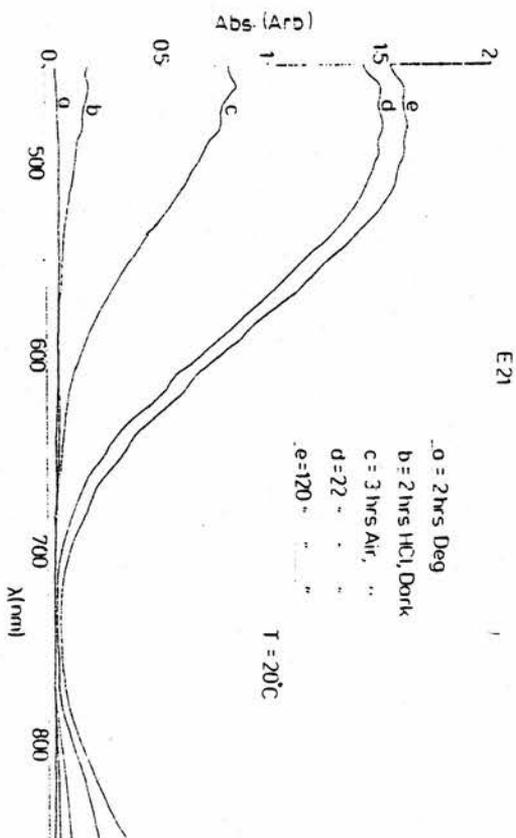
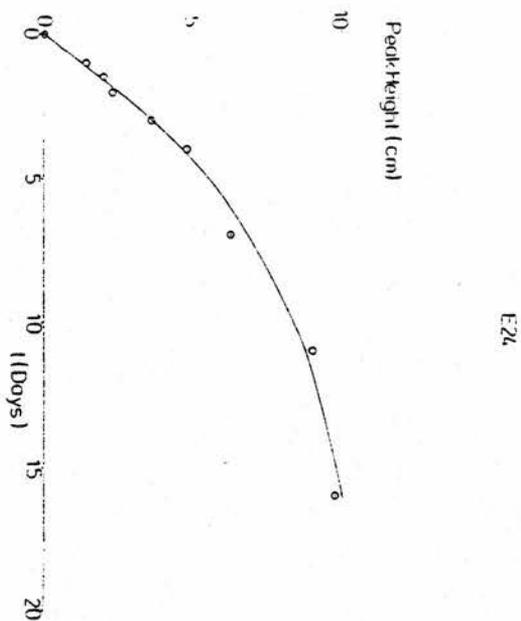
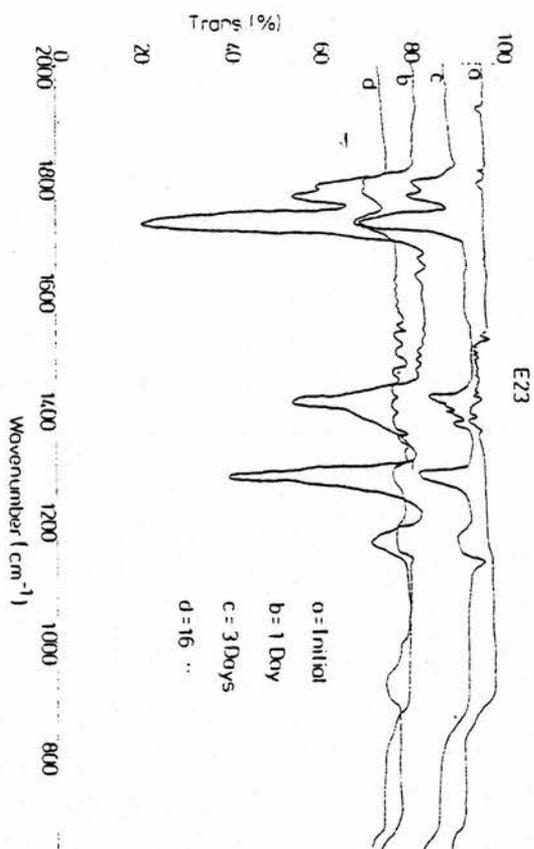
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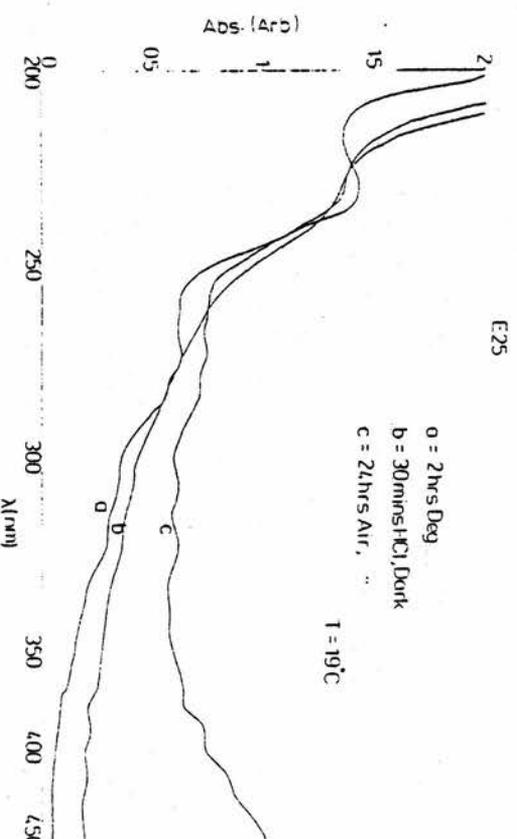
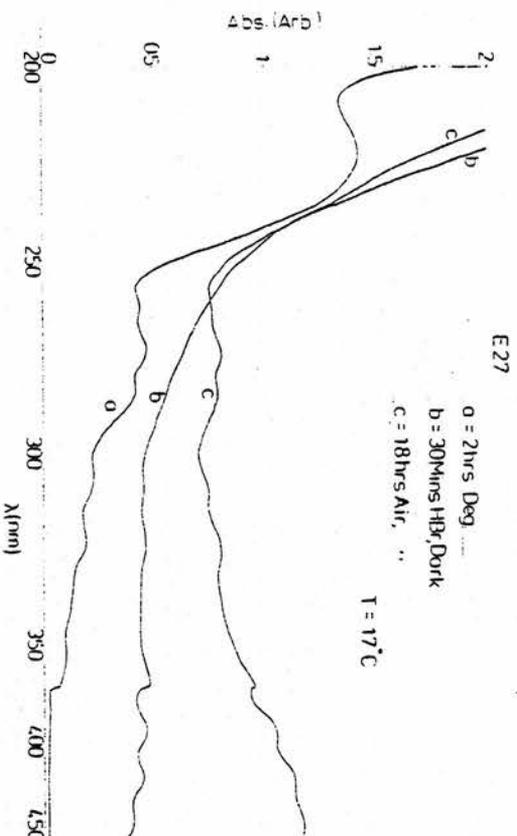
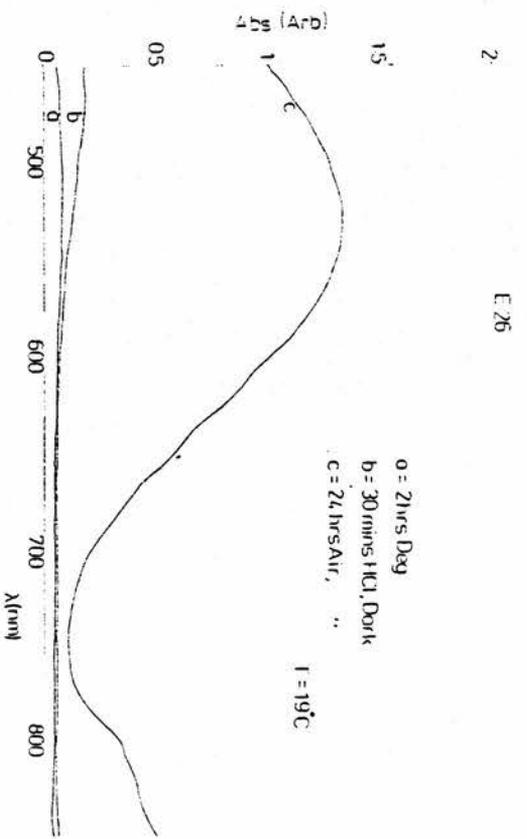
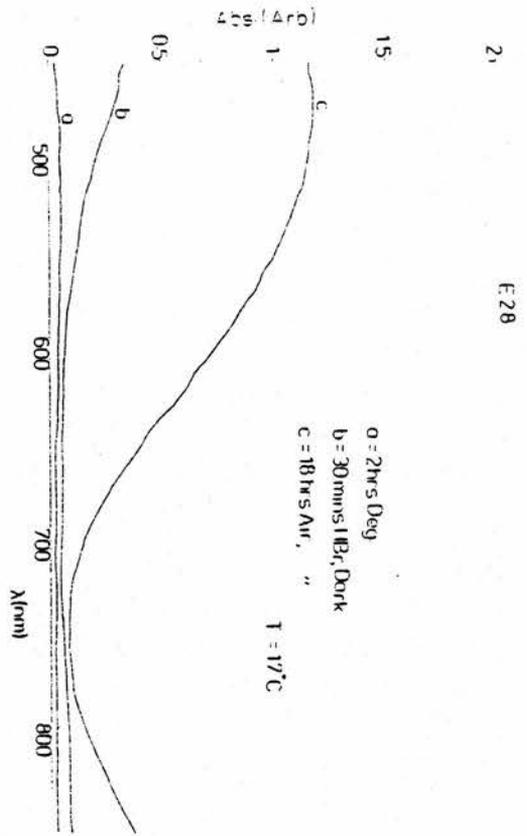


