THE SYNTHESIS AND CHARACTERISATION OF POLYMERIC DONOR-ACCEPTOR SYSTEMS.

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ABSTRACT

Charge-transfer (CT) complexes frequently have much higher electrical conductivities than their components alone and an approach to electrically conducting polymers is based on the formation of polymers carrying pendant donor and acceptor groups from which a number of possible arrangements arise, each relying on the charge-transfer interactions between the donor and acceptor groups. Of particular interest were the possible CT complexation characteristics of the phthalimido group in conjunction with a number of electron donors in polymer based systems. Donor substituents were selected from polynuclear aromatic groups based on the anthracene and phenanthrene nucleii, and also from methoxy-substituted phenols and anilines.

A series of vinyl monomers based on acrylic and methacrylic esters and amides were synthesised with the appropriate donor and acceptor functionalities incorporated in the ester/amide groupings. From these, via radical polymerisation, a range of polymer donor-acceptor (D-A) systems were prepared. Investigation of their CT complex characteristics by U.V. absorption spectroscopy revealed the phthalimido group to behave as a poor electron acceptor - no complexation was observed between the phthalimido compounds and the various donor systems. The absence of any complexation was also confirmed by their high electrical resistivities, estimated to be at least greater than 10^9 ohm-cm.

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Robert Kearney

Robert Kearney

DECLARATION

I, the undersigned, declare that this thesis represents the sole work of the author.

Robert Kearney

Robert Kearney, July 1990

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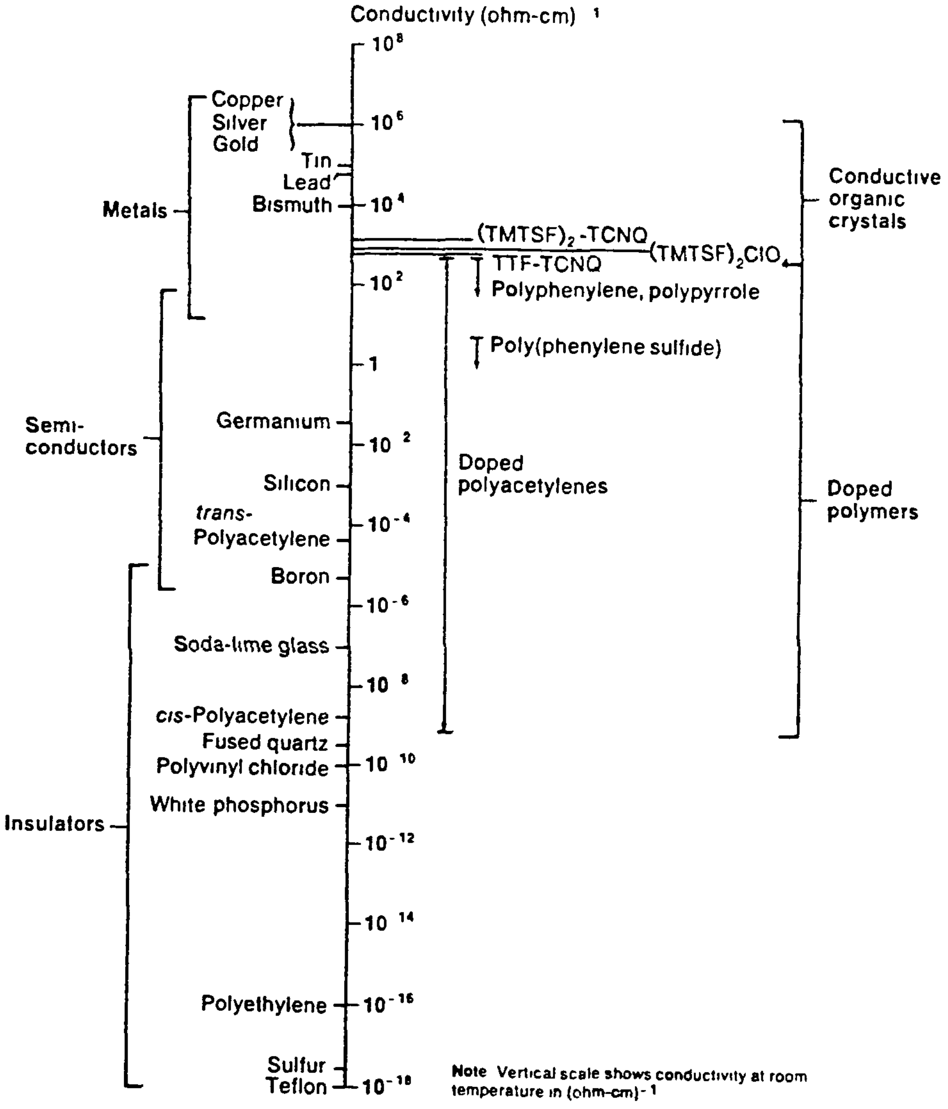
CHAPTER 1: INTRODUCTION

1.1 ELECTRICAL CONDUCTION IN POLYMERS

1.1.1 BACKGROUND

Polymers are, like most organic materials, electrical insulators and their non-conductive properties have been widely exploited in many diverse areas. Their conductivies can range from 10^{-12} to 10^{-18} S cm^{-1} at the low conductivity end with polystyrene and polyethylene being amongst the best insulators known.[1]



Note Vertical scale shows conductivity at room temperature in (ohm-cm)$^{-1}$

Fig. 1. Conductivity chart.[1]

During the last two decades there has been considerable scientific research devoted to the synthesis of electrically conducting polymers, the ultimate goal being to combine the processability and other attractive properties of polymers (low cost, light weight and mechanical toughness) with the electronic properties of metals and semiconductors. To-date polymeric materials have been prepared ranging from highly conducting through semiconducting and photoconducting to redox conducting (i.e. conducting only within a particular potential range). Some of these materials have found application in many specialist areas such as energy storage and photoreproduction, though usually with compromises in mechanical and processing properties or conductivity.[3]

The conductivity, σ, of a polymer is governed by the concentration (density) of charge carriers (n), their electronic charge which may be positive or negative (e), and the velocity of the carrier motion under unit electric field (μ), i.e. a potential gradient of 1 V cm^{-1}:

$$\sigma = n\, e\, \mu \qquad \text{eqtn. 1}$$

The velocity of carrier motion is defined as the mobility, μ, (cm^2 V^{-1} s^{-1}) and characterises the ease with which the charged species will move under the influence of an applied electrical field.[2] Conduction may be ionic or electronic, or a combination of both, depending on the charged species involved. For most polymers any conductivity observed can usually be attributed to ionic conduction. As the name implies, charge transport occurs via cation and anion pairs which are mainly derived from fragments of polymerisation catalysts, polymer degradation and dissociation products, and absorbed water. High-conductivity polymers, in contrast, are classed as electronic conductors where the presence of electrons and holes (a hole is an electron vacancy with an equivalent positive charge) contribute to the enhanced conductivity.[3] Both can contribute independently to current flow:

$$\sigma = n_+ e_+ \mu_+ + n_- e_- \mu_- \qquad \text{eqtn. 2}$$

Where the carriers are produced, i.e. generated, in the bulk of the polymer by the action of light an electronically photoconductive polymer results. In order to understand and control conduction processes in polymers it is important to know both the number and type of charge carriers, the manner in which they are generated and the magnitude of their mobilities as well as the dependence of these parameters on variables such as temperature, applied field etc.

While it has been possible to achieve high charge carrier concentrations in polymers, their mobilities are generally very low exhibiting strong electric field and temperature dependence. This can be attributed to the polymeric environment which imparts a high degree of both chemical and physical disorder. Charge carriers can become localised or trapped, thereby no longer contributing to current flow, the overall effect being to reduce the effective mobility of carriers in a sample. Traps can be chemical in nature where impurity molecules with lower ionisation potentials than the host transport molecules constitute hole traps and impurity molecules with higher electron affinities constitute electron traps. Physical traps are structural defects such as chain ends, crystalline boundaries and chain ends which can cause discontinuities in the transport pathways. Attempts to attain higher degrees of system purity and structural perfection in polymeric materials have met with very limited success and usually at the expense of processability. Consequently polymers exhibiting high mobilities, particularly at low applied fields, remain, as yet, to be developed.[2,3]

Electronic conduction in polymers is associated with electrons being extensively delocalised throughout the molecule, i.e. the conduction properties depend on the electronic structure of their energy levels. The basic concepts of band theory provide the key to understanding why certain polymers and other organic materials behave like metals.[4]

1.1.2 BAND THEORY

When a large number of atoms (as in elemental metals or semiconductors) or molecules are brought together to form a crystalline solid or polymeric chain, energy bands will form if there is sufficient interaction or overlap between the constituent atomic or molecular orbitals. These energy bands result from the splitting of energy levels with each band consisting of sets of energy levels. In many cases the interaction is strong enough for the bands to broaden and merge into one another thus forming two continuous energy bands called the valence and conduction band. These bands are analogous to the splitting of atomic energy levels as two atoms are brought together to form a molecule with higher and lower energy levels, i.e. antibonding and bonding orbitals respectively (Fig. 2).[3]

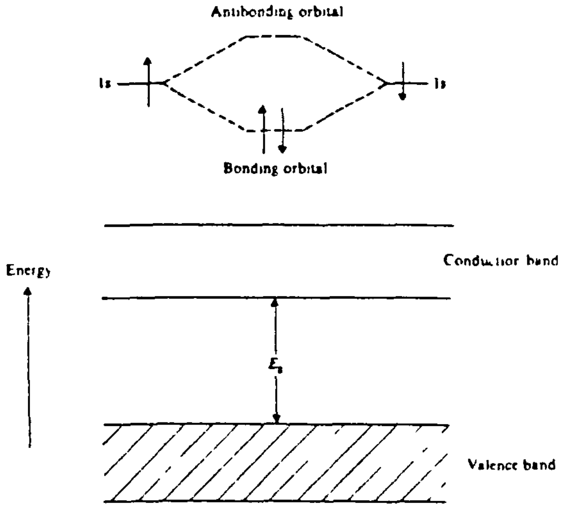


Fig. 2. Schematic interaction of hydrogen atoms and energy bands.[3]

Overlap in such solids requires extended electron states - for organics these are to be found in the p- and d-orbitals of heteroatoms and the π-electron states of unsaturated molecules. As shown below, extended overlap is possible primarily in the linear (quasi-one-dimensional) molecular arrays found in (i) stacks of planar unsaturated molecules and (ii) the chains of conjugated polymers. Consequently electronic transport in organic solids is highly anisotropic, i.e. it is associated with a preferred direction by several orders of magnitude. This is in sharp contrast to metals whose atoms overlap appreciably with those of more than one of their neighbours in a regular 3-dimensional lattice, where delocalisation of electrons reaches an extreme.[5]

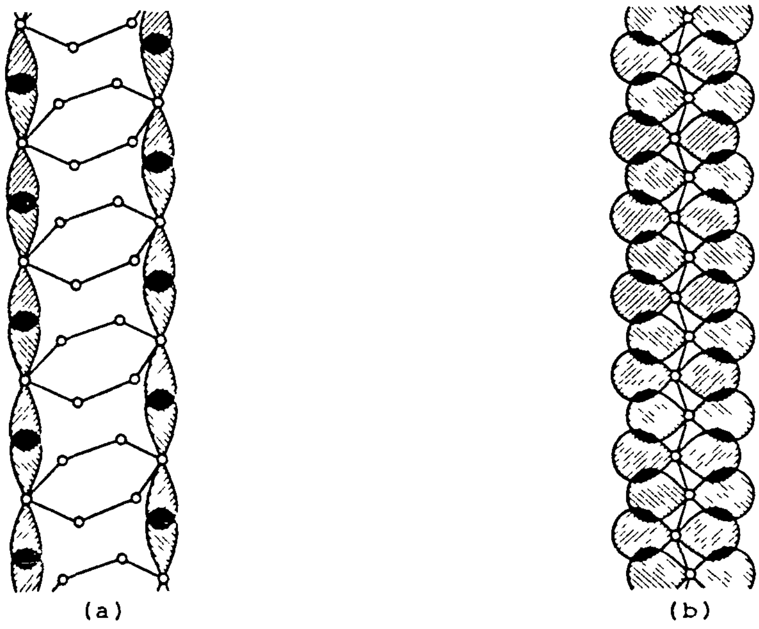


Fig. 3. Electron wave-function overlap for carbon. atom π-electrons in (a) a molecular stack and (b) a polymer chain.[5]

The interaction of energy bands however is not enough in itself to produce metallic properties in organic materials. The occupancy of these bands is critically important - electron movement requires a partially filled energy band. Most polymers have the electronic profile of insulators or semiconductors. Their lower energy or valence band is completely filled with electrons and their higher energy or conduction band is empty. A separation known as the energy gap, Eg, lies between the highest filled level in the valence band and the lowest level in the conduction band. No states or orbitals are available in the energy gap which represents a forbidden zone for electrons. Therefore for electrical conduction to occur the highest energy electrons in the ground state must gain additional energy, equal to Eg, before they reach empty orbitals in the conduction band and become mobile. When the energy gap between the highest filled and the lowest empty band is large the material is an insulator. As the gap decreases there is a probability that some electrons will be thermally excited into the lowest unoccupied molecular band, leaving behind unoccupied positive holes in the valence band. Since the electrons in the bottom of the conduction band and the positive holes in the top of the valence band are in molecular orbitals that extend throughout the entire material, both can contribute to the conduction process. Such a material is a semiconductor (Fig. 4).[4]

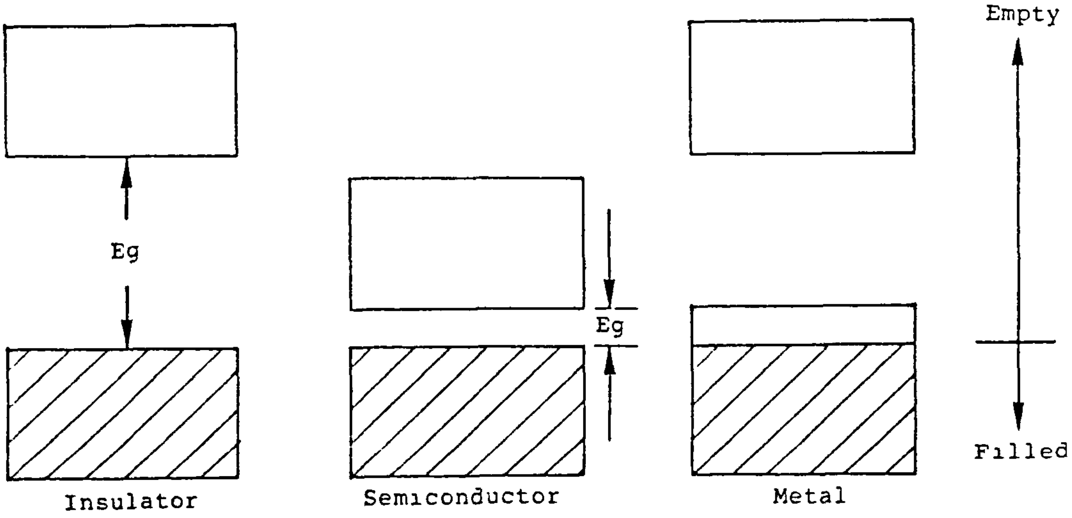


Fig. 4. Energy bands in an insulator, semiconductor and a metal. Shaded areas represent filled bands.

Promotional energy can also be obtained by direct photon absorption, i.e. photoconductivity. When the gap closes further the material will behave as a metal. It is the size of the energy gap then which determines whether thermal excitations will lead to appreciable conductivity - as the energy gap increases the charge carrier concentration becomes minute and the electrical conductivity as given in equation 1 is small. Many practical semiconductors have energy gaps (1-2 eV) somewhat larger than thermal energies (approximately 0.02 eV) at room temperature; typically Eg is over 4 eV for insulators.

In contrast, the lower or valence band of a metal is only partially filled with electrons. The highest occupied state is called the 'Fermi' level which lies at the top of the filled portion of the valence band (Fig. 4.). It is the electrons at or near the Fermi level that are involved in conduction. As a result of thermal energies electrons at the Fermi level have enough energy to populate some of the empty levels in this band. These electrons will then be in only partly occupied orbital bands and consequently, under an applied electric field, the electrons in a metal will become mobile and conduct an electric current.

In the ground state of a semiconductor then all the bands are either completely filled or completely empty, whereas in the ground state of a metal at least one band is only partially filled. Because of the differences in the electronic structure of their energy levels differences also exist with respect to their temperature dependence of conductivity. For metals, as the temperature is increased the conductivity decreases slightly because of the greater lattice vibrations which scatter electrons and thereby reduce their mobility. Charge carrier concentration is little affected by temperature. In the case of semiconductors electron mobility is also reduced with increasing temperature for the same reason but conductivity increases because the steep rise in carrier concentration swamps the more gradual decline in carrier mobility. Thus the difference between metal and semiconductor behaviour stems from the increased ease of movement of a fixed number of charge carriers in the former and a decreased number of carriers in the latter.[1,3,4]

1.1.3 APPROACHES TO POLYMER CONDUCTIVITY

There have been many different approaches to achieving enhanced conductivity in polymers and these can be separated into three main classes :

(i) conducting composites
(ii) conjugated polymers
(iii) polymeric donor-acceptor (D-A) complexes

1.1.3.1 Conducting Composites

The use of composite materials has been the traditional approach in the preparation of conducting polymers and is used to-day in the fabrication of nearly all commercial products based on conductive polymers. The desired conductivity is attained by incorporating into the polymer matrix microscopic pieces of conducting material, e.g. by adding carbon black, graphite, iron oxide, copper or aluminium particles/flakes; stainless steel fibres, metallised glass fibres and carbon fibres. Conductivities for these materials can range from 10^{-4} to 5 S cm^{-1}, though loadings of these incompatible materials are such that some desirable mechanical properties of the polymers are adversely affected. Carbon black is the most widely used additive - it is cheap and does not change the overall density of the host polymer very much.[3,6]

The alternative approach has been to develop polymers whose conductivities arise from their inherent molecular structures as evidenced below by the conjugated polymers and the polymeric donor-acceptor complexes.

1.1.3.2 Conjugated Polymers

These materials are characterised by conjugated double bonds, i.e. alternating single and double bonds, along the polymer chain. It was initially thought that conjugation in polymeric hydrocarbons would lead to extensive π-electron delocalisation, with the possibility of a narrow conduction band, derived from the π-orbitals, and consequently appreciable electron conductivity. However these materials are at best semiconductors possessing relatively large band gaps. This was explained by limited or broken sequences of electron delocalisation along the chain arising primarily from alternation of double and single bonds, i.e. unequal bond lengths, and also, in some cases, by rotation about bonds due to steric hindrances. Therefore even though conjugated polymers have backbone structures well suited to conduction, i.e. high carrier mobility, the low carrier concentration, arising from the large band gaps, results in negligible conductivity.[3]

However, it was shown in 1977 that one such polymer, polyacetylene (Fig. 5), exhibited quite a dramatic increase in conductivity on doping with strong oxidising and reducing agents (from 10^{-7} to 10^{-9} S cm^{-1} in the pure state to 10^{3} S cm^{-1} on doping).[7] This stimulated great interest in polyacetylene and other polymers.[8] As a consequence many conjugated polymers, for example poly(p-phenylene), poly(aniline), poly(pyrrole) and poly(thiophene) (Fig. 5 overleaf) have been rendered conducting by chemical or electrochemical methods.

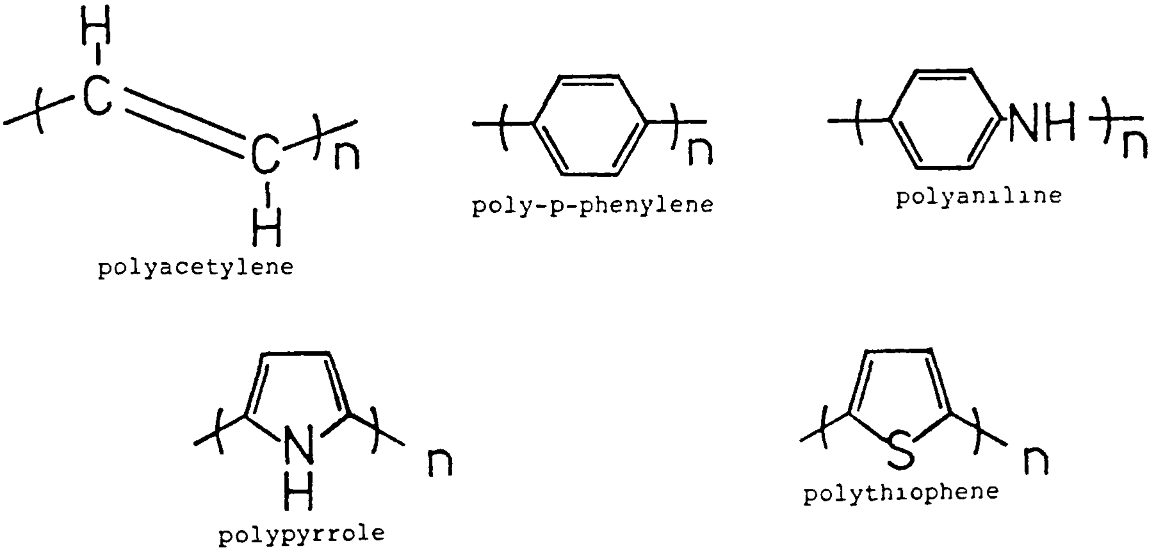


Fig. 5. Monomeric repeat units of some conjugated polymers which exhibit enhanced conductivity on doping.

The doping of conjugated polymers generates high conductivities primarily by increasing the carrier concentration. The oxidation and reduction processes are termed p- and n-type doping respectively. Typical oxidising agents are electron acceptors and include the halogens (e.g. iodine) and Lewis acids whereas the alkali metals are representative of the reducing agents which are electron donors. Although the transition from insulator to conductor on doping is quite complicated the high conductivity increase can be simply explained by an energy band picture - oxidants remove electrons from the filled valence band and reductants add electrons into the vacant conduction band. Thus in principle the polymer becomes a conductor because either the conduction or valence band ends up being partially filled. In some systems the dopant levels can be so high as to constitute a charge-transfer (CT) complex rather than a doped polymer.[4]

Polyacetylene is still considered the prototype of conducting polymers and is the most extensively studied. It has also shown the highest conductivity of any polymer and is now, essentially, as conducting as copper (approximatly one quarter the conductivity of copper by volume and twice the conductivity by weight). Prepared as stretch-oriented films polyacetylene has the highest conductivity of any organic material; σ_{rt} values of approx. 8×10^4 S cm^{-1} in the aligned direction of the film.[9]

Two basic problems have limited the applications for these conjugated polymers - their doped forms are often not amenable to processing and they can be unstable to air oxidation.[5]

1.1.3.3 Polymeric Charge-Transfer (CT) Complexes

Molecular CT complexes have been to the forefront in the development of 'organic metals' with high conductivities being reported for these materials. However a major problem with these compounds has been the extreme frailty of their crystals.[4] As a result there has been much theoretical and practical interest in combining the well-established electrical properties of the CT complexes with the mechanical toughness (and processability) of polymers. In this respect there has been some success to-date with polymeric CT complexes exhibiting enhanced conductivities and interesting photoelectric properties.[2]

1.2 CHARGE-TRANSFER COMPLEXES

1.2.1 BACKGROUND

Charge-transfer (CT) complexes, and the closely related radical-ion salts, were the first class of organic compounds to display high electronic conductivity.[4] They are typically highly crystalline solids and are formed by the interaction of strong π-molecular electron donors (D) and electron acceptor molecules (A). Additionally, these materials can exhibit photoconductive behaviour, light-initiated electron transfer from donor to acceptor leading to enhanced conductivity.[10] CT complexes may also be referred to as electron donor-acceptor (EDA) complexes.

CT complexes have a neutral ground state (DA and $D^{+\cdot}$, $A^{-\cdot}$) where there is only partial electron transfer from donor to acceptor molecule. Complexation occurs when an electron is promoted from the highest occupied molecular orbital (HOMO) of a donor to the lowest unoccupied molecular orbital (LUMO) of an acceptor (Fig. 6). The formation of the ground state CT complex is characterised by the appearance of new UV absorption spectral bands, i.e. CT absorption bands corresponding to the new transitions.[2]

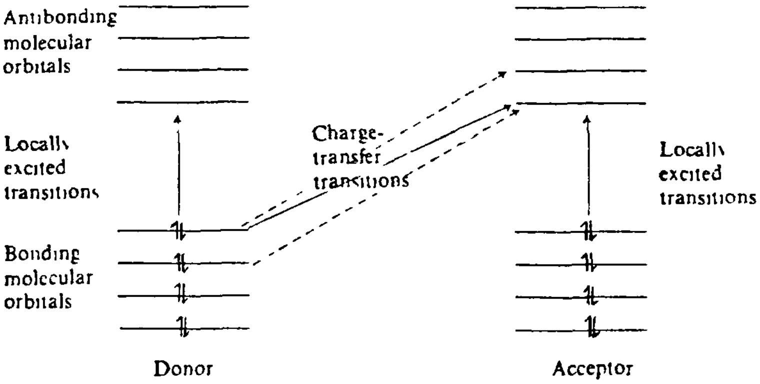


Fig. 6. Simple molecular orbital diagram showing CT transitions.[2]

Radical-ion salts ($X^{+}A^{-}$ and $D^{+\cdot}X^{-}$) however have an ionic ground state and are formed from radical ions as a result of complete electron transfer from donor to acceptor. Formation of radical ions can result from the excited state of a CT complex or by independent oxidation and reduction of donors and acceptors respectively:

$$D + A \overset{k}{\rightleftharpoons} \underset{\substack{\text{CT complex} \\ \text{(ground state)}}}{[\ D,\ A\ ]} \xrightarrow{h\nu} \underset{\substack{\text{CT complex} \\ \text{(excited state)}}}{[\ D^{+\cdot}\ A^{-\cdot}\ ]^{*}} \longrightarrow \underset{\text{ion radicals}}{D^{+\cdot},\ A^{-\cdot}}$$

Ideally electron-donor molecules possess relatively low ionisation potentials and electron-acceptors would have relatively high electron affinities. Typical donors include amines, ethers and sulphur compounds; among familiar acceptors are halogen, nitro- and cyano-substituted compounds, and quinones. Aromatic molecules may be either donor or acceptor components, and ethylenic or aromatic conjugation of any substance greatly increases its donor or acceptor capability.[2]

The majority of highly conducting materials in this class of compounds are neither CT complexes or radical-ion salts in the strictest sense as defined above. They are weak ionic salts of sorts in which there is partial transfer of an electron from donor to acceptor. These compounds have electrical conductivities ranging from 1 to 100 $\mathrm{S\ cm^{-1}}$. Typically CT complexes have conductivities of less than 10^{-6} $\mathrm{S\ cm^{-1}}$ and radical-ion salts, with complete charge-transfer, have values between 10^{-6} and 10^{-4} $\mathrm{S\ cm^{-1}}$. To avoid confusion these compounds are sometimes collectively known as EDA complexes.[5,11]

1.2.2 DEVELOPMENT OF CONDUCTING CT COMPLEXES

In the 1960s a powerful π-molecular acceptor was discovered[12], 7,7,8,8-tetracyano-p-quinodimethane (TCNQ), which has proved central to the development of conducting CT complexes and radical-ion salts. A great many complexes of TCNQ with various donors were found to be semiconductors, e.g. N-methylquinolinium salts with TCNQ had room temperature conductivities, σ_{rt}, of approximately 10^{-5} S cm^{-1}.

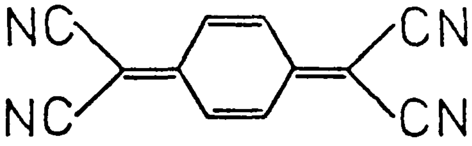


Fig. 7. TCNQ Acceptor.

The preparation of a new donor, tetrathiafulvalene[13], (TTF), in 1970 led, two years later, to the discovery that the chloride salt of TTF had high electrical conductivity (σ_{rt} = 0.2 S cm^{-1}). This in turn led in 1973 to the synthesis of the first truly 'organic metal' by J. Ferraris et al[14] when a complex of the donor TTF and acceptor TCNQ, in a 1:1 stoichiometry was found to be metallic at room temperature (σ_{rt} of 500 S cm^{-1}) increasing to σ_{max} of approximatly 10^4 S cm^{-1} on cooling. However conductivity of the complex rapidly rapidly decreased on cooling below 59 K where it became semiconducting undergoing a metal-insulator or Peierls Transition (Fig. 9). In the simplest terms, a Peierls Transition occurs where the conducting chain is

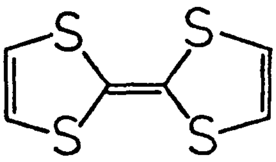


Fig. 8. TTF Donor.

stretched in one region and contracted in another, so that the conducting electrons become localised, with a filled electron band at a lower energy and an empty band at a higher energy, i.e. the distortion leads to a band gap which results in an insulating or, at best, a semiconducting material at low temperatures.[4]

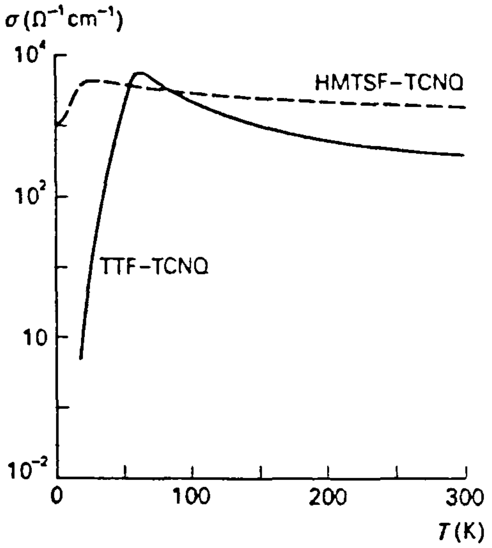
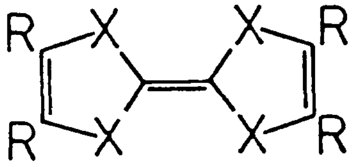
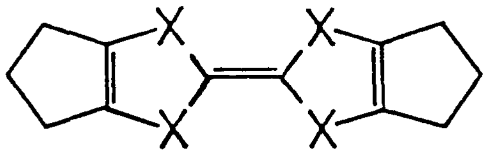


Fig. 9. Temperature dependence of conductivity of TTF-TCNQ and HMTSF-TCNQ.[5]

Since the discovery of high electrical conductivity in the TTF-TCNQ complexes there has been unabated interest in the creation of new donors (Fig. 10). Much of the work has centred



I Tetrathiafulvalene, TTF (X = S, R = H)
II. Tetraselenafulvalene, TSF (X = Se, R = H)
III. Tetratellurafulvalene, TTeF (X = Te, R = H)
IV. Tetramethylselenafulvalene, TMTSF (X = Se, R =CH_3)



V. Hexamethylenetetraselenafulvalene, HMTSF (X = Se)
VI. Hexamethylenetetratellurafulvalene, HMTTeF (X = Te)

Fig. 10. Donors which form conducting CT salts with TCNQ.

on addition of substituents onto the TTF skeleton either in place of its hydrogen atoms or by substitution of other hetero-atoms such as selenium and, more recently, tellurium[15] in place of its sulphur atoms. The greater spatial extent of the p- and d- selenium (and tellurium) based orbitals leads to larger intrachain bandwidths (relative to TTF) and hence increased metallic conductivity in addition to favouring increased interchain interactions, thereby supressing any Peierls distortions.[10]

The first of these 'organic metals' not to undergo a Peierls transition was HMTSF-TCNQ[16] which has a conductivity in excess of 10^3 S cm^{-1} down to the lowest temperatures (Fig. 9). This was followed by the observation of superconductivity under pressure in the tetramethyltetraselenafulvalene-phosphorous hexafluoride salt, $(TMTSF)_2^+ PF_6^-$, in 1980 at $T_c = 1$ K under 1.2 Kbar pressure.[17] Superconductivity has since been discovered in many TMTSF salts with $(TMTSF)_2^+ ClO_4^-$ being a superconductor ($T_c = 1.2$ K) at ambient pressure. To-date the highest temperature for the onset of superconductivity in an organic material is 10.4 K reported for the copper thiocyanate salt $(BEDT\text{-}TTF)_2\ Cu(SCN)_2$ utilising the sulphur donor, bis(ethylenedithiolo)tetrathiafulvalene, BEDT-TTF.[18]

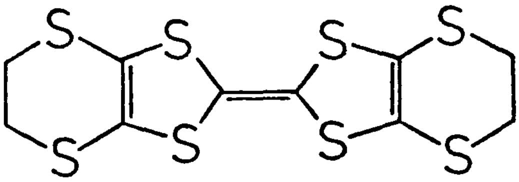
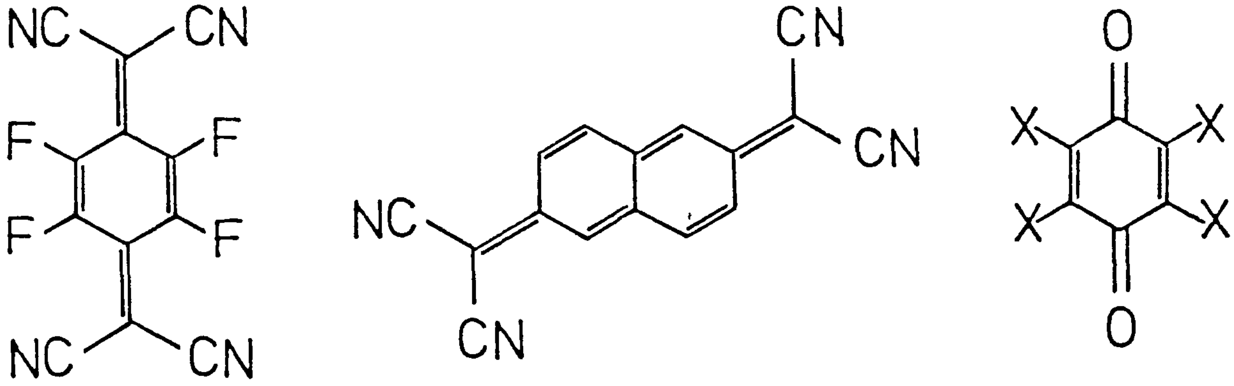


Fig. 11. BEDT-TTF Donor.

