ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS AND CHARACTERIZATION OF AROMATIC CYCLOLINEAR PHOSPHAZENE POLY(ETHER KETONE)S CONTAINING BIS-SPIRO-SUBSTITUTED CYCLO TRIPHOSPHAZENE UNIT

M.Sc. Thesis by

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

BİS-SPİRO-SUBSTİTUYE SİKLOTRİFOSFAZEN BİRİMLER İÇEREN AROMATİK SİKLOLİNEER FOSFAZEN POLİ(ETER KRTONLARIN) SENTEZİ VE ÖZELLİKLERİ

YÜKSEK LİSANS TEZİ

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LIST OF SYMBOLS

M_n	: Number average molecular weight of polymers
M_w	: Weight average molecular weight of polymers
MWD	: Molecular weight distribution of polymers
PEK	: Poly (ether ketone)
PEEK	: Poly (ether ether ketone)
PEKK	: Poly(ether ketone ketone)
PAEK	: Poly(arly ether ketone)
CP	: Cyclophosphazene
HCCP	: Hexachlorocyclophosphazene
IC	: Isophthaloyl choride
THF	: Tetrahydrofuran
DPF	: Diphenylether
T_g	: Glass Transition Temperature
T_m	: Melting Point
Ph	: Phenyl
DSC	: Differential Scanning Calorimetry
TGA	: Thermogravimetric Analysis
GPC	: Gel Permeation Chromatography

SUMMARY

SYNTHESIS AND CHARACTERIZATION OF AROMATIC CYCLOLINEAR PHOSPHAZENE POLY (ETHER KETONE)S CONTAINING BIS-SPIRO-SUBSTITUTED CYCLOTRIPHOSPHAZENE UNIT

The studies done on the high-quality macromolecules that have special fields of usage, have contributed to increasing importance of polymer science. As a result of the fact that a lot of polymeric materials used in daily life are produced by condensation polymerization, the researches done in this field have been accelerated day by day. In addition, lots of studies about the stability of the polymeric materials against the thermal degradation have been still implemented.

One of the important studies done is on poly(ether ketones) containing phosphazene units.Because the phosphazenes contain inorganic groups in their own chemical structures, they contribute stability to the polymer that they incorporate with.

In this study, a novel monomer, 2,2-bis (4'-fluorobenzoylphenoxy)-4,4,6,6-bis [spiro (2', 2''-dioxy-1', 1''-biphenylyl)] cyclotriphosphazene was synthesized and polymerized with 4,4'-difluoro benzophenone as comonomer and 4,4'-isopropylidenediphenol or 4,4'-(hexafluoroisopropylidene) diphenol in N,N-dimethyl acetamide at 162°C for 4h to give two series of aromatic cyclolinear phosphazene poly (ether ketone)s containing bis-spiro-substituted cyclotriphosphazene groups. The structure of the monomer was confirmed by ^{1}H, ^{13}C and ^{31}P NMR. The effect of the incorporation of bis-spiro-substituted cyclotriphosphazene group on the thermal properties of these polymers was investigated by DSC and TGA.

ÖZET

BİS-SPİRO-SÜBSTİTÜTE SİKLOTRİFOSFAZEN BİRİMLER İÇEREN AROMATİK SİKLOLİNEER FOSFAZEN POLİ(ETHER KETONLARIN) SENTEZİ VE ÖZELLİKLERİ

Özel kullanım alanlarına sahip kaliteli makromoleküller üzerine yapılan çalışmalar, polimer biliminin artan önemine katkıda bulunmaktadırlar. Günlük hayatta kullanılmakta olan bir çok polimer malzemenin kondenzasyon polimerleşmesi yolu ile üretildiği gerçeğinin bir sonucu olarak bu alanda yapılan araştırmalar gün geçtikçe hız kazanmaktadır. Ayrıca, polimer malzemenin ısısal bozunmaya karşı dayanıklılığı hakkında birçok çalışma gerçekleştirilmektedir.

Yapılan bu önemli çalışmalardan biri de fosfazen üniteler içeren poli(eter ketonlar) üzerinedir. Fosfazenler, kimyasal yapılarında anorganik gruplar içermeleri nedeni ile katıldıkları polimerlere ısısal dayanıklılık kazandırmaktadırlar.

Bu çalışmada, yeni bir monomer olan 2,2-bis (4'-fulorobenzoilfenoksi)-4,4,6,6-bis [spiro (2',2''-dioksi–1', 1''-bifenili)] siklotrifosfazen comonomer işlevi olan 4,4'-difloro benzofenon ve 4,4'-izopropilidendifenol veya 4,4'-(hekzafloroizopropilden) difenol ile dimetilasetamid içinde 162 °C' de, 4 saat boyunca, iki seri, bu grupları içeren aromatik siklolineerfosfazen poli(ether ketonlar) üretebilmek için polimerleştirildi. Monomerin yapısı ^{1}H, ^{13}C, ^{31}P NMR spektroskopileriyle aydınlatıldı ve alınan sonuçlar uyumluluk gösterdi. Bis-spiro-sübstitüte siklotrifosfazen grupların dahil oldukları bu polimerlerin ısısal özellikleri üzerindeki etkisi DSC ve TGA cihazlarından alınan sonuçlar doğrultusunda incelendi.

PART 1

INTRODUCTION

The development of new polymeric materials having improved and/or new mechanical and physical properties has recently become a vital face for polymer science from both an academic and industrial viewpoint.

Most half of the plastics are produced by step-growth polymerization. Step-growth polymerization reactions, also refeered to as polycondensations, are of major economic importance. Many types of polymeric materials produced in this field are used and developed in so many areas such as polyamides, polyesters, polycarbonates, polyether ketones. etc.

Aromatic polyether ketones (PEK) are classified into the engineering thermoplastics, due to their excellent thermal and chemical properties. They withstand the temperatures as high as 400°C and can be employed at high temperatures about 200°C without oxidation. PEKs displayed T_g values ranging from 100 to over 200 °C, and T_m values 300-400 °C, depending on their chemical structure. Two synthetic routes for producing PEKs have been reported. In the nucleophilic process, activated aromatic dihalides are reacted with alkali metal bisphenolates in polar aprotic solvents to produce PEK.

The incorporation of cyclotriphosphazene groups into polymer backbone is of considerable interest in recent years due to its useful thermal and chemical properties. Cyclolinear phosphazene polymers in which cyclotriphosphazene rings are recurring backbone units are synthesized from substituted cyclotriphosphazene with only two

reactive functional groups and bifunctional organic compounds of variable structures and properties.

Previous works, this concept was applied to the preparation of aromatic PEKs containing aryleneoxy-substituted cyclotriphosphazene units in the main chain via Friedel- Crafts acylation route. All of these polymers are relatively soluble and have glass transition temperatures ranging from 90 to 105°C and thermal stabilities around 410°C with 10% weight losses in nitrogen, which are nevertheless lower when compared to the wholly aromatic parent PEKs. Therefore, bis-spiro substitution through 2,2'-dioxybiphenylyl groups on the cyclotriphosphazene ring was chosen to provide a novel monomer in order to give PEKs with improved thermal stability and higher glass transition temperature.

In this study, emphasis is placed on the synthesis of a novel 2,2-bis (4'-fluorobenzoylphenoxy)- 4,4,6,6-bis [spiro (2', 2''-dioxy-1', 1''-biphenylyl)] cyclotriphosphazene monomer and its reaction with 4,4'-difluoro benzophenone as comonomer and bisphenols in the presence of K_2CO_3 and DMAC via nucleophilic aromatic substitution.

PART 2

THEORETICAL PART

2.1 STEP-GROWTH POLYMERIZATION

The class of macromoleculer products commonly defined as condensation polymers includes most of the synthetic materials manufactured world-wide and used as high-strength and/or high-toughness plastics and fibers (e.g. polyamides, polyesters, polycarbonates, etc.), as well as almost all the hard resins (unsaturated polyesters, epoxy resins. Urea-, melamine- and phenol-formaldehyde resins. etc.), covering a very wide range of applications.

Those polymeric materials used in relatively small but important industrial sectors as sealants, elastomers, foams, adhesives coatings (silicones, alkyd resins, polyimides, etc.), as well as several heavy-duty polymers (e.g. poly(arylene oxide)s, poly(arylene sulfide)s, aromatic polysulfones, etc.) and emerging engineering thermoplastics (such as aromatic poly(ether ketone)s, liquid-crystalline aromatic polyesters and polyamides, etc.) are also members of the same family. Moreover, important poymeric products of natural origin (cellulose, starch, proteins, etc.) can be considered as condensation polymers, by virtue of the processes by which they are most probably synthesized by living organisms.

From the standpoint of the polymer growth mechanism, two entirely different processes, step and chain polymerizations, are distinguishable. As is well known, step-growth polymerizations proceed via a step-by-step succession of elementary reactions between reactive sites, which are usually functional groups. But may also

be iones, complexes or even free radicals. Each independent step causes the disappearance of two coreacting centres and creates a new linking unit between a pair of molecules. In order to obtain high poymers, the reactants must be at least difunctional;monofunctinal ones act as chain-stoppers.