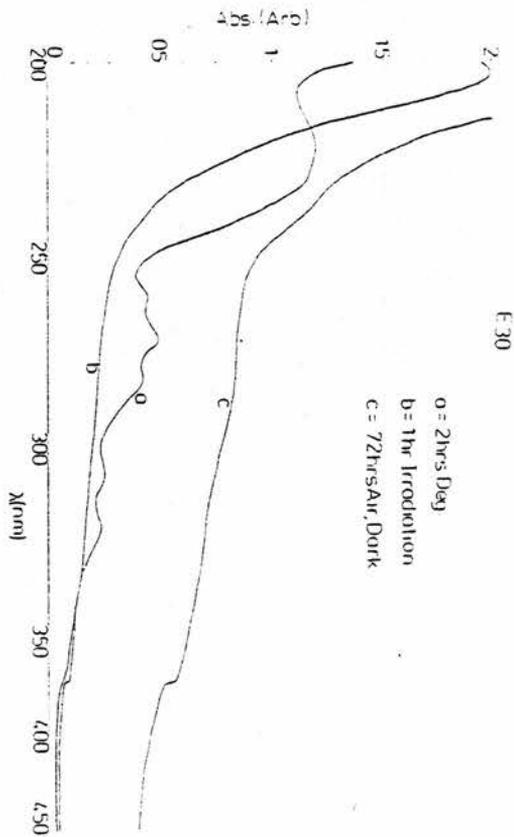
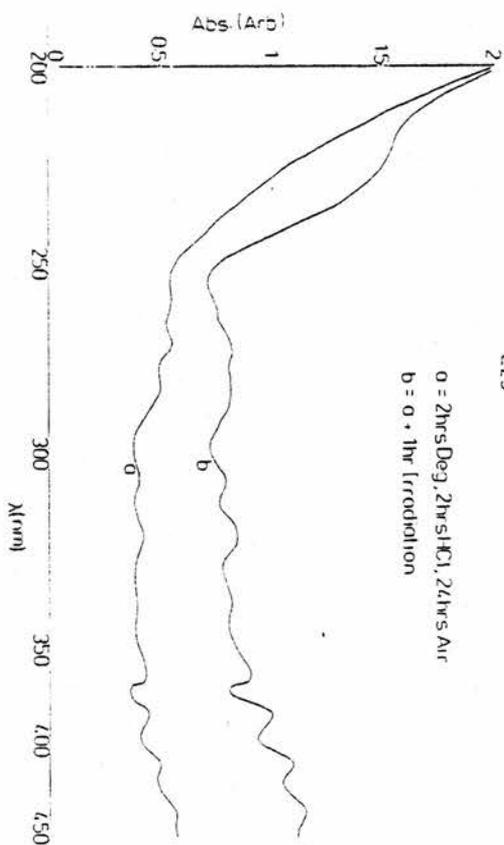
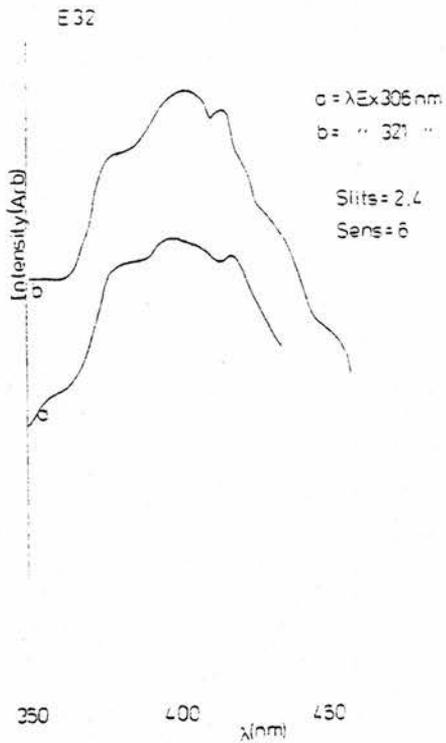
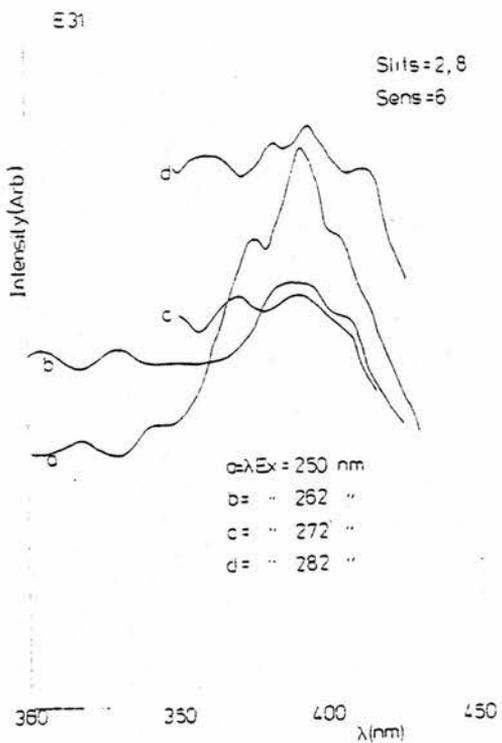
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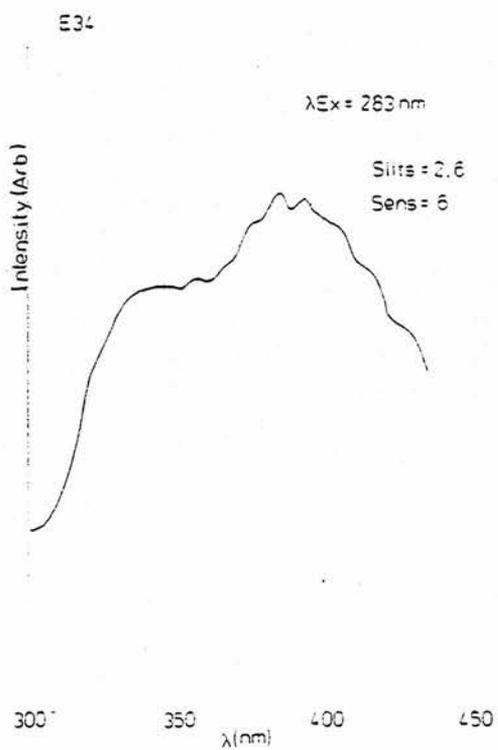
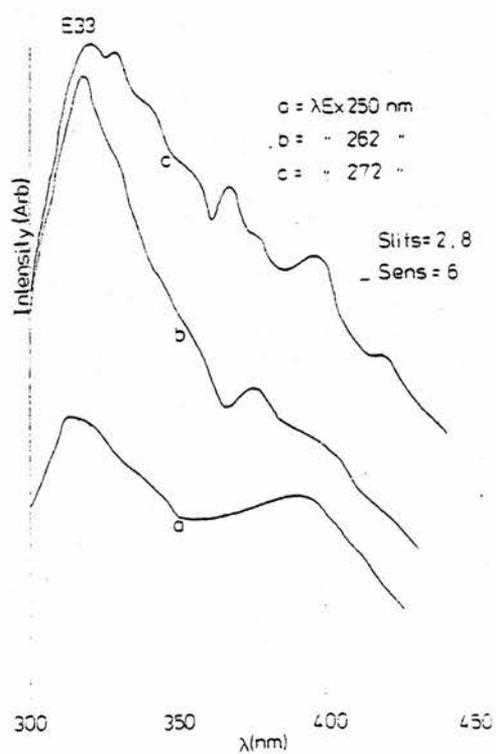
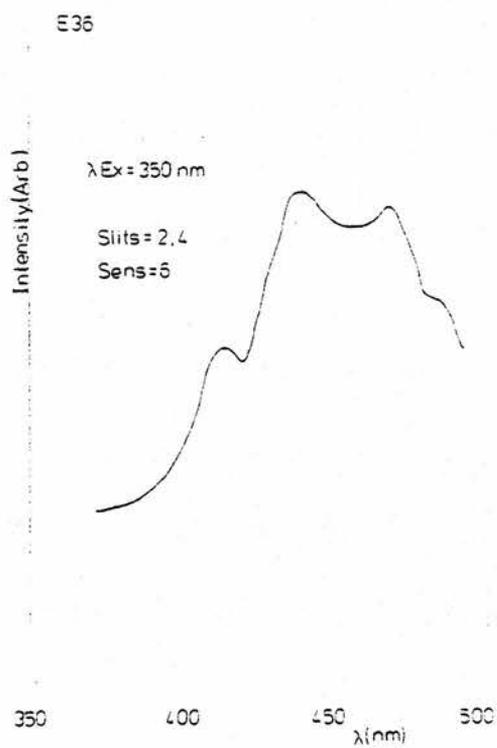
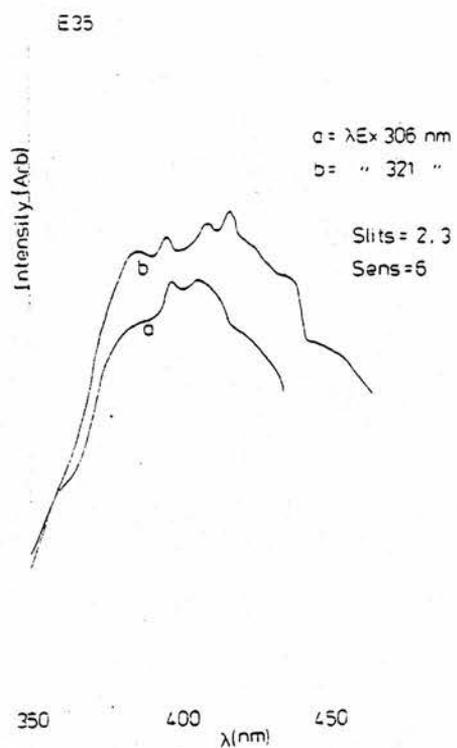