In comparison to new donors there have been very few new acceptors developed over the last decade. This is partly because the synthesis of many TCNQ derivatives is not easy to accomplish, unlike their TTF analogues.[10] In general, substitution on the basic TCNQ skeleton results in complexes that are less conducting than those of TCNQ itself. A striking example is that of the HMTSF salts of TCNQ and tetrafluoro TCNQ (Fig. 12) respectively, the former being one of the most highly conducting organic salts known (σ_{rt} = 1500 S cm^{-1}) whereas the latter has a room temperature conductivity of almost nine orders of magnitude lower (σ_{rt} of approximately 10^{-6} S cm^{-1}).[19] The key to this lies in the degree of charge transfer. For HMTSF-TCNQ salts there is only partial charge transfer (0.74 electron/molecule) whereas for HMTSF-TCNQF$_4$ charge transfer is complete and an insulator results.



I Tetrafluorotetracyano-p-quinodimethane, TCNQF$_4$
II Tetracyanonaphtho-2,6-quinodimethane, TNAP
III Tetrahalo-p-benzoquinone (x = halogen e g Br or Cl)

<u>Fig. 12.</u> Electron Acceptors.

Another TCNQ derivative is 11,11,12,12,-tetracyanonaphtho-2,6-quinodimethane, TNAP, which with an extended π system forms metallic complexes with TTF and HMTSF. The first highly conducting complexes that did not contain TCNQ, or a close derivative, as the acceptor were those with the tetrahalo-p-benzoquinones (Fig. 12, III).[10]

1.2.3 STRUCTURAL FEATURES RELATING TO CONDUCTIVITY IN CT COMPLEXES

In general a prerequisite for conductivity in this class of materials is that one or both of the components, i.e. donor and acceptor, is a planar molecule with a delocalised π-electron system. High conductivity in these crystalline solids is associated with a crystal lattice in which the donor and acceptor molecules form segregated stacks (Fig. 13) and are packed face-to-face, like a deck of playing cards, within these columns. As a result, the π-overlap and charge-transfer interaction between adjacent molecules in the stacking direction are strong, causing their unpaired electrons to be partially delocalised along these one-dimensional stacks and enabling them to conduct in that direction, i.e. formation of an energy band along the stacking axis.[10]

(a)	D A D A	(b)	D A D A
	A D A D		D A D A
	D A D A		D A D A
	A D A D		D A D A

Fig. 13. (a) Mixed donor-acceptor stacks.
(b) Segregated donor and acceptor stacks.

When this structural feature is combined with a band that is less than half filled, high conductivity can result, although highly anisotropic (this anisotropy can be as high as 10^3). In contrast mixed stacks of alternating donor and acceptors form crystalline structures which are limited to being semiconductors or insulators, arrangements which are observed within stacks of most complexes. As yet little is known about the factors controlling whether the stacking pattern will be mixed or segregated.[1]

Band filling in segregated-stack complexes is determined by the extent of charge transfer from donor to acceptor molecules. The degree of charge transfer is in turn determined by the ionisation potential and electron affinity of the donor and acceptor respectively. With exactly one electron per molecule electrical conduction (moving electrons down the chain) involves placing two electrons on the same molecule with a consequent energetic penalty because of the coulomb repulsion (repulsive forces between like charges). Therefore single electrons become associated with each molecule and insulating properties result. If, however, charge transfer is less than one, there will be some 'empty' sites onto which electrons can move, i.e. the conduction process is energetically more favourable. For a metallic donor-acceptor complex then of 1:1 stoichiometry, there must be incomplete charge transfer between the stacks. Generally an intermediate charge transfer, Z, ($0.5 \leqslant Z \leqslant 0.8$) allows the formation of a metallic band where the band is only partially occupied and conduction can take place.[1,4]

To illustrate the above points it is worth examining the structural features of the TTF-TCNQ complex salt as the majority of highly conducting complexes reported to-date are based on TTF or TCNQ derivatives.[5] Both TTF and TCNQ are of similar size; both are planar, thereby allowing the individual molecules to approach quite closely in the direction perendicular to their molecular plane, with π-delocalisation extending throughout the molecule. They both have the same high degree of symmetry.[10] In the salt, segregated stacking of the TTF and TCNQ molecules occurs (Fig. 14). The short interplanar distances between adjacent molecules, within the segregated donor and acceptor columns, (3.17 Å for TCNQ and 3.47 Å for TTF) allows significant interaction between the π-molecular orbitals of neighbours, leading to the formation of a band in the solid. Thus the direction of high conductivity is along these stacks due to the greater π-overlap in the stacking direction (in contrast non-

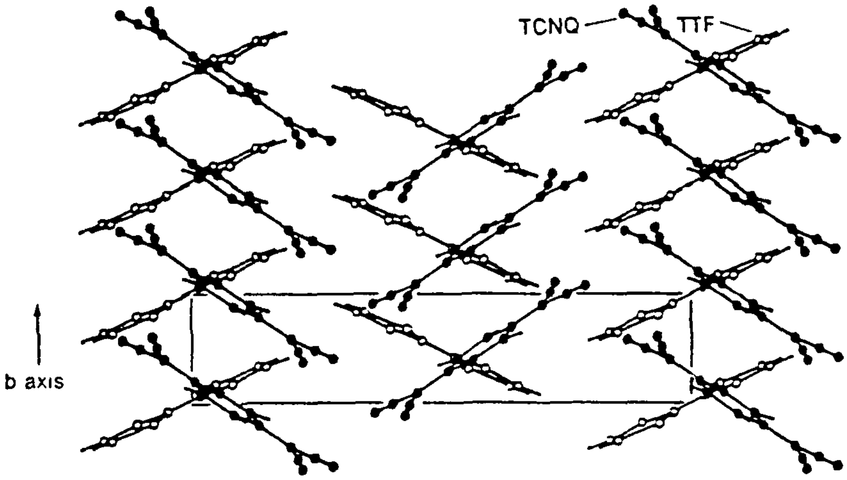


Fig. 14. X-ray crystal structure of TTF-TCNQ. The direction of high electrical conductivity is along axis b. The rectangle denotes a unit cell.[5]

stacking neighbours may be as much as up to 15 Å distant). Consequently the electrical conductivity is highly anisotropic, the ratio of conductivity in the three principle directions being approximately 500: 5: 1. The ionisation potential/electron affinity values for the pair favour incomplete charge transfer (charge transfer from TTF to TCNQ is on average 0.59, i.e. 0.59 electrons in the TCNQ band). With both TTF and TCNQ bands partially filled, both stacks contribute to the metallic conductivity.[1]

To conclude, CT or EDA complexes encompass a very broad range of materials whose conductivities can span from as low as 10^{-6} S cm^{-1} to as high as 2900 S cm^{-1} for the HMTSF-TNAP salt depending on their respective ground states. Electrical conduction arises from electron flow along supermolecular orbitals derived from the interaction of donor and acceptor molecules arranged in stacks or columns. The lowest conductivities are associated with weak complexes, where charge transfer plays a minor role in the formation of the ground-state complex. At the other extreme are the strong complexes, which exist as salts in their ground states as a result of complete electron transfer, possessing still higher conductivities with the partly ionic, mixed valence salts exhibiting the highest conductivities of all.[11] In addition CT complexes can also display photoconductive behaviour leading to enhanced conductivity - charge transfer interactions result in the occurrence of new spectroscopic transitions which greatly increase the wavelength sensitivity, i.e. possibility of visible light absorption characteristics.[10]

Most conducting complexes are characterised as single crystals or microcrystalline powders and as a result have not found extensive application because of their frailty. One approach to this problem has been the development of electroactive Langmuir-Blodgett (LB) films formed from TCNQ complexes of pyridinium cations that are substituted with long (C_{18} - C_{22}) hydrophobic alkyl chains. Conducting LB films have been deposited onto glass substrates having σ_{rt} values of approximately 10^{-1} S cm^{-1}. One such example is (N-docosylpyridinium)TCNQ on doping with iodine.[20]

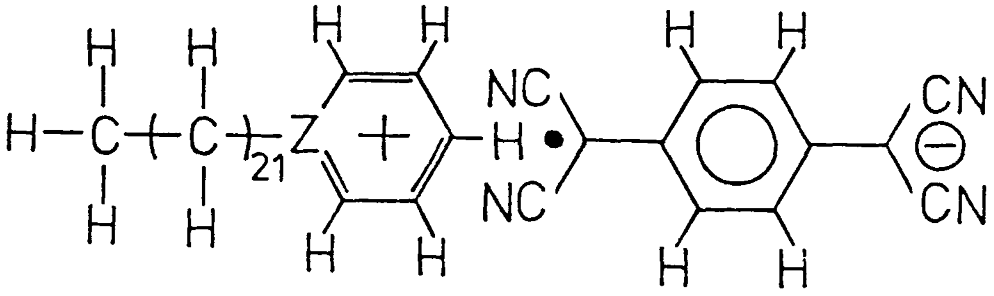


Fig. 15. N-docosylpyridinium-TCNQ CT complex.

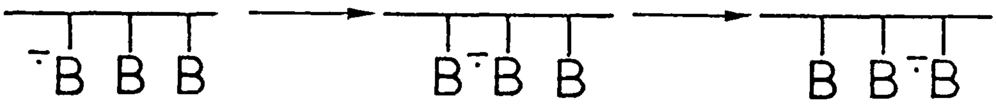
1.3 POLYMERIC CT COMPLEXES

1.3.1 BACKGROUND

Much interest has been generated in macromolecular CT (or EDA) complexes since the discovery of high electronic conduction in their low molecular weight analogues. One advantage of utilising polymer-based components lies in the enhanced material properties of given donor-acceptor (D-A) combinations coupled with the possibility of attaining higher electrical conductivities than those normally found for organic polymers.[3] Such complexes have exhibited a range of electrical properties from insulating to semiconducting, and metallic. In addition charge transfer interactions have been utilised in the areas of polymerisation and copolymerisation (as initiators and for producing alternating copolymers)[20a,b] and to study miscibility in polymer blends.[20c]

Most polymeric complex systems rely on the incorporation of pendant donor and acceptor groups along the polymer backbone. A number of possible arrangements arise, each relying on the development of charge transfer between the donor and acceptor groups within the polymer and hence endow it with the conductivity and photoelectric characteristics of simple CT complexes. Alternatively donor and acceptor groups can be built into the polymer structure, i.e. as in-chain groups such as in condensation polymers.

In an ideal situation the transport process can be envisaged as a series of electron exchanges (for hole transport the corresponding $B\text{-}B^{+}$ couple applies) between pendant functional groups (B) along a polymer chain:[2]



Thus the polymer can be viewed as simply an array of transport sites, the function of the polymer being to control the microstructure and hence the nature and degree of interaction of the donor and acceptor molecules involved in charge transport.[2] Exchange involves a hopping or tunnelling process - disorders in polymers (physical and chemical) represent a mobility gap where electrons are localised and conduction via localised electrons requires discrete jumps across an energy barrier from one site to the next (Fig. 16). An electron may hop over, or tunnel through, the top of the barrier.[3]

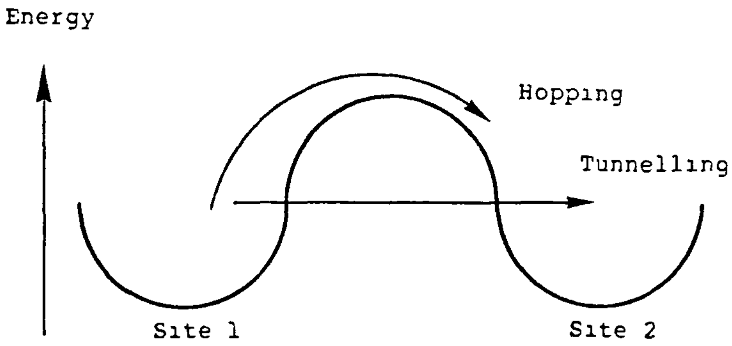


Fig. 16. Electron-transfer mechanisms between adjacent sites seperated by a potential energy barrier.

The transport states are determined by the electronic structures of the two components, i.e. the highest occupied molecular orbital (HOMO) of the donor function to hole transport and the lowest unoccupied molecular orbital (LUMO) of the acceptor to electron transport. In practice though only electron or hole transport predominates. The electrical properties are therefore governed by the concentration and distribution of the free and complexed donor/acceptor components and by the nature of the ground state of the complex.[2] In principle the determination and description of charge transport processes in disordered polymeric systems is very difficult to achieve owing to the combination of inadequate knowledge of polymer microstructure/morphology and lack of reliable electrical conductivity measurements. Consequently the majority of polymeric CT complexes are characterised purely in terms of their D-A interactions with simple conductivity measurements being sometimes carried out. Very few studies exist which attempt to relate polymer structure and electrical properties.

1.3.2 POLYMERIC DONOR-ACCEPTOR COMBINATIONS

Macromolecular complexes have at least one polymeric component; these can be considered as follows:

(i) complexes between a donor (or acceptor) polymer and a low molecular weight acceptor (or donor) compound (type I and II respectively).

(ii) complexes between a donor polymer and an acceptor polymer (type III).

(iii) complexes of a donor-acceptor (D-A) copolymer (type IV and V, representing inter- and intramolecular charge-transfer respectively).

These CT complexes, formed from polymer donor or acceptor components, are considerably more complex than their low molecular weight models. The presence and nature of CT interactions between appropriate donor-acceptor combinations are greatly influenced by the conformational freedom within a given polymer backbone as well as the precise structure (and

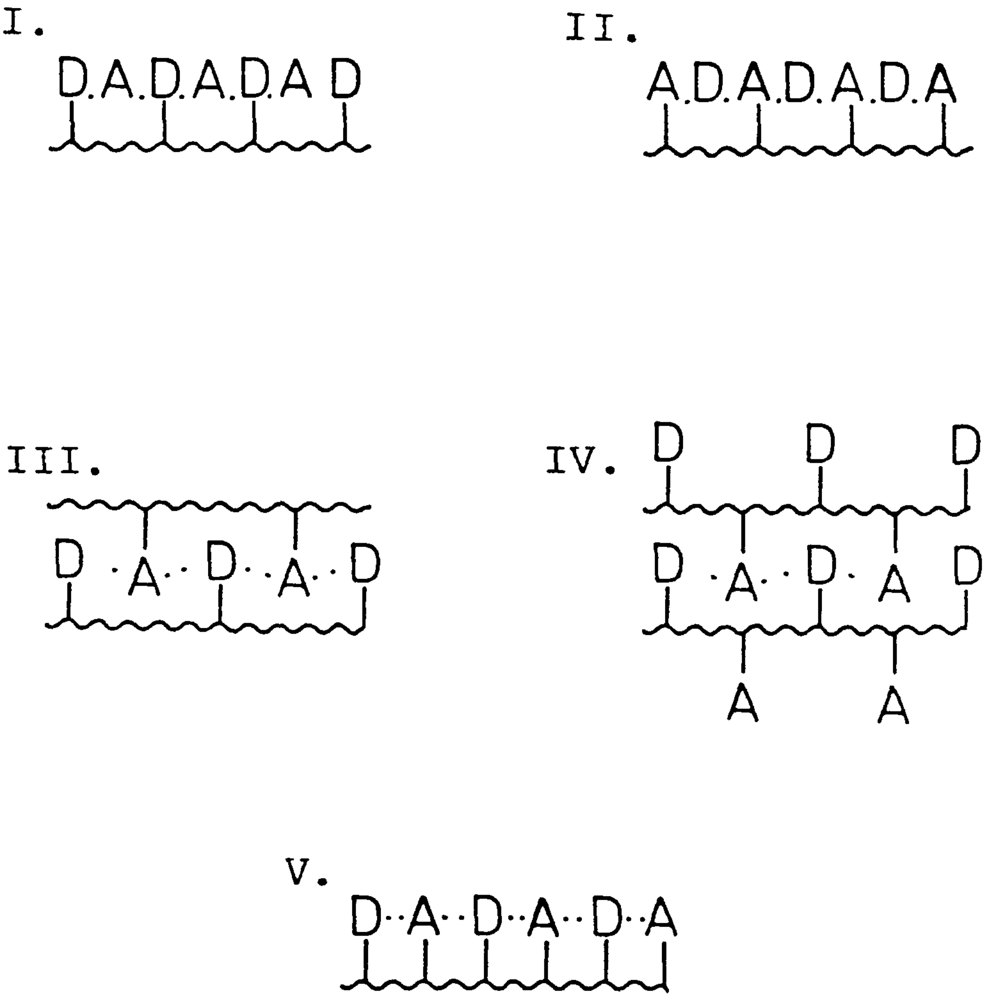
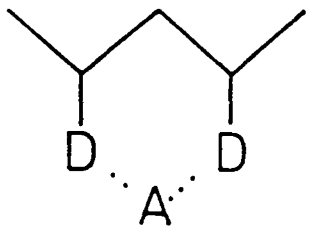
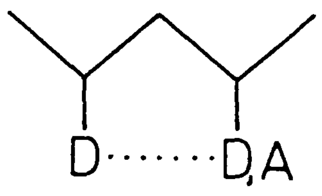


Fig. 17. Macromolecular CT complexes.

configuration) of the pendant interacting units. Polymeric donors and acceptors are subject to conformational changes, arising from the individual polymer backbones, which introduce orientation and concentration effects, absent in simple molecular systems. Such effects may result, for example, in an increased population of sites comprising more than one donor or acceptor unit and the formation of higher order complexes[2], i.e. $(D)_nA$ or $(A)_nD$:



DAD complex



DDA complex

Where there are neighbouring pendant aromatic groups there may be the possibility of excimer formation[21] - excimers are collisional interactions of a ground-state molecule with a corresponding excited-state molecule (singlet or triplet). Association of a suitable acceptor molecule with the units of an excimer-forming site would provide the basis for the formation of a DAA (or AAD) complex. Evidence for the formation of such higher order complexes can be provided by UV absorption studies - in polymer CT complexes they are characterised by values of λ_{max} at longer wavelengths (lower energies) than those for corresponding low molecular weight models.[22] In addition there can be conformational restrictions imposed by the polymer chain (and side chains) on the degree of interaction between donor and acceptor groups, i.e. the degree of overlap of donor HOMO and acceptor LUMO orbitals. For studies of complex formation in solution these phenomena are largely controlled by the actual donor-acceptor pair and the polymer-solvent interactions which influence chain conformation.[2] The situation becomes very complicated and is much less well resolved in the polymeric solid, e.g. polymer films, owing to the general lack of detailed information regarding polymer microstructure.

An approximation as to the extent of complexation in a polymer system (in comparison to their low molecular weight model compounds) can be provided by their $K\epsilon$ values (K - association constant, ϵ - absorption, or extinction coefficient) as determined by Benesi-Hildebrand plots from their UV spectra.[23,24] Spectroscopic and mass density measurements have been used to obtain quantitive estimations of D-A complexation in the amorphous solid state.[25-27]

1.3.2.1 Polymers as Donors

The combination of a polymeric donor and a small acceptor molecule is the most widely studied of all the polymeric CT complex systems.[2] This can be attributed, in part, to their relative ease of fabrication but also to the interest generated by the unique electric and photoelectric properties exhibited by CT complexes of poly(vinyl carbazole), (PVK), which have found practical applications in electrography. For the majority of such systems the donor groups are pendantly joined to the macromolecules and are complexed with low molecular weight acceptors (Fig. 18). These polymers are, in most cases, obtained through free-radical or ionic polymerisations. Some donor polymers have also been produced by polycondensation.

In view of their successful commercial applications it is not surprising that PVK, and related polymers containing the carbazole moiety, have been the most extensively studied of all the polymeric donors.

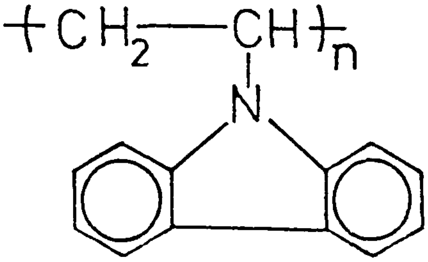
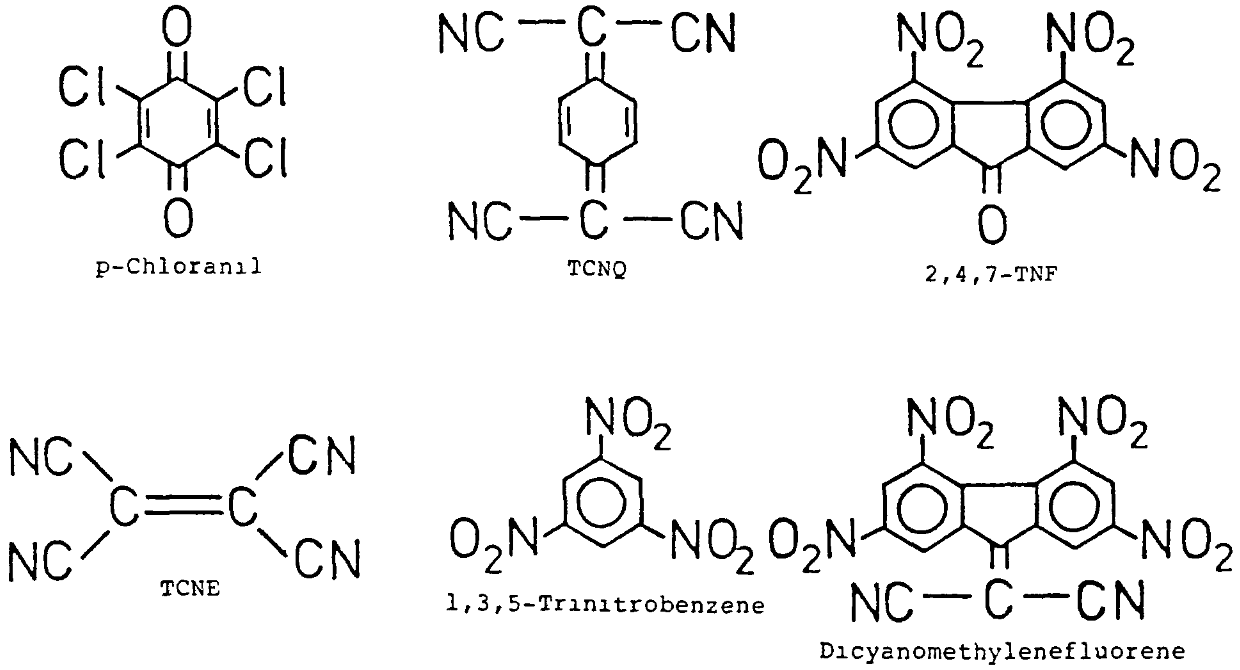


Fig. 18. Poly(vinylcarbazole), PVK.

PVK, on account of the strong electron-donating properties of the carbazole group, forms CT complexes with a variety of different compounds having acceptor properties as evidenced by the appearance of a new band, the 'charge-transfer (CT) band' in their absorption spectra. These complexes are characterised by high photoelectric sensitivity in the visible region. Commonly used acceptors are illustrated in Fig. 19 and complexes of PVK with iodine, tetracyanoethylene (TCNE), tetracyanoquinodimethane

(TCNQ), and 2,4,7-trinitro-9-fluorenone (TNF) have been widely reported in the literature. Generally these polymer complexes


p-Chloranil

TCNQ

2,4,7-TNF

TCNE

1,3,5-Trinitrobenzene

Dicyanomethylenefluorene

Fig. 19. Low molecular weight acceptors.

have enhanced electrical and photoconductive properties (relative to uncomplexed PVK), e.g. conductivities as high as 10^{-5} S cm^{-1} were reported for PVK-I_2.[28] While their Kf values were lower than the corresponding values for complexes with their model compounds, N-ethylcarbazole and N-isopropylcarbazole, this was attributed to the steric interference to intermolecular association caused by the bulky carbazole groups directly bonded to the polymer backbone.[29,30]

Initially work was directed towards increasing the visible light photosensitivity of the PVK polymer by doping with low levels (up to 10 mole %) of acceptor molecules[31] - formation of coloured CT complexes absorb in the visible range and so increase photogeneration efficiency. Acceptors with especially high electron affinities were employed in order to shift the absorption bands further into the long-wave region. TNF is so effective with PVK that the combination is used in xerographic copiers. As a consequence the electrical and photoelectrical properties of PVK-TNF complexes have been thoroughly investigated. Although the actual mechanism of charge transport in PVK-TNF is not fully understood it has been shown that the system is unique in that it is bipolar, i.e. capable of transporting both electrons and holes. Hole transport is associated with the PVK (carbazole) component and electron transport with the TNF component, the electronic properties being very dependent on composition with hole mobility decreasing as the TNF content increases.[32]

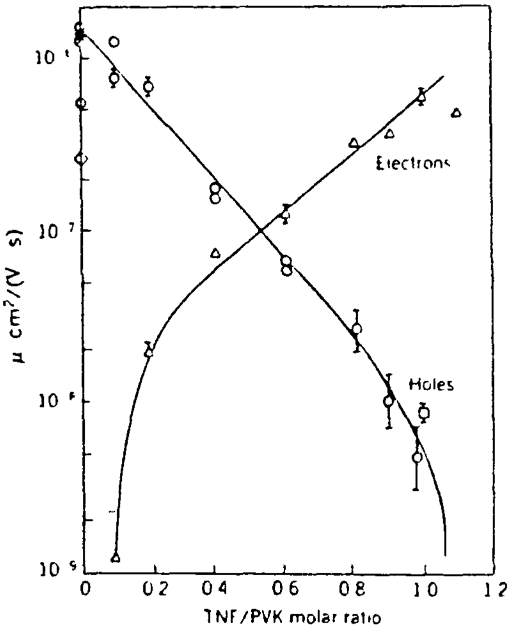
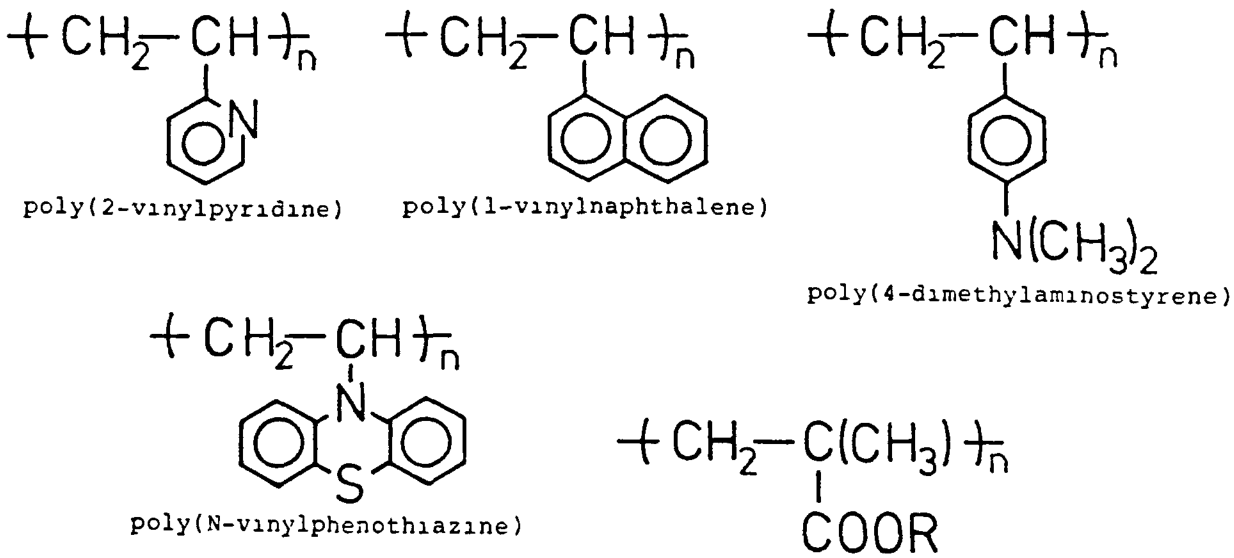


Fig. 20. Hole and electron mobilities in PVK-TNF at E approximately 10^5 V/cm as a function of TNF loading.[32] Δ Ref. 33; ● Ref 34; ⊗ Ref 35; ☐ Ref 32.

Many other carbazole-containing polymers have been synthesised many of which exhibit photoconductivity. Among the latest are poly(2-N-carbazoylethyl methacrylate)[36] and poly(N-carbazoylethyl glycidyl ether)[37] which have sought to overcome the high degree of steric hindrance to complex formation in PVK caused by the bulky carbazole group. PVK-TNF is unique in that high loadings of TNF can be accommodated in the amorphous polymeric solid without phase separation or crystallisation of the small molecule unlike other acceptor molecules. Up to 1.2 moles TNF per mole of vinyl carbazole repeat unit can be achieved.[32]

Other polymeric donors have been reported, being mostly either vinyl backbone polymers or polyacrylates and polymethacrylates with attached donor substituents, and their CT complex properties investigated. These include the vinylpyridines, vinylphenothiazines and polymers containing large polynuclear aromatic groups (e.g. anthracene, naphthalene) or aromatic amino groups. Representative examples are shown in Fig. 21 below. Some of these polymers display some degree of photoconductivity, though only in the UV range. Their complexes are, at best, semiconductors where their electrical conductivities are generally lower than that of their corresponding monomeric complexes.[3] The poly(2-vinylpyridine)iodine (P2VP-I_2) complexes are particularly significant because of their commercial application in solid-state electrochemical cells


poly(2-vinylpyridine)

poly(1-vinylnaphthalene)

poly(4-dimethylaminostyrene)

poly(N-vinylphenothiazine)

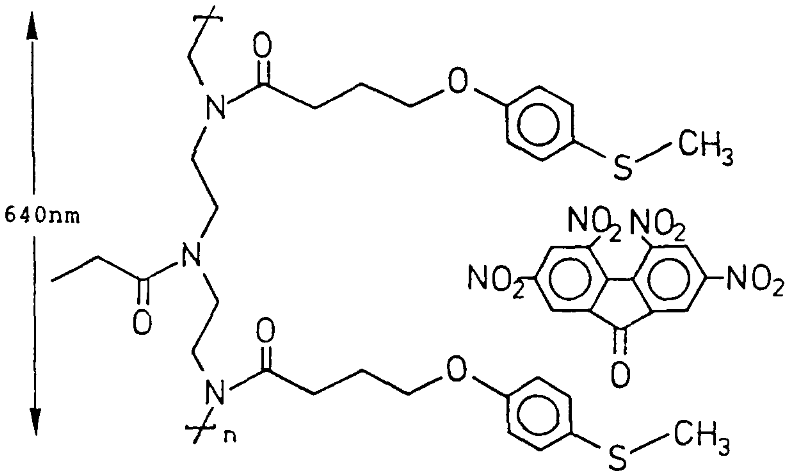
polymethacrylate R: phenyl
anisyl or
naphthyl

Fig. 21. Donor polymers.

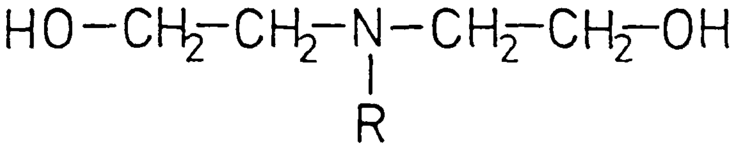
where the complex serves as a convenient source of iodine for the cell reaction:

$$2\ \mathrm{Li} + \mathrm{I_2} \longrightarrow 2\ \mathrm{LiI}$$

P2VP-I_2 complexes have conductivities of the order of 10^{-4} to 10^{-7} S cm^{-1}. Litt and Summers attributed incorrect spacing of repeat units to the low conductivities in the above systems and synthesised a novel semiconducting polymeric CT complex based on a polyethylene-imine backbone.[38] Because of its ordered structure this polymer allows control over the donor repeat distance along the chain (0.635nm) as well as the space required for accommodating the complexing acceptor molecules. With 2,4,5,7-tetranitrofluorenone as the acceptor groups and 4-(methylthio)phenoxy as the donor groups such polymeric complexes had conductivities 10^3 times that for the corresponding small molecule model complexes (one of the very few instances where the trend has been claimed):



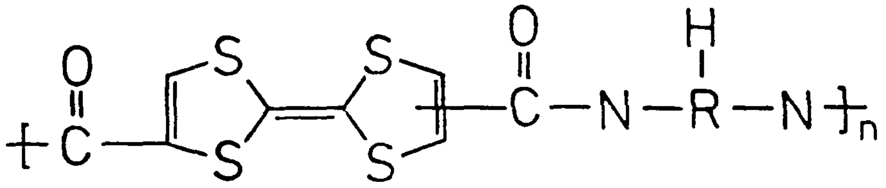
There are also a number of condensation polymers with donor groups along the main chain. The earliest examples were polyesters from the diols:[39]



$$\mathrm{HO{-}CH_2{-}CH_2{-}\underset{\displaystyle R}{\underset{|}{N}}{-}CH_2{-}CH_2{-}OH}$$

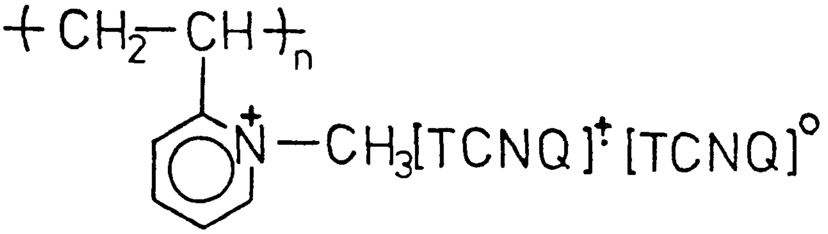
R: phenyl, m-tolyl,
p-anisyl, 2-fluorenyl.