With both the step and chain mechanism, the polymerizations processes can be based on either one of two types of propagation reactions: condensation and addition polymerizations are called simply 'polycondensations' and 'polyadditions'.

Most of the polycondensation processes, which occur via a suitable choice of condensation, reactions (such as esterification, amidation, acetalization, nucleophilic or electrophilic substitutions, etc.), follow a step-growth mechanism. In contrast, although a chain mechanism is the usual feature of polyaddition processes, several of them proceed by a stepwise addition of pairs of functional groups brought by the reactants (isocyanate/hydroxyl, isocyanate/amine or Diels-Alders reaction, Michael-type adducts formation, etc). Such polyadditions display the same functionality criteria and the same features as any step polymerizations [1].

As stated before, step-growth polymerization are merely classical organic reactions that are used to produce linear macromolecules starting from bifunctional base molecules or "monomers", or to produce polymer networks from mixtures of bifunctional and multifunctional base molecules [2].

Step-growth polymerization is a process involving at the beginning one or more reactants (monomer) carrying at least two reactive functional groups. These monomers, on reacting between themselves, with or without the elimination of small molecules, give rise to oligomeric products which still contain functional groups and which are able to react again, either between themselves or with the monomer. In this way products of ever growing moleculer weigth are formed, from monomer to dimer, trimer, tetramer,pentamer and so on, as illustrated in Scheme 2.1 [3].

-●- + -●- → -●-●-

monomers dimers

-●- + -●-●- → -●-●-●-

trimer

-●-●- + -●-●- → -●-●-●-●- addition of monomer

-●- + -●-●-●- → -●-●-●-●-

tetramer

-●- + -●-●-●-●- → -●-●-●-●-●-

-●-●- + -●-●-●- → -●-●-●-●-●-

pentamer

and

-●-●-●-●-●- + -●-●-●-●-●- → -●-●-●-●-●-●-●-●-●-●-

combination of oligomers

Scheme 2.1 Formal illisturation of stept-growth polymerization

and, provided the stoichiometric ratio of monomers used is unity, the chains can grow extremely large [4].What step-growth polymerization is of characteristics can be summarized as follows;

• Mole weight of polymer increases steadily throughout reaction.

• Monomer disappears early in the reaction (DP_n=10 less than %1 of monomer remains)

• Any two moleculer species present can react

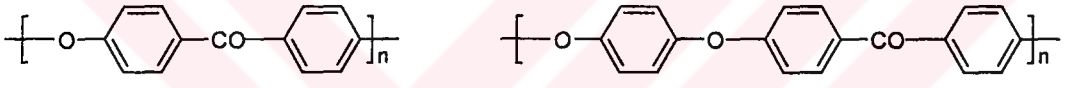
• Long reaction times are essential to obtain high moleculer weight polymers

• At any stage all moleculer species are present in a calculate distribution.

2.2 AROMATIC POLY(ETHER KETONE)S

Poly(ether ketones) comprise the class of polymers in which arylene groups are linked by ether and carbonyl groups. Since alkylene linkages are generally not present, and are undesirable, the acronym PAEK [poly(arly ether ketone)] may be used [5] to describe the general class.

A polymer marketed as Stilan (RTM) by the Raychem Corporation had structure (1), usually referred to as PEK, while the polymer with structure (2) is PEEK, produced commercially by Imperial Chemical Industries as Victrex PEEK (RTM). The systematic name of (2) is poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene), which is sufficiently cumbersome to justify the use of the acronym. As seen in scheme (2.2).



(1) (2)

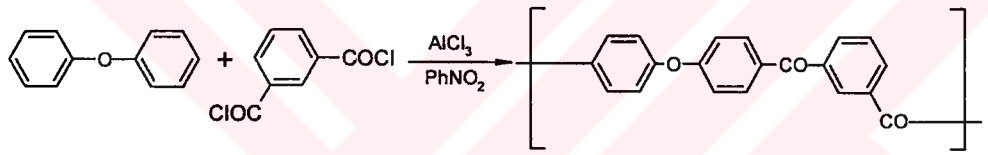
Scheme 2.2 General illustration of PEK and PEEK

In these cases 1,4-phenylene groups have been assumed, but other poly(ether ketones) may contain such groups as 1,3-phenylene, biphenylene, naphthylene, etc.

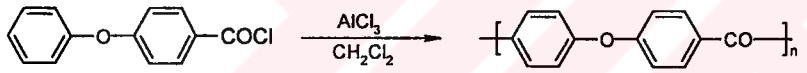
The poly(ether ketones) are a desirable class of polymers which are attracting increasing interest at the present time. Their development has been the subject of recent reviews: however, new publication, mainly in the form of patents, are becoming ever more frequent. Their desirability stems from their extremely high thermal stability, and in this they resemble the polysulfones [6,7]. However, the polysulfones are, with few exceptions, amorphous and subject to attack by solvents. Liquids which may cause cracking, softening, etc. Are present among those which occur in or around aircraft, e.g. dicholoromethane, isopropinol, hydraulic fluid, kerosene, etc. Poly(ether ketones) are usually crystalline and are therefore resistant to attack by solvents, which is especially important when they are used, as is commonly the case, in aerospace environment. The only common room-temperature solvent known for PEK or PEEK is concentrated sulfuric acid.

While crystallinity gives the poly(ether ketones) a unique set of properties among thermoplastic, it is the property, coupled with melting points generally above 300 °C, which makes their synthesis so difficult. The problem is how to keep the polymers in solution and so obtain high moleculer weights. This can be achieved by working at very high temperatures (the nucleophilic process) or by working in strongly acidic media [8] (the electrophilic process) in which the carbonly groups are protonated, allowing the polymer to remain in solution.

The first generally acknowledged attempt [9] to produce a poly(ether ketone) (Scheme (2.2)) failed to produce high moleculer weigth polymer because the product came out of solution prematurely. This was an example of the electrophilic approach to the synthesis, as was the first attempt to make PEK ; again, the moleculer weight was too low to give useful mechanical properties. As given in (2.1) and (2.2).



(2.1)



(2.2)

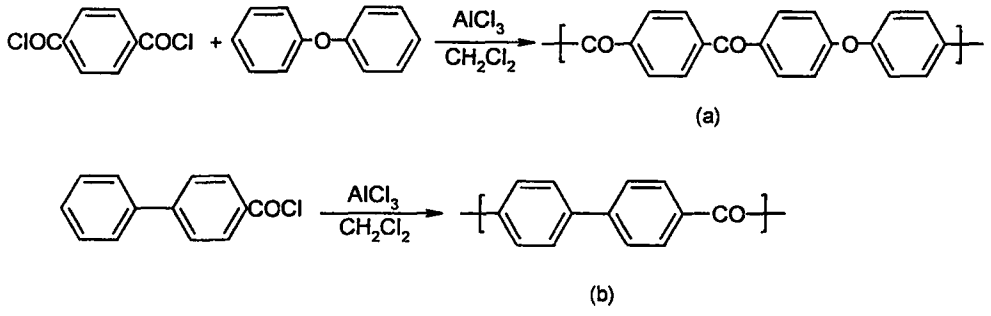
The properties of the PAEKs are such that high selling prices are possible, allowing the use of costly raw materials and/or costly processes. However, there is undoubted pressure to utilize cheap and avaible starting materials, such as phosgene, diphenyl ether, terephthaloyl chloride, etc., to produce another generation of these polymers, and in this respect the first attepts at synthesizing PAEKs are instructive.

Two synthetic routes for producting aromatic PEKs have been described in literature. One involves electrophilic condensation and the other nucleophilic displacement.

2.2.1 Electrophilic Route

The first attempt to produce poly(ether ketones) used aluminum chloride in nitrobenzene to condense isophthaloyl chloride (IC) or terephthaloyl chloride (TC) with diphenyl ether (DPE) or biphenyl. Poly(ether ketone ketone) (PEKK) was

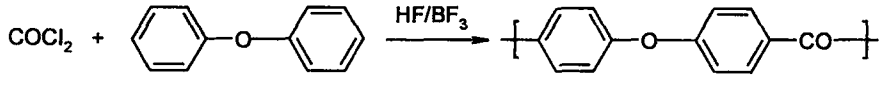
produced (2.1) at 65°C from IC/DPE, from which fibres could be drawn. The materials 'softened' at 250 °C and was soluble in *m*-cresol and tetrachloroethylene. The first PEK was produced in a similar manner using aluminum chloride in dichloromethane to condense *p*-phenoxybenzoyl chloride at room temperature (2.2). The polymer was soluble in dichloroacetic acid. Among others, the polymers **(a)-(b)** were also synthesized as seen in equation (2.3).



(2.3)

It is clear that, in general, the polymer made in these first experiments were too low in moleculer weigth to give really useful properties, and in some cases must have been of low crystallinity, as shown by their solubility, this possibly being due to the presence of aberrant structures.