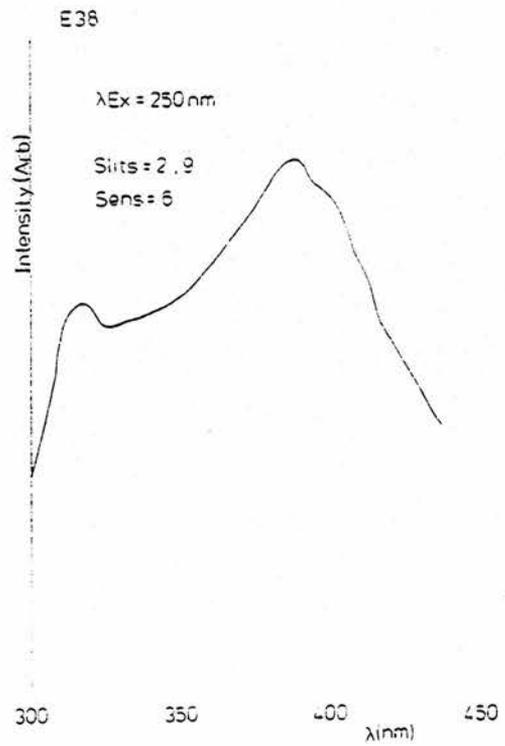
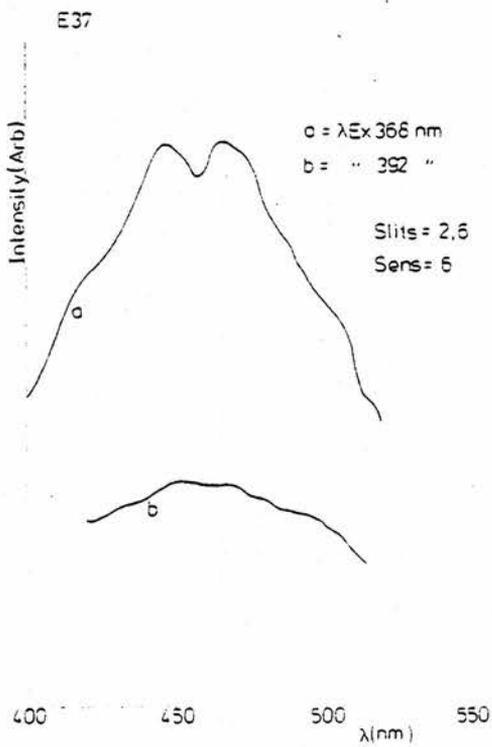
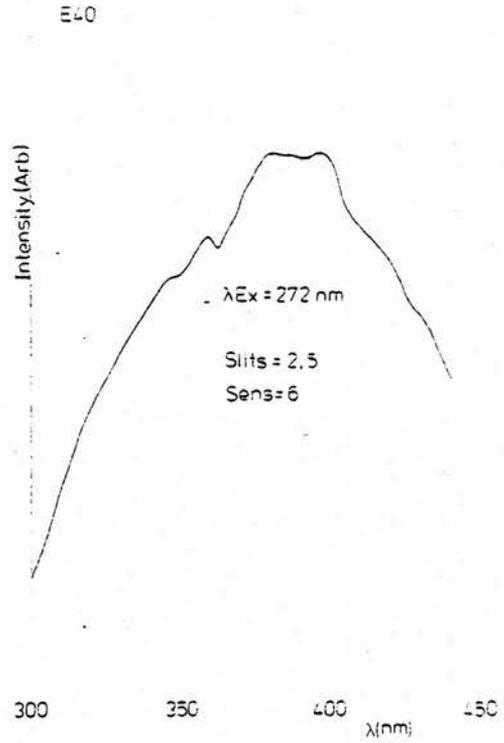
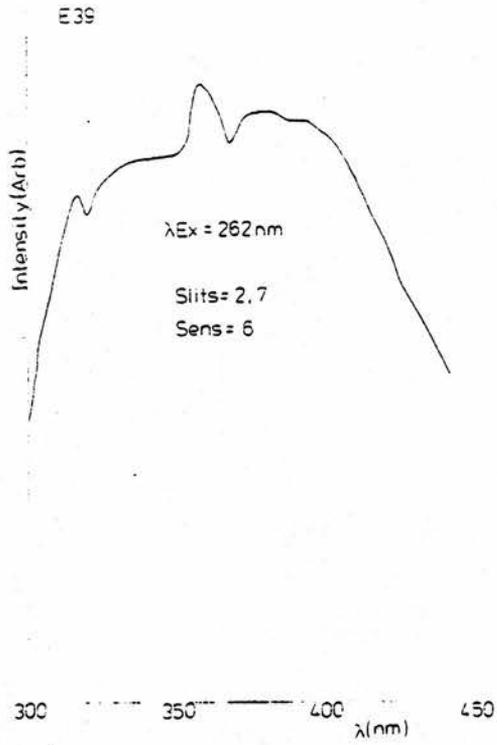