Ohno reported complex formation in linear and network, i.e. cross-linked, polyurethanes containing phenylimino groups as donor units by complexing with p-chloranil.[40] Their electrical properties were not investigated. Recently Watanabe et al synthesised polyamides containing TTF moieties within the main chain. Electrical conductivities ranged from 10^{-5} to 10^{-9} S cm^{-1} on complexing with bromine. Electrical conduction in the bromine complexes was attributed to the hopping of odd electrons from TTF to adjacent TTF †.[41]



R: aromatic derivatives

In addition to the above systems polymeric TCNQ complexes have been synthesised and their electrical properties studied. The first such examples were those based on poly(vinylpyridines):

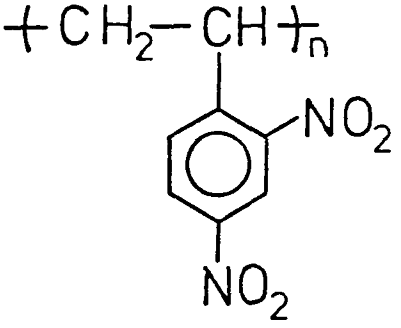


Addition of excess neutral TCNQ gave products with conductivities as high as 10^{-3} to 10^{-2} S cm^{-1}.[42-44] The presence of neutral TCNQ was critical in achieving the high conductivity where the TCNQ$^{\bar{\cdot}}$-TCNQ arrays are responsible for charge-carrier (electron) transport. The more order the matrix polymer provides for these molecular arrays the higher the conductivity. Similarly TCNQ polymer complex salts with high conductivities were reported for poly(vinylacetals)[39] and PVK.[45]

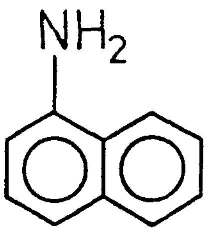
1.3.2.2 Polymers As Acceptors

In contrast to the large number of polymeric donor-small molecule acceptors reported the reverse is true for the acceptor polymer-donor molecule combinations where few high molecular weight polymers with electron-acceptor functions have been synthesised. Synthetic difficulties are mainly responsible for the lack of suitable structures. For the majority of vinyl type polymers, where the acceptor function is pendant to the backbone, free-radical polymerisation techniques are unfeasible as most acceptors are free-radical inhibitors. Additionally anionic polymerisation of monomers containing strong acceptor groups would prove impossible because of electron-transfer reactions.[2]

Polymers containing pendant nitrated phenyl groups account for most acceptor polymers and the first such example was poly(2,4-dinitrostyrene), prepared by nitration of polystyrene:



poly(2,4-dinitrostyrene)



α -naphthylamine

Its CT characteristics with α-naphthylamine were reported by Smets et al[46] but no study of the conductivity of this system was performed. Because of the polymerisation problems discussed above, the majority of acceptor polymers have been prepared by condensation techniques. Sulzberg and Cotter[42] synthesised a series of polyesters utilising nitrated phthalic acid isomers as the acceptor units. One such example was poly(hexane-1,6-diol-5-nitroisophthalate) as illustrated below. The CT complex characteristics of these polymers were evaluated by forming EDA blends with donor polymers and are discussed later.[39]

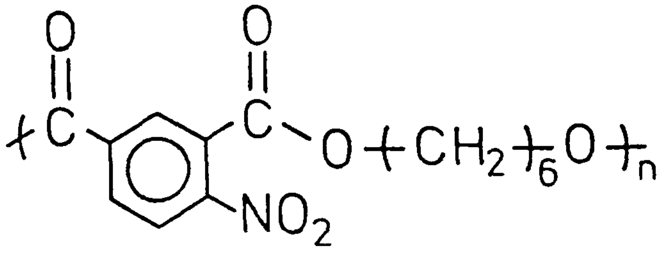
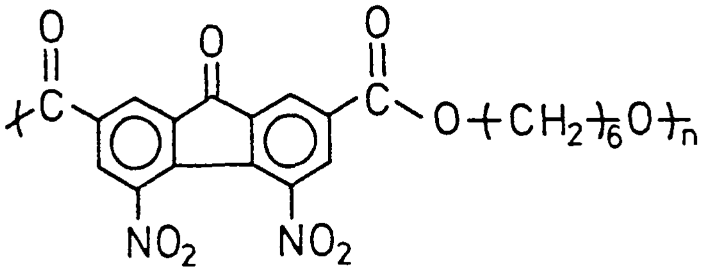
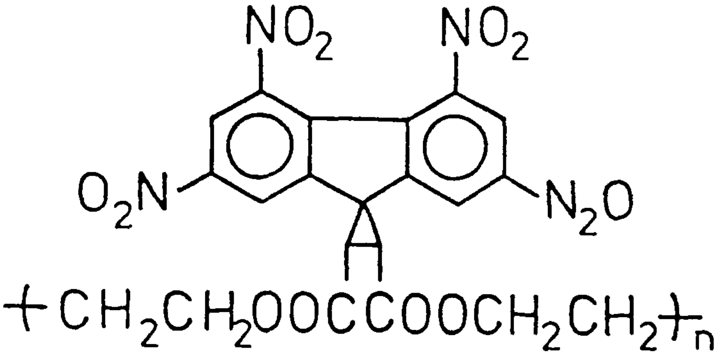


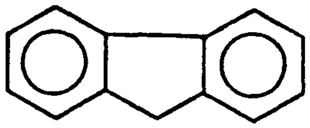
Fig. 22. Poly(hexane-1,6-diol-5-nitroisophthalate)

These authors also described acceptor polymers based on the fluorene ring system.[47] An example is the polyester based on dinitrofluorenonedicarboxylic acid and hexane-1,6-diol:



Again no complexing studies were reported for these polymers other than EDA blends with donor polymers (they form polymer complexes with donor molecules and their complexes exhibit semiconducting properties). Other acceptor polymers based on the nitrofluorenones have been prepared and studied.[48] These are polyesters containing the spirocyclopropane-tetranitrofluorene units:

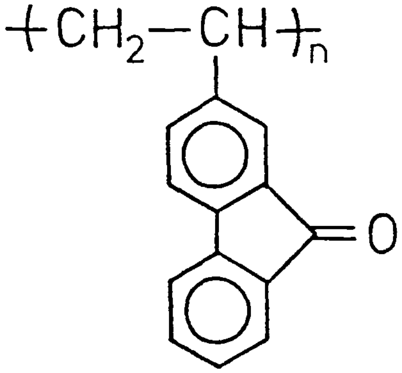




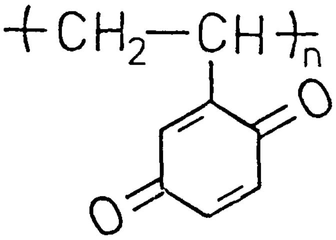
fluorene

Complexing studies of this strong acceptor polymer were carried out with fluorene as the small donor molecule. $K\epsilon$ values were larger in these polymer complexes than in the monomer model complexes, i.e. they complex more efficiently than their model compounds.

Despite the problems associated with polymerisation some vinyl-type polymers containing acceptor groups have been prepared and include the vinylfluorenones[49] and the quinone-containing polymers[50,51] (which exhibit interesting redox behaviour):

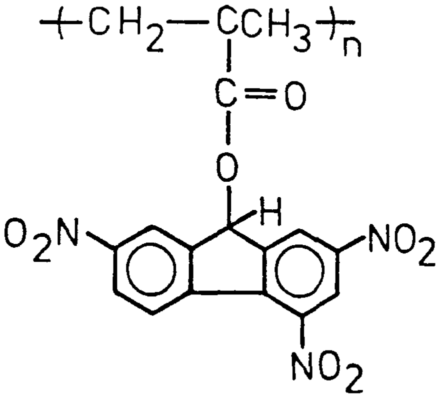


poly(2-vinylfluorenone)

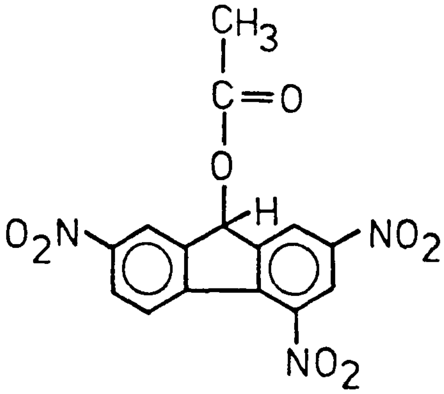


There is no data available concerning the complexing characteristics of the quinone polymers. Although the vinylfluorenone polymers formed complexes with a variety of donors in solution very low complexing levels were observed in the solid state. This was attributed to the fluorenone group being such a weak acceptor. The polymers exhibited poor electron transport capabilities.

Turner and AuClair[23] synthesised an acceptor polymer based on the trinitrofluorene nucleus, poly(2,4,7-trinitro-9-fluorenyl) methacrylate. This strong acceptor polymer formed



poly(2,4,7-trinitro-9-fluorenyl) methacrylate



2,4,7-trinitro-9-fluorenyl acetate

complexes with anthracene - the polymer complex had a λ_{max} at 495nm versus 475nm in the corresponding small molecule model system, 2,4,7-trinitro-9-fluorenyl acetate (Fig. 23. below). The Kϵ value, as determined by Benesi-Hildebrand analysis, for the polymer and anthracene was 2000 mol^{-2} l^{2} cm^{-1} at 495nm compared to the small molecule model system which gave a Kϵ value of 1100 mol^{-2} l^{2} cm^{-1} at 475nm, i.e. enhanced complexation in polymer acceptor when compared to the small molecule model.

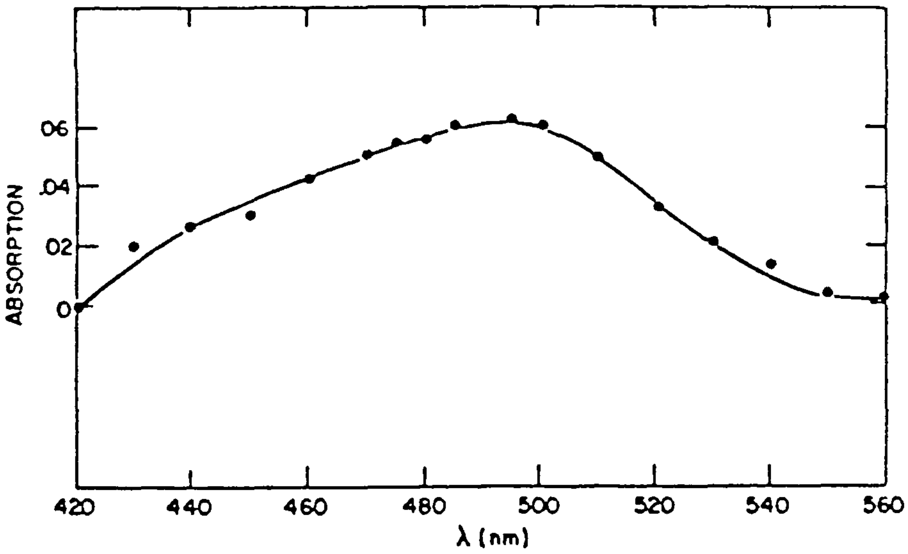


Fig. 23. Charge transfer absorbance of poly(2,4,7-trinitro-9-fluorenyl) methacrylate/anthracene, 5 x 10^{-3} M, THF, 25^{o}C, 1-cm cell.[23]

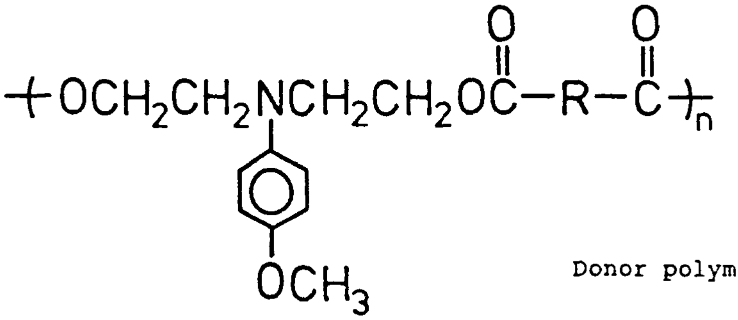
While other acceptor-type polymers have been developed many are insoluble thereby precluding any investigation of their complexing behaviour or electrical properties.

1.3.2.3 Polymer Donor-Polymer Acceptor Blends

The insertion of a low molecular weight compound into the matrix of a polymer (to obtain a CT complex) causes a deterioration of the mechanical properties of the polymer, and the restoration of these properties by plasticisation, for example, seriously supresses any enhancement of the electrical properties. In an effort to overcome these disadvantages polyblends of polymeric donors and polymeric acceptors have been prepared by either solution casting or melt mixing of the components. These materials, in contrast to many of the polymer-small molecule complexes, have well-defined structures, good mechanical properties and are easily processed. Their interchain electron donor-acceptor (EDA) interactions have also been used as model systems to study miscibility in polymer blends.[52]

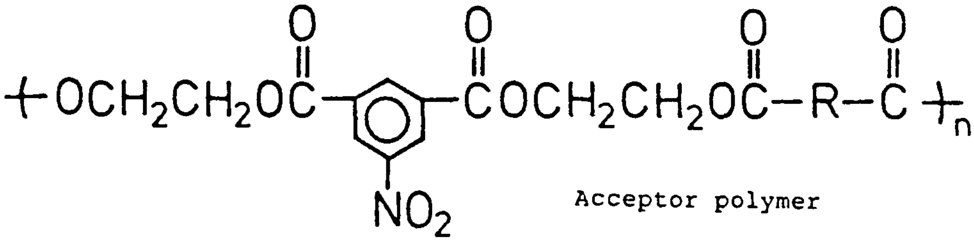
Though there are only a few published electrical investigations of these polymer combinations their intermolecular CT interactions have been extensively reported. Much of the work has concentrated on mixtures of condensation polymers containing appropriate donor and acceptor groups. The first reported example of a polymeric donor-polymeric acceptor CT complex was by Sulzberg and Cotter[53] who prepared a 50:50 mixture (by weight) of poly(p-anisyliminodiethanol bisphenol A carbonate) and poly(bis(2-hydroxyethyl)-5-nitroisophthalate bisphenol A carbonate) as illustrated below (I and II respectively):

(I)



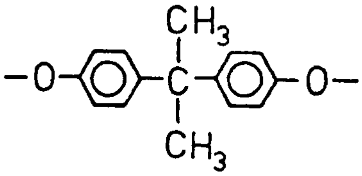
Donor polymer

(II)



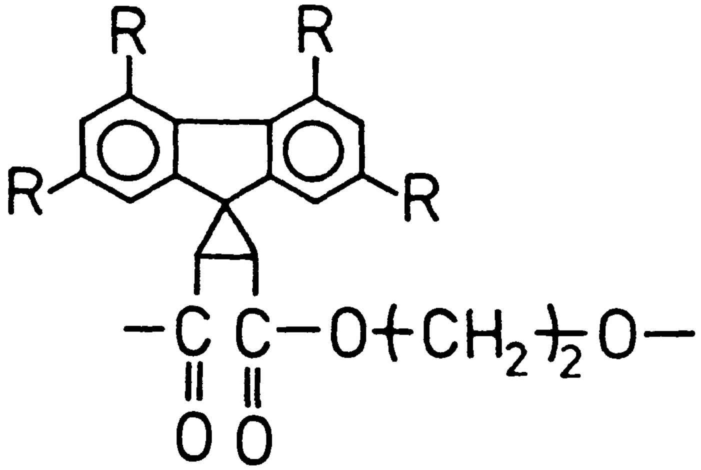
Acceptor polymer

R = bis(4,4'-oxyphenyl)-2,2-propane,



The resulting films from this combination exhibited volume resistivities a factor of 10^3 lower than the individual component polymers and were of a bright yellow-orange colour as a result of complexation. The same authors investigated mixtures of acceptor polyesters (prepared from nitrophthalic acids) with polyester and polycarbonate donors which gave highly coloured blends with volume resistivities as low as 10^5 to 10^6 S cm^{-1} (the majority of mixtures though had volume resistivities as low as 10^{11} to 10^{13} S cm^{-1})[39]. Donor groups were selected from phenyl, p-anisyl and di- and tri-substituted methoxyphenyl groups.

Schulz and Tanaka[48] evaluated the CT complex characteristics of polymer EDA blends based on the spirocyclopropanefluorene group. The presence or absence of nitro groups on the fluorene ring yield acceptor or donor polyesters accordingly:

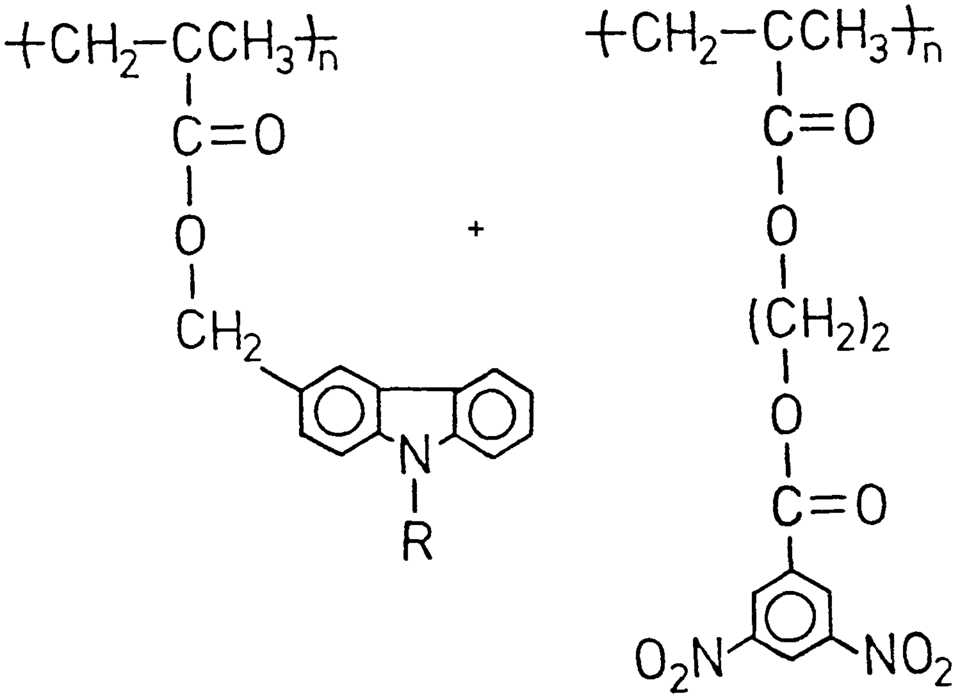


Donor: R = H

Acceptor : R = NO_2

Complexation of a mixture of these two polymers resulted in considerably higher Kε values (up to four times) than the model compounds or the acceptor polymer-small molecule system.

Polymer EDA blends have also been prepared from appropriate vinyl acceptor and donor polymers. There are few examples but one such system utilises the electron donating characteristics of the carbazole group, incorporated in the side chain of a series of polymethacrylates. These form interpolymeric EDA complexes with the acceptor polymer, poly(2-(3,5-dinitrobenzoyloxy) ethyl methacrylate).[52] Their CT complex interactions were used to study miscibility in polymer blends. The influence of EDA complex formation on the rheological and mechanical properties of polymer blends have also been investigated.[54,55]



1.3.2.4 Donor-Acceptor (D-A) Copolymers

As with the polymer donor-polymer acceptor blends donor-acceptor (D-A) copolymers were developed primarily to overcome the poor mechanical properties associated with the polymer-(simple molecule) CT complexes. These copolymers, with either in-chain or pendant donor and acceptor groups, behave as intramolecular CT complexes in dilute solutions - the interacting groups need not be on adjacent positions in the chain (Fig. 24). The intramolecular nature of these CT interactions can be readily established by observing that the intensity of the CT band follows the Beer-Lambert Law, i.e. CT absorption varies linearly with concentration. This is in contrast to the behaviour of intermolecular associations where the concentration of complex, and hence the absorption, is dependent on the equilibrium constant, K, - intermolecular interaction would be expected to vary in a non-linear fashion with concentration of the donor and acceptor components. In the solid state D-A copolymers can exhibit both inter- and intramolecular complexation, the relative amounts depending on the sequence distribution of donor and acceptor units and the configuration and conformations of the side chains and chain segments.

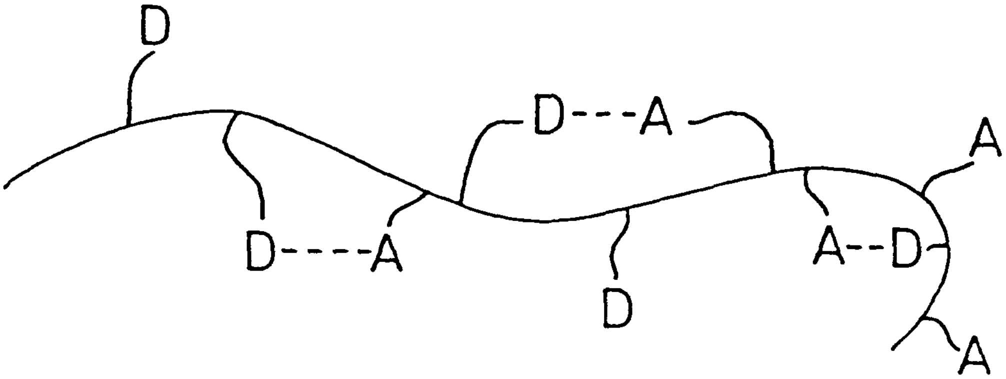


Fig. 24. Intramolecular complexation interactions. for a D-A copolymer.

D-A copolymers have been prepared by a variety of methods - chemical modification of existing polymers, polycondensation between a donor and acceptor monomer, and radical copolymerisation of donor-acceptor monomer pairs. Condensation polymerisation affords the greatest degree of control over copolymer microstructure allowing the preparation of materials with an alternating sequence of donor and acceptor units along the polymer chain, thus maximising the degree of intramolecular complexation. Any tendency for a reduction in polymer flexibility, i.e. brittleness, owing to CT complex formation can be modified by variation of the separation between consecutive pendant groups along the chain and also by variation of the length of the side-chain linking the pendant groups to the backbone. Alternation of donors and acceptors is more difficult to achieve in copolymers based on vinyl monomers though CT interactions may ensure a reasonable degree of specificity in this respect during polymerisation. Radical polymerisation provides the most convienent method to obtain D-A copolymers.

The earliest examples of polymeric intrachain complexes were those prepared by partial nitration of poly(acenaphthlene) homopolymers.[56] Degrees of nitration ranged from 7.9 to 40.6% and their CT complex properties were proved by their colour and increased photoconductivity. Enhancement in the photoconductivity of these nitrated polymers was attributed to formation of intramolecular complexes between the aromatic and nitro-aromatic groups along the polymer backbone resulting in an increased photogeneration of charge carriers. Similarly nitration of poly(vinylnaphthalene)[57] and poly(vinylcarbazole)[58] leads to D-A copolymers. Gipstein et al[59] obtained vinylfluorene-vinylfluorenone copolymers by a partial oxidation of poly-(vinylfluorene). They also synthesised a terpolymer of the

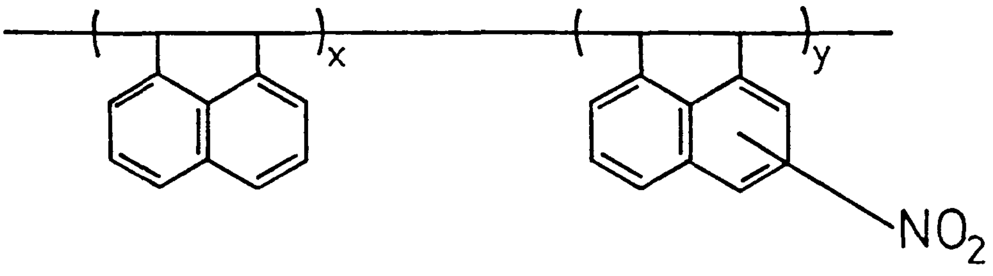
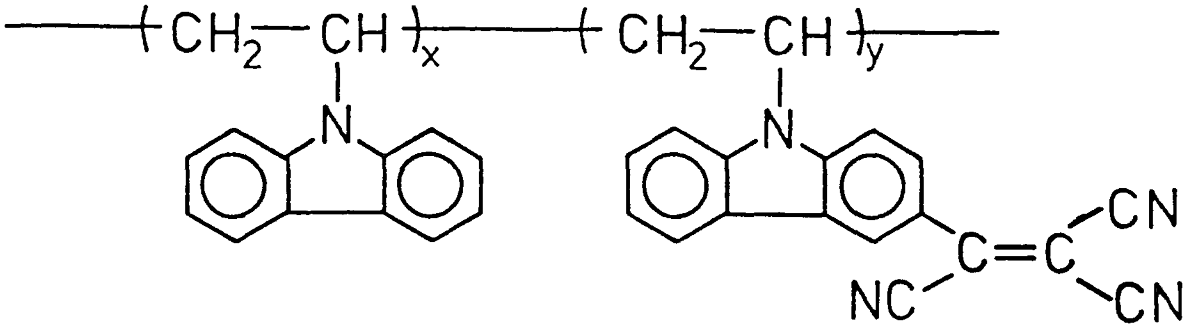
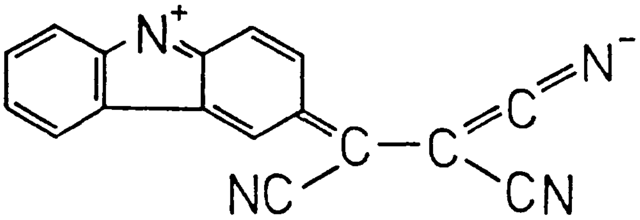


Fig. 25. Nitrated poly(acenaphthalene).

vinylfluorene-vinylfluorenone-vinylcarbazole type by oxidation of a vinylfluorene-vinylcarbazole copolymer. Other D-A copolymers have been prepared by analogous reaction methods and include those derived from vinylcarbazole-vinylacetate and vinylcarbazole-acryloyl chloride copolymers.[60] Recently Schulz and Geissler[61] synthesised polyvinyl alcohol acetal with naphthyl and carbazoyl donor groups and dinitrobenzoyl and trinitrofluorenyl acceptor groups. All the above copolymers exhibited photoconductivities higher than that of poly(vinylcarbazole), PVK. A unique D-A copolymer has been described in which an intramolecular CT complex comprises the pendant group.[62] This polymer was synthesised by reaction of PVK with tetracyanoethylene, TCNE, under controlled conditions to give the vinylcarbazole-vinyl-3-tricyanovinyl-carbazole copolymer:

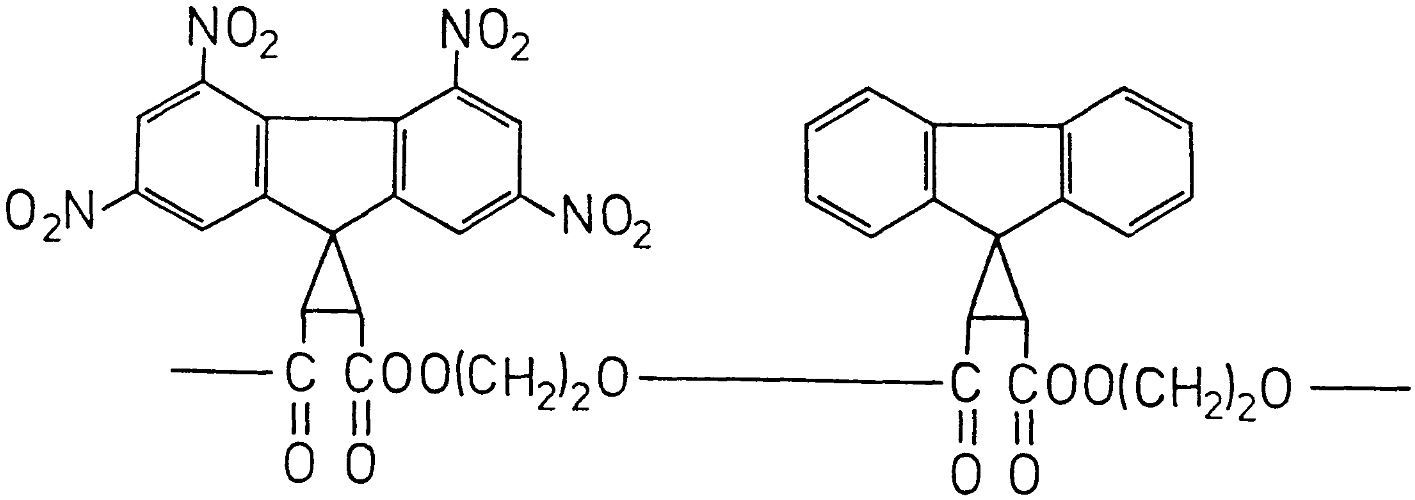


High degrees of substitution can be achieved but at the expense of molecular weight and solubility. Enhancement in conductivity was attributed to contributions from intramolecular polarisation reactions of the type:



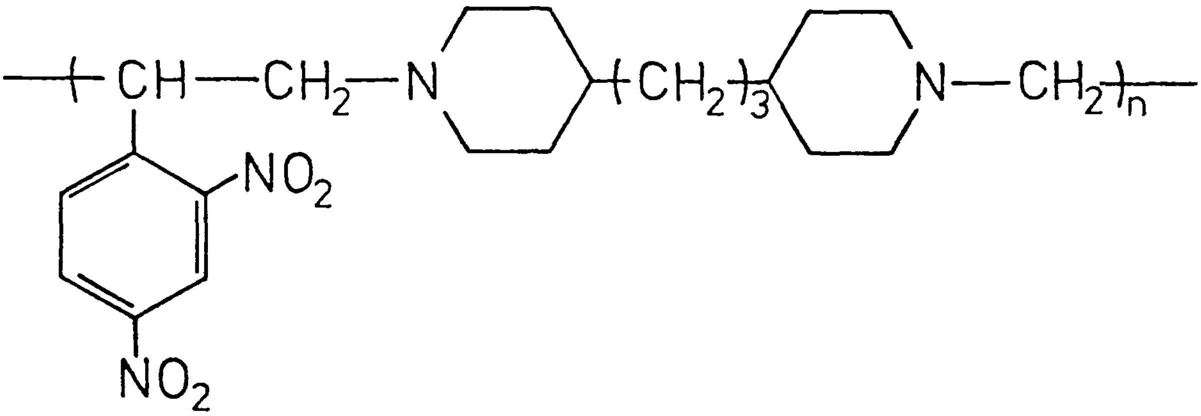
Copolymers containing low levels of tricyanovinylcarbazole groups were considerably more conductive than PVK owing to the high extinction coefficient and visible light absorption characteristics (λmax. approximately 500nm). Hole mobilities decrease with increasing concentration of tricyanovinylcarbazole groups.[2]

In contrast to the chemically modified D-A copolymers polycondensation provides a means of accuratly controlling the sequence distribution of donor and acceptor units and hence the degree of complexation. Schulz and Tanaka[48] prepared copolymers from the spiro cyclopropane-tetranitrofluorene monomer unit and its corresponding non-nitrated fluorene analogue:

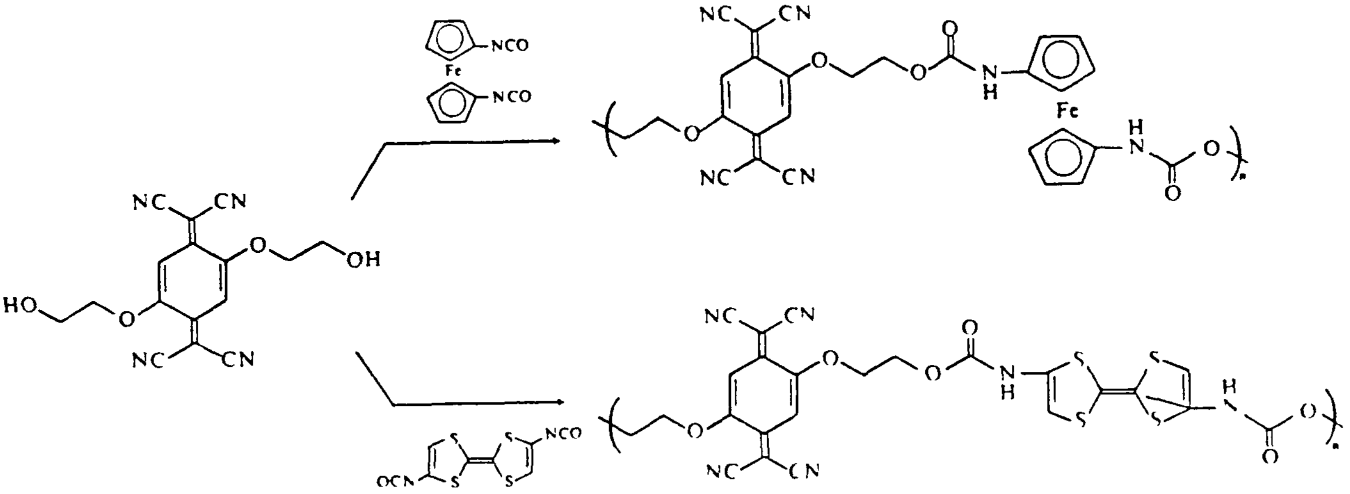


These copolyesters had D:A ratios of approximatly 4:1 and 14:1 and their reaction mixtures attained an intense green-brown colour. A strong absorption band was observed from 600 to 650nm. The intramolecular nature of the interaction was verified by the linear change in the CT absorption with concentration. By comparing with model compounds it was estimated that only 10% of the acceptor groups available were complexed. The very rigid nature of the complexed groups arising from the spiran structure was thought to play a role in this behaviour. No electrical analyses were made on these materials.