An attempt to produce PEK by reaction of phosgene with diphenly ether under these conditions, gave only a low yield of low moleculer weight material is seen in (2.4).



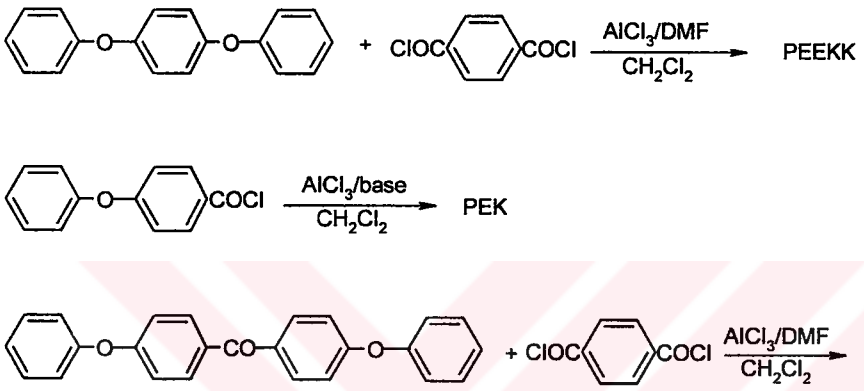
(2.4)

2.2.1.1 $AlCl_3$ Route

The crystalline poly(ether ketones) are insoluble in the commonly used Friedel-Crafts reaction solvents such as dichloromethane, 1,2-dichloroethane, nitrobenzene, carbon disulfide, etc., and it is this which prevents attainment of high moleculer weight. Nevertheless, because of its ease as a laboratory technique, the $AlCl_3$-catalyzed process has been extensively used. [10-11] to produce research quantities of , usually, low moleculer weigth polymers.

The realization that the polymer/catalyst complex is solubilized if large excesses of $AlCl_3$ are used has enabled the production of high moleculer weigth polymers[12,13].

The use of $AlCl_3$ in the ratio of 2,6-5,6 mol per mol of reacting acid chloride group, in the precence of a Lewis base (which is believed to reduce alkylation by the reaction solvents), has yielded a number of high moleculer weigth compositions. As given in (2.5)

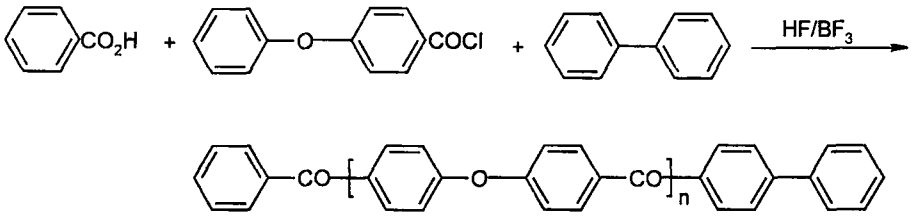


(2.5)

2.2.1.2 HF Process

Polymerization in HF/BF_3 has also seen considerable development [5,23-26] and has been used commercially. When *p*-phenoxybenzoyl chloride is polycondensed in a non-metallic reactor, e.g. of poly(tetrafluoroethylene) (PTFE) construction, PEK of improved colour and melt stability, capable of elongations of 50% or more, is obtained [14].

The mechanical properties of PEK made by this process are improved when low polymer is removed by acetone extraction [15]. Further improvements in colour, stability and reduced branching are achieved by 'double end capping' [16], in which a nucleophilic and an electrophilic reagent are included in the recipe, as shown in (2.6)



(2.6)

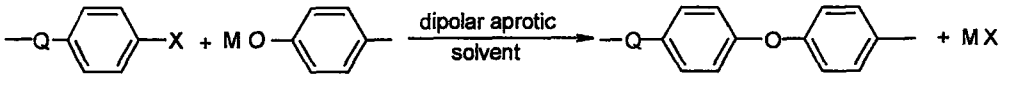
2.2.1.3 Use of Phosgene

The synthesis of useful (tough,high moleculer weight) PEK from the cheap reagents phosgene and diphenly ether (2.7) has long been a desirable target, but one not so far achieved. Generally, low yields of low moleculer weight material have been obtained [17,18], no systematic study of the reasons for this has been carried out, but instability of diphenly ether under certain conditions has been postulated [19], and clearly there is increased scope for non-*para* structures.

(2.7)

2.2.2 Nucleophilic Route

The polymerization process by nucleophilic displacement, originally developed for the production of polysulfones [20], has been successfully adapted by ICI to the production of poly(ether ketones). Essential features in the reactions (2.8) of aromatic halides and alkali metal salts of phenols, to produce sulfone and ketone polymers, are the use of a dipolar aprotic solvent and activation of the halide X by an electron-withdrawing group Q in the *ortho* or *para* position.



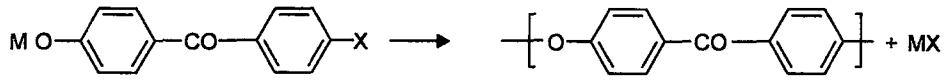
(2.8)

The nature of the electron-withdrawing group, the halide, the cation and the solvent all have a marked influence on the course and rate of reaction. The power of the electron-withdrawing group lies in the order $NO_2 \sim SO_2 > C{=}O > N{=}N$; for the

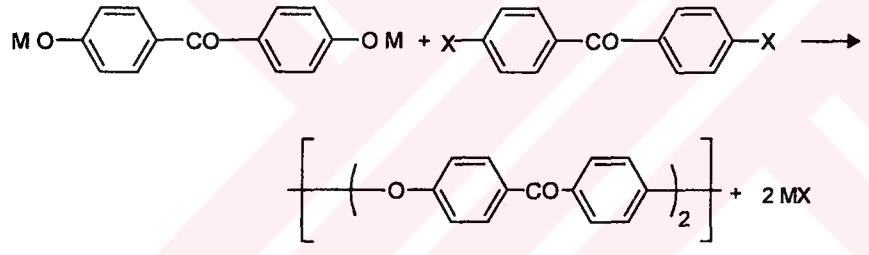
halogenes, F≥ CI > Br > I; and for the alkali metal cations in the order Cs > K > Na > Li. The choice of solvents is complicated, with dimethyl sulfoxide being favoured for polymers.

Crystalline poly(ether ketones) generally require a solvent which can be used at higher temperatures without decomposition which may have a reduced catalytic effect; diphenly sulfone is a favoured example.

Poly(ether ketones) will usually be prepared from a halide activated by the carbonyl group, and can be produced from one-monomer or two-monomer reactions, of which equation (2.9) and (2.10) are examples.



(2.9)



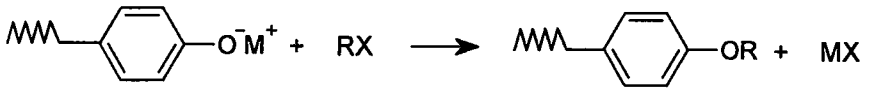
(2.10)

2.2.2.1 Stoichiometry and Moleculer Weight Control

The attainment of high moleculer weight is dependent upon accurate control of stoichiometry, i.e. the molar ratios of reactants (which may also include the base) undergoing polycondensation.

Since it is usually possible to obtain a polymer of undesirably high moleculer weight when the monomers are stoichiometrically in balance, it is usual [21] to arrange for a reactant, most often the dihalide, to be in a slight excess. In the case of the one-monomer reaction (2.9) it is necessary to incorporate a small amount of another reactant, which could be a mono- or di-halide.

Moleculer weight control can also be achieved by monitoring the course of the polymerization and, at the desired point, making an addition of a monofunctional reagent, which may be a phenol or phenoxide or an active halogen compound. This technique not only stops the polymerization but may be used to convert unstable end groups, such as phenoxide or phenol, to the more stable ether end group (2.11).

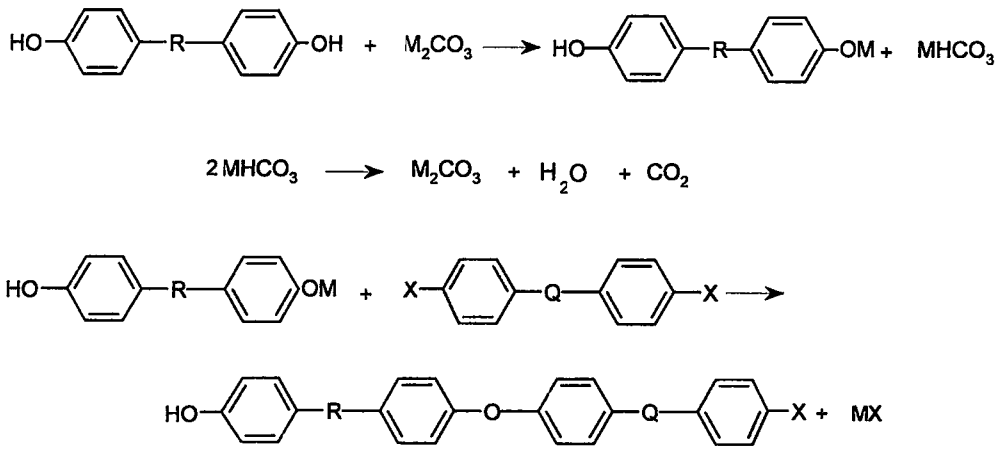


(2.11)

2.2.2.2 Carbonate Process

Controlling stoichiometry on an industrial scale can be problematic. The use of alkali metal hydroxides to prepare phenoxide monomers requires careful stoichiometric control in addition to that required for the balance with dihalide. If the salt formation is carried out in *situ* by reaction of the phenol with alkali metal carbonate [22,23] it is found that the amount of the latter is not critical, since excess carbonate (unlike hydroxide) does not lead to hydrolysis of the halo monomer.