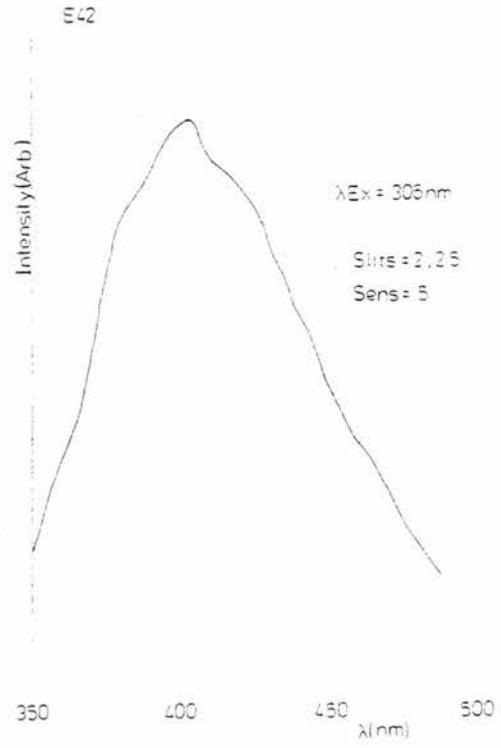
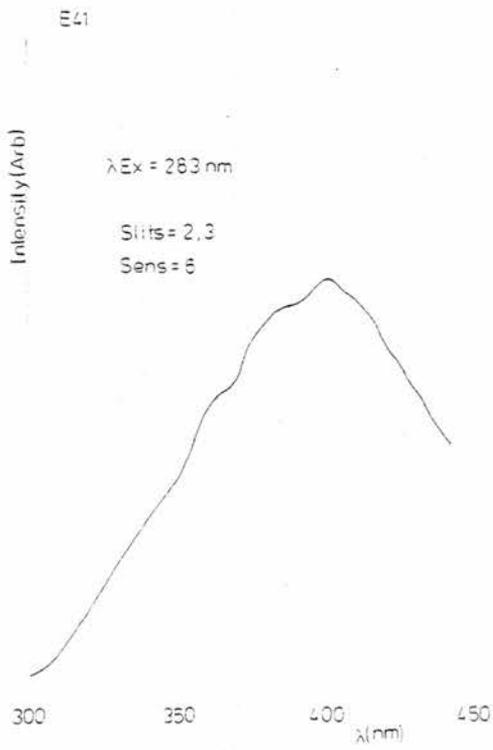
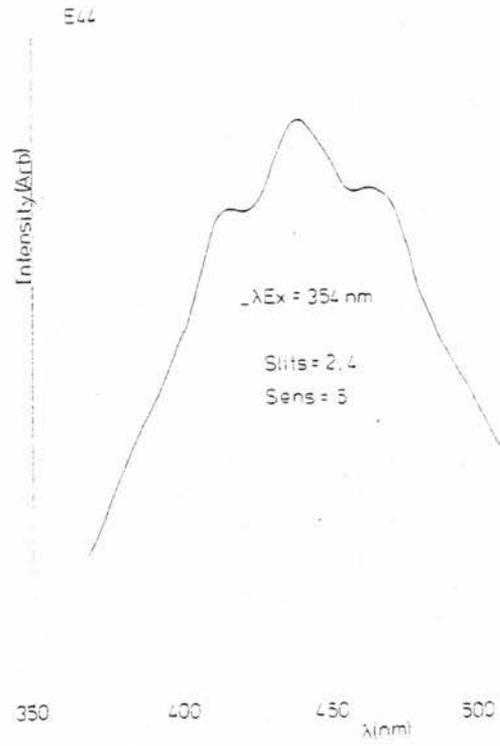
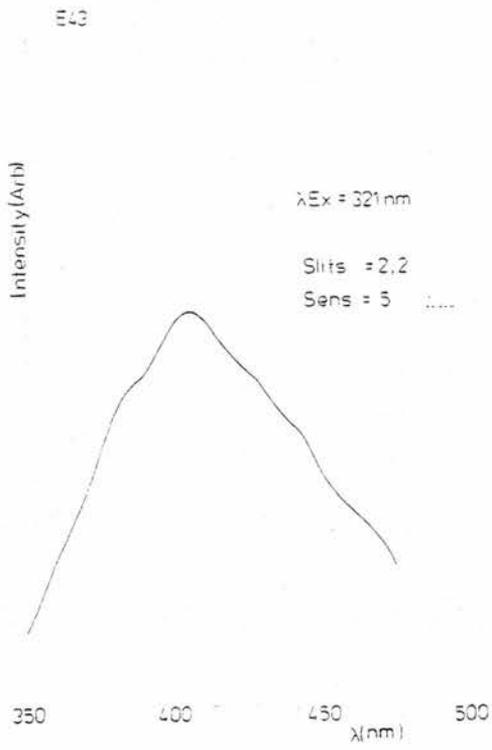


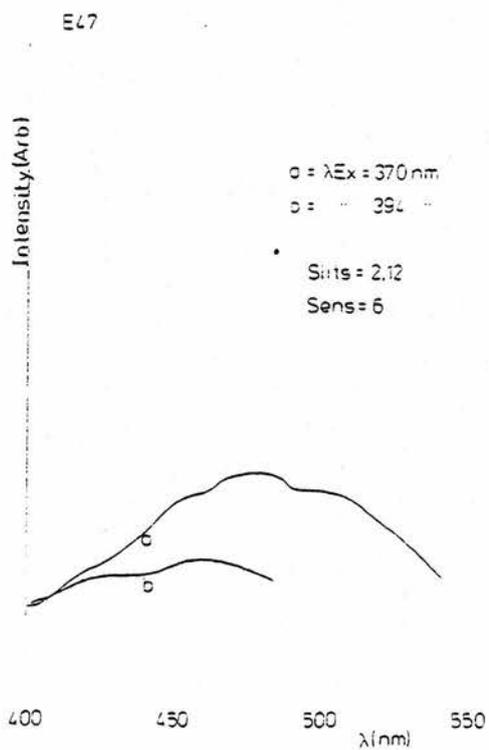
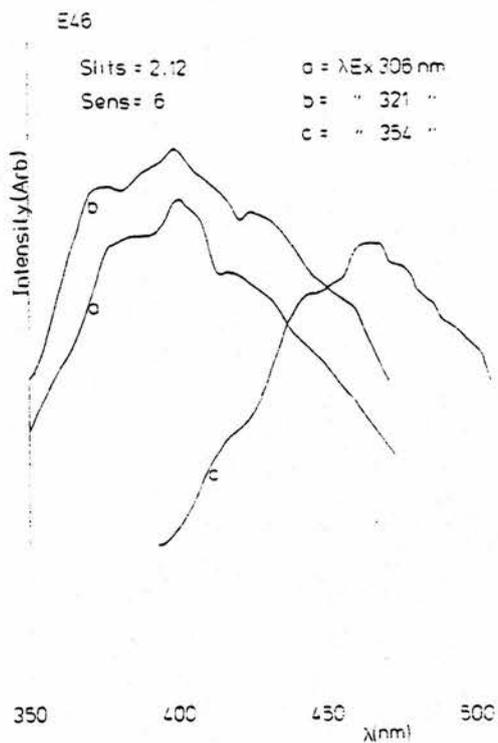
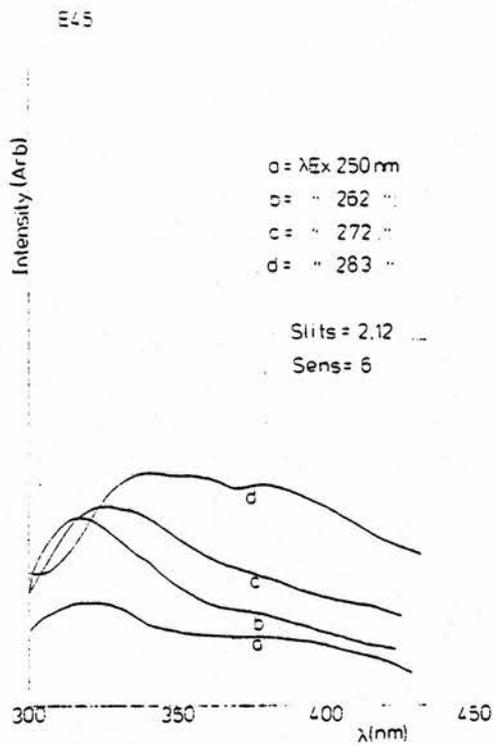