Tsuchida et al[63] used the Mannich reaction starting from 2,4-dinitrotoluene, 1,3-di-(4-piperidinyl)-propane and formaldehyde to yield an unusual D-A copolymer. It was unique in that the π-type acceptor group was pendant to the backbone while the n-type donor was in the backbone:

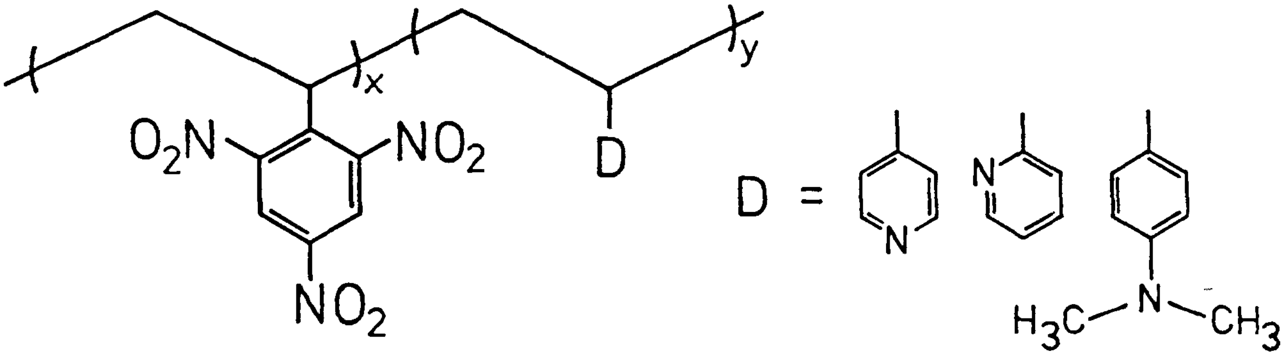


The polymer had a CT absorption band in the 450-550nm region and polymer solutions obeyed the Beer-Lambert Law over a wide range of concentrations. D-A copolyurethanes were prepared[64] by condensation of a diol derivative of TCNQ, 2,5-bis(2-hydroxyethoxy)-TCNQ with donor functional monomers containing ferrocene or TTF. These polymers were insoluble in organic solvents and black. The ferrocene-containing polyurethane had a conductivity of 3.3 x 10^{-4} S cm^{-1} (two orders of magnitude lower than that of the complex formed between the corresponding TCNQ and ferrocene model compounds). The TTF polyurethane had a conductivity of 1.6 x 10^{-11} S cm^{-1}. It was proposed that



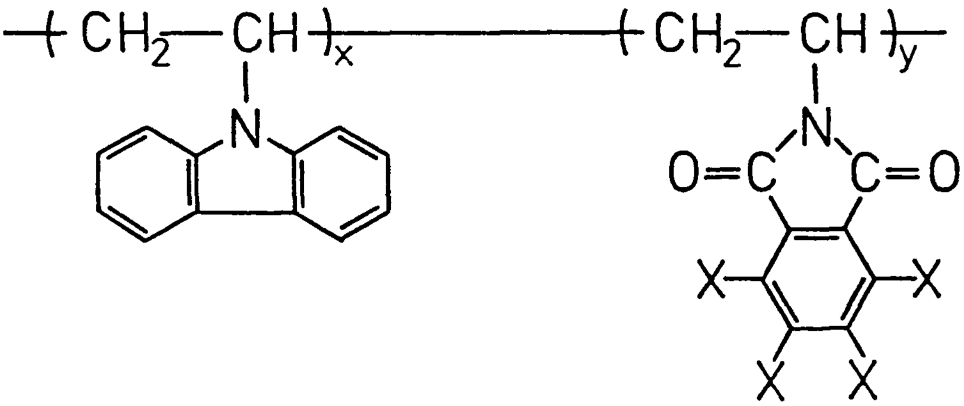
due to the rigid chain structures of these polymers interchain complexes dominate in the solid state. Recently Tazuke et al[65] reported on the inter- and intramolecular interactions of a polyester containing pyrene and N,N-dimethylaniline groups by absorption and fluoresence spectroscopy. No electrical measurements were carried out.

The first D-A copolymer obtained by radical polymerisation was synthesised by Yang and Gaoni.[66] They reported the formation of ·polymers having an alternating D-A structure where the acceptor monomer 2,4,6-trinitrostyrene underwent spontaneous copolymerisation in the presence of 4-vinylpyridine, 2-vinylpyridine and 4-dimethylaminostyrene as donor monomers:



These copolymers exhibited intramolecular complexations with CT absorptions bands in the 450-550nm region. Their conductivities were of the order of 10^{10} S cm-1.

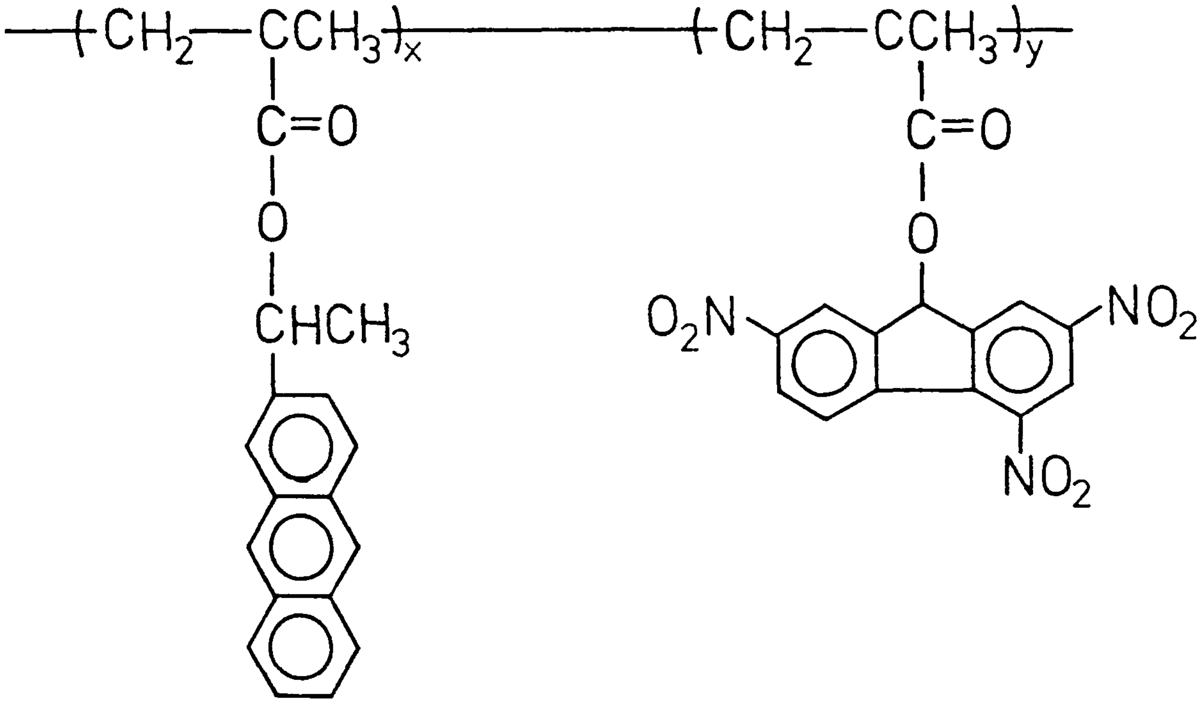
Seanor and Limburg[67] made detailed investigations into a series of vinylcarbazole-vinylphthalimide random copolymers prepared by free-radical techniques. A broad CT band was observed from 350-470nm which did not appear for a mixture of the two homopolymers or for the PVK-ethylphthalimide model system. The intramolecular nature of the CT interaction was confirmed by observing that the intensity of the CT band followed the Beer-Lambert Law and by the presence of a broad CT emission band from 400-600nm. Other D-A systems were prepared from the vinylcarbazole-vinylphthalimide copolymers by varying the structure of the phthalimide group via an exchange reaction:



x = H, Cl, Br or I

The photoconductivity of these copolymers decreased along the series X = H, Cl, Br, I. This was attributed to steric factors with complexation becoming more difficult with increasing size of the acceptor group. As with the PVK-TNF system it was observed that the effective hole mobility in these copolymers decreased with increasing acceptor content.

Stolka and Turner[68] obtained a 1:1 D-A copolymer by the copolymerisation of anthracene and trinitrofluorenone methacrylates:



The copolymer exhibited a strong intramolecular CT band in the 450-550nm region with the absorption in the 490nm range about one order of magnitude greater in intensity than the CT band in the model systems (see Fig. 26 below). This enhancement was attributed to the influence of the polymer environment on the interacting chromophores (a higher effective concentration of complex, in comparison to the model systems, is obtained as a result of constrained intramolecular chromophoric interaction). Again the intramolecular character of the CT interaction of the pendant anthracene and trinitrofluorenyl groups was established by the linear dependence of absorption of the CT band with concentration. No electrical or photoconductivity measurements were carried out on this copolymer.

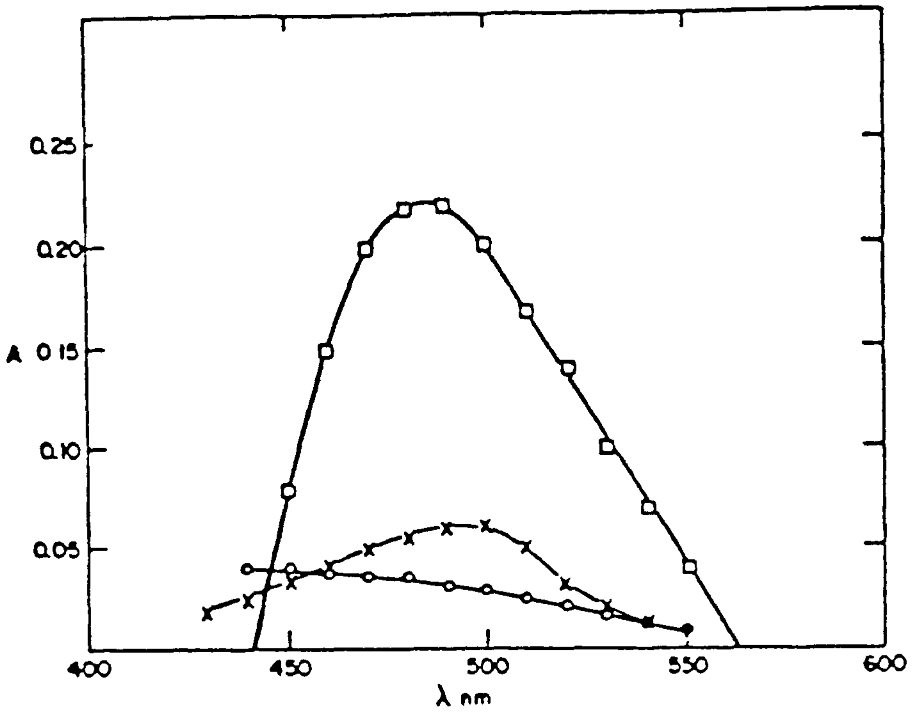


Fig. 26. Charge-transfer spectra of (O) anthracene/2,4,7-trinitro-9-fluorenyl acetate; (×) anthracene/poly(TNFMA); (□) poly(TNF-co-AEMA), 5 x 10^{-3} M in each chromophore, THF, 25°C, 1-cm cell.[68]

Simionescu et al[25,69,70] have recently synthesised a series of polymeric intramolecular CT complexes by radical copolymerisation of acrylate and methacrylate monomer pairs. The complexing groups were carbazoyl, anthryl, phenothiazinyl and p-dimethylaminobenzyl as the donor groups, and picryl, dinitrobenzyl and trinitrofluorenyl as the acceptor groups. Evidence for intramolecular complexation in these D-A copolymers was provided by ^{1}H-nmr and electronic absorption spectra. CT bands showed a maximum of 1:1 composition for all the copolymers. Differences in complexation intensities for the various systems were explained by configurational changes arising from α-substitution at the vinyl group or side-chain length. Photoconductivity studies showed that photogeneration reached a maximum at 1:1 compositions where the density of excited CT states reached maximum values. Conductivities in the dark were very low (10^{-16} to 10^{-17} S cm^{-1}).

1.3.3 DOPING WITH CT COMPLEXES

Crystallisation of highly-conducting CT complexes, i.e. TTF-TCNQ, in polymeric matrices during the process of film casting provides an extremely effective method of making commercial polymers conductive.[71,72] Such polymers include poly(carbonate), poly(styrene), poly(methyl methacrylate), and poly(phenylene oxide). Under carefully controlled conditions crystallisation takes place resulting in the formation of very fine and branched microcrystals of the complex. At appropriate casting temperatures and solvent evaporation rates dendrite-like crystals penetrate the polymer matrix and form a conducting network. This technique, called reticulate doping, provides conductive films at a surprisingly low additive content - well below 1 wt % - with specific conductivity in the range 10^{-1} to 10^{-3} S cm^{-1}. Casting of these polymer films is on glass substrates. The concentration dependence of conductivity is presented in Fig. 27 for TTF-TCNQ in poly(carbonate) (PC) and poly(methyl methacrylate) (PMMA) cast from o-dichlorobenzene.

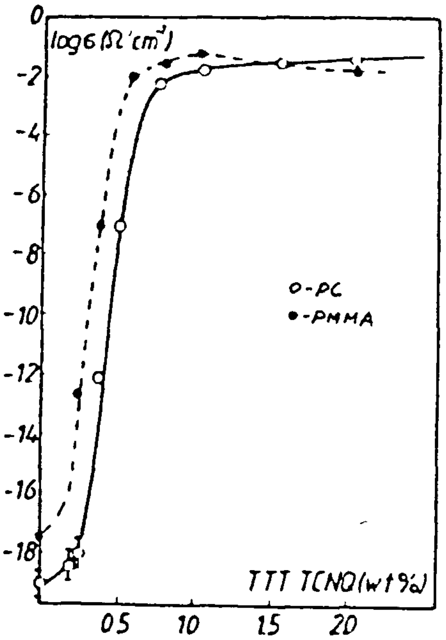


Fig. 27. The dependence of specific conductivity of PC and PMMA films on the content of TTF-TCNQ complex.[72]

The morphology of the crystalline network depends qualitatively on the concentration of the CT complex and on the solvent used for film casting as well as on the polymer (amorphous or crystalline, inert or not). Very high mobilities and charge carrier densities have been reported for these systems (e.g. for PC + 1 wt % TTF-TCNQ, 10^{-2} cm^2 V^{-1} s^{-1} and 10^{19} cm^{-3} respectively). As a consequence of the low dopant content involved many of the mechanical properties of these conducting polymers are practically unchanged when compared with pure films cast under the same conditions.

In contrast, polymers doped with molecularly dispersed CT complexes generally lead only to enhanced photoconductivity exhibiting low dark conductivities. Attempts to achieve high conductivity require rather high concentrations of the conducting CT complex (20-30%) leading to adverse effects on the mechanical and thermal properties of the polymeric binder. Recently it has been shown that when such homogeneous solid solutions of conductive CT complex are treated with particular solvents, precipitation of the additives (i.e. donor and acceptor) occurs and under favourable conditions a conducting network will form making the film surface conducting.[73] In addition concentration of the molecularly dispersed CT complex can be as low as 0.3 wt %. The surface conductivity of poly(carbonate) films, containing 0.3 wt% TTF-TCNQ, treated with dioxane vapours is of the order of 10^{-4} S cm^{-1}. The thickness of the conducting layer can be lower than 5μm thus making it possible to obtain 20μm thick polymer films conducting on both sides independently. Using appropriate masks it is possible to 'print' required conducting patterns on the surface of an object made of suitable doped polymer.

1.4 OUTLOOK

Despite extensive research into a variety of polymer based CT complex systems only a few have been commercially exploited. This can in general be attributed to the fact that these materials tend to be quite brittle and have much lower electrical conductivities in comparison to their lower molecular weight analogues. The more notable successes include materials such as poly(2-vinylpyridine)-iodine and poly(vinylcarbazole)-trinitrofluorenone: P2VP-I_2 has found commercial use in highly efficient solid-state batteries and the PVK-TNF system has many important applications in the electrophotographic industry, in particular xerography.

Provided that the appropriate combination of conductive (or photoconductive), mechanical and processing properties can be achieved with polymeric CT complexes further applications in the electronics and energy industries seem possible. It would appear from current research trends that the majority of development work will continue to concentrate on further developing the polymer-small molecule CT complex systems and systems where small molecule complexes are dispersed in an inert polymeric binder. It is felt that these are the areas most likely to lead to successful commercial exploitation where tailored electrical, photoelectrical and mechanical properties for specialised applications are more likely to be realised. Donor-acceptor copolymer systems are primarily of theoretical interest as yet though there may be interesting applications due to, for example, their photoelectrical properties and the possibility of controlling their microstructure, and therefore their mechanical properties.

CHAPTER 2: DISCUSSION

2.1 INTRODUCTION

As outlined in the abstract the aim of this work was to prepare a series of novel polymer systems, tailored in such a way that their various pendant electron donor (D) and electron acceptor groups (A) would interact and give rise to both inter- and intrachain electron donor-acceptor (EDA) complexes thereby endowing these polymers with the conductivity and photoelectric characteristics of simple charge-transfer complexes.

The systems chosen for study were based on a vinyl polymer type backbone (i.e. polyethylene type) with pendant ester or amide groups providing the link unit for incorporation of the donor and acceptor units onto the polymer chain. The approach was to synthesise a series of comblike polymers containing the electron acceptor phthalimido moiety in the side chain and to study their EDA interactions with a range of electron donor polymers, donor substituents being selected from polynuclear aromatic compounds, such as anthryl and phenanthryl groups, and methoxy-substituted phenyl and aniline groups. The structures of the synthesised monomers are illustrated below.

Originally it was envisaged that the two aspects of preparation of the polymer systems, and investigation of their electrical and electrochemical properties would proceed in parallel following initial preparation of a few of the desired materials. Their CT interactions were to be characterised utilising U.V. and visible spectroscopy. However owing to considerable difficulties encountered in the early stages in developing satisfactory synthetic routes for these vinyl monomers it was decied to proceed first with the preparation of the different polymer systems - investigation of their CT properties and those for analogous simple models were to follow as photoinitiated electron transfer reactions involving the above mentioned acceptor and donor substituent groups had previously been documented in the literature. This chapter then falls naturally into two distinct parts, the first detailing the syntheses and characterisation of the various monomers, polymer and copolymer systems, the second dealing mainly with the charge transfer complex (CTC) properties of the different D-A systems investigated, as evidenced by U.V. and visible spectroscopy.

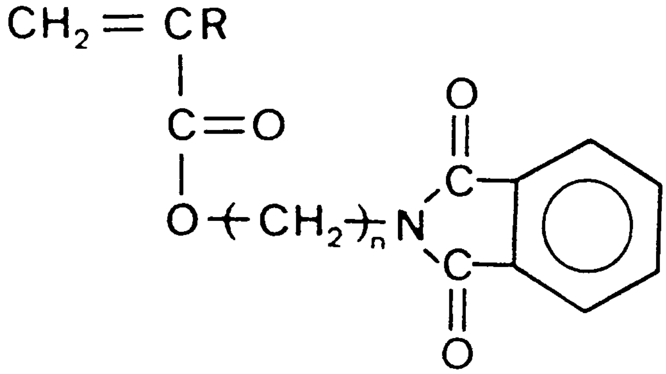
2.2 SYNTHESIS AND CHARACTERISATION

2.2.1 MONOMERS

All the monomers were of the vinyl type, either esters or amides of acrylic and methacrylic acid with the appropriate functionalities incorporated into the ester/amide groupings. Both acrylates and methacrylates were chosen for study as it has been shown that degrees of complexation tend to be somewhat higher for methacrylate-acrylate than for methacrylate-methacrylate copolymers with acrylate-acrylate type systems expected to have the stongest intramolecular interactions.[25] Similarly a series of acrylamides and methacrylamides were also prepared - although there is the possibility that such a similar relationship holds true for acrylamide/methacrylamide copolymer combinations there is no confirmatory evidence as yet. These intramolecular complexation differences between the systems were explained by configurational differences which are due to steric determination (through the α-methyl substituent) of substituent arrangements with respect to the main chain.[69]

2.2.1.1 Phthalimido Esters

It is possible to tailor interchain EDA interactions by changing the length of the side chains linking pendant donor or acceptor groups to the polymer backbone.[74] It was with such in mind that a series of N-alkylphthalimido acrylate and methacrylate monomers were synthesised with the number of carbon atoms separating the phthalimido nitrogen from the ester oxygen being varied from 1 to 5 in order to investigate the effects of such steric hindrances on the strength of interchain EDA complexations. It has been demonstrated in such systems that interchain interactions are reduced on increasing the alkyl side chain lengths where it has been possible in the higher



n	R	
1	H	PMA (15)
1	CH3	PMMA (16)
2	H	2-PEA (17)
2	CH3	2-PEMA (18)
3	H	3-PPA (19)
3	CH3	3-PPMA (20)
5	H	5-PPA (21)
5	CH3	5-PPMA (22)

Fig. 28. Phthalimido monomer system.

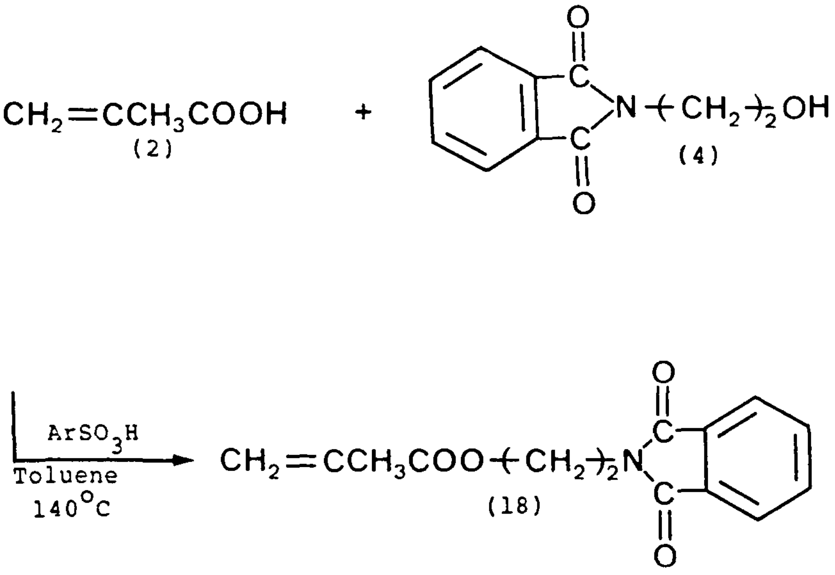
homologues to examine intrachain charge transfer in copolymer systems relatively free of interchain EDA complexation.[25,74] Additionally the presence of these alkyl groups in the side chains would reduce any tendencies for such polymer systems to exhibit increased brittleness arising from their involvement in CT complex formation.

These electron-acceptor phthalimido monomers were prepared by esterification of the corresponding N-hydroxyalkylphthalimides with the appropriate acrylic/methacrylic acid derivatives. The N-hydroxyalkylphthalimides were initially synthesised in high yields using established literature methods as detailed in the Experimental chapter.

2-(N-Phthalimido)ethyl acrylate (2-PEA, 17) was the first monomer in this series to be synthesised, though in low yields (maximum of 36%), following a method similiar to that used by Nikolayev and Zhelobayeva[75] for preparation of its methacrylate analogue, 2-(N-phthalimido)ethyl methacrylate (2-PEMA, 18) - the reaction was a base-catalysed acylation reaction with pyridine as the base/HCl-acceptor and copper (I) chloride as a polymerisation inhibitor. Attempts to increase the yield by further purification of the reacting species, choice of different solvent systems and varying the molar ratios of the reactants all proved unsuccessful - TLC analysis consistently indicated the presence of starting material irrespective of the length of time, or temperature, at which the reactions were carried out. In addition a variety of stirring aids were employed to offset any adverse effects that the hydrochloride salt deposits may have had on the homogeneity of the reaction mixtures, particularly during the initial stages of the reaction as the acid chloride was added. Kato et al[76,77] had reported the synthesis of (17) with yields of up to 65% using a similar reaction scheme with triethylamine (Et_3N) as the base catalyst/HCl acceptor.

In contrast the corresponding methacrylate ester, 2-PEMA (18), was readily synthesised in high yield (89%) by acid-catalysed esterification of methacrylic acid with N-(2-hydroxyethyl)-phthalimide (4).[76] p-Toluenesulphonic acid was employed as the acid catalyst and the equilibrium was driven towards favouring ester formation by azeotropic distillation of water from the reaction mixture:

Scheme 1: Acid catalysed acylation

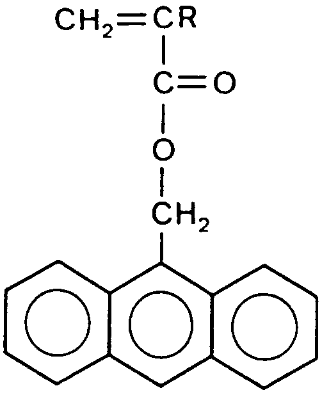


Attempts to synthesise the other phthalimido esters in this series using the direct esterification route used for (18) were unsuccessful. 2-PEMA was also synthesised by a base-catalysed reaction similar to that used for (17) above.

The other phthalimido monomers in the series, namely N-phthalimidomethyl acrylate (PMA, 15) and methacrylate (PMMA, 16), 3-(N-phthalimido)propyl acrylate (3-PPA, 19) and methacrylate (3-PPMA, 20), and 5-(N-phthalimido)pentyl acrylate (5-PPA, 21) and methacrylate (5-PPMA, 22) were all prepared in good yield by the condensation of acryloyl or methacryloyl chloride with the corresponding imidoalcohols in the presence of Et_3N as the base catalyst and HCl acceptor. Choice of solvent system was important particularly for the lower homologues in the series where more polar solvents such as acetonitrile were required. With the exception of PMA (15) the above compounds have not previously been reported in the literature - Kiyoshi et al[76] reported the synthesis of (15) with a melting point of 117-120.5°C though characterisation was not complete with elemental analysis data being reported for nitrogen only; this compares unfavourably with the value of 133-136°C for PMA (15) obtained in this work which also includes full CHN analysis data in addition to ^1H-nmr and ^{13}C-nmr spectra.

It is of interest to note that the phthalimido methacrylates in this series were obtained in greater yields than their acrylate counterparts. As expected melting points decreased as the length of the spacer methylene chain increased - in general acrylates had higher melting points than their methacrylate analogues, these differences becoming less significant with increasing number of carbons in the spacer group.

2.2.1.2 Anthryl/Phenanthryl Esters



R = H : 9-AMA (23)
R = CH3 : 9-AMMA (24)

Fig. 29. Anthryl monomer systems.

The anthryl monomers were prepared by esterification of the hydroxy compound 9-(hydroxymethyl)anthracene (8) with acryloyl and methacryloyl chlorides utilising base-catalysed reactions, typically with Et3N. Much of the early work centred on the synthesis of the (9-anthryl)methyl methacrylate ester (9-AMMA, 24) which required considerable development work prior to its successful synthesis, work which was later successfully applied in the preparation of the other monomer systems.

Early attempts to synthesise (24) using reaction sequences similar to those used in the syntheses of the phthalimido esters proved unsuccessful, leading instead to a mixture of products - from TLC analysis of the reaction mixtures there was evidence of unreacted starting material in addition to as many as six products in some instances. Similar results were also obtained using alternative acylation reaction schemes. Conversion of (8) to its alkoxide salt, by means of n-butyllithium, and reacting this with an equivalent of methacryloyl chloride following a procedure developed by Kaiser and Woodruff[78] (Scheme 2) was unsuccessful, again yielding an array of products; likewise using a phase transfer catalysis (PTC) acylation route.[79] In a parallel reaction benzyl alcohol was readily converted to its corresponding ester by methacryloyl chloride using tetrabutylammonium bromide (TBAB) as the catalyst and sodium hydride as the base. Use of the direct acid-catalysed esterification technique also proved unsuccessful.

Scheme 2: Dehydrogenation / acylation route

$$\mathrm{ROH} \xrightarrow[\text{THF - hexane}]{n\text{-}C_4H_9Li} \mathrm{ROLi} \xrightarrow[\text{1 hour}]{\text{R'COCl}} \mathrm{R'COOR} + \mathrm{LiCl}$$

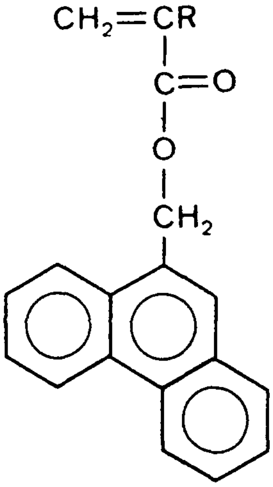
The 9-AMMA ester (24) was eventually synthesised via a base-catalysed acylation route following a number of modifications to both the reaction conditions and reagents as follows:

1) commercial grades of methacryloyl chloride, which were only of approximately 90% purity and containing phenothiazine as a stabiliser, were freshly distilled prior to use where previously they had been used as received - in addition laboratory prepared acid chlorides were also distilled before use, the acid chlorides prepared from the benzoyl chloride route being favoured over those prepared via the thionyl chloride route. Also, between use, the acid chlorides were stored at -20°C;

2) because of the highly exothermic nature of the initial reaction the acid chloride was added to the reaction mixture at temperatures between -10 and -5°C. The use of a greater volume of solvent also helped to dissipate heat and facilitated a more efficient stirring action thereby leading to greater homogeneity of the reaction mixture.

Either Et_3N or pyridine could be used as the base in the reaction process.[80] TLC analysis indicated one product with no unreacted starting material present. Both yield and melting point were higher than those reported in the literature (58% and 84-84.5°C respectively; c.f. 42% and 82-83°C.[80]).

(9-Anthryl)methyl acrylate (9-AMA, 23), unlike its methacrylate counterpart (9-AMMA, 24), was successfully prepared following a procedure similar to that of Simionescu et al[81] without the need for further purification of the acryloyl chloride - chloroform was the choice of solvent with Et_3N as the base. The temperature of the reaction mixture at the initial stage was not as critical as it had been for the synthesis of 9-AMMA (24), with reaction taking place at approximately 5°C, although the large amount of solvent present dissipated efficiently any heat generated during the initial phase of the reaction. The melting point for the 9-AMA ester was considerably higher (86-87°C) than that quoted by Simionescu et al (78-79°C).

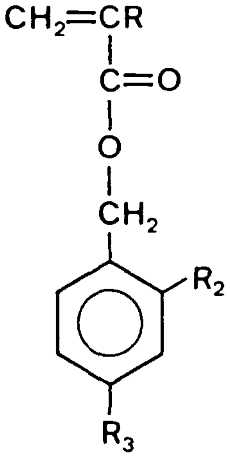


R = H : 9-PhMA (25)
R = CH3 : 9-PhMMA (26)

Fig. 30. Phenanthryl monomer systems.

The phenanthryl acrylate and methacrylate esters were synthesised in a similar manner. (9-Phenanthryl)methyl acrylate (9-PhMA, 25), a compound previously not reported in the literature, was prepared in high yield following esterification of (9-hydroxymethyl)phenanthrene (7) by acryloyl chloride with Et_3N as the base. Purification by repeated crystallisation from MeOH was required as TLC analysis of the reaction product indicated the presence of two impurities. (9-Phenanthryl)methyl methacrylate (9-PhMMA, 26) was prepared in good yield (65% and m.p. 74-76°C; c.f. 23.5% and m.p. 70.6-73.8°C[82]).

2.2.1.3 Methoxyphenyl Esters



R1	R2	R3	
H	OCH3	H	2-MPhA (27)
CH3	OCH3	H	2-MPhMA (28)
H	H	OCH3	4-MPhA (29)
CH3	H	OCH3	4-MPhMA (30)

Fig. 31. Methoxyphenyl ester monomer system.