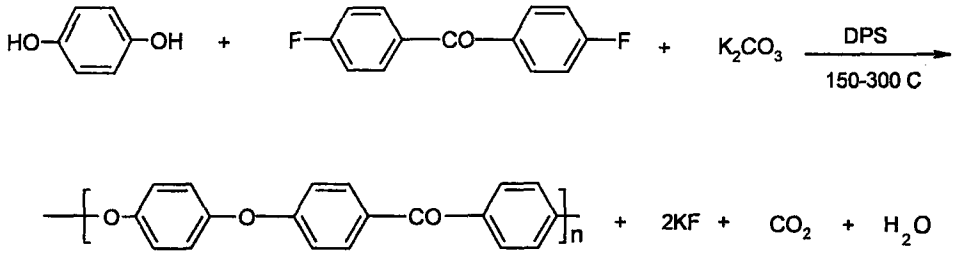
The problems of insolubility and instability of the salts, most marked in the case of hydroquinone, are alleviated, because disalts do not appear to be formed. Monosalt, as soon as it is formed, reacts with dihalo compound to form a soluble phenol ether, which goes on to react with more carbonate, as shown in (2.12)



(2.12)

2.2.2.3 Poly(ether ether ketone) PEEK

The nucleophilic process can be illustrated by the specific example of PEEK, a polymer produced commercially by the chemistry of equation (2.13) [24]. 4,4'-difluorobenzophenone (BDF) can be used; this monomer is not a commodity material but can be produced via a variety of Friedel-Crafts processes.



(2.13)

PEEK has a melting point (T_m) of 334 °C, and, in order to keep the polymer in solution, the final reaction temperature must be not less than about 300 °C.

2.2.3 Properties of Poly(ether ketones)

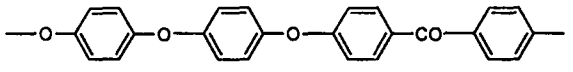
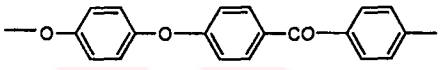
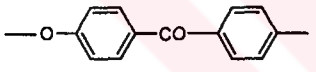
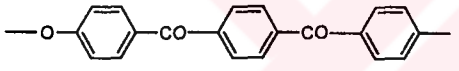
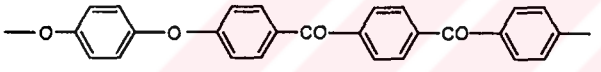
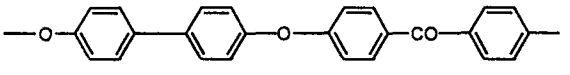
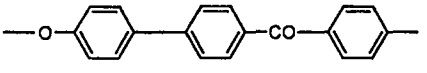
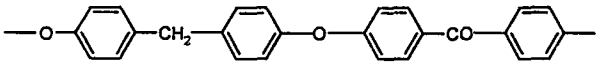
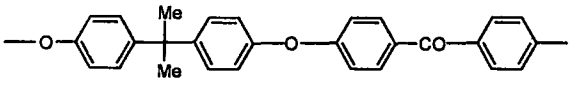
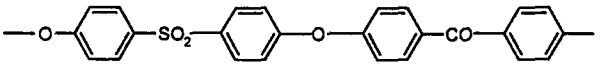
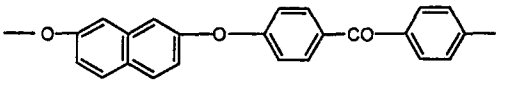
The crystalline poly(ether ketones) are stiff and tough, and resist wear, abrasion and fatigue. They exhibit high temperature performance; that it is the polymers withstand the high (400 °C) temperatures required for processing and, subsequently, can be used at high temperatures (≥200 °C) without oxidation and loss in properties.

They possess low flammability and, when burning, give low levels of smoke and toxic gas. They are solvent resistant and resistant to radiation. The important properties of glass transition temperatures, T_g, and crystalline melting point, T_m, of polymers can be observed by differential scanning calorimetry. The important properties of glass transition temperature, T_g, and crystalline melting point, T_m, obtained by differential scanning calorimetry, are shown for a number of polymer structures in Table 2.1.

It can be seen that the T_g values can range from about 100 °C to over 200 °C and T_m values from about 300 °C to well over 400 °C. Relatively small changes in structure, such as substitution of methylene for carbonyl in the chain, can prevent

crystallization from occurring. There are several parameters that effect the mobility of a polymer chain: backbone flexibility, pendant groups. A polymer chain that can move around fairly easily will have a very low T_g if chain does not move so well will have a high T_g.

Table 2.1 Glass transition temperature (T_g) and crystalline melting point (T_m) for some representative poly(ether ketones).

Structure	T_g (°C)	T_m (°C)
	129	324
	144	335
	154	367
	165	391
	150	365
	167	416
	210	440
	123	f
	155	f
	181	f
	155	f

f :does not crystallise on cooling at 20 °C min^{-1} from the melt.

2.2.3.1 Miscibility and Isomorphism

An interesting and unusual property of the poly(ether ketones) is that blends may exhibit miscibility and isomorphic or immiscible behaviour [25]. The proposed explanation is that the unit cells of the PEAKs are nearly identical, i.e. the units PhO- and PhCO- are interchangeable in the crystalline lattice [26], and, if a blend is miscible in the melt, the two types of chains can be in close proximity during crystallization and will be isomorphic. PEEK is miscible with PEK but not with PEKK; while PEKK is miscible with PEK and PEEKK.

2.2.4 Chemistry of Poly(ether ketones)

Analysis and characterization of PAEKs is made difficult by the absence of room temperature solvents; in spite of this, many of the laboratory techniques applicable to polymers have been successfully employed. IR spectroscopy is possible using powder or film samples, NMR spectroscopy may be carried out in sulfuric or triflic acids, etc.

2.2.4.1 Characterization

Crystallinity and crystal structure have been elucidated by means of wide and small angle X-ray diffraction. Morphology has been studied by electron microscopy and light-polarizing microscopy [27].

Moleculer weight have been measured by light scattering and by gel permeation chromatography (GPC), run in a mixed phenol/trichlorobenzene solvent at 115 °C.

2.2.4.2 Stabilization

The poly(ether ketones) are inherently very stable, but their high melting points lead to elevated processing temperatures, generally above those at which conventional antioxidants can function, and under these conditions oxidative changes can occur. It has been found [28] that certain amphoteric oxides can function as antioxidants for PAEKs, with γ-alumina apparently being most effective.

2.2.4.3 Thermal decomposition

Isothermal decomposition of PEEK and PEK has been studied by thermogravimetry [29]. Volatile decomposition products were analyzed by mass spectroscopy and were found to contain phenol and dibenzofuran.

2.2.4.4 Sulfonation

Poly(ether ketones) containing phenylene groups unprotected by an electron-withdrawing group, such as in PEEK, may be sulfonated in sulfuric acid [30,31,32]. The sulfonated polymer can be converted into its sodium salts [33] by neutralization with sodium acetate. The T_g increases from 143 °C to 415 °C for 100% sodium sulfonate PEEK; ionic clustering is believed to occur at below 25-30 % sodium sulfonate. Fully sulfonated PEEK polymer is water soluble.

2.2.4.5 Crosslinking

Crosslinking may be deliberately induced to improve high temperature performance. This has been achieved using elemental sulfur [34], by insertion of biphenlylene into the chain, by incorporation of by butadiene moieties [35].