SECTION F - DISCUSSION

1. Directly Synthesised Polyenes

The methods used for the synthesis of PPA⁴³ and PMP⁵³ produced high MW soluble polyene systems in good yield. Characterisation of products showed these materials to have no significant differences from the literature products.

a) Emission Spectroscopy

The disappointing results obtained for the emission spectra of these systems have a series of contributing causes. The sensitivity of these species to light and to O₂ has been noted⁴⁵, and decrease of fluorescence intensity of PPA with increasing MW has already been mentioned¹¹². A third important factor is the decrease of quantum yield (QY), or efficiency, of fluorescence with increasing length of conjugation¹²⁵. The high MW of the compounds used has already been noted, and in the case of PPA, the intense colouration of the product does not change on reprecipitation, which shows that this is not due to crystallinity preserving the conjugation, as found by Holob and Ehrlich¹²³, but to an inherently high degree of conjugation of the polymer.

The excitation spectrum of PPA taken at $\lambda_{Em} = 470$ nm (Fig. D12) shows a broad spectrum with contributions coming mainly from $\lambda_{Ex} = 350-440$ nm showing that the predominant polyenes in the system have n double bonds where $n = 6-10$, correlating absorption maxima with those found for a series of dimethyl polyenes¹¹⁶. The excitation spectrum differs from the absorption, mainly due to the two discrete peaks found at 409 and 435 nm, which suggest that the species involved are efficient emitters.

b) Chemical Effects

The interaction between iodine and Poly(Acetylene) ($(\text{CH})_x$) produces a dramatic increase in conductivity²⁸. Recent Raman studies on these interactions have indicated the presence of I_3^- in the crystalline polymer¹²⁶, but without the concomitant discovery of I^+ . Consequently, the electron attached to I_3^- seems to come from the polyene as a result of Charge Transfer (CT). The transfer of e^- to the polyhalide appears to be almost complete, since the UV spectrum obtained with lightly doped $(\text{CH})_x$ is almost identical with that of the undoped material²⁸. In this state, the cationic polymer chain and the polyhalide anion may be independent of one another.

Reactions between I_2 and PPA have been reported^{119,123}, but no emission study has been carried out on the species formed. There are no literature reports of interactions between I_2 and PMP.

The fact that the emission intensity of both polyenes is greatly enhanced by I_2 is puzzling, in that I_2 would be expected to enhance non-radiative decay from the excited state to the ground state, and thus quench the emission. A possible general explanation of this phenomenon is that, in some way, I_2 causes a perturbation of the polyene, the spectroscopic properties of poly conjugated polymers being extremely sensitive to configuration¹²⁷. Specific causes may include a shift in the cis-trans ratio of the polyene towards the all-trans side, which has a higher fluorescence quantum yield; eg. all trans Retinol $Q = 0.02$, 9-cis retinol $Q = 0.007$ ¹²⁸. However, a systematic study of the QY's of a series of isomers of a long chain polyene has not yet appeared, and indeed would be extremely difficult. Increased mixing of the ^1Bu and $^1\text{Ag}^-$ excited states could also be caused by

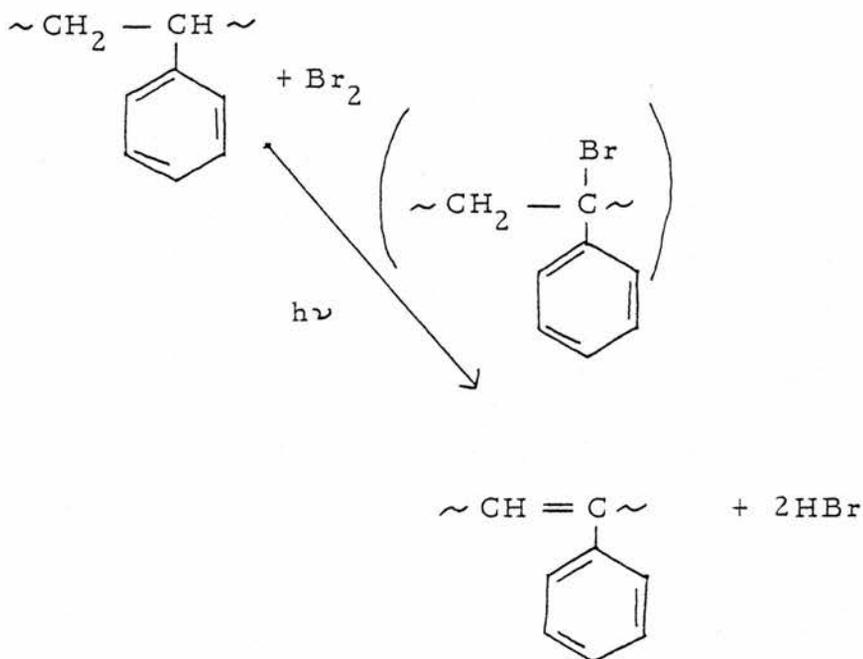
addition of I_2 , and this would contribute to an increase in emission intensity.

The acute differences noted between the absorption spectra of IPPA and IPMP (Figs. E2, 8, 9) can be explained as being brought about by different degrees of CT efficiency. The IPPA spectrum, which shows some evidence of rearrangement of polyene ratios, contains no extra CT peaks, and may be taken to be evidence of an efficient electron transfer situation, with the polyenic cation being only loosely attached to its counter-ion. Complex formation between the phenyl groups of PPA and I_2 is ruled out, as a strong CT band would be expected around 290-320 nm, similar to that found for interactions between I_2 and substituted benzenes¹²⁹.

PMP, on the other hand, has very bulky side groups which can prevent a close approach and efficient transfer of electrons to iodine; the large bands noted in the absorption spectrum may thus be due to a "conventional" CT complex between I_2 and the backbone polyene system. Attempts to judge the efficiency of transfer from the electrical conductivity are of dubious value, since the exact ratio of I_2 actually taking part in a CT interaction, and the type of conducting species involved, cannot be ascertained.

That the increase in conductivity is a genuine movement towards a semi-conducting state can be deduced from the extremely broad excitation spectra obtained for both complexes; a continuous excitation spectrum denoting an "organic metal" state, as noted for high doped $I_2/(CH)_x$ ¹³⁰.