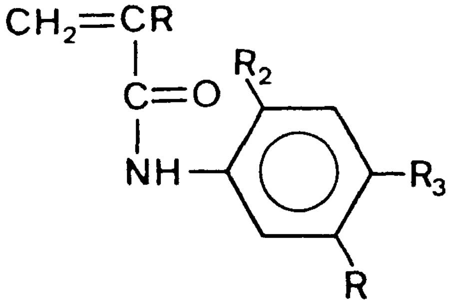
This series of monomers, both acrylates and methacrylates, were monosubstituted, with the methoxy group in either the ortho or para positions. The compounds, whose syntheses have not previously been reported, were prepared by condensation of monosubstituted methoxyphenols with the corresponding acid chlorides. With the exception of 4-methoxyphenyl methacrylate (4-MPhMA, 30), the three remaining compounds in the series, namely 2-methoxyphenyl acrylate (2-MPhA, 27), 2-methoxyphenyl methacrylate (2-MPhMA, 28), and 4-methoxyphenyl acrylate (4-MPhA, 29), were all successfully synthesised by base-catalysed acylation, Et3N being used as the base, and the freshly distilled acid chlorides added in 20% excess at sub-zero temperatures. Both 2-MPhA and 2-MPhMA, being oils, were purified by vacuum distillation over hydroquinone on a Kugelrohr short-path distillation apparatus and stored at -20°C.

Attempts to synthesise 4-MPhMA using similar reaction methods were unsuccessful - TLC analysis of the initial crude products indicated the presence of both starting material and two products; purification by recrystallisation and vacuum distillation on the Kugelrohr apparatus yielded chromatographically pure material though this was not apparent from ^{1}H-nmr spectra and melting point determinations where multiple solid-liquid phase transitions were observed over a broad range from 50-60°C. 4-MPhMA was eventually synthesised by phase transfer catalysed (PTC) acylation in high yield following a method by Illi[79] using sodium carbonate as the HCl acceptor and tetrabutylammonium bromide (TBAB) as the PTC catalyst. TLC analysis of the reaction mixture indicated that the reaction had gone to completion, the crystallised product being chromatographically pure and exhibiting a sharp melting point, 60-60.5°C.

2.2.1.4 Methoxyphenyl Amides

Monomers included both mono- and disubstituted methoxy acrylamides and methacrylamides (Fig. 31 below). In general their syntheses were relatively straightforward via base-catalysed reaction of the appropiate substituted aniline with the appropriate acid chlorides, addition being at sub-zero temperatures, employing either pyridine or Et_3N as the base. To improve yields, and guard against diacylation, the methoxyanilines were used in about 20% excess. A number of amides were also successfully synthesised by PTC acylation, and in high yield.

From literature surveys it would appear that the amides described below have not been previously synthesised. The monosubstituted methoxyphenyl amides include N-2-methoxyphenyl acrylamide (N-2-MPhA, 31) and methacrylamide (N-2-MPhMA, 32), and N-4-methoxyphenyl acrylamide (N-4-MPhA, 33) and methacrylamide (N-4-MPhMA, 34), substituted in the ortho and para positions respectively. The disubstituted amides were N-2,4-dimethoxyphenyl acrylamide (N-2,4-MPhA, 35) and methacrylamide (N-2,4-MPhMA, 36), and N-2,5-dimethoxyphenyl acrylamide (N-2,5-MPhA, 37) and methacrylamide (N-2,5-MPhMA, 38).



R1	R2	R3	R4	
H	OCH3	H	H	N-2-MPhA (31)
CH3	OCH3	H	H	N-2-MPhMA (32)
H	H	OCH3	H	N-4-MPhA (33)
CH3	H	OCH3	H	N-4-MPhMA (34)
H	OCH3	OCH3	H	N-2,4-MPhA (35)
CH3	OCH3	OCH3	H	N-2,4-MPhMA (36)
H	OCH3	H	OCH3	N-2,5-MPhA (37)
CH3	OCH3	H	OCH3	N-2,5-MPhMA (38)

Fig. 32. Methoxyphenyl amide monomer system.

A feature of the ^{1}H-nmr spectra of these amido compounds was the location of their NH signals as broadened peaks in the region 7.7-8.3ppm. It was also observed in the ^{1}H-nmr spectra of those methoxy- or dimethoxy-phenyl acrylamides and methacrylamides which contain a methoxy substituent ortho to the amido nitrogen that one of the aromatic protons was shifted considerably downfield, appearing in the 8.1-8.5ppm region. One such example is N-2,4-MPhMA (36) whose ^{1}H-nmr spectrum is shown in Fig. 33(a).

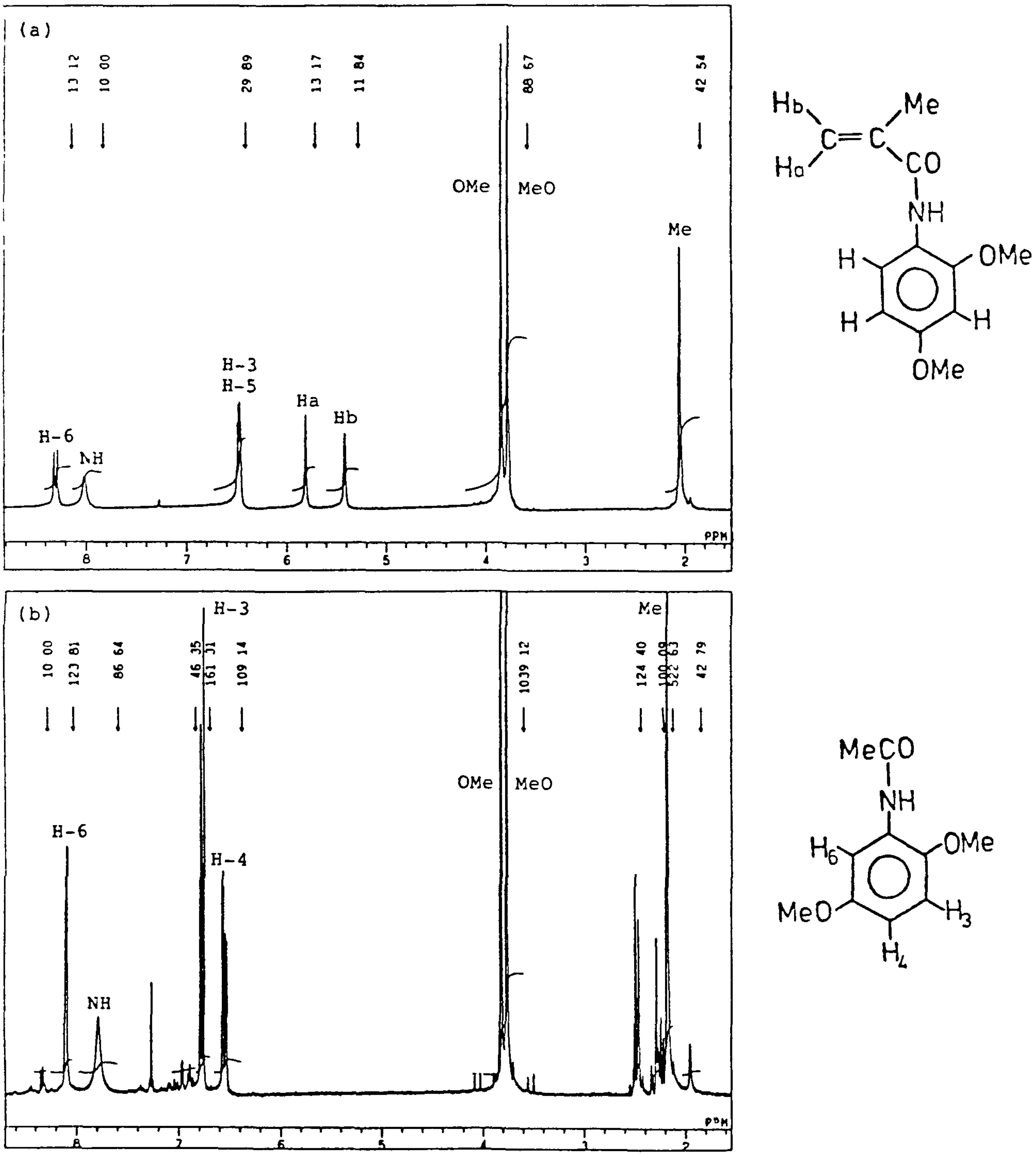


Fig. 33. ^{1}H-nmr spectra for (a) N-2,4-MPhMA (36); and (b) N-2,5-Dimethoxyphenyl acetamide (40) (slightly impure).

Analysis of the aromatic coupling constants exhibited by this series of amides confirmed that the deshielded proton in each case was H-6, that ortho to the amido nitrogen.

That the vinyl group is not responsible for the observed deshielding is confirmed by observation of the NMR spectrum of the model compound N-2,5-dimethoxyphenyl acetamide (40) which also displayed a large downfield shift for one of its aromatic protons [Fig. 33(b) above].

In the absence of a methoxy group otho to the amido nitrogen essentially no deshielding of the proton in the other ortho position occurs. For example the NMR spectrum of N-4-MPhMA (34) (Fig. 34) shows a normal 1,4-disubstituted pattern for the aromatic protons with the chemical shifts for H-2/H-6 at 7.44ppm. This is the value anticipated from examination of the NMR spectrum of acetanilide (PhNHCOMe) or acetoacetanilide ($PhNHCOCH_2COMe$). Phenacetin ($4EtOC_6H_4NHCOMe$) also displays the anticipated resonance for H-2/H-6 at δ 7.5.[83]

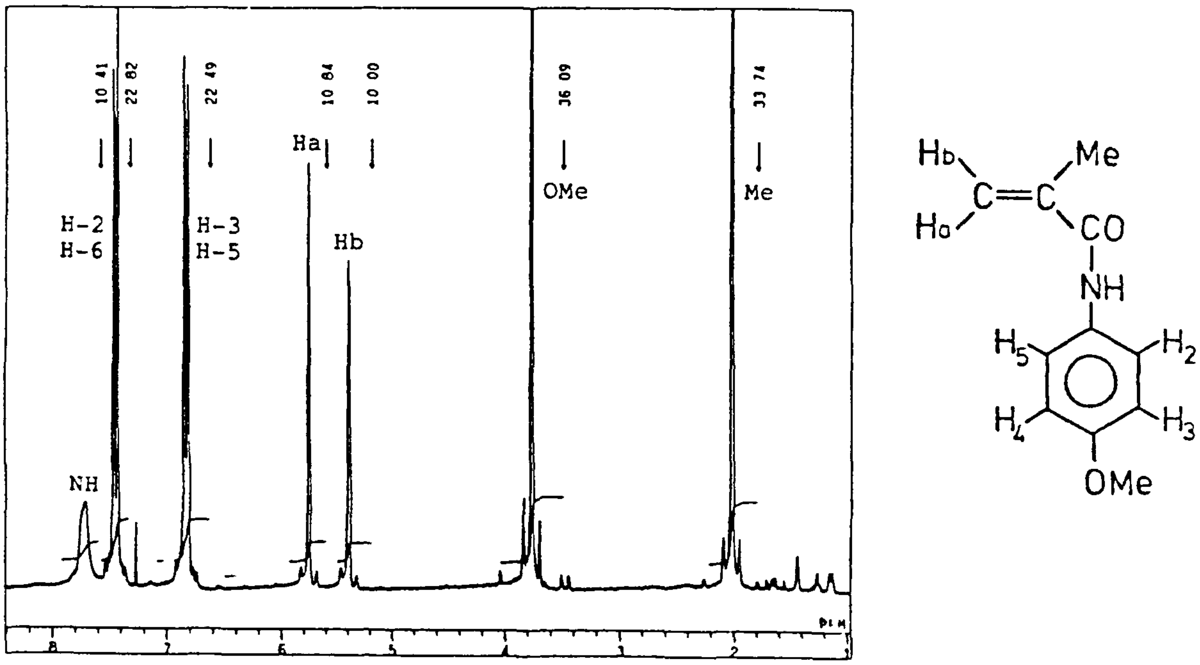
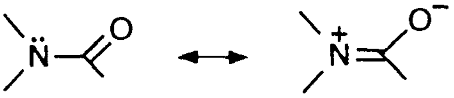


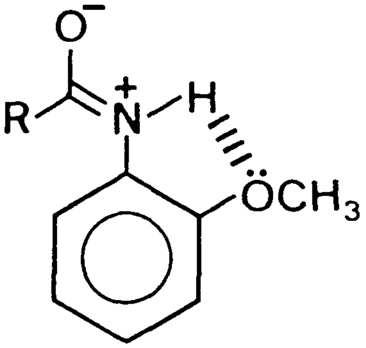
Fig. 34. 1-H-nmr spectrum of N-4-MPhMA (34).

In agreement with our observations above on the effect of a methoxy group ortho to the acylamino function, 2-acetoacetanisidide ($2\text{-}MeOC_6H_4NHCOCH_2COMe$) displays an aromatic resonance at δ 8.15 whereas both 4-acetoacetanisidide ($4\text{-}MeOC_6H_4NHCOCH_2COMe$) and 2-acetoacetaotoluidide ($4\text{-}MeC_6H_4\text{-}NHCOCH_2COMe$) display their lowest field aromatic absorption at δ 7.5.[83] It therefore appears that a 2-methoxy group may interact with an acylamino group to result in a deshielding effect on a hydrogen in the 6-position.

Restricted rotation about the amide C-N bond is a well known phenomenon[84] arising from cojugation between the carbonyl group and the nitrogen lone pair:



The zwitteronic canonical form which contributes to the amide resonance hybrid would be expected to be deshielding with respect to a hydrogen ortho to it on an aromatic ring. Possibly hydrogen bonding between a 2-methoxy substituent and an adjacent amido NH may enhance the stability of the zwitteronic form of the amido group increasing its contribution and thereby increasing the deshielding effect of the acylamino function on a proton sited at C-6. Further work will be necessary to elucidate the origin of this interesting effect.



2.2.2 POLYMERS

In general radical-induced addition polymerisation leads to vinyl polymers of 1,2-type structures:

$$n\,CH_2{=}CHX \xrightarrow{In^{\bullet}} \left[CH_2{-}CHX\right]_n$$

This was confirmed by the IR and ^{1}H-nmr spectra of the polymers prepared in this study. A typical example is the polymerisation of 2-(N-phthalimido)ethyl methacrylate (2-PEMA, 18) - the infrared spectra for both monomer and polymer are shown in Fig. 35 (a) and (b) respectively below. Characteristic bands of the monomer which disappeared on polymerisation were those due to C=C stretching vibrations in the vinyl group at about 1630 cm^{-1} and the CH bending vibrations in the same group.

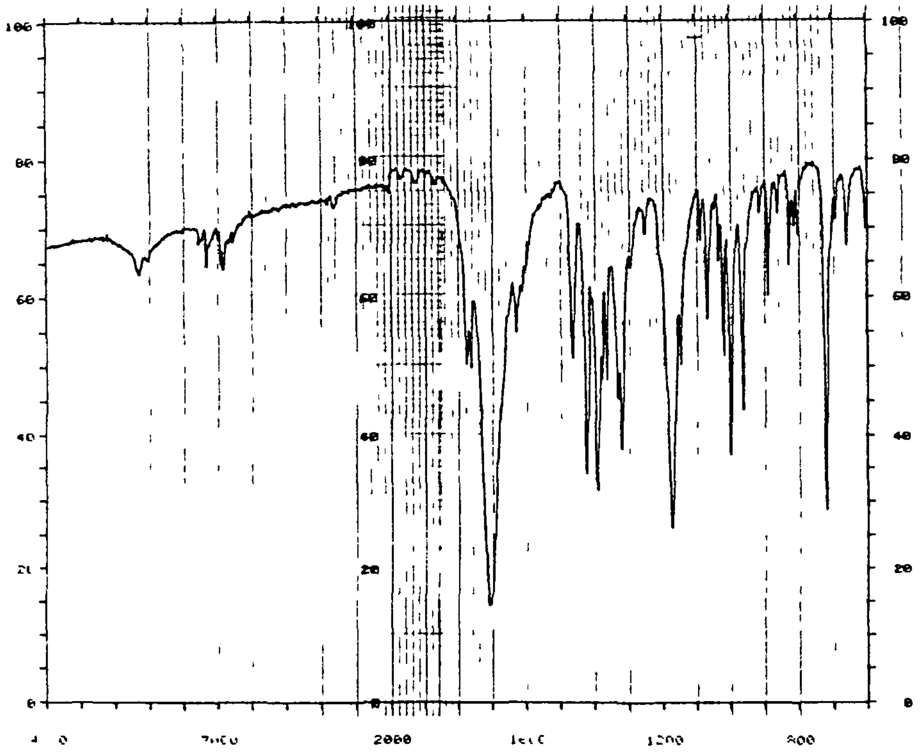


Fig. 35(a). IR spectrum (KBr) for 2-(N-phthalimid)oethyl methacrylate monomer (2-PEMA, 18).

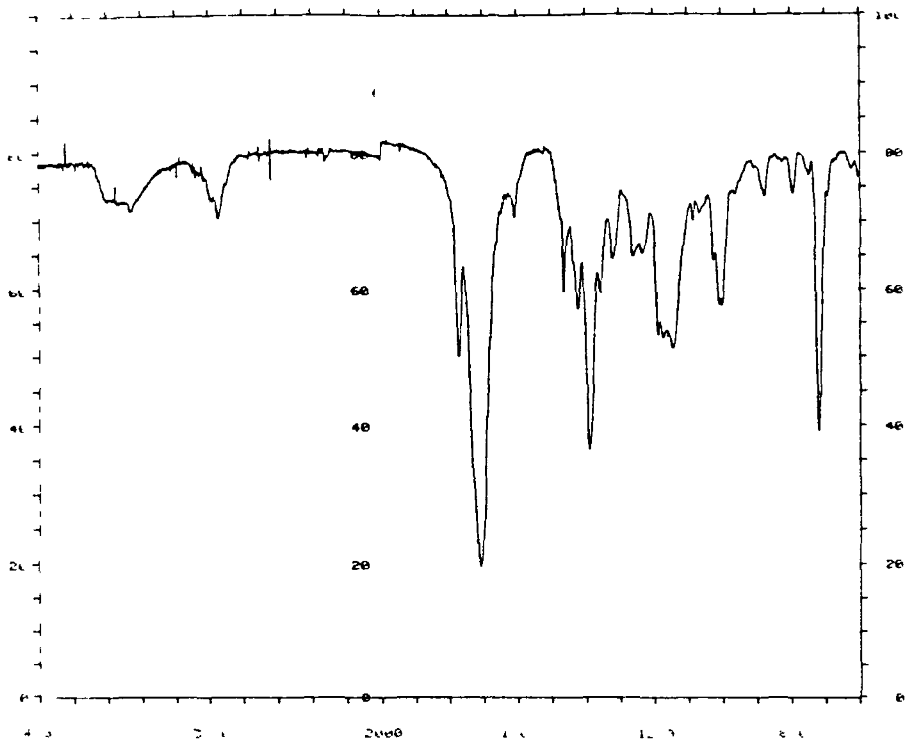


Fig. 35(b). IR spectrum (KBr) for poly(2-PEMA) (44) polymer.

Their ^1H-nmr spectra, illustrated below in Fig. 36 (a) and (b) were also in agreement with the normal 1,2-type polymer structures - saturation in the polymers result, as expected, in considerable upfield shifts for the previously olefinic

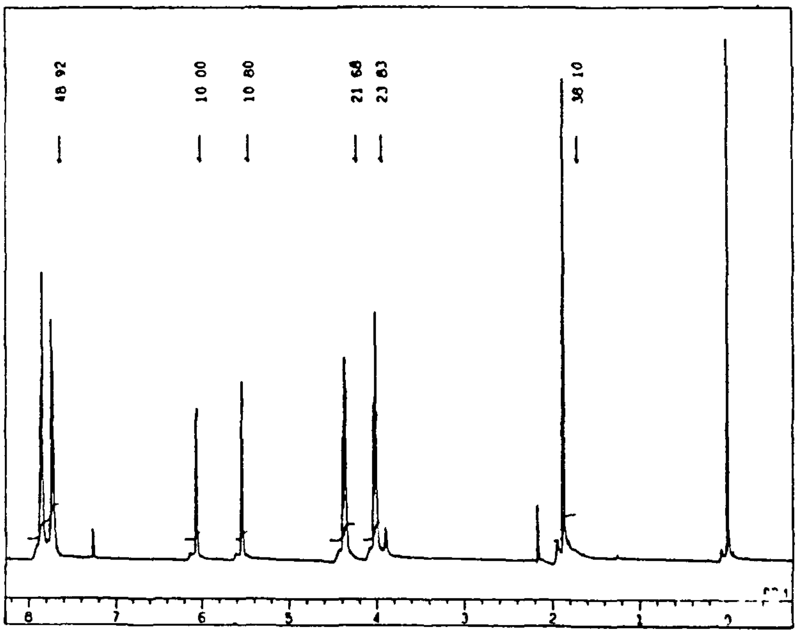


Fig. 36(a). ^1H-nmr spectrum of 2-PEMA (18) monomer.

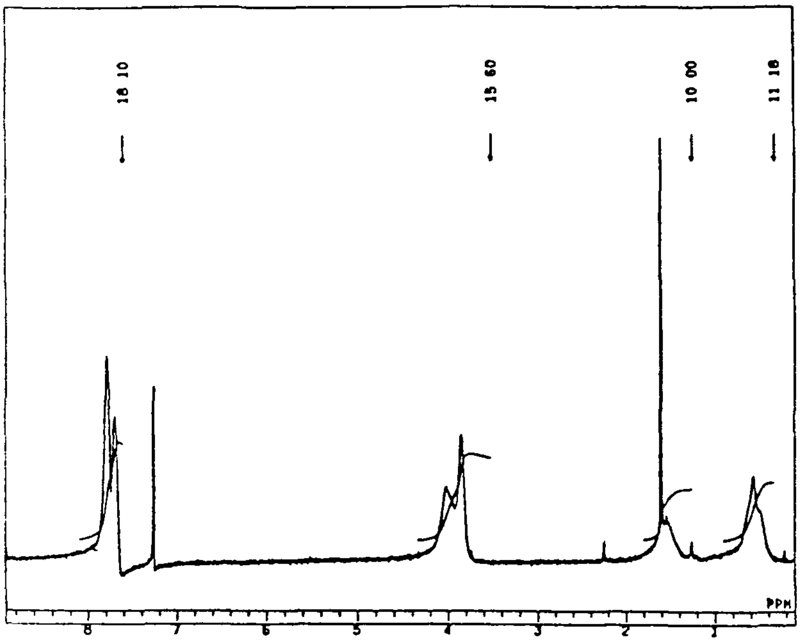
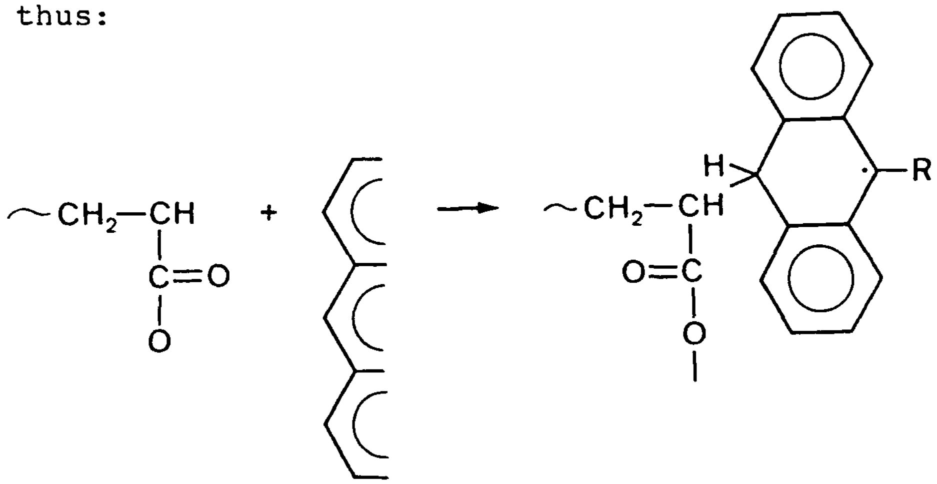


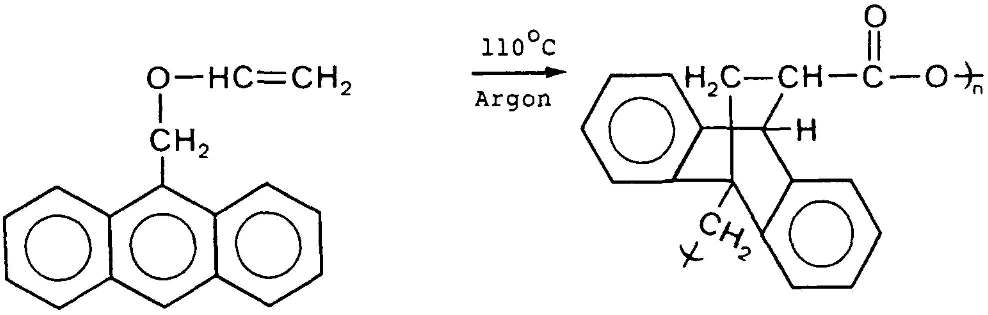
Fig. 36(b). ¹H-nmr spectrum of poly(2-PEMA) (44) polymer.

protons. Attempts to polymerise the phthalimido ester, 5-PPA (21) using free-radical initiation gave low conversion, low molecular weight products. Monomer recovery was high and monomer purity did not appear to be the cause of this anomalous finding.

A notable exception to the above was (9-anthryl)methyl acrylate (9-AMA, 23) which failed to polymerise by the free-radical route. The failure of the radical-induced polymerisation of this acrylate monomer was attributed to the fact that the anthracene group itself behaves as an efficient radical quencher and inhibitor leading to unreactive dibenzylic radicals thus:



However, at higher temperatures in the absence of AIBN, thermal polymerisation of 9-AMA occurred, probably via a Diels-Alder cycloaddition process of the acrylate group of one monomer molecule to the meso-anthracene positions of another molecule to yield a 9,10-type polymer (48) as proposed by Simionescu et al:[81]



Due to the presence of rigid and bulky side groups in these polymer systems they exhibited high melting points, with broad transition ranges. The absence of clearly defined melting points was indicative of high molecular weight amorphous polymers. The bulky nature of the side groups, coupled with the likelihood of lack of stereoregularity along the polymer chains, inhibited the ability to pack and crystallise and thus the polymers might reasonably be expected to be amorphous in nature. This was confirmed by differential scanning calorimetry (DSC) studies - a typial plot is illustrated for poly(2-PEMA) (44) in Fig. 37 overleaf. Although not readily apparent, owing to the sloping baseline (associated with a damaged sample pan in the DSC cell), it can be observed that the trace only yields peaks relating to endothermic transitions, namely glass transition (Tg), melting transition (Tm), and a transition associated with degradation (Td), (oxidation or crosslinking). No exothermic reaction indicative of crystallisation was observed.

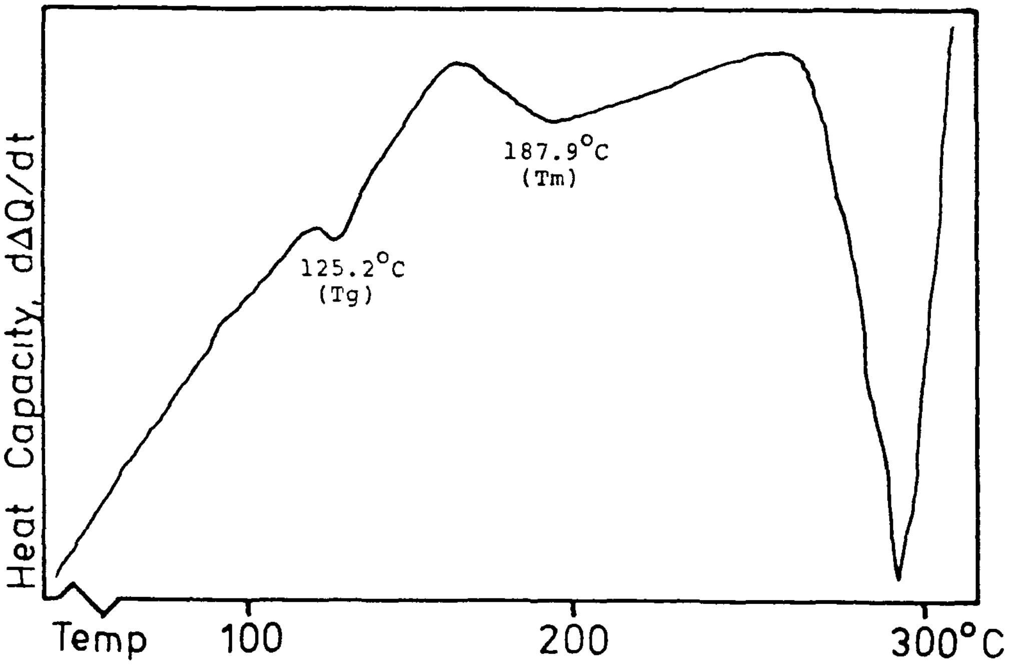


Fig. 37. DSC trace for poly(2-PEMA) (44).

The introduction of flexible alkyl side chains, as in the phthalimido series of polymers, resulted in a decrease in melting point, as expected, in ascending the series. The anthryl polymers exhibited no discernable transitions, decomposing on heating. Processing of these polymers in the molten state should be thus avoided. The polyamides exhibited the highest melting points, attributed to perhaps intermolecular H-bonding and also to the possibility of hindrance associated with the greater difficulty of rotation around the C-N bond. With few exceptions the methacrylate/methacrylamide polymers had higher melting points than their corresponding acrylic/ acrylamide counterparts - the presence of the methyl group causes a slight stiffening of the polymer chain by impeding rotation about the single C-C bond, this in turn effecting the increase in melting temperatures.

2.2.3 COPOLYMERS

A series of copolymers was prepared by radical copolymerisation of the electron-acceptor (A; phthalimido esters) and electron-donor (D; anthryl, phenanthryl and methoxyphenyl esters, and the methoxyphenyl amides) monomer pairs as detailed in the 'Experimental' chapter. For all the systems studied it was observed, on mixing solutions of the two monomer pairs prior to the copolymerisation reaction, that no colour change occurred which might have been indicative of intermolecular complexation between the donor and acceptor moieties - the significance of this will be discussed in detail in the proceeding section.

All the acrylate-acrylate and methacrylate-methacrylate type systems were successfully copolymerised. With the exception of 2-MPhMA/2-PEA (78) attempts to copolymerise acrylate-methacrylate copolymer systems failed - monomer recovery was high. This fact was rather surprising as there are many examples in the literature of such systems undergoing successful radical copolymerisation. Two of the attempted copolymerisation reactions involved the pairing of the donor monomer 9-AMMA (24) with the two acceptor monomers, PMA (15) and 2-PEA (17) respectively - these failures may possibly be attributed to the anthracene group acting as an efficient radical quencher and inhibitor leading to unreactive dibenzylic radicals as discussed above for the attempted radical-induced polymerisation of the 9-AMA (23) acrylate monomer.

Copolymer compositions were estimated from 'CHN' elemental analysis data. The majority of copolymers had equimolar compositions, also confirmed by their respective ^{1}H-nmr spectra - this is an important feature as intermolecular CT complexations are at a maximum for copolymers of 1:1 composition.^{25} IR spectra showed 'inter alia' broad carbonyl bands at approximatly 1710 cm^{-1} - for copolymers containing both ester and amide functionalities the carbonyl 'bands' was significantly broader due to the two seperate bands overlapping each other.

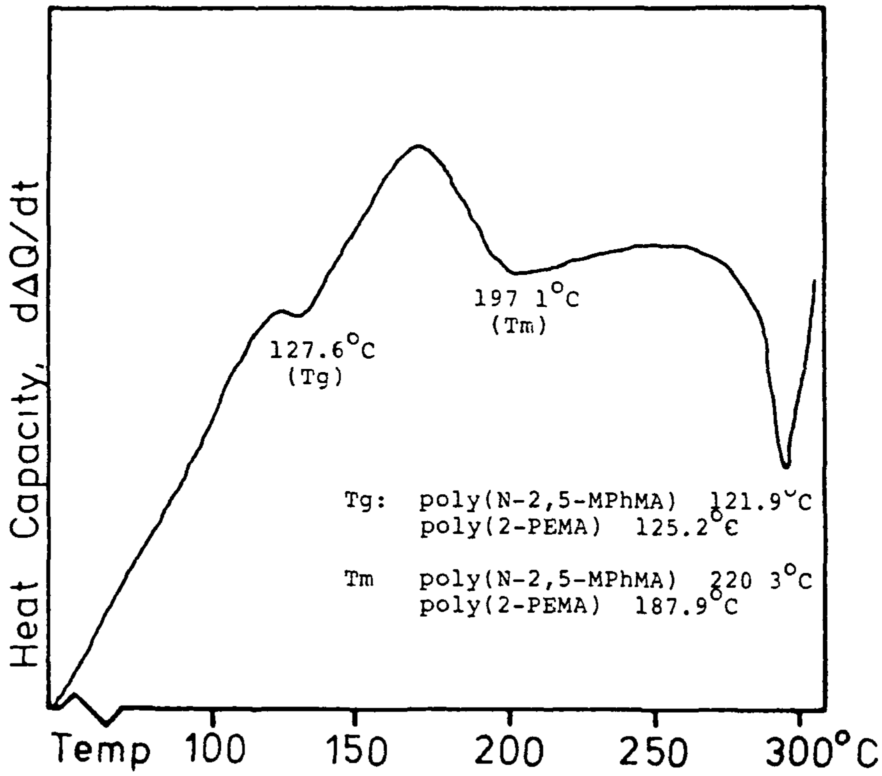


Fig. 38. DSC trace for poly(N-2,5-MPhMA-co-N-2-PEMA) (86) copolymer.