2.3 PHOSPHAZENES

Phosphazenes are substrates that contain –P=N- units in their chemical structures. The singular characteristic of these molecules is the great variety of different compounds that can be embodied in this class of materials, ranging from high polymers to low-moleculer-weigth oligomers. Why phosphazene compounds and their derivations are of importance can be summarize as follows:

- Linear phosphazene polymers show unusual flexibility, high thermal stability, flame resistance, high oxygen index values, low smoke evolution properties and chemical stability against strong acid, bases and aggressive chemicals. Thus they have potential applications in biomedicine, photochemistry, resist technology, organometallic chemistry, membranes, liquid crystals, non-linear optics, photo-chromism, catalysis, electrical conductivity, hybrid materials, silicon-containing substrates, ceramics, piezo-electricity, tribology, electrochromism and holography.
- Cyclic phosphazene oligomers behave as biologically active materials as a result of their antitumor, insect chemosterilant, pesticide and fertilizer activities, show potential applicability as flame-retardant additives (for cellulose materials, synthetic fibers, textiles, polyurethanes and several different commercial organic macromolecules) with a considerably high limiting oxygen index (LOI), clathrates for solvent separation or stereoregulated free-radical polymerizations and high-temperature resistant fluids. Resently, they have also been found to be excellent phase-transfer catalysts as polypodants or cryptands, photoinitiators for radical polymerization, photo-stabilizers and antioxidants for organic commercial polymers, such as polystyrene or polyolefins, and dendrimers.
- Cyclolinear polymers have attracted some attention as flame-resistant materials in the past, but no significant commercialization of these substrates has occured to date. In contrast, cyclomatrix polymers have proved to be very interesting products, with potential application as structural plastics, protective coatings resistant to strongly aggressive chemicals, thermal-and fire- stable matrices, high-temperature adhesives, heat- and radiation-resistant electrical components, and

laminating resins; for these materials industrial development on a commercial scale has been attempted.

- Organic, carbon-backboned polymers containing pendant side cyclophosphazene moieties show interesting characteristics as flame-retardant additives chemically attached to a polymeric organic chains or as ionic conductive materials for light batteries [36].

2.3.1 Synthesis of Cyclophosphazenes

Cyclophosphazenes (CP) are cyclic molecules formed of three (or more) –P=N- repeating units, and contain 'formal' unsaturations in the cycle and two substituents at the phosphorus atom. The chemical structures of both cyclotriphosphazenes and cyclotetraphosphazenes, the most common members of this series, are reported in Scheme 2.3. Other homologues, containing five, six, seven, etc. –P=N- groups are known, but are less frequently encountered.

Scheme 2.3 General structure of trimeric and tetrameric cyclophosphazenes

Although several methods have been established over the years to prepare different types of cyclophosphazene derivative (e.g. reactions between phosphorus(III) halides with sodium azide, cyclization of linear 1,3-diamines with halophosphoranes, etc.), the general procedure for synthesizing these substrates deals with the reactions of halophosphoranes with ammonium halides in boiling *syn*-tetrachloroethane or *o*-dichlorobenzene, according to the following reaction (2.14)

$$n\mathrm{R_1R_2PX_3} + n\mathrm{NH_4X} \rightarrow (\mathrm{NPR_1R_2})_n + 4n\mathrm{HX} \qquad (2.14)$$

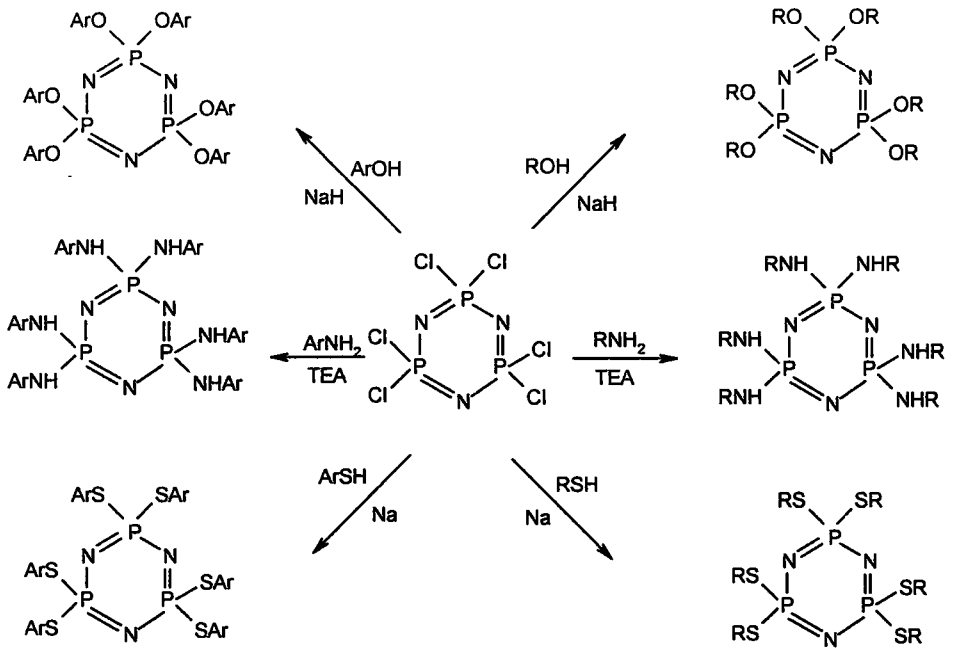
where R_1 and R_2 may be Cl, Br or organic groups, and X are Cl or Br. In these reactions, cyclotri- and cyclotetraphosphazenes are predominantly formed; they contain only one type or mixed types of halogens, and/or alkyl or phenly groups bonded at the phosphorus, depending on the chlorophosphorane exploited for these reactions.

The oldest member of the cyclophosphaneze series, and also the most important one, is hexachlorocyclotriphosphazene (HCCP), $(NPCl_2)_3$ as seen in Scheme 2.3. It is a white, crystalline compound that was synthesized for the first time by Liebig and Wöhler in 1834 by reacting phosphorus pentachloride with gaseous ammonia. Subsequently, it took more than a century to have the composition and moleculer weigth of this substrate recognized, its chemical reactivity explored and its synthetic procedure established definitively.

The key role played by hexachlorocyclotriphosphazene in the chemistry of phosphazene materials has emerged clearly only recently, when;

- This compound was used as a starding point for the synthesis of substituted and partially substituted cyclophosphazenes containing organic and/or organo-metallic residues; and
- Allcock succeeded in the polymerization of this compound to polydichlorophosphazene, $(NPCl_2)n$, thus opening up the way to poly(organophosphazene)s, accompletely new series of organo-inorganic macromolecules [37].

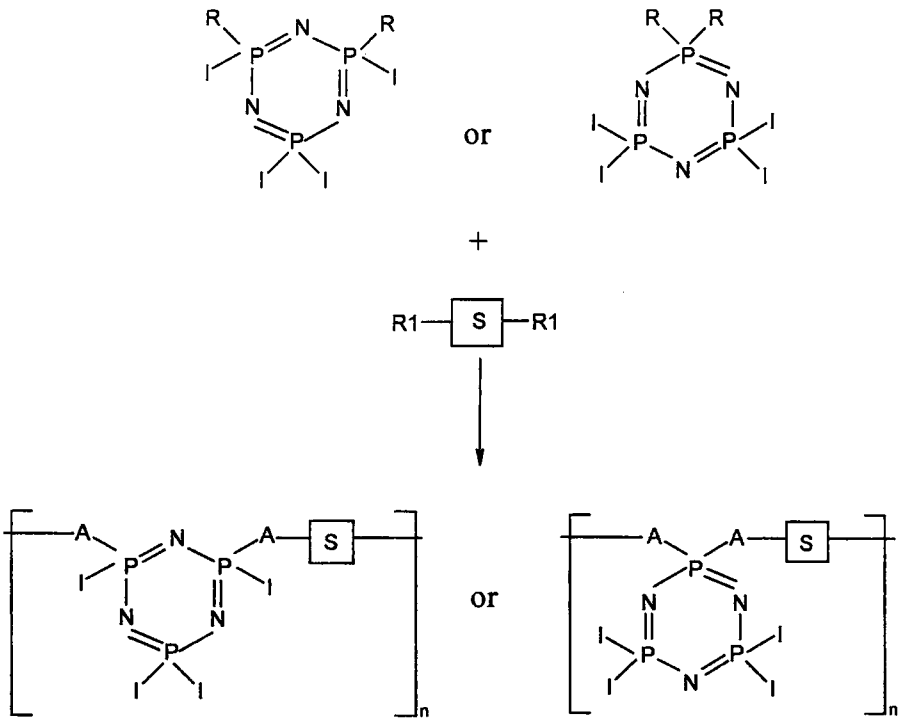
Cyclo(organo)phosphazenes, in fact, are usually prepared by nucleophilic displacement of the reactive chlorines of HCCP and their substitution with variable type of aliphatic and aromatic amines and thio organic derivaties according to the routes reported in Scheme 2.4.



Scheme 2.4 General reaction scheme for the preparation of hexa-substituted cyclo(organo-phosphazene)s.

2.3.2 Synthesis of cyclolinear polymers

Cyclolinear polymers are, in general, low-moleculer-weigth phosphazene oligomers in which cyclophosphazene rings are part of the repetitive skeletal units of these materials. They are the result of the reaction between substituted cyclophosphazenes containing only two reactive functions and bifunctional organic reagents of variable structures and properties. The general scheme for the preparation of these substrates is reported in Scheme 2.5., while the different types of chemical reaction that have been established over time for the synthesis of these materials are collected in Table 2.1. Here, the reactive function 'R_1' of the organic difunctinal reagents, the function 'A' resulting from the reaction of R + R_1 and the low-moleculer-weigth substances eventually eliminated during the process are indicated for all the species involved in the chemical process.