In Section C, it was seen that the products of the photoreaction, and the subsequent thermal processing, possessed very similar spectroscopic properties, implying the creation of polyene sequences during the first stage of the reaction. A more accurate rendition of the reaction scheme therefore may be written as shown below:-



The use of NMR studies to follow the gradual creation of styrene-phenylacetylene random copolymers by this method showed that ^1H NMR does not yield a great deal of information about double bond formation, but does show that the bromine attack is exclusively on the α proton of the styrene unit. Test sample spectra were essentially the same as that of the control PS, and the literature values for PS^{107, 132}. The use of ^{13}C NMR is more useful in the study of polymers¹³³, due to the wide range of chemical shifts, and the lack of spin-spin coupling in the manner of proton NMR. Comparisons with the ^{13}C spectra of poly(butadiene)¹¹⁰ and Poly(Phenylacetylene)⁴⁴ have shown the presence of double bonds in

the polymer backbone, but only to a small extent, indicating that a highly conjugated state has not been achieved.

Difficulties encountered with the Perkin-Elmer MPF-44 spectrofluorimeter at this stage of the project prevented the gathering of a large amount of data on the emission properties of these systems, the only concrete fact emerging being their general similarity to the spectra of the other polyene systems investigated.

The fact that sunlight ($\lambda > 300$ nm) gives a better result than low wavelength irradiation is probably due to additional photochemical reactions, brought about by the higher energy radiation involved, superceding the bromination/dehydrobromination reaction.

b) Poly(Vinyl Chloride)

I. Photochemical Degradation

As can be seen from the absorption and emission spectra in Section D, the conditions of irradiation show little effect on the overall spectroscopic properties of the degraded material. Retention of HCl during the irradiation does appear to inhibit the reaction to a certain extent, and this is in agreement with previous work⁷⁸.

The intensity of the emission spectra obtained shows a sudden increase in going from $\lambda_{Ex} < 300$ to $\lambda_{Ex} > 300$ nm, this effect is also noted, more clearly, for degraded PVAc and will be discussed fully under that section.

Absorption spectra show that, due to the generally accepted "zipper" mechanism^{66, 84} of PVC degradation, the length of the polyene sequences created increases with increasing degradation time. The effect of this on the emission characteristics of the degraded material is to reduce the intensity of emission with

increasing degradation time due to re-absorption by higher, non-emitting polyene sequences.

The excitation spectra of the samples are similar to those of PVAc and will again be more fully discussed under that heading.

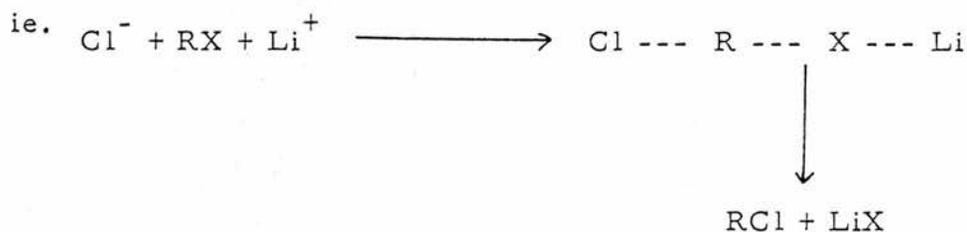
Both the emission and excitation spectra found compare well with those found in the preliminary experiments of Owen and Read¹²⁰.

II. Chemical Degradation

Chemical degradation of PVC in solution produces highly coloured polymers containing long sequences of double bonds. Investigation of those species is difficult however, due to their often being partially or totally insoluble, and to their extreme sensitivity to air and light⁶⁴.

1) LiX (X=halide):- Of the series of lithium halides used to dehydrohalogenate PVC, only LiCl and LiBr succeeded. The two possible mechanisms put forward for this type of reaction may give some indication of why this is so:-

a) The removal of HX requires a trans elimination therefore it is suggested that an exchange of halogen atoms first occurs, with the replacement X being in the preferred trans position -



the now trans Cl can then be removed by simultaneous attack by Li^+ and the lone pair of DMF:-

The slightly stronger reactivity of LiBr over LiCl evidenced in the microanalysis results would seem to indicate that its lesser bond strength is a contributory factor, and this points to the first mechanism. The presence of a LiCl_2^- species in the second scheme casts some doubts on its validity, but is not impossible. The second scheme is favoured by other authors^{69,70}, and by the fact that isolable complexes can be formed between LiCl and DMF⁶⁷.

2) KOH:- The reaction scheme involved in this degradation is much simpler than the above, consisting of a simple base catalysed elimination, as noted by the original authors⁶¹.

The spectra show that increasing reaction time brings about increased production of long polyenes, but this is attended by increasing insolubility, probably caused by cross-linking, and O_2 effects.

Emission and excitation spectra are in excellent agreement with the preliminary data on chemically degraded PVC published by Owen and Read¹²⁰.

c) Poly(Vinyl Acetate)

Of all the polymers used in the indirect synthesis of polyenes, PVAc has provided the most interesting and consistent spectroscopic and chemical results. Much less attention has been paid to the degradation behaviour of PVAc than that of PVC, and observations made during this work may cast some light on the processes involved in the deacetylation process.

I. Thermal Degradation

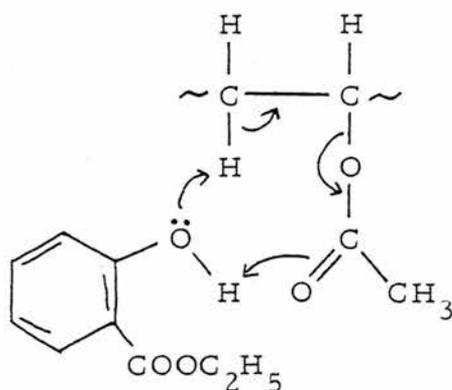
As noted in Section C, the thermal degradation of PVAc under vacuum, with constant removal of volatiles, gives a product which shows clear maxima in the UV/Visible spectrum, which indicate the presence of a series of polyene units. It is noted that the length of conjugation of the double bonds in this system is limited, not as in the case of thermally degraded PVC¹³⁴. This may be put forward as evidence of a random deacetylation process as suggested by some authors⁹⁵⁻⁹⁷, as opposed to the "unzipping" mechanism of PVC degradation, since the build-up of long sequences would not be favoured. The ability of the lower MW PVAc samples to produce longer sequences of double bonds within the same time scale however, would seem to be in favour of Grassie^{89, 90}, in that the higher number of end group double bonds available provides a larger number of initiation sites, and therefore may increase the rate of formation of long conjugated sequences.

That PVAc cross-links early in the degradation process is a well documented fact^{89, 90, 95-97} but the mechanism of the process is not conclusively proven. Kholchlova et al⁹⁷ suggest a Diels-Alder type reaction between adjacent chains, and a catalytic contribution by acetic acid dissolved in the degraded polymer is a possible method for this. The continuing cross-linking is brought forward as a very important factor in the degradation behaviour of PVAc by Servotte and Desreux⁹⁶, who state that the polymer is changed from a series of chains to a 3-D matrix by the cross-linking. This could have an important effect on the deacetylation behaviour and, linked with evidence from emission spectroscopy, will be seen to have possible

great significance.

II. Solution Thermal Degradation

As stated by Varma and Sadhin¹⁰⁰, the solvent used during this particular experimental series participates in the reaction itself, therefore this process might be more strictly referred to as a chemical degradation. Investigation of the degradation in inert solvent with catalytic amounts of ethyl salicylate might confirm whether the mechanism cited is true:-



III. Chemical Degradation

As noted in Section C, the use of p-toluic acid, p-cresol, pentachlorophenol, etc. failed to produce a deacetylation reaction of the type catalysed by p-toluenesulphonic acid¹⁰¹. Comparing the almost total ionisation of pTSA in aqueous solvent to the high pKa values of the other compounds (p-toluic acid = 4.36, p-cresol = 10.17), it can be seen why this is so.