Studies of some of the copolymers using differential scanning calorimetry (DSC) indicated that they are random copolymers as both glass transition temperature (Tg), and melting transition temperature (Tm), do not fall between those of the corresponding homopolymers as would be expected of alternating copolymer systems. A typical example is that of poly(N-2,5-MPhMA-co-2-PEMA) whose DSC trace is shown in Fig. 38 above. The random nature of these copolymer systems provides further evidence for the absence of intermonomeric CT complexation in the copolymerisation reactions.

2.3 CHARGE TRANSFER STUDIES

In most complexes CT absorption can be detected as a weak long wavelength tail. However there was no such evidence of CT complexation as provided by U.V. and visible spectroscopy for any of the polymer based donor-acceptor (D-A) combinations studied in this work, i.e. polymer-small molecule, polymer-polymer or copolymer. Similarly for their respective monomers and model compounds no CT absorption peaks could be detected in the accessible range of the spectrometer up to 820nm, e.g. anthracene /N-methyl phthalimide in Fig. 39(c) overleaf. All mixtures, blends etc had been prepared in a 1:1 stoichiometry for the donor and acceptor components.

As no new absorption bands, associated with complex formation, were observed at the longer wavelengths the absence of colour changes on mixing the donor and acceptor components in both the the solid-state and in solution was not significant. However there was the possibility that CT bands may have been present but were being overlapped by the stronger absorptions of the parent donor and acceptor compounds. Accordingly the presence, or absence, of CT bands was determined by subtracting out the contribution of either the acceptor or donor (the choice depending on which component absorbs at the greater wavelength) from the absorption of the donor-acceptor mixtures, or copolymer, using a specialised software package in conjunction with the U.V. diode array spectrometer (for example, Fig. 39 overleaf). The results, as stated above, were negative for all D-A systems investigated using the phthalimido moiety as the acceptor group.

Recording of D-A solutions with either donor or acceptor solutions in the reference beam, each of the same concentration, and reading the differences directly yielded identical results. One such example was the D-A monomer pair 9-AMMA/N-2-PEMA (Fig. 40, page 78) prepared in an equimolar ratio.

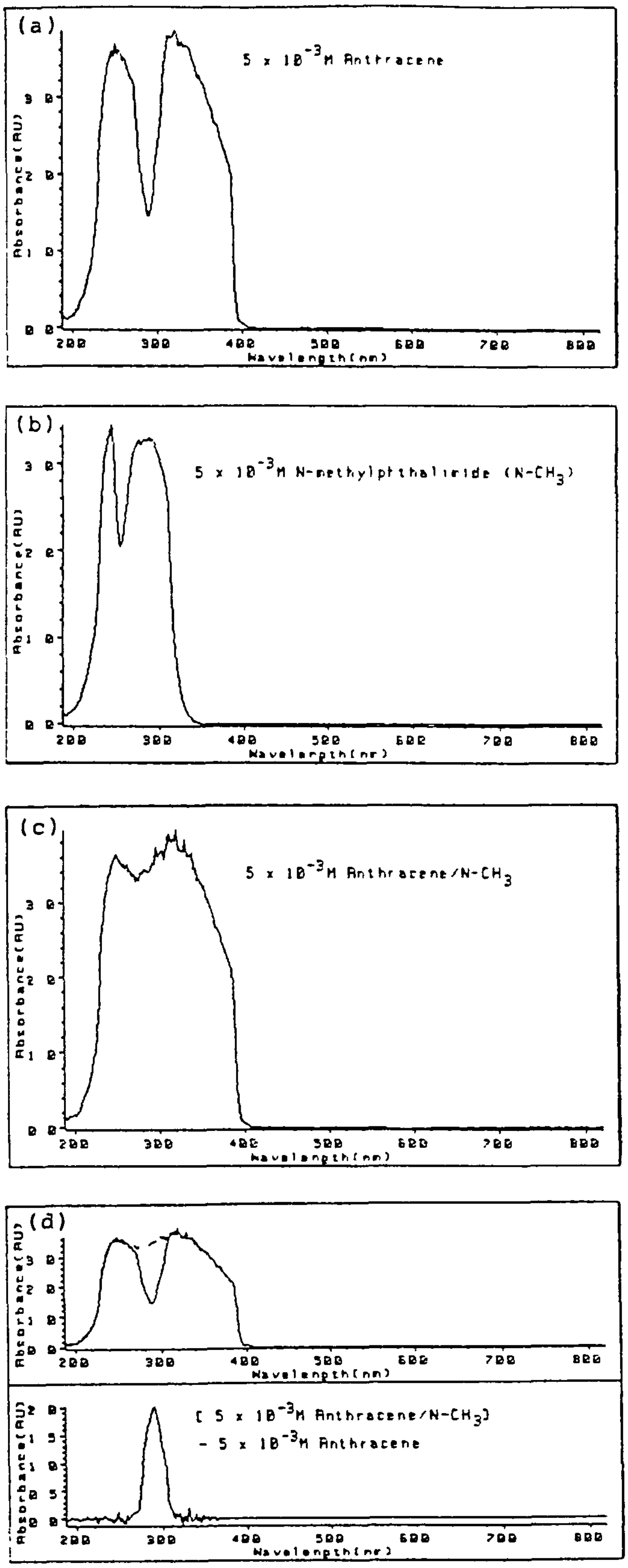


Fig. 39. U.V. spectra for (a) anthracene; (b) N-methyl phthalimide; (c) anthracene/N-methylphthalimide; (d) anthracene/N-methyl phthalimide with anthracene contribution subtracted out; total concentration 5×10^{-3}M, 1-cm cell, CH_2Cl_2.

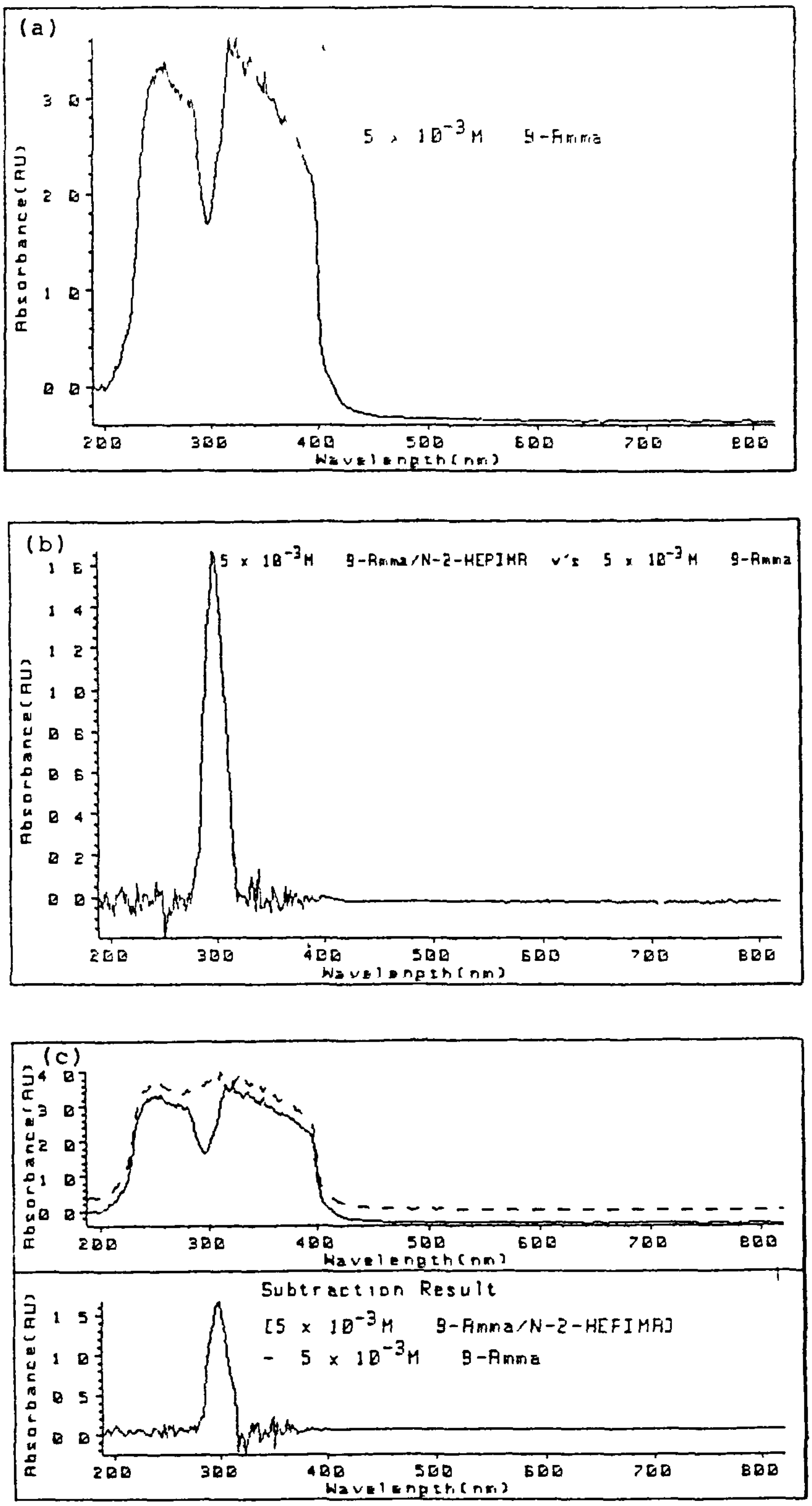
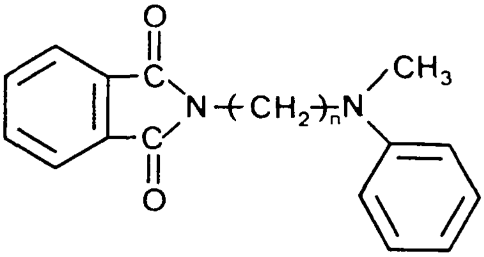


Fig. 40. U.V. spectra for (a) 9-AMMA/2-PEMA; (b) 9-AMMA/2-PEMA against 9-AMMA in reference cell; (c) 9-AMMA/2-PEMA with 9-Amma contribution subtracted out; total concentration 5 x 10^{-3}M, 1-cm cell, CH_2Cl_2.

The apparent failure of the phthalimido compounds to interact and complex with the various aromatic donor systems investigated was surprising, since CT interactions involving phthalimido compounds have been previously reported in the literature. Mazzocchi and co-workers have provided evidence for excited state electron transfer processes in N-methylphthalimide/ alkene systems.[85,86] Davidson and Lewis observed ground state intramolecular D-A complexes for a series of N-(aminoalkyl)-phthalimides by the appearance of CT transition bands in their



n = 0, 1, 2, 3, 4.

U.V. absorption spectra[87] - the intramolecular interaction between amine and imide groups was obtained over a wide concentration range (1 x 10^{-4}M to 1 x 10^{-2}M). J.H. Borkent and co-workers[88] reported inter- and intramolecular complexes containing the N-alkyltetrachlorophthalimide group as an electron acceptor and a variety of aromatic compounds as electron donors (e.g. carbazole, anisole, p-methylanisole etc.) where in most of the complexes CT absorption was detected as a long wavelength absorption tail.

D-A combinations for which U.V spectral studies were carried out are listed in the 'Experimental' chapter under section 3.5 titled 'U.V.Studies'. For a number of such D-A pairs investigations were made using a variety of solvent systems.

2.4 RESISTIVITY DETERMINATIONS

Attempts to measure the volume resistivities of the polymeric (D-A) systems, and for mixtures of their model donor and acceptor compounds, using the van der Pauw 4-point probe method[89], as detailed in Section 3.6, were unsuccessful. This was not perhaps surprising considering the poor CT complexation properties exhibited by these complexes. The 4-point probe arrangement is limited to measuring resistivities up to 10^9 ohms-cm. Similarly no values for electrical conductivity could be determined for a selection of samples tested at the Centre d'Etudes Nucleaire de Grenoble (CENG), France by Dr. J.G. Vos of the School of Chemical Sciences, DCU, also using a 4-point probe technique. Donor-acceptor systems investigated were as follows:

Acceptor	Donor
1. N-methylphthalimide (39)	- anthracene
	- phenanthrene
	- 9-AMA (23)
	- poly(9-AMA) (48)
	- 9-AMMA (24)
	- poly(2-MPhA) (52)
	- poly(4-MPhA) (54)
2. PMA (15)	- anthracene
	- phenanthrene
3. PMMA (16)/poly(PMMA) (42)	- anthracene
	- phenanthrene
	- 9-AMA (23)
	- poly(9-AMA) (48)

Acceptor	Donor
4. 2-PEA (17)/poly(2-PEA) (43)	- anthracene
	- phenanthrene
	- 9-AMA (23)
	- poly(9-AMA) (48)
	- 9-AMMA (24)
5. 2-PEMA (18)/poly(2-PEMA) (44)	- anthracene
	- phenanthrene
	- 9-AMA (23)
	- poly(9-AMA) (48)
	- 9-AMMA (24)

2.5 CONCLUDING REMARKS

From the evidence of their U.V. absorption spectra it would appear that there was no CT complexation for any of the D-A combinations investigated using the phthalimido group as the acceptor. Presumably more effective donor groups, for example aromatic amines, might have proved more effective.

CHAPTER 3: EXPERIMENTAL

3.1 GENERAL TECHNIQUES

Unless otherwise stated the following apply. Melting points were recorded in glass capillary tubes. The boiling points of oils were determined during purification on a Kugelrohr short-path distillation apparatus. Reaction courses and product mixtures were routinely monitored by TLC on precoated silica gel plates (Riedel-de Haen DC ALF) treated with a fluorescent indicator and after development were examined under an ultraviolet light operating at 254nm.

Infrared spectra were measured on a Perkin-Elmer 983 G spectrometer as thin films on NaCl plates (oils) or in nujol mulls or KBr discs (solids). Nuclear Magnetic Resonance (^1H-nmr) spectra were initially run on a Perkin-Elmer R12-B instrument operating at 60 MHz. The majority of spectra reported below were recorded on a Jeol GX 270 S.C.M. spectrometer operating at 270 MHz by the NMR section, Department of Chemistry, University College Galway, Ireland. Spectra were run in deuterochloroform ($CDCl_3$) and peak positions are given in parts per million downfield from tetramethylsilane (TMS) as the internal reference. ^{13}C-nmr were generally referenced to the centre peak of the solvent (77.10 for $CDCl_3$).

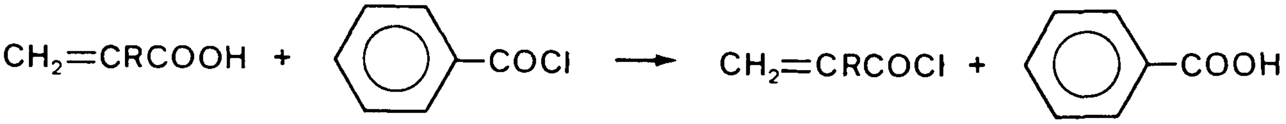
Micranalyses were carried out by the Microanalysis Department, University College Dublin, Belfield, Dublin 4, Ireland.

3.2 SYNTHESIS

3.2.1 STARTING MATERIALS

Acryloyl Chloride (1): Acryloyl chloride was prepared by reaction of acrylic acid and benzoyl chloride (Scheme 2).[90] A mixture of acrylic acid (36g, 0.5 mole; Riedel-de Haen - 99%) and benzoyl chloride (140g, 1 mole; Riedel-de Haen - 98%) was distilled rapidly over hydroquinone (0.5g) through a 25cm column containing Raschig rings. Distillate boiling up to 85°C was collected over hydroquinone (0.5g) in a receiver immersed in an ice/acetone bath and redistilled through a Claisen head containing Raschig rings, the fraction boiling in the range 72-74°C being collected. Yields of 25-30mL (50-60%) acryloyl chloride were obtained which was stored at -20°C.

Scheme 3: Preparation of acryloyl chloride



R = H, CH3

Methacryloyl Chloride (2): Methacryloyl chloride was prepared from methacrylic acid (Riedel-de Haen - 99%) following a similiar procedure to that used for acryloyl chloride above. Fractional distillation was carried out under reduced pressure and the fraction boiling at 93-96°C was collected. Typical yields were approximately 40mL (70%) and the acid chloride was stored at -20°C.

The above acid chlorides were also prepared from their corresponding acids and thionyl chloride,[91] $SOCl_2$, (though in poor yields) and were obtained commercially from both Aldrich and Janssen. Commercial grades of methacryloyl chloride were stabilised with phenothiazine (typically at levels of 150ppm) and being technical grades of approximately 90% purity required further purification prior to use.

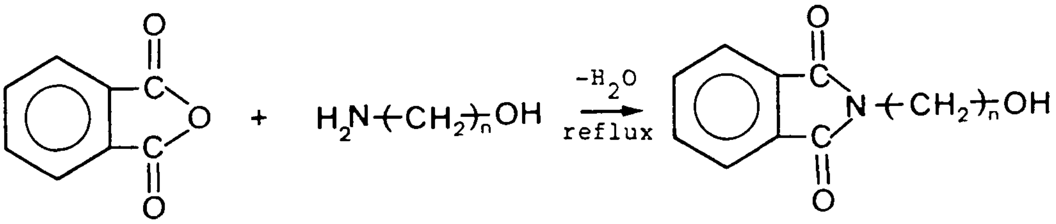
N-(Hydroxymethyl)phthalimide (3): was prepared as follows.[92] A mixture of phthalimide (102g, 0.7 mole; Aldrich - 98%), 40% formalin (52mL, 0.7 mole) and 350mL H_2O were boiled under reflux for 10-15 minutes until a clear solution resulted. The solution was allowed to cool overnight and the white crystalline product was filtered with suction, washed with ice-water and air dried to give N-(hydroxymethyl)phthalimide (107g, 86%), m.p. 136-139°C, no improvement on recrystallising from ethanol (lit.,[93] 149.5°C); $\nu_{max.}$ 3440br (OH), 1774 and 1696cm^{-1} (C=O); δ_H (60 MHz; DMSO-d_6/$CDCl_3$) 5.05 (2H, d, $NC\underline{H}_2$), 6.45 (1H, t, $O\underline{H}$) and 7.7-8.0 (4H, m, aromatic).

N-(Hydroxymethyl)phthalimide was also obtained commercially (Aldrich - 97%).

N-(2-Hydroxyethyl)phthalimide (4): To a well-stirred mixture of phthalic anhydride (74g, 0.5 mole; Riedel-de Haen - 99%) in 200mL toluene was added ethanolamine (30mL, 0.5 mole; Hopkins & Williams - 99%) dropwise over 15-20 minutes. The reaction mixture was then heated under reflux for 4 hours in a Dean-Stark apparatus and allowed to cool overnight during which the crude product crystallised out. N-(hydroxyethyl)phthalimide was recrystallised twice from H_2O yielding colourless crystals (yields $\geqslant$ 85%), m.p. 127-128°C (lit.,[94] 127°C); $\nu_{max.}$ 3460br (OH), 1762 and 1689cm^{-1} (C=O); δ_H (60 MHz; $CDCl_3$) 2.65 (1H, s, $O\underline{H}$), 3.9 (4H, s, $(C\underline{H}_2)_2$), and 7.65-8.05 (4H, m, aromatic).

N-(3-Hydroxypropyl)- and N-(5-hydroxypentyl)phthalimide (see below) were prepared in a similar manner to above from the corresponding amino alcohols, i.e. 3-aminopropan-1-ol (Riedel-de Haen - 99%) and 5-aminopentan-1-ol (Aldrich - 97%) respectively:

Scheme 4: Preparation of N-hydroxyalkylphthalimides



n = 2, 3 or 5

N-(3-Hydroxypropyl)phthalimide (5): Yield 93.5%, white crystals, m.p. 75-77°C (from 30% EtOH) (lit.^{95}, 78-81°C) - TLC indicated product was chromatographically pure; νmax. 3404br (OH), 1756 and 1710cm^{-1} (C=O); δ_H (60MHz; $CDCl_3$) 1.9 (2H, q, C$\underline{H}_2$), 2.85 (1H, s, O$\underline{H}$), two overlapping triplets centred at 3.65 and 3.85 (4H, HOC$\underline{H}_2$ and C$\underline{H}_2$N respectively), and 7.6-8.05 (4H, m, aromatic)

N-(5-Hydroxypentyl)phthalimide (6): Yield 73%, opaque waxy solid, m.p. 39-41.5°C (35% MeOH); νmax. 3393br (OH), 1768 and 1706cm^{-1} (C=O); δ_H (60 MHz; $CDCl_3$) 1.05-2.0 (6H, m, $(C\underline{H}_2)_3$), 3.15 (1H, s, O$\underline{H}$), 3.4-3.95 (4H, m, HOC$\underline{H}_2$ and NC$\underline{H}_2$), and 7.65-8.05 (4H, m, aromatic).

9-(Hydroxymethyl)phenanthrene (7): was prepared by $NaBH_4$ (2.2g, 0.058 mole) reduction of phenanthrene-9-carboxaldehyde (10g, 0.048 moles; Aldrich) in 250mL refluxing MeOH.^{96} After 4 hours the solution was cooled and diluted with warm water and the white crystals precipitated were filtered, dried overnight in vacuo - yield 96%, white crystals, m.p. 150.5°C (from benzene) (lit.,[97] 149-149.5°C); $\nu_{max.}$ 3183br cm^{-1} (OH); δ_H (60 MHz; $CDCl_3$/DMSO-d_6) overlapping triplet and doublet at 4.9-5.03 (3H, O<u>H</u> and C<u>H</u>$_2$O respectively) and 7.4-8.8 (9H, m, aromatic).

The following materials were obtained commercially and used without further purification: 9-(hydroxymethyl)anthracene (8) (Aldrich - 97%), 2-methoxyphenol (9) (BDH - 99%), 4-methoxyphenol (10) (BDH -98%), 2-methoxyaniline (11) (BDH - 98%), 4-methoxyaniline (12) (Aldrich - 97%), 2,4-dimethoxyaniline (13) (Riedel-de Haen - 97%), and 2,5-dimethoxyaniline (14) (Aldrich - 97%). Their purities were determined by IR and ^{1}H-nmr spectroscopy, and TLC prior to use.

3.2.2 MONOMERS

The monomers described below are either esters or amides prepared from the condensation of acryloyl/methacryloyl chloride with the corresponding alcohol/phenol or aniline respectively. Two general procedures, and variations thereof, were employed for their syntheses. In all cases the acid chlorides were freshly distilled prior to use and solvents and reagents were purified and dried according to standard procedures.[98]

<u>General Preparation Of Esters/Amides</u>: These were base-catalysed reactions where pyridine or triethylamine served also as HCl acceptors. Typically the appropriate alcohol/phenol (0.025 moles) was vigorously stirred in 25mL solvent (MeCN, THF, or $CHCl_3$) containing pyridine or Et_3N as the base (in equimolar quantities to the acid chloride) for approximately 15 minutes. The resulting mixture was then cooled to sub-zero temperatures (-5 to -10°C) in an ice/acetone bath and treated during 10-15 minutes by the dropwise addition of the acid chloride (0.03-0.05

moles in 10-15mL solvent) (Scheme 5(i).). The solution was heated gradually to 50°C in an oil bath and maintained at this temperature for 3 hours after which it was cooled in an ice bath and 50mL H_2O added. The aqueous phase was extracted with three 50mL portions of diethyl ether/$CHCl_3$ and the combined organic phases were successively washed with 5% aq. HCl, 5% aq. $NaHCO_3$, H_2O and saturated NaCl solution, and then dried over anhydrous $MgSO_4$. After solvent removal on a rotary evaporator the crude product was purified by vacuum distillation (over hydroquinone) or recrystallisation using activated charcoal. Oils were stored at -20°C.

<u>Scheme 5</u>: Base-catalysed acylation

(i) Ester

$$\underset{\text{excess}}{CH_2{=}CRCOCl} \qquad R_1OH \xrightarrow[<0^{\circ}C]{Et_3N} CH_2{=}CRCOOR_1$$

(ii) Amide

$$CH_2{=}CRCOCl \qquad \underset{\text{excess}}{R_1NH_2} \xrightarrow[<0^{\circ}C]{Et_3N} CH_2{=}CRCONHR_1$$

R = H, CH_3; R_1 = appropriate donor or
acceptor group.

Amides were prepared in a similar manner except that the anilines were used in excess (approximately 20%) over the acid chlorides and any unreacted starting material remaining at the end was removed by washing with a 5% aq. HCl solution.

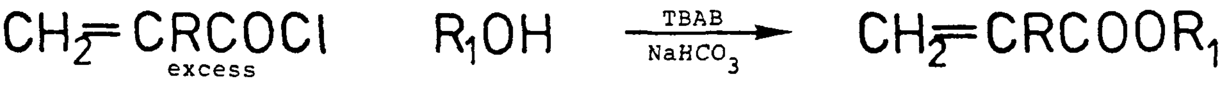
Alternative Procedure - Phase Transfer Catalysed (PTC) Acylation:[79]

This route utilised tetrabutylammonium bromide (TBAB; Aldrich - 99%) as the phase transfer catalyst with the HCl acceptor being an inorganic base, powdered sodium carbonate, used in large excess (see Scheme 6.). As above, ester syntheses required an excess of acid chloride over the alcohol/phenol whereas for the synthesis of amides the amines were used in excess.

To a well-stirred mixture of alcohol/phenol (0.04 moles), CH_2Cl_2 (100mL), TBAB (46mg) and powdered Na_2CO_3 (10g) a solution of the appropriate acid chloride (0.048 moles), in CH_2Cl_2 (20mL), was added dropwise, over 30-40 minutes, at room temperature. Stirring was continued for an additional 2 hours whereupon the mixture was filtered, washed with solvent and concentrated on the rotary evaporator. The resulting crude product was then purified by the usual methods, with oils being stored at -20°C.

Scheme 6: PTC acylation

(i) Ester



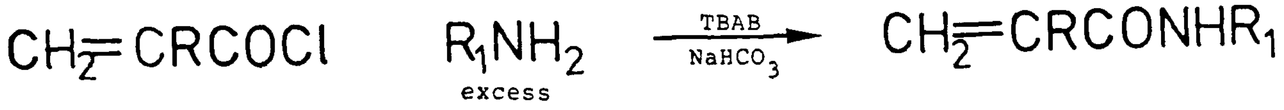
$$\underset{\text{excess}}{CH_2{=}CRCOCl} \qquad R_1OH \xrightarrow[NaHCO_3]{TBAB} CH_2{=}CRCOOR_1$$

R = H, CH_3;
R_1 = appropriate donor or acceptor group.

Although the above procedure pertains to ester syntheses it was similar to that used for acylation of the anilines with one exception - the excess starting material at the end of the reaction had to be removed, as determined by TLC, by thoroughly

Scheme 6: PTC acylation cont'd...

(ii) Amide



$$CH_2{=}CRCOCl \quad \underset{\text{excess}}{R_1NH_2} \xrightarrow[NaHCO_3]{TBAB} CH_2{=}CRCONHR_1$$

R = H, CH_3;

R_1 = appropriate donor or acceptor group.

washing the organic phase with a 5% aq. HCl solution and drying over anhydrous $MgSO_4$ before removal of the solvent to yield the crude product.

Esters and amides that have been prepared successfully by PTC acylation are marked with an asterix (*) below.

(N-Phthalimido)methyl Acrylate (15): from (3) and (1), yield 70%, pale yellow crystals, m.p. 133-136°C (from MeOH) (lit.,[76] 117-120.5°C); (Found: C, 60.96; H, 3.70; N, 5.71. $C_{12}H_9NO_4$ requires C, 62.34; H, 3.92; N, 6.05%); $\lambda_{max.}$ (MeOH) 218 (ϵ 50,700 dm^3 mol^{-1} cm^{-1}), 238sh (10,500), and 294nm (2,100); $\nu_{max.}$ 1780 and 1711vs cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 5.74 (2H, s, $COC\underline{H}_2N$), 5.78-5.83 (1H, dd, J 1.4 and 10.4Hz, Hb), 5.97-6.07 (1H, dd, J 10.4 and 17.2Hz, Hc), 6.35-6.42 (1H, dd, J 1.4 and 17.2Hz, Ha), 7.71-7.75 (2H, m, aromatic), and 7.84-7.89 (2H, m, aromatic); δ_C ($CDCl_3$) 60.96 ($-\underline{C}H_2-$), 124.11, 127.46, 131.83w, 132.33, 134.80 (aromatic and vinyl), 164.98 and 166.81 (carbonyl). Compound (15) is referred to in abbreviated form as PMA.

(N-Phthalimido)methyl Methacrylate (16): from (3) and (2), yield 86%, white crystals, m.p. 134°C (from MeOH); (Found: C, 64.10; H, 4.60; N, 5.64. $C_{13}H_{11}NO_4$ requires C, 63.67; H, 4.52; N, 5.71%); $\lambda_{max.}$ (MeOH) 218 (ε 51,400 dm^3 mol^{-1} cm^{-1}), 238sh (9,500), and 294nm (2,000); $\nu_{max.}$ 1779 and 1707vs cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 1.92 (3H, s, $C\underline{H}_3$), 5.60 (1H, s, Hb), 5.79 (2H, s, $OC\underline{H}_2N$), 6.12 (1H, s, Ha), 7.77-7.8 (2H, m, aromatic) and 7.92-7.95 (2H, m, aromatic); δ_C ($CDCl_3$) 18.06 (w, $\underline{C}H_3$), 61.15 ($\underline{C}H_2$), 123.92, 126.83w, 131.76w, 134.61, 135.37 (aromatic and vinyl), 166.12w and 166.69w (carbonyl); Compound (16) is referred to in abbreviated form as PMMA.

2-(N-Phthalimido)ethyl Acrylate (17): from (4) and (1) in a similar manner to general procedure above except that the acid chloride was added at room temperature. Yield 36%, white crystals, m.p. 111-112°C (from MeOH) (lit.,[76] yield 65%; m.p. 112-113.5°C); (Found: C, 63.50; H, 4.61; N, 5.66. Calc. for $C_{13}H_{11}NO_4$: C, 63.67; H, 4.52; N, 5.71%); $\nu_{max.}$ 1767 and 1722vs cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 3.99-4.04 (2H, t, J 5.5Hz, $C\underline{H}_2N$), 4.39-4.43 (2H, t, J 5.5Hz, $OC\underline{H}_2$), 5.80-5.85 (1H, dd, J 1.4 and 10.4 Hz, Hb), 6.01-6.12 (1H, dd, J 10.4 and 17.2Hz, Hc), 6.34-6.41 (1H, dd, J 1.4 and 17.2Hz, Ha), 7.71-7.76 (2H, m, aromatic) and 7.83-7.89 (2H, m, aromatic). Compound (17) is referred to in abbreviated form as 2-PEA.

2-(N-Phthalimido)ethyl Methacrylate (18): was prepared from the condensation of methacrylic acid (Riedel-de Haen - 99%) and (4) using p-toluenesulphonic acid (BDH - 98%) as the acid catalyst as follows:[99] N-2-(hydroxyethyl)phthalimide (4) (19.1g, 0.1 moles) and methacrylic acid (8.6g, 0.1 moles) were refluxed over hydroquinone (1.0g) in 75mL toluene at 140°C for 6 hours in the presence of p-toluenesulphonic acid (0.5g) using a Dean-Stark apparatus.

The reaction mixture was allowed to cool, the toluene removed using a rotary evaporator and the concentrate cooled overnight in a fridge which resulted in the crude product crystallising out as a white mass. This was then dissolved in diethyl ether and washed thoroughly with 2% aq. NaOH solution to remove the hydroquinone and any traces of unreacted methacrylic acid, being finally dried over $MgSO_4$. Removal of the solvent yielded ester (18) (23g, 89%), white crystals, m.p. 99-100°C (from acetone) (lit.,[76] 100.5-101.5°C); (Found: C, 65.09; H, 4.85; N, 5.37. Calc. for $C_{14}H_{13}NO_4$: C, 64.85; H, 5.05; N, 5.37); $\lambda_{max.}$ (MeCN) 218 (ϵ 43,800 dm^3 mol^{-1} cm^{-1}), 240sh (13,200), and 292nm (2,800); $\nu_{max.}$ 1760 and 1705vs (C=O); δ_H (270MHz; $CDCl_3$) 1.87 (3H, s, $C\underline{H}_3$), 3.96-4.08 (2H, t, J 5.5Hz, $C\underline{H}_2N$), 4.32-4.46 (2H, t, J 5.5Hz, $OC\underline{H}_2$), 5.54 (1H, s, Hb), 6.08 (1H, s, Ha), 7.67-7.79 (2H, m, aromatic) and 7.83-7.91 (2H, m, aromatic). Compound (18) is referred to in abbreviated form as 2-PEMA.