Where:

'R' are reactive functions supported onto the cyclophosphazene compounds;

'I' are inert groups supported onto the cyclophosphazene compounds;

'R1' are reactive functions contained in the organic bifunctional molecules;

'A' is an organic function resulting from the reaction of R and R1;

'S' is an aliphatic or an aromatic spacer group.

Scheme 2.5 General Synthetic Patterns for the Preparation of Cyclolinear Phoshazene Polymers.

From this table it is evident that comparatively much less work has been devoted to the preparation of cyclolinear phosphazene polymers compared with the efforts dedicated to the cyclomatrix substrates. It is also evident that the same type of reactions (i.e. condensation, esterification, elimination, substitution, etc.) were exploited for the preparation of both types of phosphazene macromolecule. The only exception to this rule seems to be the thermally or photochemically induced opening of the unsaturated double bonds attached to cyclophosphazene compounds.

Finally, the industrial utilization of cyclolinear phosphazene polymers appears to be considerably lower than that of the corresponding cyclomatrix substrates which are

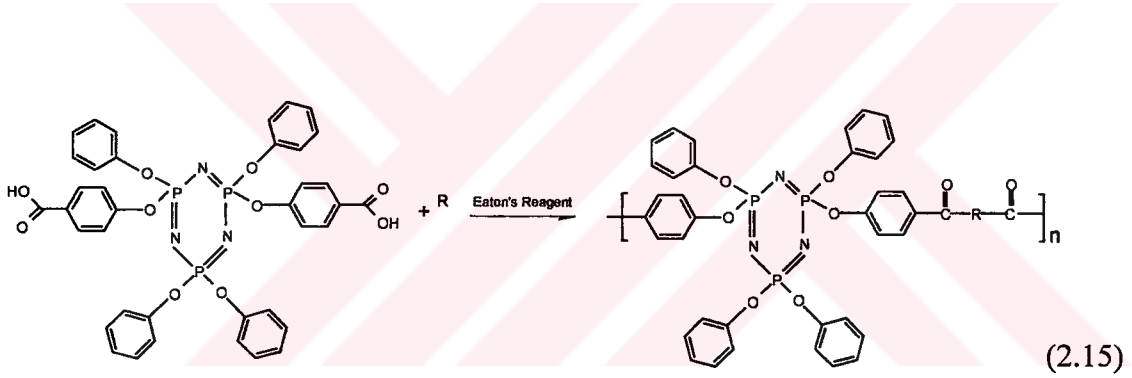
widely used as thermosetting resins, heat-resistant mouldings, reinforced structural plastics or laminates, and thermally stable surface coatings. A lot of polymer which containing cyclotriphosphazene units have been synthesized. A several examples can be given as follows.

Table 2.2 Reactive groups and generated chemical functions in the preparation of cyclolinear phosphazene polymers.

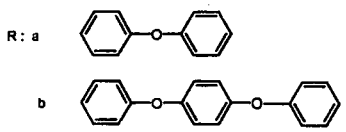
R	R_1	A	Evolved Product
$-NH_2$	HO-Alkyl-	P-O-Alkyl-	NH_3
$-NH_2$	Cl-Si-$(Ph)_2$-O-	-NH-Si-$(Ph)_2$-O-	HCl
$-NH_2$	$-NH_2$	-NH-	NH_3
$-NH_2$	OCN-Aryl-	-NH-CO-NH-Aryl-	-
$-NH_2$	Cl-CO-$Alkyl_1$	-NH-CO-$Alkyl_1$-	HCl
$-NH_2$	Cl-P-	-NH-P-	HCl
$-NO_2$	Na^{+-}O-Ar-	-O-Ar-	$NaNO_2$
-Cl	HO-Aryl-	-O-Aryl-	HCl
-Cl	HO-P-	-O-P-	HCl
-Cl	CH_2=CH-CH_2-	-CH_2-CHCl-CH_2-	-
-OH	Cl-Si-$(Ph)_2$-	-O-Si-$(Ph)_2$-	HCl
-OH	OCN-Aryl-	-O-CO-NH-Aryl-	-
-O-Alkyl	HO-$Alkyl_1$-	-O-$Alkyl_1$-	Alcohol
-O-Alkyl	HO-Aryl-	-O-phenyl-	Aryl alcohol
-O-Alkyl	Cl-Si-$(Ph)_2$-	-O-Si-$(Ph)_2$-	Alkly-Cl
$-N_3$	Ph_2P-$(CH_2)_n$-	-N=PPh_2-$(CH_2)_n$-	N_2
-NCS	HO-$Alkyl_1$-	-NH-CS-$Alkyl_1$-	-

2.3.2.1 Aromatic Poly(ether ketone)s Containing Cyclotriphosphazene Units

Tunca and Hızal described the synthesis and characterization of novel PAEKs containing tetrakisphenoxy substituted cyclotriphosphazene units containing. PAEK's were prepared by direct polycondensation of bis(4-oxybenzoic acid) tetrakis (phenoxy) cyclotriphosphazene (1) with diphenylether or 1,4-diphenoxybenzene using Eaton's reagent as condensing agent and solvent as seen in (2.15). polycondensation at 120 °C gave polymer of high moleculer weight. Incorporation of cyclophosphazene groups in the aromatic poly(ether ketone) backbone greatly enhanced the solubility of these poymers in common organic polar solvents. Thermal stabilities by TGA for polymer series ranged from 390 to 354 °C in nitrogen at 10% weight loss and glass transition temperatures (T_g) ranged from 81.4 to 89.6 °C by DSC [38].



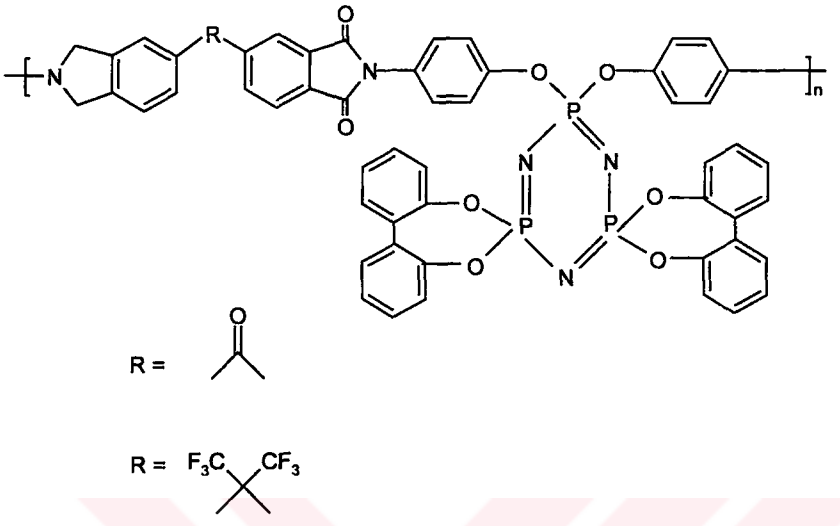
(2.15)



2.3.2.2 Aromatic Cyclolinear Phosphazene Polyimides

Kumar and Gupta have developed a new class of cyclolinear polyimides containing bis(aryleneoxy)spirocyclotriphosphazene as an integral part of polymer chain and reported them . The polyimides offer advantages of thermooxidative stability and high char yield in air. The observation of high char yield in an air atmosphere, colorless to light-yellow color films, and bulky bis-spiro-substituted pendants makes cyclotriphosphazene-containing polyimides potential candicates for a variety of applications in space, aerospace, microelectronics, and membrane technologies. The

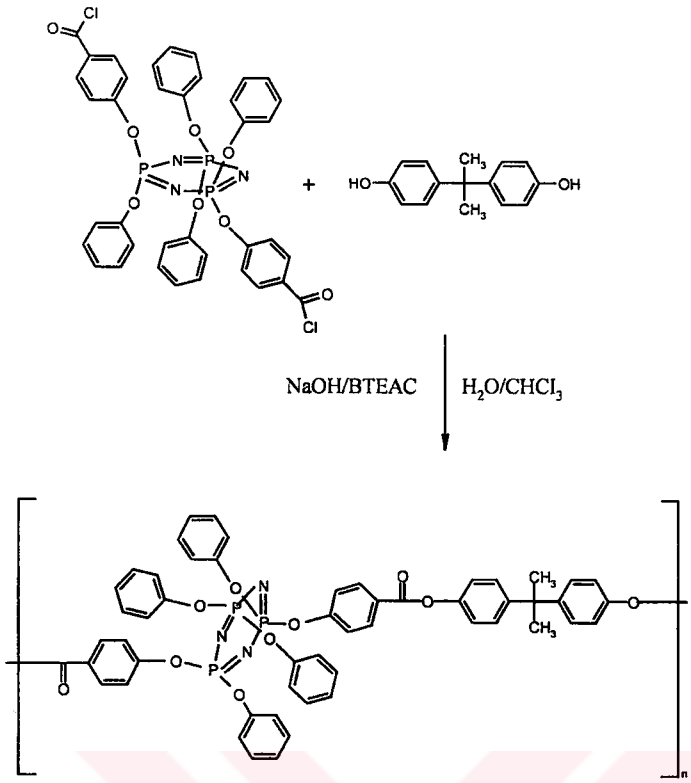
thermal stability of the polymers was investigated by dynamic thermogravimetry in air, and showed thermooxidative decomposition starting at ~ 410 °C and a char yield in the range of 58-50 % at 800 °C in an air atmosphere [39]