IV. Emission Spectroscopy

As can be appreciated from the spectra shown in Section D, thermally degraded PVAc provided the best and most interesting

emission and excitation spectra. The general pattern of emission spectra can be summarised, in terms of the absorption spectrum, as shown in Fig. F1 and set out below: - (bearing in mind that the dividing lines are probably not nearly so sharp as represented)

1. Here we are seeing the parent, undegraded, polymer, plus a large amount of $n=1, 2$ polyenes. The emission spectra from $\lambda_{Ex} = 250$ nm shows two widely separated bands, one due to short sequences, the higher wavelength one due to Energy Transfer (ET) processes to higher polyenes. The spectra are very weak, indicating that the fluoresce QY of the short sequences is low, and that ET is not efficient.

2. In this section occurs discrete absorbance at 262.5, 273, and 284 nm, which can be tentatively correlated to sequences of $n=3-4$ double bonds¹¹⁶. The emission intensity increases for emissions between 380 and 400 nm, while the low wavelength emission is lost.

3. The two peaks at 307 and 322 nm can be correlated to $n=4-5$ sequences. The emission intensity here is very much stronger than from excitations at lower λ , indicating that species with $n=4$ and 5 have high fluorescence QY. Side bands in the emission at 440 and 470 nm indicate a low efficiency ET process towards higher polyenes.

4. Two peaks at 334-354 nm - correlatable to $n=5-6$. The emission here shows a marked shift in emphasis from emission at 385 and 400 nm towards high intensity emissions at 415 and 440 nm, with side bands at 470 nm, and tentatively at 495 nm.

5. This region shows little in the way of discrete maxima and the emission intensity again decreases rapidly, most probably due to the sharp decrease in oscillator strength of the fluorescence transition encountered at high n values.

Taking the above observations together, it may be said that, while ET between polyene sequences is inefficient, it is not negligible; the presence of emissions at 440 and 470 nm, even at low λ_{Ex} confirming this. That polyenes with $n=4-5$ straddle the arbitrary regions shown in Fig. F1 is also obvious.

Variations in emission intensity on changing the excitation wavelength can be explained as being brought about by differences in the fluorescence quantum yield of the various polyene sequences; in that polyenes of $n=4-5$ have a higher QY than the others. In the case of shorter sequences, perhaps the low QY is caused by the uncertainty of the identity of the lowest excited state for such species noted by Andrews and Hudson¹⁵. For longer sequences, the lowering of the oscillator strength of the fluorescence transition will be the overriding factor.

Excitation spectra show that the species noted below region 3 in Fig. F1 do not contribute a great deal to the emissions at 385, 400 nm, or above, and that, as the emission wavelength increases, the higher absorptions become more involved. The excitation spectrum of $\lambda_{\text{Em}} = 315$ nm shows a contribution from the region 255-270 nm. A similar spectrum is seen for photodegraded PVC (Fig. D19), which shows this to be a genuine polyene excitation/emission couple, and not an artifact of the parent PVAc.

Emission spectra of these degraded PVAc samples at $\lambda_{\text{Ex}} = 283\text{-}321$ nm, and the excitation spectra thereof correlate remarkably well with literature spectra of deca-2,4,6,8-tetraene¹³⁵.

As is clearly seen in the emission spectra in Section D, degraded PVAc provides sharper, stronger, spectra than degraded PVC. This is probably due to some perturbation effect of HCl dissolved in the degraded PVC, though not to a Heavy Atom Effect, as noted for the interactions of aromatic compounds with halide salts¹³⁶, as this has been found not to occur in polyene fluorescence¹³⁷.

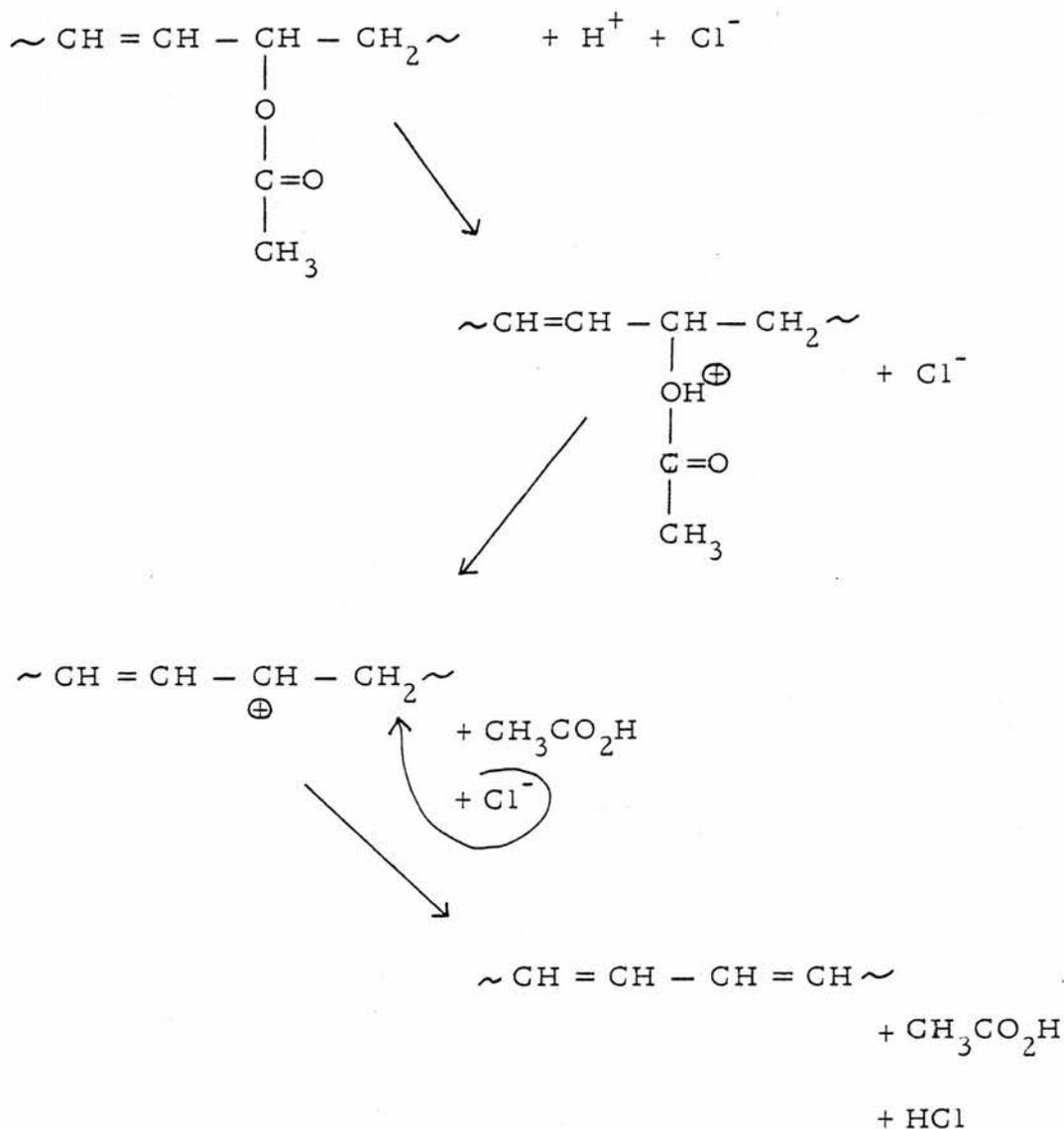
Emission spectra taken of degraded PVAc samples at 77 K under vacuum show only a slight sharpening of the bands of the RT spectrum; although very few reproducible spectra were found, due to difficulties with the scattering factors involved. From this observation it may be assumed that there is no phosphorescence present in the spectra illustrated for thermally degraded PVAc.