<u>3-(N-Phthalimido)propyl Acrylate</u> (19): from (5) and (1), yield 42%, cream crystals, m.p. 63-64°C (from MeOH); (Found: C, 64.53; H, 5.05; N, 5.37. $C_{14}H_{13}NO_4$ requires C, 64.85; H, 4.95; N, 5.40%); $\lambda_{max.}$ (MeCN) 220 (ϵ 36,500 dm^3 mol^{-1} cm^{-1}), 240sh (9,900), and 294nm (1,800); $\nu_{max.}$ 1765 and 1706vs cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 2.00-2.15 (2H, sextet, J 6.5Hz, $CH_2C\underline{H}_2CH_2$), 3.80-3.86 (2H, t, J 6.5Hz, $C\underline{H}_2N$), 4.19-4.24 (2H, t, J 6.5Hz, $OC\underline{H}_2$), 5.77-5.82 (1H, dd, J 1.4 and 10.2Hz, Hb), 6.0-6.11 (1H, dd, J 10.2 and 17.5Hz, Hc), 6.34-6.41 (1H, dd, J 1.4 and 17.5Hz, Ha), 7.71-7.81 (2H, m, aromatic) and 7.83-7.86 (2H, m, aromatic); δ_C ($CDCl_3$) 27.55 (β-$\underline{C}H_2$), 35.08 ($\underline{C}H_2N$), 61.91 ($O\underline{C}H_2$), 123.22, 128.16, 130.75, 132.02w, 133.91 (aromatic and vinyl), 165.93w and 168.27w (carbonyl). Compound (19) is referred to in abbreviated form as 3-PPA.

<u>3-(N-Phthalimidopropyl) Methacrylate</u> (20): from (5) and (2), yield 73%, cream crystals, m.p. 59-61°C (from MeOH); (Found: C, 65.68; H, 5.52; N, 5.05. $C_{15}C_{15}NO_4$ requires C, 65.92; H, 5.53; N, 5.12%); $\lambda_{max.}$ (MeCN) 218 (ϵ 38,500 dm^3 mol^{-1} cm^{-1}), 240sh (9,800), and 294nm (1,800); $\nu_{max.}$ 1764 and 1708 cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 1.92 (3H, s, $C\underline{H}_3$), 2.05-2.15 (2H, quintet, J 6.5Hz, $CH_2C\underline{H}_2CH_2$), 3.81-3.86 (2H, t, J 6.5Hz, $C\underline{H}_2N$), 4.19-4.23 (2H, t, J 6.5Hz, $OC\underline{H}_2$), 5.52 (1H, s, Hb), 6.08 (1H, s, Ha), 7.70-7.75 (2H, m, aromatic) and 7.81-7.86 (2H, m, aromatic); δ_C ($CDCl_3$) 18.19 (=$\underline{C}H_3$), 27.62 (β-$\underline{C}H_2$), 35.09 ($\underline{C}H_2N$), 61.98 ($OCO\underline{C}H_2$), 123.22, 125.50, 132.08w, 133.92, 136.13w (aromatic and vinyl), 167.19w and 168.31w (carbonyl). Compound (20) is referred to in abbreviated form as 3-PPMA.

<u>5-(N-Phthalimido)pentyl Acrylate</u> (21): from (6) and (1), yield 35%, clear colourless oil, b.p. approx. 130°C/0.015mbar; (Found: C, 65.99; H, 6.02; N, 4.64. $C_{16}H_{17}NO_4$ requires C, 66.88; H, 5.96; N, 4.87%); $\nu_{max.}$ 1767 and 1707vs cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 1.27-1.47 (2H, m, $CH_2C\underline{H}_2CH_2$), 1.69-1.79 (4H, m, J 7.2Hz, $OCH_2C\underline{H}_2$ and $C\underline{H}_2CH_2N$), 3.66-3.71 (2H, t, J 7Hz, $C\underline{H}_2N$), 4.12-4.17 (2H, t, J 6.6Hz, $OC\underline{H}_2$), 5.79-5.84 (1H, dd, J 1.6 and 10.2Hz, Hb), 6.06-6.16 (1H, dd, J 10.2 and 17.2Hz, Hc), 6.34-6.41 (1H, dd, J 1.6 and 17.2Hz, Ha), 7.71-7.76 (2H, m, aromatic) and 7.80-7.82 (2H, m, aromatic); δ_C ($CDCL_3$) 22.75 (γ-$\underline{C}H_2$), 27.68 (β-$\underline{C}H_2$), 37.11 ($\underline{C}H_2N$), 63.68 ($O\underline{C}H_2$), 122.52, 128.09, 129.86, 131.64w, 133.34 (aromatic and vinyl), 165.36w and 167.57w (carbonyl). Compound (21) is referred to in abbreviated form as 5-PPA.

<u>5-(N-Phthalimido)pentyl Methacrylate</u> (22): from (6) and (2), yield 78%, white waxy solid, m.p. 29.5-30.5°C (from MeOH); (Found: C, 67.64; H, 6.55; N, 4.55. $C_{17}H_{19}NO_4$ requires C, 67.75; H, 6.35; N,

4.64%); $\lambda_{max.}$ (MeCN) 218 (ϵ 38,400 dm^3 mol^{-1} cm^{-1}), 240sh (9,500), and 294nm (1,700); vmax. 1768 and 1710vs cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 1.36-1.47 (2H, m, $CH_2C\underline{H}_2CH_2$), 1.69-1.77 (4H, m, J 7Hz, $OCH_2C\underline{H}_2$ and $C\underline{H}_2CH_2N$), 1.91 (3H, s, $C\underline{H}_3$), 3.68-3.73 (2H, t, J 7.0Hz, $C\underline{H}_2N$), 4.12-4.16 (2H, t, J 6.4Hz, $OC\underline{H}_2$), 5.53 (1H, s, Hb), 6.08 (1H, s, Ha), 7.70-7.78 (2H, m, aromatic), and 7.80-7.85 (2H, m, aromatic); δ_C ($CDCl_3$) 18.19 ($=\underline{C}CH_3$), 23.25 (γ-$\underline{C}H_2$), 28.13 (β-$\underline{C}H_2$), 37.62 ($\underline{C}H_2N$), 64.32 ($O\underline{C}H_2$), 123.10, 125.12, 132.08w, 133.79, 136.83w (aromatic and vinyl), 167.13w and 168.07 (carbonyl). Compound (22) is referred to in abbreviated form as 5-PPMA.

(9-Anthryl)methyl Acrylate (23): from (8) and (1), yield 77%, orange crystals, m.p. $86-87^{o}C$ (from MeOH) (lit.,[81] yield 73%, m.p. $78-79^{o}C$); (Found: C, 81.96; H, 5.31. $C_{18}H_{14}O_2$ requires C, 82.42; H, 5.37%); $\lambda_{max.}$ (MeOH) 254 (ϵ 140,800 dm^3 mol^{-1} cm^{-1}), 348 (6,300), 366 (9,500), and 384nm (8,700); vmax. 1706vs cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 5.76-5.80 (1H, dd, J 1.5 and 10.2Hz, Hb), 6.06-6.22 (1H, dd, J 10.2 and 17.2Hz, Hc), 6.22 (2H, s, $C\underline{H}_2O$), 6.37-6.44 (1H, dd, J 1.5 and 17.2Hz, Ha) and 7.45-8.49 (9H, m, aromatic); δ_C ($CDCl_3$) 59.51 ($\underline{C}H_2O$), 124.55, 125.75, 126.70w, 127.27, 128.85, 129.74, 129.86, 131.83, 132.02 (aromatic and vinyl), and 167.0 (w, $\underline{C}=O$). Compound (23) is referred to in abbreviated form as 9-AMA.

(9-Anthryl)methyl Methacrylate (24): from (8) and (2), yield 57.5%, yellow-orange crystals, m.p. $84-84.5^{o}C$ (from MeOH) (lit.,[80] yield 42%, m.p. $82-83^{o}C$); (Found: C, 82.18; H, 5.78. Calc. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.83%); $\lambda_{max.}$ (MeOH) 254 (ϵ 173,000 dm^3 mol^{-1} cm^{-1}), 348 (7,500), 366 (12,000), and 384nm (11,000); vmax. 1703vs cm^{-1} (C=O); δ_H (270MHz;

$CDCl_3$) 1.90 (3H, s, $C\underline{H}_3$), 5.47 (1H, s, Hb), 6.03 (1H, s, Ha), 6.18 (2H, s, $C\underline{H}_2O$), and 7.42-8.44 (9H, m, aromatic); δ_C ($CDCl_3$) 18.32 ($C\underline{C}H_3$), 59.13 ($O\underline{C}H_2$), 124.04, 125.06, 126.0, 126.19w, 126.57, 129.11, 131.13w, 131.38w, 136.19w aromatic and vinyl), and 167.58 (w, $O\underline{C}=O$). Compound (24) is referred to in abbreviated form as 9-AMMA.

(9-Phenanthryl)methyl Acrylate (25): from (7) and (1), yield 74%, white crystals, m.p. 94-97°C (from MeOH); (Found: C, 81.99; H, 5.44. $C_{18}H_{14}O_2$ requires C, 82.42; H, 5.38%); $\lambda_{max.}$ (MeOH) 252 (ϵ 70,800 $dm^3\ mol^{-1}\ cm^{-1}$), 210 (43,500), 220sh (33,400), 276sh (15,300), and 296nm (13,900); $\nu_{max.}$ 1723vs cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 5.68 (2H, s, $C\underline{H}_2O$), 5.81-5.85 (1H, dd, J 1.4 and 10.2Hz, Hb), 6.13-6.23 (1H, dd, J 10.2 and 17.2Hz, Hc), 6.42-6.49 (1H, dd, J 1.4 and 17.2Hz, Ha), and 7.55-8.72 (9H, m, aromatic); δ_C ($CDCl_3$) 64.67 ($O\underline{C}H_2$), 122.14, 122.84, 123.85, 126.26, 126.45, 126.57, 126.83, 127.90w, 128.16, 128.47, 129.36, 130.37w, 130.81 (aromatic and vinyl), and 165.68 (w, $\underline{C}=O$). Compound (25) is referred to in abbreviated form as 9-PhMA.

(9-Phenanthryl)methyl Methacrylate (26): from (7) and (2), yield 65%, white crystals, m.p. 74-75°C (from MeOH) (lit.,[100] 74-76°C); (Found: C, 82.29; H, 5.77. Calc. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.83%); $\lambda_{max.}$ (MeOH) 252 (ϵ 63,100 $dm^3\ mol^{-1}\ cm^{-1}$), 212 (42,000), 222sh (31,000), 276sh (13,500), 284 (10,800), and 296nm (10,200); $\nu_{max.}$ 1709vs cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 1.96 (3H, s, $C\underline{H}_3$), 5.55 (1H, s, Hb), 5.66 (2H, s, $OC\underline{H}_2$), 6.15 (1H, s, Ha), and 7.54-8.72 (9H, m, aromatic); δ_C ($CDCl_3$) 18.44 ($=C\underline{C}H_3$), 65.33 ($O\underline{C}H_2$), 122.52, 123.22, 124.30, 126.07, 126.64, 126.89, 127.21, 128.47, 128.85, 129.93, 130.43, 130.69, 131.19w, 136.26w (aromatic and vinyl), and 167.32 (w, $\underline{C}=O$). Compound (26) is referred to in abbreviated form as 9-PhMMA.

2-Methoxyphenyl Acrylate (27): from (9) and (1), yield 30%, colourless oil, b.p. 93-94°C/0.8mbar; (Found: C, 67.75; H, 5.81. $C_{10}H_{10}O_3$ requires C, 67.40; H, 5.65%); $\lambda_{max.}$ (MeOH) 272nm (ϵ 2,400 dm^3 mol^{-1} cm^{-1}); $\nu_{max.}$ 1739vs cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 3.79 (3H, s, $OC\underline{H}_3$), 5.96-6.0 (1H, d, J 10Hz, Hb), 6.29-6.39 (1H, dd, J 10 and 18Hz, Hc), 6.57-6.63 (1H, d, J 18Hz, Ha), and 6.92-7.23 (4H, m, aromatic); δ_C ($CDCl_3$) 55.84 ($O\underline{C}H_3$), 112.53, 120.75, 122.84w, 126.95, 127.65, 132.46, 139.61w, and 151.19w, (aromatic and vinyl). Compound (27) is referred to in abbreviated form as 2-MPhA.

2-Methoxyphenyl Methacrylate (28): from (9) and (2), yield 69%, colourless oil, b.p. 100-105°C/0.5mbar; (Found: C, 68.27; H, 6.35. $C_{11}H_{12}O_3$ requires C, 68.73; H, 6.29%); $\lambda_{max.}$ (MeOH) 210 (ϵ 19,600 dm^3 mol^{-1} cm^{-1}), and 272nm (2,400); $\nu_{max.}$ 1734vs cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 2.02 (3H, s, $C\underline{H}_3$), 3.73 (3H, s, $OC\underline{H}_3$), 5.68 (1H, s, Hb), 6.34 (1H, s, Ha), and 6.71-7.19 (4H, m, aromatic); δ_C ($CDCl_3$) 18.08 ($=C\underline{C}H_3$), 55.46 ($O\underline{C}H_3$), 112.21, 120.37, 122.52, 126.45, 126.64, 139.73w, 151.0w (aromatic and vinyl), and 164.98 (w, $\underline{C}=O$). Compound (28) is referred to in abbreviated form as 2-MPhMA.

4-Methoxyphenyl Acrylate (29): from (10) and (1), yield 34%, yellow oil, b.p. 78-79°C/ 0.2mbar; (Found: C, 67.79; H, 6.07. $C_{10}H_{10}O_3$ requires C, 67.40; H, 5.67%); $\lambda_{max.}$ (MeOH) 220sh (ϵ 9,600 dm^3 mol^{-1} cm^{-1}), and 272nm (2,700); $\nu_{max.}$ 1737vs cm^{-1} (C=O); δ_H (60MHz; $CDCl_3$) 3.6 (3H, s, $OC\underline{H}_3$), 5.6-5.9 (1H, Hb), 6.25-6.4 (1H, Hc), 6.5-6.65 (1H, Ha), and 6.7-7.05 (4H, m aromatic). Compound (29) is referred to in abbreviated form as 4-MPhA.

4-Methoxyphenyl Methacrylate (30)*: from (10) and (2), yield 79%, cream-white crystals, m.p. 60-60.5^{o}C (from MeOH/H_2O); (Found: C, 69.12; H, 6.35. $C_{11}H_{12}O_3$ requires C, 68.73; H, 6.29%); $\lambda_{max.}$ (MeOH) 276nm (ϵ 2,700 dm^3 mol^{-1} cm^{-1}); $\nu_{max.}$ 1724vs cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 2.05 (3H, s, $C\underline{H}_3$), 3.78 (3H, s, $OC\underline{H}_3$), 5.72 (1H, s, Hb), 6.32 (1H, s, Ha), 6.87-6.90 (2H, m, aromatic) and 7.00-7.05 (2H, m, aromatic); δ_C ($CDCl_3$) 18.89 (=$\underline{C}H_3$), 56.03 ($O\underline{C}H_3$), 114.93, 122.84, 127.46, 136.51w, 144.92w, 157.70w (aromatic and vinyl), and 166.69 (w, $\underline{C}$=O). Compound (30) is referred to in abbreviated form as 4-MPhMA.

N-2-Methoxyphenyl Acrylamide (31): from (11) and (1), yield 31%, cream-brown crystals, m.p. 67-68^{o}C (from MeOH/H_2O); (Found: C, 67.40; H, 6.10; N, 7.65. $C_{10}H_{11}NO_2$ requires C, 67.78; H, 6.25; N, 7.90%); $\lambda_{max.}$ (MeOH) 296 (ϵ 9,800 dm^3 mol^{-1} cm^{-1}). and 278nm (8,500); $\nu_{max.}$ 3226br (NH), and 1655vs cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 3.87 (3H, s $OC\underline{H}_3$), 5.72-5.76 (1H, dd, J 1.8 and 9.5Hz, Hb), 6.24-6.33 (1H, dd, J 9.5 and 16.8Hz, Ha), 6.39-6.45 (1H, dd, J 1.8 and 16.8Hz, Hc), 6.86-6.89 (1H, d, J 8Hz, aromatic H-3), 6.94-7.08 (2H, m, aromatic H-4 and H-5), 7.92br (1H, N$\underline{H}$), and 8.45-8.48 (1H, d, J 8Hz, aromatic H-6); δ_C ($CDCl_3$) 55.71 ($O\underline{C}H_3$), 109.87 , 119.93, 121.13, 123.91, 127.20, 127.52w, 131.57, 147.0w (aromatic and vinyl), and 163.26 (w, $\underline{C}$O). Compound (31) is referred to in abbreviated form as N-2-MPhA.

N-2-Methoxyphenyl Methacrylamide (32): from (11) and (2), yield 39%, v.light yellow oil, b.p. 118^{o}C/0.3mbar; (Found: C, 66.70; H, 6.50; N, 7.06. $C_{11}H_{13}NO_2$ requires C, 69.09, H, 6.85, N, 7.32%); $\lambda_{max.}$ (MeOH) 212 (ϵ 19,200 dm^3 mol^{-1} cm^{-1}), 260 (6,400), and 290nm (6,900); $\nu_{max.}$ 3426br (NH), and 1673cm^{-1}

(C=O); δ_H (270MHz; $CDCl_3$) 2.05 (3H, s, $C\underline{H}_3$), 3.84 (3H, s, $OC\underline{H}_3$), 5.42 (1H, s, Hb), 5.81 (1H, s, Ha), 6.82-6.86 (1H, dd, J 1.7 and 7.9, aromatic H-3), 6.91-7.05 (2H, m, aromatic H-4 and H-5), 8.22br (1H, s, N$\underline{H}$), and 8.40-8.44 (1H, dd, J 1.8 and 7.7Hz, aromatic H-6); δ_C ($CDCl_3$) 55.60 ($O\underline{C}H_3$), 109.74, 119.52, 119.79, 120.86, 123.62, 127.49, 140.73, 147.93 (aromatic and vinyl), and 165.94 ($\underline{C}$O). Compound (32) is referred to in abbreviated form as N-2-MPhMA.

<u>N-4-Methoxyphenyl Acrylamide</u> (33): from (12) and (1), yield 36%, beige crystals, m.p. 96-98°C (from $MeOH/H_2O$); (Found: C, 67.37; H, 6.41; N, 7.73. $C_{10}H_{11}NO_2$ requires C, 67.78; H, 6.41; N, 7.90%); $\lambda_{max.}$ (MeOH) 286nm (ϵ 12,400 dm^3 mol^{-1} cm^{-1}); $v_{max.}$ 3292br (NH), and 1656vs cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 3.67 (3H, s, $OC\underline{H}_3$), 5.58 (1H, dd, J 2.7 and 9Hz, Hc), 6.22 (2H, m, Ha and Hb), 6.62 (2H, d, J 9Hz, aromatic H-3 and H-5), 7.40 (2H, d, J 9Hz, aromatic H-2 and H-6) and 8.29br (1H, s, N$\underline{H}$); δ_C ($CDCl_3$) 55.39 ($O\underline{C}H_3$), 114.05, 122.14, 127.08, 131.07w, 131.38, 156.50w (aromatic and vinyl), and 163.97 (w, $\underline{C}$O). Compound (33) is referred to in abbreviated form as N-4-MPhA.

<u>N-4-Methoxyphenyl Methacrylamide</u> (34)*: from (12) and (2), yield 90%, purple crystals, m.p. 82-84°C (from MeOH); (Found: C, 69.25; H, 6.90; N, 7.00. $C_{11}H_{13}NO_2$ requires C, 69.09; H, 6.85; N, 7.32%); λ_{max} (MeOH) 272nm (ϵ 9,900 dm^3 mol^{-1} cm^{-1}); $v_{max.}$ 3306br (NH), and 1651vs (C=O); δ_H (270MHz; $CDCl_3$) 2.02 (3H, s, $C\underline{H}_3$), 3.72 (3H, s, $OC\underline{H}_3$), 5.39 (1H, s, Hb), 5.76 (1H, s, Ha), 6.81-6.85 (2H, d, J 9Hz, aromatic H-3 and H-5), 7.42-7.46 (2H, d, J 9Hz, aromatic H-2 and H-6), and 7.71br (1H, s, N$\underline{H}$); δ_C ($CDCl_3$) 18.76 ($=C\underline{C}H_3$), 55.46 ($O\underline{C}H_3$), 114.05, 119.68, 122.08, 130.94w, 140.75w, approx. 156w (aromatic and vinyl), and 166.75 (w, $\underline{C}$O). Compound (34) is referred to in abbreviated form as N-4-MPhMA.

N-2,4-Dimethoxyphenyl Acrylamide: (35): from (13) and (1), yield 34%, beige crystals, m.p. 121-123°C (from MeOH); (Found: C, 62.85; H, 5.98; N, 6.57. $C_{11}H_{13}NO_3$ requires C, 63.75; H, 6.32; N, 6.76%); $\lambda_{max.}$ (MeOH) 302 (ϵ 9,500 dm^3 mol^{-1} cm^{-1}), and 288nm (9,500); $\nu_{max.}$ 3233br (NH), 1663, 1649, and 1609vs cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 3.78 (3H, s, $OC\underline{H}_3$), 3.84 (3H, s, $OC\underline{H}_3$), 5.69-5.73 (1H, dd, J 1.3 and 9.7Hz, Hb), 6.22-6.32 (1H, dd, J 9.7 and 16.8Hz, Ha), 6.36-6.40 (1H, dd, J 1.3 and 16.8Hz, Hc), 6.46 (2H, m, aromatic H-3 and H-5), 7.74br (1H, s, $N\underline{H}$), and 8.34 (1H, d, J 9.5Hz, aromatic H-6); δ_C ($CDCl_3$) 55.46 ($O\underline{C}H_3$), 55.65 ($O\underline{C}H_3$), 98.54, 103.80, 120.82, 121.07w 126.76, 131.57, 149.29w, 156.56w (aromatic and vinyl), and 162.96 (w,$\underline{C}$O). Compound (35) is referred to in abbreviated form as N-2,4-MPhA.

N-2,4-Dimethoxyphenyl Methacrylamide (36)*: from (13) and (2) yield 69.5%, white crystals, m.p. 53-54°C (from $MeOH/H_2O$); (Found: C, 64.90; H, 6.73; N, 6.14. $C_{12}H_{15}NO_3$ requires C, 65.14; H, 6.83; N, 6.14%); $\lambda_{max.}$ (MeOH) 284nm (ϵ 9,600 dm^3 mol^{-1} cm^{-1}); $\nu_{max.}$ 3332 (NH), and 1652cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 2.06 (3H, s, $=CC\underline{H}_3$), 3.78 (3H, s, $OC\underline{H}_3$), 3.85 (3H, s, $OC\underline{H}_3$), 5.42 (1H, s, Hb), 5.81 (1H, s, Ha), 6.46-6.49 (2H, m, aromatic H-3 and H-5), 8.02br (1H, s, $N\underline{H}$), and 8.28-8.32 (1H, d, J 10Hz, aromatic H-6); δ_C ($CDCl_3$) 18.44 ($=C\underline{C}H_3$), 55.58 ($O\underline{C}H_3$), 56.16 ($O\underline{C}H_3$), 105.76, 108.54, 110.57, 119.93, 128.16w, 140.68w, 142.20w, 153.78 aromatic and vinyl), and 165.98 (w, $\underline{C}$O). Compound (36) is referred to in abbreviated form as N-2,4-MPhMA.

N-2,5-Dimethoxyphenyl Acrylamide (37): from (14) and (1), yield 56%, white crystals, m.p. 100-101°C (from $MeOH/H_2O$); (Found: C, 63.71; H, 6.47; N, 6.67. $C_{11}H_{13}NO_3$ requires C, 63.75; H, 6.32; N, 6.76%); $\lambda_{max.}$ (MeOH) 314nm (ϵ 8,700 dm^3 mol^{-1} cm^{-1});

$v_{max.}$ 3219br (NH), and 1654cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 3.78 (3H, s, $OC\underline{H}_3$), 3.83 (3H, s, $OC\underline{H}_3$), 5.72-5.76 (1H, d, J 10Hz, Hb), 6.23-6.32 (1H, dd, J 10 and 16.8Hz, Ha), 6.38-6.45 (1H, d, J 16.8Hz, Hc), 6.56-6.60 (1H, dd, J 3 and 9Hz, aromatic H-4), 6.77-6.80 (1H, d, J 9Hz, aromatic H-3), 7.93br (1H,s, N$\underline{H}$), and 8.21 (1H, d, J 3Hz, aromatic H-6); δ_C ($CDCl_3$) 55.71 ($O\underline{C}H_3$), 56.15 ($O\underline{C}H_3$), 106.08, 108.92, 110.69, 127.33, 128.16w, 131.51, 142.20w, 153.84w (aromatic and vinyl), and 163.27 (w, $\underline{C}O$). Compound (37) is referred to in abbreviated form as N-2,5-MPhA.

<u>N-2,5-Dimethoxyphenyl Methacrylamide</u> (38): from (14) and (2), yield 76%, yellow oil, b.p. 130-138°C/0.2mbar; (Found: C, 64.70; H, 7.12; N, 6.29. $C_{12}H_{15}NO_3$ requires C, 65.14; H,6.83; N, 6.33%); $\lambda_{max.}$ (MeOH) 308nm (ϵ 8,300 dm^3 mol^{-1} cm^{-1}); $v_{max.}$ 3423 (NH), and 1674vs cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 2.05 (3H, s, $=CC\underline{H}_3$), 3.77 (3H, s, $OC\underline{H}_3$), 3.82 (3H, s, $OC\underline{H}_3$), 5.45 (1H, s, Hb), 5.82 (1H, s, Ha), 6.53-6.58 (1H, dd, J 3 and 9Hz, aromatic H-4), 6.57-6.75 (1H, d, J 9Hz, aromatic H-3) 8.17-8.18 (1H, d, J 3Hz, aromatic H-6) and 8.26br (1H, s, N$\underline{H}$); δ_C ($CDCl_3$) 18.63 ($=\underline{C}CH_3$), 55.46 ($O\underline{C}H_3$), 55.77 (3H, s, $O\underline{C}H_3$), 98.55, 103.80, 119.62, 120.57, 121.20w, 140.88w, 149.35w, 156.44w (aromatic and vinyl), and 165.81 (w, $\underline{C}O$). Compound (38) is referred to in abbreviated form as N-2,5-MPhMA.

3.2.3 OTHER MATERIALS

<u>N-Methylphthalimide</u> (39): To phthalic anhydride (52g, 0.35 moles; Riedel-de Haen - 99%) was added, with intermittent shaking and cooling, 25% excess of aqueous methylamine (55g, 0.44 moles; Aldrich - 25% aqs) dropwise over 20 minutes. Water was removed slowly by heating to 100°C and kept there for 90 minutes after which the

residual cream-coloured material was heated to 210°C for 2.5 hours. The hot liquid was poured into a mortar, allowed to cool and the hard cake was crushed to a fine powder. The crude product was recrystallised twice from chloroform to give cream-white crystals of (39) (42.3g, 75%), m.p. 133°C (lit.,[101] 133-134°C); $\lambda_{max.}$ (MeCN) 218 (ϵ 38,000 dm^3 mol^{-1} cm^{-1}), 242sh (11 700), and 292nm (2,200); $\nu_{max.}$ 1754 and 1717cm^{-1} (C=O); δ_H (60MHz; $CDCl_3$) 3.14 (3H, s, $NC\underline{H}_3$), and 7.5-7.95 (4H, m, aromatic).

N-2,5-Dimethoxyphenyl Acetamide (40): prepared from acetylation of (14) using acetic anhydride - 0.5g of (14) was dissolved in 25mL 2M HCl to which was added crushed ice. A solution of 5g of hydrated sodium acetate in 25mL H_2O was introduced and the mixture was shaken well in an ice bath until the smell of acetic anhydride disappeared. The solid acetyl derivative was collected and recrystallised (from H_2O) to yield brown crystals of (40) (106mg, 17%), m.p. 90.5-91°C; (Found: C, 61.67; H, 7.01; N, 7.13. $C_{10}H_{13}NO_3$ requires C, 61.52; H, 6.71; N, 7.17%); $\nu_{max.}$ 3243 (NH), and 1652vs cm^{-1} (C=O); δ_H (270MHz; $CDCl_3$) 2.19 (3H, s, $C\underline{H}_3$), 3.77 (3H, s, $OC\underline{H}_3$), 3.83 (3H, s, $OC\underline{H}_3$), 6.53-6.58 (1H, dd, J 3 and 9Hz, aromatic H-4), 6.76-6.79 (1H, d, J 9Hz, aromatic H-3), 7.79br (1H, s, $N\underline{H}$), and 8.09-8.10 (1H, d, J 3Hz, aromatic H-6).

3.3 POLYMERISATION

The polymers described below were prepared by 2,2'azo-bis-(isobutyronitrile) (AIBN; Merck - 98%) initiated free radical polymerisation. Typically a 10% w/v solution of the monomer in dichloroethane with 2 mol% AIBN (based on monomer) was deoxygenated by bubbling through argon for approximately 15 minutes in an ice/acetone bath at -10°C. Polymerisation was carried out in an oil bath at 60 ± 2°C for a specified period of time. Polymers were purified by two precipitations from dichloroethane into rapidly stirring methanol, filtered and washed with methanol, and dried in vacuo at 60°C to constant weight. An exception to the above was the monomer 9-AMA (24) which was converted to its polymer by thermal polymerisation at 110°C under nitrogen, i.e. bulk polymerisation.[76] Polymerisation data for all the polymers are given in Table I below.

Characterisation of the polymers was by elemental analysis, IR, UV, and in some cases ^{1}H-nmr spectroscopy. Polymer melt temperatures were determined in capillary tubes. Being predominantly amorphous in nature these polymers exhibited broad softening/melting ranges - those that decomposed on heating with no discernable transition are indicated accordingly.

TABLE I : Polymerisation Data[a]

Polymer	Mass of AIBN in mg.	Temp. in °C	Time in hrs.	Conv. in %
poly(PMA)	14.2	62	40	52.7
poly(PMMA)	13.4	62	24	62.8
poly(2-PEA)	13.4	62	24	64.2
poly(2-PEMA)	12.7	62	24	71.8
poly(3-PPA)	12.7	60	27	41.8
poly(3-PPMA)	11.8	60	29	86.9
poly(5-PPA)[b]	11.5	62	20	-
poly(5-PPMA)	10.9	59	48	75.1

a) Polymerisation conditions - solvent: dichloroethane (10mL); initiator: 2mol-% AIBN, and 10% w/v monomer conc.

b) Failed to polymerise by free-radical route.

TABLE I : Polymerisation Data[a] cont'd...

Polymer	Mass of AIBN in mg.	Temp. in ^{o}C	Time in hrs.	Conv. in %
poly(9-AMA)[c]	-	108	24	50.8
poly(9-AMMA)	11.8	64	40	69.0
poly(9-PhMA)	12.5	62	24	44.5
poly(9-PhMMA)	11.8	63	45	67.2
poly(2-MPhA)	19.8	62	50	75.0
poly(2-MPhMA)	17.0	62	30	88.3
poly(4-MPhA)	19.8	62	49	54.7
poly(4-MPhMA)	17.0	62	49	87.9
poly(N-2-MPhA)	18.5	62	20	70.2
poly(N-2-MPhMA)	17.3	62	22	72.2
poly(N-4-MPhA)	18.5	62	21	86.6
poly(N-4-MPhMA)	17.2	62	21	31.4
poly(N-2,4-MPhA)	15.8	61	23	17.8
poly(N-2,4-MPhMA)	14.8	61	22	27.1
poly(N-2,5-MPhA)	15.8	61	66	83.1
poly(N-2,5-MPhMA)	14.8	61	39	84.9

a) Polymerisation conditions - solvent: dichloroethane (10mL); initiator: 2mol-% AIBN, and 10% w/v monomer conc.

c) Thermal Polymerisation.

Poly(PMA) (41): cream ppt, m.p.149-157^{o}C; (Found: C, 61.55; H, 3.59; N, 5.76. $C_{12}H_{9}NO_{4}$ requires C, 62.34; H, 3.92; N, 6.05%); $\lambda_{max.}$ ($CH_{2}Cl_{2}$) 232 (ϵ 13,900 dm^{3} mol^{-1} cm^{-1}), 256 (2,700), and 296nm (1,900).

Poly(PMMA) (42): white ppt., m.p. 184-193°C; (Found: C, 62.77; H, 4.36; N, 5.56. $C_{13}H_{11}NO_4$ requires C, 63.67; H, 4.52; N, 5.71%); $\lambda_{max.}$ (CH_2Cl_2) 232 (ϵ 10,200 dm^3 mol^{-1} cm^{-1}), 294 (1,900), and 300nm (1,600); δ_H (270MHz; $CDCl_3$) 0.95br (3H, $-CC\underline{H}_3$), 1.86br (2H, Ha and Hb), 5.52br (2H, $OC\underline{H}_2N$), and 7.78br (4H, aromatic).

Poly(2-PEA) (43): white ppt., m.p. 116-122°C; (Found: C, 63.38; H, 4.31; N, 5.86. $C_{13}H_{11}NO_4$ requires C, 63.67; H, 4.52; N, 5.71%); $\lambda_{max.}$ (CH_2Cl_2) 236 (ϵ 11,000 dm^3 mol^{-1} cm^{-1}), and 296nm (1,700); δ_H (270MHz; $CDCl_3$) 1.24br and 1.72br (2H, Ha and Hb), 2.24br (1H, Hc), 3.78br (2H, $C\underline{H}_2N$), 4.13br (2H, $OC\underline{H}_2$), and 7.68br (4H, aromatic).

Poly(2-PEMA) (44): white ppt., m.p. 156-165°C; (Found: C, 64.13; H, 4.57; N, 5.31. $C_{14}H_{13}NO_4$ requires C, 64.85; H, 5.05; N, 5.40%); $\lambda_{max.}$ (CH_2Cl_2) 232 (ϵ 18,000 dm^3 mol^{-1} cm^{-1}), and 294nm (3,000); δ_H (270MHz; $CDCl_3$) 0.56br (3H, $-CC\underline{H}_3$), 1.59br (2H, Ha and Hb), 3.83br (2H, $C\underline{H}_2N$), 4.02br (2H, $OC\underline{H}_2$), and 7.58-7.87 (4H, aromatic).