(2.16)

2.3.2.3 Synthesis of Polyesters from Cyclotriphosphazenes

Miyata at al prepared polyesters containing cyclotriphosphazene units by phase transfer catalyzed two-phase polycondensation and direct polycondensation. The polycondensation of the acid chloride of (trans-2,4-dicarboxyphenoxy-2,4,6,6-tetraphenoxy) cyclotriphosphazene (trans-CPP) and bisphenol A (BA) in the presence of benzyltriethylammonium chloride (BTEAC) as phase transfer reagent gave a polyester with a moleculer weight of 22,000 as given in (2.17). the homopolyester prepared from trans-CPP and BA exhibited a significantly low glass transition temperature of 65°C, and the copolymers had glass transition temperatures in the range 220-91°C, depending on the contents of trans-CPP units. Thermogravimetric analysis showed that the homopolyester was stable up to 390°C in a nitrogen atmosphere, and the char yield of copolyester with 5.5 mol % of trans-CPP units was 36% at 600°C, which was seven times higher than that of the polyester without cyclotriphosphazene units [40].



(2.17)

PART 3

EXPERIMENTAL PART

3.1 Chemicals

Hexachlorocyclotriphosphazene (Fluka), 2,2'- dihydroxy-1, 1'-biphenyl (Fluka), tetrabutylammonium bromide (TBAB) (Aldrich), 4-fluoro-4'-hydroxy benzophenone (Aldrich), 4,4'-difluoro benzophenone (Fluka), 4,4'-isopropylidenediphenol (Aldrich), 4,4'-(hexafluoroisopropylidene) diphenol (Fluka) and sodium hydride (80 %) (Fluka) were used as received. Tetrahydrofuran (THF) and N, N-dimethylacetamide (DMAc) were purified by conventional drying and distillation procedures.

3.2 Synthesis of 2,2-dichloro-4, 4,6,6- bis [spiro (2,2'-dioxy-1', 1''-biphenylyl)] cyclotriphosphazene (1)

The compound 1 was synthesized as described in literature [41]. m.p.: 325 °C (325.7°C Lit. [41]) Elem. Anal. Calcd. for $C_{24}H_{16}C_{l2}N_3O_4P_3$: C % 50.14, H % 2.78, N % 7.31; Found: C % 50.66, H % 2.83, N % 7.25. ^{1}H NMR ($CDCl_3$, δ ppm): 7.3-7.6 (m, 16 H, aromatic protons of two dioxybiphenyl groups); ^{31}P NMR ($CDCl_3$, δ ppm): 30.77 (t, P-Cl_2, Jpp= 79.33 Hz), 21.05 (d, P-dioxybiphenyl groups, Jpp=79.13Hz)

3.3 Synthesis of 2,2-bis (4'-fluorobenzoylphenoxy)-4,4,6,6-bis [spiro (2', 2''-dioxy-1', 1''-biphenylyl)] cyclotriphosphazene (2)

2 g (3.48 mmol) of (**1**), 1.88 g (8.7 mmol) of 4-fluoro-4'-hydroxy benzophenone and 0.266 g (8.7 mmol) of sodium hydride (80 %) were dissolved in 100 mL of dry THF. The reaction mixture was refluxed under nitrogen for 48 hours and then filtered. The filtrate was concentrated to a volume of 40 mL and precipitated drop wise into hexane. The obtained white solid was washed with ethanol several times and dried to give 2.95 g (Yield: 91 %). m.p.: 144 °C (by DSC). Elem. Anal. Calcd. for $C_{50}H_{32}F_2N_3O_8P_3$: C % 64.25, H % 3.42, N % 4.50; Found: C % 64.62, H % 3.50, N % 4.44. ^{1}H NMR ($CDCl_3$, δ ppm): 7.7-7.9 (m, 8H, ortho carbonyl groups), 7.29-7.43 (m, 8H, aromatic protons of dioxybiphenyl groups), 7.49-7.55 (m, 8H, aromatic protons of dioxybiphenyl groups), 7.0-7.2 (m, 8H, meta to carbonyl groups) ^{13}C NMR ($CDCl_3$, δ ppm), 193.9(C=O), 167.56, 163.51, 154.20, 154.09, 148.18, 134.76, 133.97, 133.92, 132.63, 132.48, 131.77, 129.79, 129.75, 128.83, 126.27, 121.84, 121.24, 121.15, 11.76, 115.42, is given Appendix 3.1.;^{31}P NMR ($CDCl_3$, δ ppm): 26.66 (d, P-dioxybiphenyl groups, Jpp= 93.8 Hz), 10.70 (t, P- 4'-fluorobenzoylphenoxy groups, Jpp= 93.8 Hz)

3.4 A Typical Polymerization Procedure of Polymer I

A flask equipped with a magnetic stirrer, a Dean-Stark trap and condenser was charged with a difluoro compound **2** (1.115 g, 1.195 mmol), bisphenol **4a** (0.272g, 1.195mmol), DMAc (6 mL), toluene (6 mL), and anhydrous K_2CO_3 (0.335 g, 2.42 mmol). The mixture was refluxed for 1 h to remove the water produced. The toluene was then removed, and the reaction was continued at low reflux for 4 h at 162°C. After cooling, the reaction mixture diluted with DMAc was poured into methanol containing a small amount of acetic acid. The resulting polymer was filtered, washed with methanol and dried at 100°C.

The THF soluble polymers are dissolved in THF, filtered and poured into methanol to precipitate out the polymer.

3.5 The Polymerization Procedure for Polymer II-VI

a) For Polymer II

A flask equipped with a magnetic stirrer, a Dean-Stark trap and condenser was charged with a difluoro compound **2** (0.7805 g, 0.8365 mmol), bisphenol **4b** (0.4013, 1.195mmol), 4,4'-difluorobenzophenone **3** (0.0782 g, 0.3585 mmol), DMAc (6 mL), toluene (6 mL), and anhydrous K_2CO_3 (0.335 g, 2.42 mmol). The mixture was refluxed for 1 h to remove the water produced. The toluene was then removed, and the reaction was continued at low reflux for 4 h at 162°C. After cooling, the reaction mixture diluted with DMAc was poured into methanol containing a small amount of acetic acid. The resulting polymer was filtered, washed with methanol and dried at 100°C.

The THF soluble polymers are dissolved in THF, filtered and poured into methanol to precipitate out the polymer.

b) For Polymer III-VI

These polymers were synthesized through the same procedure by taking the mole rate given in Table 4.1.

3.6 A Typical Polymerization Procedure of Polymer VII

A flask equipped with a magnetic stirrer, a Dean-Stark trap and condenser was charged with a difluoro compound **2** (1.115 g, 1.195 mmol), bisphenol **4b** (0.4013, 1.195mmol), DMAc (6 mL), toluene (6 mL), and anhydrous K_2CO_3 (0.335 g, 2.42 mmol). The mixture was refluxed for 1 h to remove the water produced. The toluene was then removed, and the reaction was continued at low reflux for 4 h at 162°C. After cooling, the reaction mixture diluted with DMAc was poured into methanol containing a small amount of acetic acid. The resulting polymer was filtered, washed with methanol and dried at 100°C.

The THF soluble polymers are dissolved in THF, filtered and poured into methanol to precipitate out the polymer.

3.7 The Polymerization Procedure for Polymer VIII-XII

a) For Polymer VIII

A flask equipped with a magnetic stirrer, a Dean-Stark trap and condenser was charged with a difluoro compound **2** (0.7805 g, 0.8365 mmol), bisphenol **4b** (0.4013, 1.195 mmol), 4,4'-difluorobenzophenone **3** (0.0782 g, 0.3585 mmol), DMAc (6 mL), toluene (6 mL), and anhydrous K_2CO_3 (0.335 g, 2.42 mmol). The mixture was refluxed for 1 h to remove the water produced. The toluene was then removed, and the reaction was continued at low reflux for 4 h at 162°C. After cooling, the reaction mixture diluted with DMAc was poured into methanol containing a small amount of acetic acid. The resulting polymer was filtered, washed with methanol and dried at 100°C.

The THF soluble polymers are dissolved in THF, filtered and poured into methanol to precipitate out the polymer.

b) For Polymer IX-XII

These polymers were synthesized through the same procedure by taking the mole rate given in Table 4.2.