V. Correlation of Emission Intensity Variation to Degradation Mechanism

As seen in Fig. D57 (this is only a representative diagram, the emissions at 385 and 400 nm also show this behaviour) plotting the emission intensity for specific peaks against degradation time for selected λ_{Ex} shows there to be two maxima. A possible explanation for this phenomenon involves there being two distinct deacetylation reactions occurring at different stages of the degradation process. If, as Grassie proposes⁸⁹, the degradation is initiated at or near chain end double bond sites (unlike PVC, PVAc does not appear to contain internal ethylenic linkages¹³⁸, at least for high MW material),

The mechanism proposed is as follows:-

Consider HCl dissolved in the polymer matrix. The equilibrium $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$ may be set up at this low T, and a reaction scheme devised as below:-



Carbonium ions, being planar¹⁴⁰, will allow the conjugation to be easily continued. This mechanism has the advantage of explaining the need for backbone double bonds, which provide the driving force for the reaction at such a low T.

The marked difference in the photolytic behaviour of PVAC samples, as shown in Figs. E29, 30, indicates that once the above

reaction has been initiated, any energy input will tend to accelerate that reaction. The loss of absorption noted on immediate irradiation of degraded PVAc is probably a bleaching reaction similar to that found for degraded PVC irradiation under HCl⁸⁵.

The changes in emission behaviour noted during reaction of degraded PVAc with HCl are complex. The emission bands from 380-415 nm are much less intense, while an enhancement of the emission at c. 320 nm is noted for $\lambda_{Ex} = 250-272$ nm; this would seem to indicate a rearrangement of the medium length polyenes to shorter sequences, in addition to the continuing HCl catalysed deacetylation. The fact that HBr quenches all the fluorescence bands quickly indicates that, being the stronger acid, its catalysis of the deacetylation reaction is more powerful, and that a great deal of the emission energy from the medium length polyene fluorophores will be reabsorbed by the long sequences created.

In addition to these points, HX may reduce the fluorescence efficiency of the polyenes by favouring inter-system crossing, or some other non-radiative process.

3. General Comments

a) Spectroscopy

Examining the emission spectra of all the directly and indirectly synthesised polyenes, the fact that stands out is the general similarity, indicating that, in the case of mixed polyenes in polymer molecules,

the substituents do not have such a profound effect on the emission properties as noted for simpler systems¹³⁵.

The main difference in spectroscopic behaviour between directly, and indirectly, synthesised polyenes is that in indirectly synthesised systems the proportion of the different lengths of conjugated system can be controlled by altering the period of degradation, or the type of degradation used (photochemical, thermal, chemical). For directly synthesised systems, made from alkyne monomers, it is very difficult to predict the types and ratios of conjugated units, since the control over originally created conjugation is much less (depending on reaction conditions and catalyst), and the products are very prone to change their ratios unpredictably depending on solvent, light, etc.

The general type and position of emission spectra noted for both types of system matches quite well with reported spectra for natural polyenes such as Vitamin A alcohol and ethers¹⁴¹ (retinal does not compare quite so well, due to the $n-\pi^*$ transition of the carbonyl group), and for various diphenyl and unsubstituted polyenes^{12,14}. Exact correlations between the spectra in Section D, and those of individual polyene systems cannot be made due to two factors:-

a) The polyene containing polymers have an unknown mixture of different lengths of conjugated polyene, and their spectra cannot be resolved due to an inefficient but non-negligible ET process between them.

b) Practically all the literature spectra are of all-trans systems, whereas it is not known in which isomeric ratios any of the species in these systems are.

Comparison between this work and the preliminary paper of Owen and Read¹²⁰ shows excellent agreement between their PVC emission spectra and the PVC spectra shown in Section D, and a general agreement with all featured emission spectra. However, they have found a weak emission spectrum for the undegraded material in solution, which was not detected in the film samples investigated here.

For further investigation, some way of measuring fluorescence lifetimes might lead to more information being obtained from the spectroscopic investigation of these systems.

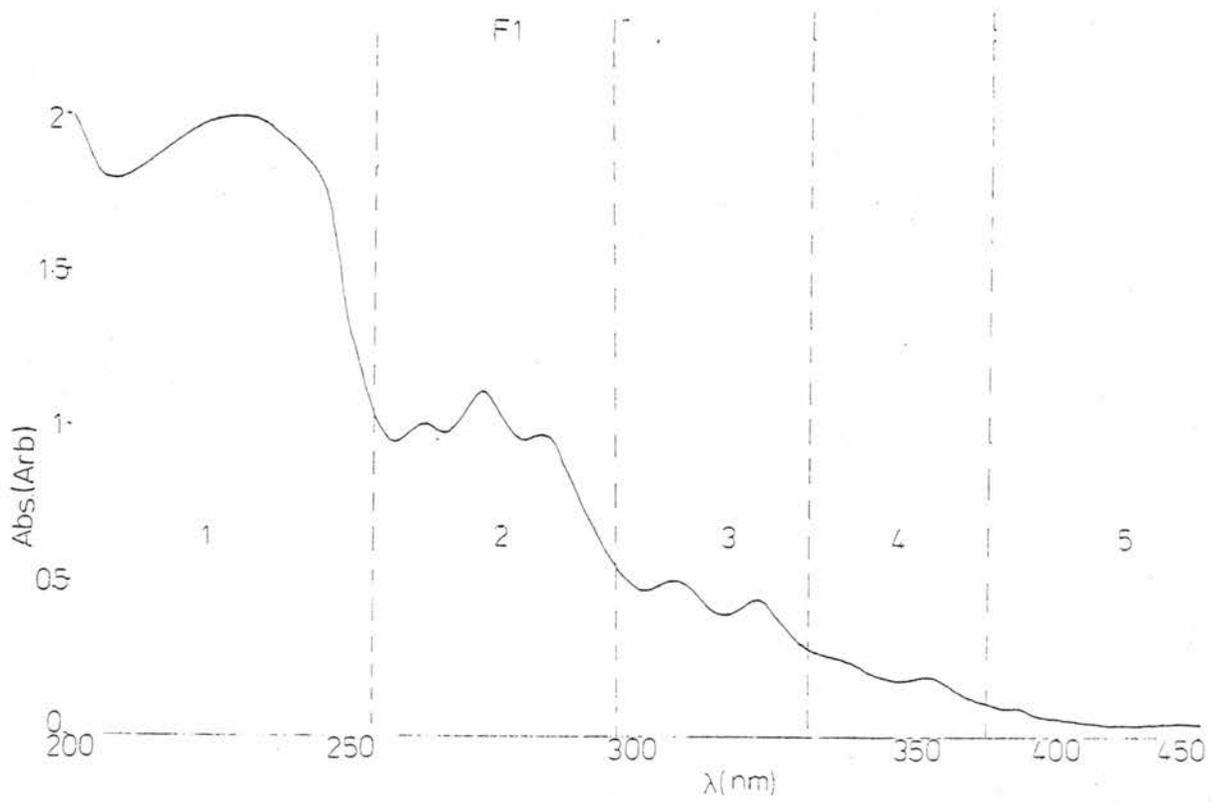
b) Chemical Effects

1) HCl/Degraded PVAc

The finding of this reaction mechanism was unexpected, and could be important, particularly in the field of VC/VAc copolymer degradation^{142, 143}. A more rigorous study of this reaction, particularly at low T, might yield some interesting results.

2) I₂/PPA, I₂/PMP

These reactions gave the expected increase in conductivity¹²³, but some unusual effects on the fluorescence behaviour. Investigation of very low levels of I₂ doping might be profitable, while a gradual, carefully monitored, increase might shed some light on the differences between the I₂/PPA and I₂/PMP reactions. Different dopants might also be used, such as AsF₅²⁸ or H₂SO₄¹⁴⁴.



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