Poly(3-PPA) (45): white ppt., m.p. 82-86°C; (Found: C, 63.34; H, 5.18; N, 5.07. $C_{14}H_{13}NO_4$ requires C, 64.85; H, 5.05; N, 5.40%; $\lambda_{max.}$ (CH_2Cl_2) 236 (ϵ 14,600 dm^3 mol^{-1} cm^{-1}), and 296nm (2,000).

Poly(3-PPMA) (46): white ppt., m.p. 118-121°C; (Found: C, 65.18; H, 5.45; N, 4.85. $C_{15}H_{15}NO_4$ requires C, 65.92; H, 5.53; N, 5.12%); $\lambda_{max.}$ (CH_2Cl_2) 234 (ϵ 13,500 dm^3 mol^{-1} cm^{-1}), and 296nm (1,800).

Poly(5-PPMA) (47) white ppt., m.p. 84-90°C; (Found: C, 68.16; H, 6.60; N, 4.56. $C_{17}H_{19}NO_4$ requires C, 67.75; H, 6.35, N, 4.64%); $\lambda_{max.}$ (CH_2Cl_2) 234 (ϵ 12,900 dm^3 mol^{-1} cm^{-1}), and 292nm (1,800).

Poly(9-AMA) (48)^a: v. pale yellow ppt., m.p. 230-235°C (decomp.); (Found: C, 80.53; H, 5.33. $C_{18}H_{14}O_2$ requires C, 82.42; H, 5.37%); $\lambda_{max.}$ (CH_2Cl_2) 258 (ϵ 12,400 dm^3 mol^{-1} cm^{-1}), 230 (5,100), 368 (1,500), 388 (1,300), and 350nm (980).

Poly(9-AMMA) (49): pale yellow ppt., m.p. 182-187°C (decomp.); (Found: C, 82.27; H, 5.72. $C_{19}H_{16}O_2$ requires C, 82.58; H, 5.83%); $\lambda_{max.}$ (CH_2Cl_2) 248 (ϵ 23,800 dm^3 mol^{-1} cm^{-1}), 368 (6,500), 388 (6 000), and 352nm(4 500); δ_H (270Mhz; $CDCl_3$) 0.6br ($-CC\underline{H}_3$), 1.58br (Ha and Hb), 5.7br ($OC\underline{H}_2$-aryl), and 6.7-8.8 (aromatic).

Poly(9-PhMA) (50): white ppt., m.p. 131-137°C; (Found: C, 82.27; H, 5.16. $C_{18}H_{14}O_2$ requires C, 82.42; H, 5.37%); $\lambda_{max.}$ (CH_2Cl_2) 254 (ϵ 43,900 dm^3 mol^{-1} cm^{-1}, and 300nm (8,900).

Poly(9-PhMMA) (51): white ppt., m.p. 188-199°C; (Found: C, 82.45; H, 5.75. $C_{19}H_{16}O_2$ requires C, 82.58; H, 5.83%); $\lambda_{max.}$ (CH_2Cl_2) 256 (ϵ 56,500 dm^3 mol^{-1} cm^{-1}), and 300nm (13 300); δ_H (270MHz; $CDCl_3$) 0.68br ($-CC\underline{H}_3$), 1.72br (Ha and Hb), 5.05br ($OC\underline{H}_2$-aryl), and 7.0-8.6br (aromatic).

a) synthesised by thermal polymerisation.

Poly(2-MPhA) (52): white ppt., m.p. 103-106°C; (Found: C, 66.90; H, 5.40. $C_{10}H_{10}O_3$ requires C, 67.40; H, 5.65%); $\lambda_{max.}$ (CH_2Cl_2) 272nm (ϵ 1,800 dm^3 mol^{-1} cm^{-1}).

Poly(2-MPhMA) (53): white ppt., m.p. 185°C (no transition observed); (Found: C, 66.39; H, 6.07. $C_{11}H_{12}O_3$ requires C, 68.73; H, 6.29%); $\lambda_{max.}$ (CH_2Cl_2) 272nm (ϵ 2,300 dm^3 mol^{-1} cm^{-1}).

Poly(4-MPhA) (54): white ppt., m.p. 92-96°C; (Found: C, 67.61; H, 5.72. $C_{10}H_{10}O_3$ requires C, 67.40; H, 5.65%); $\lambda_{max.}$ (CH_2Cl_2) 234 (ϵ 4,800 dm^3 mol^{-1} cm^{-1}), 278 (2,500), and 284sh nm (2,100).

Poly(4-MPhMA) (55): white ppt., m.p. 167-182°C; (Found: C, 68.88; H, 5.98. $C_{11}H_{12}O_3$ requires C, 68.73; H, 6.29%); $\lambda_{max.}$ (CH_2Cl_2) 232 (ϵ 6,200 dm^3 mol^{-1} cm^{-1}), and 278nm (2,100).

Poly(N-2-MPhA) (56): v.light brown crystalline matl., m.p. 190 -206°C; (Found: C, 65.04; H, 6.26; N, 7.39. $C_{10}H_{11}NO_2$ requires C, 67.78; H, 6.25; N, 7.90%); $\lambda_{max.}$ (CH_2Cl_2) 246 (ϵ 8,500 dm^3 mol^{-1} cm^{-1}), and 282nm (4,000).

Poly(N-2-MPhMA) (57): white ppt., m.p. 196-212°C; (Found: C, 68.89; H, 7.05; N, 7.17. $C_{11}H_{13}NO_2$ requires C, 69.09; H, 6.85; N, 7.32%); $\lambda_{max.}$ (CH_2Cl_2) 248 (ϵ 21,200 dm^3 mol^{-1} cm^{-1}), and 284nm (9,400).

Poly(N-4-MPhA) (58): pink-brown crystalline matl., m.p. 254 -260°C; (Found: C, 65.22; H, 6.23; N, 7.25. $C_{10}H_{11}NO_2$ requires C, 67.78; H, 6.25; N, 7.90%).

Poly(N-4-MPhMA) (59): grey-white ppt., m.p. 240-254°C; (Found: C, 64.45; H, 6.67; N, 6.70. $C_{11}H_{13}NO_2$ requires C, 69.09; H, 6.85; N, 7.32%); $\lambda_{max.}$ (CH_2Cl_2) 252nm (ϵ 10,700 dm^3 mol^{-1} cm^{-1}).

Poly(N-2,4-MPhA) (60): orange-cream crystalline matl., m.p. 274-286°C; (Found: C, 63.08; H, 6.51; N, 6.56. $C_{11}H_{13}NO_3$ requires C, 63.75; H, 6.32; N, 6.76%); $\lambda_{max.}$ (CH_2Cl_2) 254 (ϵ 11,500 dm^3 mol^{-1} cm^{-1}), and 288nm (5 100).

Poly(N-2,4-MPhMA) (61): white ppt., m.p. 190-204°C; (Found: C, 64.42; H, 6.92; N, 5.97. $C_{12}H_{15}NO_3$ requires C, 65.14; H, 6.83; N, 6.33%); $\lambda_{max.}$ (CH_2Cl_2) 254 (ϵ 14,000 dm^3 mol^{-1} cm^{-1}), and 292nm (5,800).

Poly(N-2,5-MPhA) (62): v.light green crystalline matl., m.p. 152-160°C; (Found: C, 60.41; H, 6.16; N, 5.93. $C_{11}H_{13}NO_3$ requires C, 63.75; H, 6.32; N, 6.76%); $\lambda_{max.}$ (CH_2Cl_2) 230 (ϵ 14,900 dm^3 mol^{-1} cm^{-1}), 246 (13,700), and 300nm (9,700).

Poly(N-2,5-MPhMA) (63): white ppt., m.p. 162-170°C; (Found: C, 65.56; H, 7.02; N, 5.84. $C_{12}H_{15}NO_3$ requires C, 65.14; H, 6.83; N, 6.33%); $\lambda_{max.}$ (CH_2Cl_2) 230 (ϵ 10,200 dm^3 mol^{-1} cm^{-1}), 246 (9,400), and 300nm (6,200).

3.4 COPOLYMERISATION

Copolymerisation reactions were carried out at 60 ± 2^{o}C using dichloroethane as the solvent. The concentration of each monomer was 0.25 mol/l in all cases, the ratio of monomers being kept constant on a 1:1 mole ratio. AIBN was used as the initiator (2 mol%, relative to monomers) and all syntheses were performed under argon in sealed vessels. As for the polymerisation procedure detailed previously, the copolymers were precipitated twice with methanol, filtered and dried in vacuo at 60^{o}C to constant weight.

Copolymerisation data is contained in Table II. All copolymers were characterised by IR, UV, and ^{1}H-nmr spectroscopy and their compositions determined by elemental analysis data.

9-Amma / N-HMPIA (64)
9-Amma / N-HMPIMA (65)
9-Amma / N-2-HEPIA (66)
9-Amma / N-2-HEPIMA (67)
9-Amma / N-3-HPPIMA (68)
9-Amma / N-5-HPPIMA (69)
9-Phmma / N-HMPIMA (70)
9-Phmma / N-2-HEPIMA (71)
9-Phmma / N-3-HPPIMA (72)
2-MPhA / N-HMPIA (73)
2-MPhA / N-2-HEPIA (74)
4-MPhA / N-HMPIA (75)
4-MPhA / N-2-HEPIA (76)
2-MPhMA / N-HMPIMA (77)
2-MPhMA / N-2-HEPIA (78)
2-MPhMA / N-2-HEPIMA (79)
4-MPhMA / N-HMPIMA (80)
4-MPhMA / N-2-HEPIMA (81)
N-2,5-MPhA / N-2-HEPIA (82)
N-2,5-MPhA / N-3-HPPIA (83)
N-2,5-MPhMA / N-HMPIMA (84)
N-2,5-MPhMA / N-2-HEPIA (85)
N-2,5-MPhMA / N-2-HEPIMA (86)
N-2,5-MPhMA / N-3-HPPIMA (87)

Fig. 41. Copolymer Systems and references

Table II: Copolymerisation Data[a]

Copolymer	Temp. in °C	Time in hrs.	Conv. in %
poly(9-AMMA-co-PMA)[b]	62	24	-
poly(9-AMMA-co-PMMA)	63	50	59.9
poly(9-AMMA-co-2-PEA)[b]	63	50	-
poly(9-AMMA-co-2-PEMA)	63	48	50.2
poly(9-AMMA-co-3-PPMA)	59	50	80.3
poly(9-AMMA-co-5-PPMA)	59	50	80.3
poly(9-PhMMA-co-PMMA)	62	43	88.4
poly(9-PhMMA-co-2-PEMA)	62	41	68.7
poly(9-PhMMA-co-3-PPMA)	62	42	90.2
poly(2-MPhA-co-PMA)	64	37	56.5
poly(2-MPhA-co-2-PEA)	62	25	54.5
poly(4-MPhA-co-PMA)[b]	64	43	-
poly(4-MPhA-co-2-PEA)	64	43	54.9
poly(2-MPhMA-co-PMMA)	62	63	81.7
poly(2-MPhMA-co-2-PEA)	63	50	75.9
poly(2-MPhMA-co-2-PEMA)	64	42	85.4
poly(4-MPhMA-co-PMMA)	62	50	76.6
poly(4-MPhMA-co-2-PEMA)	62	50	86.0
poly(N-2,5-MPhA-co-2-PEA)	62	45	63.5
poly(N-2,5-MPhA-co-3-PPA)	61	47	80.1
poly(N-2,5-MPhMA-co-PMMA)	61	43	52.5
poly(N-2,5-MPhMA-co-2-PEA)[b]	61	45	-
poly(N-2,5-MPhMA-co-2-PEMA)	61	42	69.6
poly(N-2,5-MPhMA-co-3-PMMA)	61	48	75.3

a) Copolymerisation conditions - solvent: dichloroethane (10mL); initiator: 2 mol-% AIBN and concentration of monomer 0.25 mol/l; monomer ratio 1:1

b) Failed to polymerise by free-radical polym. route.

Poly(9-AMMA-co-PMMA) (65): Found: C, 73.19; H, 5.25; N, 2.36. Anal. calcd. for $C_{32}H_{27}NO_6$ (1:1 copolymer): C, 73.69; H, 5.21; N, 2.68%; $\lambda_{max.}$ (CH_2Cl_2) 258 (ϵ 78,900 dm^3 mol^{-1} cm^{-1}), 368 (6,500), 388 (5,800), and 350nm (4,500); δ_H (270MHz; $CDCl_3$) 0.9br (6H, 2 x $-CC\underline{H}_3$), 1.7br (4H, 2 x Ha, 2 x Hb), 5.5br (2H, $OC\underline{H}_2$-aryl), 5.78br (2H, $OC\underline{H}_2N$), and 6.8-8.4 (13H, aromatic).

Poly(9-AMMA-co-2-PEMA) (67): Found: C, 73.34; H, 5.46; N, 2.48. Anal. calcd. for $C_{33}H_{29}NO_6$ (1:1 copolymer): C, 74.00; H, 5.45; N, 2.61%; $\lambda_{max.}$ (CH_2Cl_2) 258 (ϵ 88,800 dm^3 mol^{-1} cm^{-1}), 368 (7,800), 388 (7,200), and 350nm (5,500); δ_H (270MHz; $CDCl_3$) 0.6br (2 x $-CC\underline{H}_3$), 1.58br (Ha and Hb), 3.8br ($C\underline{H}_2N$ and $COC\underline{H}_2$), 5.8br ($OC\underline{H}_2$-aryl), and 7.1-8.4 (aromatic).

Poly(9-AMMA-co-3-PPMA) (68): Found: C, 73.57; H, 5.59; N, 2.27. Anal. calcd. for $C_{34}H_{31}NO_6$ (1:1 copolymer): C, 74.30; H, 5.68; N, 2.54%; $\lambda_{max.}$ (CH_2Cl_2) 258 (ϵ 86,600 dm^3 mol^{-1} cm^{-1}), 368 (7,500), 388 (7,000), and 350nm (5,000); δ_H (270MHz; $CDCl_3$) 0.8br (6H, 2 x $-CC\underline{H}_3$), 1.8br (6H, 2 x Ha, 2 x Hb, and $CH_2C\underline{H}_2CH_2$), 3.6br (4H, $C\underline{H}_2N$ and $OC\underline{H}_2$), 5.9br (2H, $OC\underline{H}_2$-aryl), and 7.0-8.5 (13H, aromatic).

Poly(9-AMMA-co-5-PPMA) (69): Found: C, 74.75; H, 6.21; N, 2.28. Anal. calcd. for $C_{36}H_{35}NO_6$ (1:1 copolymer): C, 74.85; H, 6.10; N, 2.42%; $\lambda_{max.}$ (CH_2Cl_2) 258 (ϵ 101,200 dm^3 mol^{-1} cm^{-1}), 368 (8,200), 388 (7,500), and 350nm (5,500); δ_H (270MHz; $CDCl_3$) 0.7br (6H, 2 x $-CC\underline{H}_3$), 1.0-2.0 (10H, 2 x Ha, 2 x Hb, and $-C\underline{H}_2C\underline{H}_2C\underline{H}_2-$), 3.6br (4H, $OC\underline{H}_2$ and $NC\underline{H}_2$), 5.9br (2H, $OC\underline{H}_2$-aryl), and 7.0-8.8 (13H, aromatic).

Poly(9-PhMMA-co-PMMA) (70): Found: C, 71.83; H, 4.97; N, 2.30. Anal. calcd. for $C_{32}H_{27}NO_6$ (1:1 copolymer): C, 73.69; H, 5.21; N, 2.68%; $\lambda_{max.}$ (CH_2Cl_2) 256 (ϵ 51,600 dm^3 mol^{-1} cm^{-1}), and 298nm (11,500); δ_H (270MHz; $CDCl_3$) 0.9br (6H, 2 x $-CC\underline{H}_3$), 1.8br (4H, 2 x Ha, 2 x Hb), 5.35br (4H, $OC\underline{H}_2N$ and $OC\underline{H}_2$- aryl), and 7.0-8.6 (13H, aromatic).

Poly(9-PhMMA-co-2-PEMA) (71): Found: C, 72.09; H, 5.51; N, 2.44. Anal. calcd. for $C_{33}H_{29}NO_6$ (1:1 copolymer): C, 74.00; H, 5.45; N, 2.61%; $\lambda_{max.}$ (CH_2Cl_2) 256 (ϵ 52,400 dm^3 mol^{-1} cm^{-1}), and 298nm (11,600); δ_H (270MHz; $CDCl_3$) 0.6br (6H, 2 x $-CC\underline{H}_3$), 1.6br (4H, 2 x Ha, 2 x Hb), 3.7br (4H, $C\underline{H}_2N$ and $OC\underline{H}_2$), 5.2br (2H, $OC\underline{H}_2$-aryl), and 7.0-8.6 (13H, aromatic).

Poly(9-PhMMA-co-3-PPMA) (72): Found: C, 72.30; H, 5.57; N, 2.18. Anal. calcd. for $C_{34}H_{31}NO_6$ (1:1 copolymer): C, 74.30; H, 5.68; N, 2.54%; $\lambda_{max.}$ (CH_2Cl_2) 256 (ϵ 46,900 dm^3 mol^{-1} cn^{-1}), and 298nm (10,800); H (270MHz; $CDCl_3$) 0.85br (6H, 2 x $-CC\underline{H}_3$), 1.8br (6H, 2 x Ha, 2 x Hb, and $CH_2C\underline{H}_2CH_2$), 3.2-4.1 (4H, $C\underline{H}_2N$ and $OC\underline{H}_2$), 5.3br (2H, $OC\underline{H}_2$-aryl), and 7.2-8.6 (13H, aromatic).

Poly(2-MPhA-co-PMA) (73): Found: C, 64.69; H, 4.56; N 3.22. Anal. calcd. for $C_{22}H_{19}NO_7$ (1:1 copolymer): C, 64.54; H, 4.67; N, 3.42%; $\lambda_{max.}$ (CH_2Cl_2) 230 (ϵ 15,800 dm^3 mol^{-1} cm^{-1}), 272 (3,400), and 294nm (1,800); δ_H (270MHz; $CDCl_3$) 1.8br (Ha and Hb), 2.7br (Hc), 3.7br ($OC\underline{H}_3$), 5.6 ($OC\underline{H}_2N$), 6.4-7. (aromatic - phenyl), and 7.35-7.9 (aromatic - phthalimido).

Poly(2-MPhA-co-2-PEA) (74): Found: C, 65.01; H, 4.98; N, 3.05. Anal. calcd. for $C_{23}H_{21}NO_7$ (1:1 copolymer): C, 65.24; H, 4.99; N, 3.30%; $\lambda_{max.}$ (CH_2Cl_2) 232 (ϵ 14,300 dm^3 mol^{-1} cm^{-1}), 272

(3,500), and 294nm (2,000); δ_H (270MHz; $CDCl_3$) 1.85br (2 x Ha, 2 x Hb), 2.6br (2H, 2 x Hc), 3.65br (5H, OC$\underline{H}_3$ and C$\underline{H}_2$N), 4.17br (2H, OC$\underline{H}_2$), 6.4-7.2 (4H, aromatic - phenyl), and 7.3-7.9 (4H, aromatic - phthalimido).

<u>Poly(4-MPhA-co-2-PEA)</u> (76): Found: C, 64.66; H, 4.99; N, 3.38. Anal. calcd. for $C_{22}H_{19}NO_7$ (1:1 copolymer): C, 64.54; H, 4.99; N, 3.30%; $\lambda_{max.}$ (CH_2Cl_2) 232 (ϵ 17,100 dm^3 mol^{-1} cm^{-1}), 284 (3,200), and 260nm (1,400); δ_H (270MHz; $CDCl_3$) 1.7br (4H, 2 x Ha, 2 x Hb), 2.5br (2H, 2 x Hc), 3.7br (5H, OC$\underline{H}_3$ and C$\underline{H}_2$N), 4.2br (2H, OC$\underline{H}_2$), 6.5-7.2 (4H, aromatic - phenyl), and 7.4-8.0 (4H, aromatic - phthalimido).

<u>Poly(2-MPhMA-co-PMMA)</u> (77): Found: C, 66.11; H, 5.33; N, 2.95. Anal. calcd. for $C_{24}H_{23}NO_7$ (1:1 copolymer): C, 65.89; H, 5.29; N, 3.20%; $\lambda_{max.}$ (CH_2Cl_2) 230 (ϵ 13,800 dm^3 mol^{-1} cm^{-1}), 256 (4,300), 274 (3,600), and 294nm (1,800); δ_H (270MHz; $CDCl_3$) 1.25br (6H, 2 x -CC$\underline{H}_3$), 2.2br (4H, 2 x Ha, 2 x Hb), 3.65br (3H, OC$\underline{H}_3$), 5.6br (2H, OC$\underline{H}_2$N), 6.6-7.3 (4H, aromatic - phenyl), and 7.3-7.9 (4H, aromatic - phthalimido).

<u>Poly(2-MPhMA-co-2-PEA)</u> (78): Found: C, 65.97; H, 5.43; N, 2.90. Anal. calcd. for $C_{24}H_{23}NO_7$ (1:1 copolymer): C, 65.89; H, 5.29; N, 3.20%; $\lambda_{max.}$ (CH_2Cl_2) 232 (ϵ 17,400 dm^3 mol^{-1} cm^{-1}), 274 (5,700), and 294nm (2,100); δ_H (270MHz; $CDCl_3$) 0.7-1.9 (7H, -CC$\underline{H}_3$, and 2 x Ha, 2 x Hb), 2.25br (1H, Hc), 3.7br (5H, OC$\underline{H}_3$ and C$\underline{H}_2$N), 4.2br (2H, OC$\underline{H}_2$), 6.6-7.2 (4H, aromatic - phenyl) and 7.35-7.9 (4H, aromatic - phthalimido).

<u>Poly(2-MPhMA-co-2-PEMA)</u> (79): Found: C, 65.92; H, 5.45; N, 2.92. Anal. calcd. for $C_{25}H_{25}NO_7$ (1:1 copolymer): C, 66.50; H, 5.29; N, 3.10%; $\lambda_{max.}$ (CH_2Cl_2) 232 (ϵ 14,600 dm^3 mol^{-1} cm^{-1}), 274

(3,400), and 294nm (1,800); $_{H}$ (270MHz; $CDCl_3$) 0.4-2.6 (10H, 2 x $-CC\underline{H}_3$, and 2 x Ha, 2 x Hb), 3.7br (3H, $OC\underline{H}_3$), 3.9br (2H, $C\underline{H}_2N$), 4.1br (2H, $OC\underline{H}_2$), 6.7-7.35 (4H, aromatic - phenyl), and 7.4-7.9 (4H, aromatic - phthalimido).

Poly(4-MPhMA-co-PMMA) (80): Found: C, 66.04; H, 5.35; N, 2.71. Anal. calcd. for $C_{24}H_{23}NO_7$ (1:1 copolymer): C, 65.89; H, 5.29; N, 3.20%; max. (CH_2Cl_2) 232 (ϵ 17,300 dm^3 mol^{-1} cm^{-1}), 278 (3,600), and 304nm (1,800); $_{H}$ (270MHz; $CDCl_3$) 1.3br (6H, 2 x $-CC\underline{H}_3$), 2.1br (4H, 2 x Ha, 2 x Hb), 3.8br (3H, $OC\underline{H}_3$), 5.65br (2H, $OC\underline{H}_2N$), 6.6-7.2 (4H, aromatic - phenyl), and 7.5-7.9 (4H, aromatic - phthalimido).

Poly(4-MPhMA-co-2-PEMA) (81): Found: C, 65.84; H, 5.33; N, 2.52. Anal. calcd. for $C_{25}H_{25}NO_7$ (1:1 copolymer): C, 66.50; H, 5.58; N, 3.10%; $\lambda_{max.}$ (CH_2Cl_2) 232 (ϵ 20,800 dm^3 mol^{-1} cm^{-1}), and 280nm (3,400); δ_H (270MHz; $CDCl_3$) 0.9br (6H, 2 x $-CC\underline{H}_3$), 1.9br (2 x Ha, 2 x Hb), 3.8 (3H, $OC\underline{H}_3$), 3.9br (2H, $C\underline{H}_2N$), 4.1br (2H, $OC\underline{H}_2$), 6.65-7.1 (4H, aromatic - phenyl), and 7.45-7.9 (4H, aromatic - phthalimido).

Poly(N-2,5-MPhA-co-2-PEA) (82): Found: C, 62.82; H, 5.27; N, 5.78. Anal.calcd. for $C_{24}H_{24}N_2O_7$ (1:1 copolymer): C, 63.70; H, 5.34; N, 6.19%; $\lambda_{max.}$ (CH_2Cl_2) 232 (ϵ 21,700 dm^3 mol^{-1} cm^{-1}), and 300nm (7,800); δ_H (270MHz; $CDCl_3$) 1.9br (4H, 2 x Ha, 2 x Hb), 2.65br (2H, 2 x Hc), 3.9 (8H, 2 x $OC\underline{H}_3$, and $C\underline{H}_2N$), 4.4br (2H, $OC\underline{H}_2$), 6.4-7.2 (2H, aromatic - phenyl), 7.75-8.35 (4H, aromatic - phthalimido), and 8.5br (2H, aromatic - phenyl, and $N\underline{H}$.

Poly(N-2,5-MPhA-co-3-PPA) (83): Found: C, 64.31; H, 5.82; N, 5.89. Anal.calcd. for $C_{25}H_{26}N_2O_7$ (1:1 copolymer): C, 64.36; H, 5.61; N, 6.00%; $\lambda_{max.}$ (CH_2Cl_2) 234 (ϵ 20,800 dm^3 mol^{-1} cm^{-1}), and 300nm (7,800); δ_H (270MHz; $CDCl_3$) 1.3-2.2 (6H, 2 x Ha, 2 x Hb, and $CH_2C\underline{H}_2CH_2$), 2.45br (2H, 2 x Hc), 3.6br (8H, 2 x $OC\underline{H}_3$, and $C\underline{H}_2N$), 3.9br (2H, $OC\underline{H}_2$), 6.05-6.7 (2H, aromatic - phenyl), 7.45-8.05 (4H, aromatic - phthalimido), and 8.3br (2H, aromatic - phenyl, and $N\underline{H}$).

Poly(N-2,5-MPhMA-co-PMMA) (84): Found: C, 63.09; H, 5.27; N, 5.36. Anal.calcd. for $C_{25}H_{26}N_2O_7$ (1:1 copolymer): C, 64.36; H, 5.61; N, 6.00%; $\lambda_{max.}$ (CH_2Cl_2) 230 (ϵ 20,900 $dm^3\ mol^{-1}\ cm^{-1}$), and 300nm (8,400); δ_H (270MHz; $CDCl_3$) 0.7-1.5 (6H, 2 x $-CC\underline{H}_3$), 1.5-2.3 (4H, 2 x Ha, 2 x Hb), 3.7 (6H, 2 x $OC\underline{H}_3$), 5.55br (2H, $OC\underline{H}_2N$), 6.25-6.85 (2H, aromatic - phenyl), 7.4-8.0 (4H, aromatic - phthalimido), and 8.1br (2H, aromatic - phenyl, and $N\underline{H}$).

Poly(N-2,5-MPhMA-co-2-PEMA) (86): Found: C, 64.26; H, 5.69; N, 5.31. Anal.calcd. for $C_{26}H_{28}N_2O_7$ (1:1 copolymer): C, 64.98; H, 5.87; N, 5.82%; $\lambda_{max.}$ (CH_2Cl_2) 234 (ϵ 29,900 $dm^3\ mol^{-1}\ cm^{-1}$), and 300nm (11,900); δ_H (270MHz; $CDCl_3$) 1.0br (6H, 2 x $-CC\underline{H}_3$), 1.85br (4H, 2 x Ha, 2 x Hb), 3.75br (8H, 2 x $OC\underline{H}_3$, and $C\underline{H}_2N$), 4.05br (2H, $COC\underline{H}_2$), 6.3-6.85 (2H, aromatic - phenyl), and 7.4-8.2 (6H, aromatic - phthalimido /phenyl, and $N\underline{H}$).

Poly(N-2,5-MPhMA-co-3-PPMA) (87): Found: C, 65.93; H, 6.28; N, 5.51. Anal.calcd. for $C_{27}H_{30}N_2O_7$ (1:1 copolymer): C, 65.57; H, 6.11; N, 5.66%; $\lambda_{max.}$ (CH_2Cl_2) 232 (ϵ 26,400 $dm^3\ mol^{-1}\ cm^{-1}$), and 300nm (9,700); δ_H (270MHz; $CDCl_3$) 1.1b (6H, 2 x $-CC\underline{H}_3$), 1.95br (6H, 2 x Ha, 2 x Hb, and $CH_2C\underline{H}_2CH_2$), 3.65 (8H, 2 x $OC\underline{H}_3$, and $C\underline{H}_2N$), 3.95br (2H, $COC\underline{H}_2$), 6.25-6.75 (2H, aromatic - phenyl), 7.5-7.8 (4H, aromatic - phthalimido), 7.9br (1H, $\underline{N}H$), and 8.15br (1H, aromatic - phenyl).

3.5 U.V. STUDIES

CT interactions were investigated using U.V. spectroscopy. Spectra were measured on a Hewlett Packard 8452 U.V. Diode Array Spectrometer using standard techniques. CT absorption bands overlapped by strong absorptions from either donor and/or acceptor components were determined by subtracting out the respective contribution(s) from the spectra of the donor/ acceptor (D-A) combinations. The results were verified by subtraction of the individual spectra using the in-built 'ChemStation' software package.

All spectra were determined for freshly prepared solutions, i.e. were run on the same day. The following solvents were used as received: methanol (Labscan - HPLC grade); acetonitrile (Labscan - HPLC grade); tetrahydrofuran (Rathburn Chemicals Ltd. - HPLC grade), and dichloromethane (Riedel-de Haen - 99.8%). Investigations with commercially available low molecular weight electron acceptors included picric acid (2,4,6-trinitrophenol) (Riedel-de Haen - 99%), maleic anhydride (BDH - 98.5%), tetrachlorophthalic anhydride (BDH - 98.5%), and N-methyl tetrachlorophthalimide, all used without further purification. No CT interactions were observed for D-A combinations of these acceptor compounds with the donor monomer/polymer systems synthesised in this work. Investigations were carried out on the following D-A pairs:

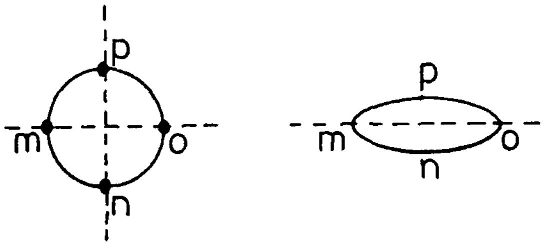
Acceptor	Donor
1. N-methyl phthalimide	- anthracene
	- 9-AMMA (24)
	- 9-PhMMA (26)
2. Tetrachlorophthalic anhydride	- 9-AMMA (24)

Acceptor	Donor
3. Maleic anhydride	- anthracene
	- 9-AMMA
4. N-Methyl tetrachlorophthalimide	- anthracene
	- 9-AMMA (24)
5. Picric acid	- anthracene
	- 9-AMMA (24)
	- 9-PhMMA (26)
	- N-4-MPhA (33)
	- N-2,4-MPhA (35)
	- N-2,4-MPhMA (36)
6. 2-PEMA (18)/poly(2-PEMA) (44)	- anthracene
	- phenanthrene
	- 9-AMMA (24)
	- poly(9-AMMA) (49)
	- N-2,4-MPhMA (36)
	- poly(N-2,4-MPhMA) (61)

3.6 ELECTRICAL MEASUREMENTS

With the exception of the copolymers, D-A mixtures were first prepared by mixing dilute solutions of the respective components in chloroform using an ultrasonic bath. After removal of the solvent on a Rotovap, the resulting solid phase was ground and dried in vacuo at $60^{o}C$. The powder mixtures were then compacted into thin circular pellets (0.5-1.0 mm x 13 mm Ø) in a stainless steel press at a pressure of approximately 5×10^{3} Kg cm^{-2} at ambient temp. Copper wire was attached to the circumference of these thin discs in a 4-point van der Pauw arrangement[89] with silver-loaded epoxy resin, the discs being fixed in a jig and the resin contacts cured at 60°C in vacuo. Conductivity measurements were carried out at ambient pressure and temperature. The voltage source was a d.c. Thurlby power supply (Radionics No. 610-461) and a Fluka 8060A digital electrometer was used to measure current passing through the sample discs.

3.6.1. VAN DER PAUW 4-POINT PROBE METHOD[89]



This method is used for measuring the resistivity, P, of thin samples. It entails the placing of four small contacts, M, N, O, and P on the periphery and applying a current i_{MN} to contact M and taking it off at contact N. The potential difference $V_p - V_o$ is measured. The resistence $R_{MN,OP}$ is obtained from the relationship:

$$R_{MN,OP} = V_p - V_o / i_{MN}$$

When the sample possesses a line of symmetry with M and O being placed on the line of symmetry and N and P disposed symmetrically with respect to this line (as above in diagram) then P is obtained from the equation:

$$P = (\pi d / \ln 2) \times R_{MN,OP}$$ where d is the sample thickness

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