3.8 Characterization

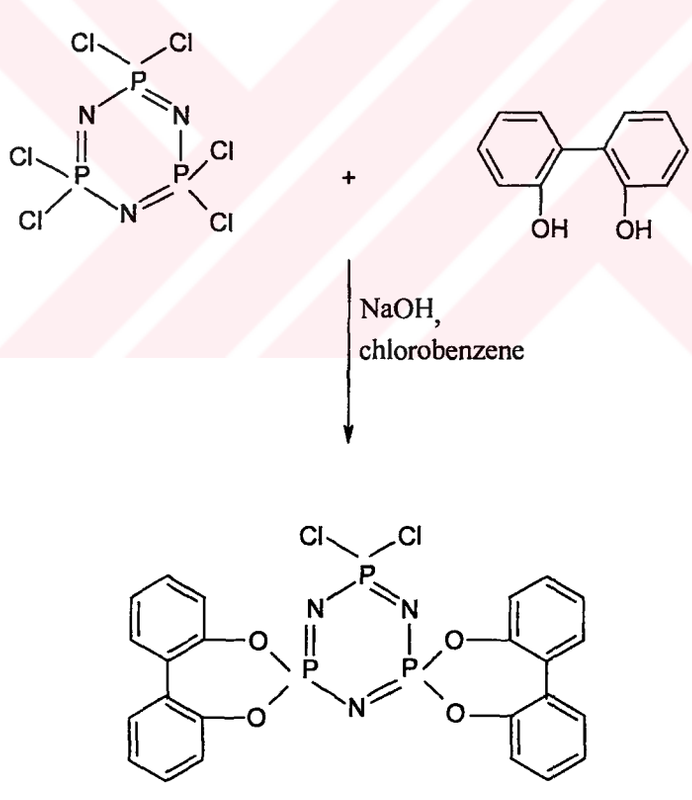
The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker spectrometer (250 MHz for proton and 62.86 MHz for carbon). The ^{31}P NMR spectra were obtained with a Bruker spectrometer at 121 MHz. The chemical shifts were referenced to 85% H_3PO_4 in $CDCl_3$ at 0 ppm. ^{31}P NMR spectra were observed under conditions of ^1H decoupling. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were conducted on a Perkin Elmer DSC 6 and Shimadzu TG 50, respectively.

Gel permeation chromatography (GPC) analyses were performed with an Agilent Model 1100 instrument consist of pump and RI detector and three Waters Styragel columns (HR 4, HR 3, and HR 2). THF was eluent at a flow rate of 0.3 mL /min at 30 ^{o}C. The molecular weight of polymers was calculated with the aid of polystyrene standards.

PART 4

RESULTS AND DISCUSSION

4.1 Synthesis of 2,2-dichloro-4, 4,6,6-bis [spiro (2,2'-dioxy-1', 1''-biphenylyl)] cyclotriphosphazene (1)

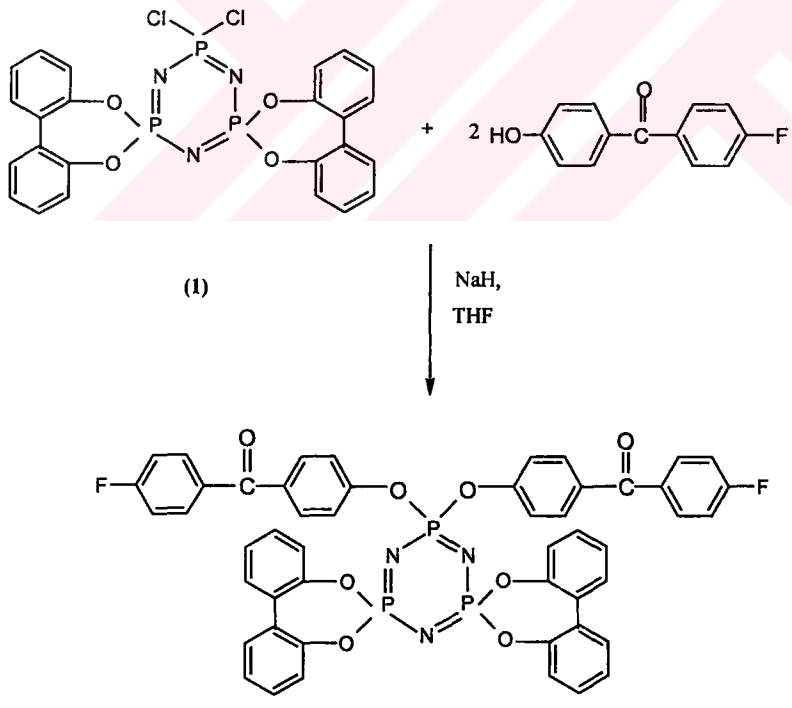


(1)

Scheme 4.1 Synthesis of 2,2-dichloro-4,4,66-bis[spiro(2,2'-dioxy-1',1''-biphenylyl)] cyclotriphosphazene

Hexachlorocyclotriphosphazene was first reacted with 2 moles of 2,2'- dihydroxy-1, 1'-biphenyl to give 2,2-dichloro-4,4,6,6- bis [spiro (2,2'-dioxy-1',1''-biphenylyl)] cyclotriphosphazene **1** in heterogeneous system containing water and chlorobenzene and in the presence of a phase transfer catalyst (TBAB) and NaOH as shown in Scheme 4.1. The dichloro compound 1 was characterized by elemental analysis, ^{1}H and ^{31}P NMR spectroscopy. ^{1}H NMR spectrum showed a large multiplet which can be assigned to the protons of biphenyl groups as given in Appendix 4.1. However, it was not informative, ^{31}P NMR spectrum is of AB_2 type corresponding to the two differently substituted phosphorus atoms in the cyclotriphosphazene ring as seen in Appendix 4.2. The characterization of 1 revealed that no mono spiro product was isolated, therefore affording a clean pathway to synthesize difluoro monomer 2.

4.2 Synthesis of 2,2-bis (4'-fluorobenzoylphenoxy)-4,4,6,6-bis [spiro (2', 2''-dioxy-1', 1''-biphenylyl)] cyclotriphosphazene (2)



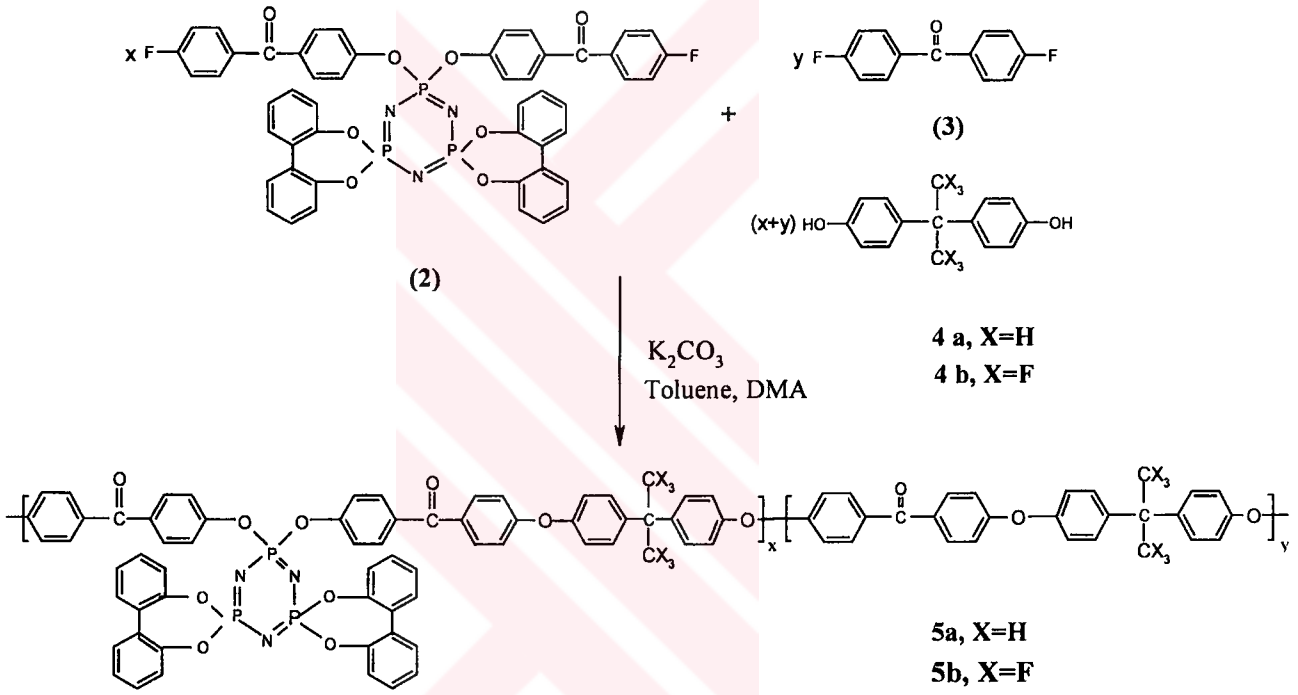
(2)

Scheme 4.2 Synthesis of 2,2-bis (4'-fluorobenzoylphenoxy)-4,4,6,6-bis [spiro (2',2''-dioxy-1',1''-biphenylyl)] cyclotriphosphazene (2)

The reaction of **1** with sodium salt of 4-fluoro-4'-hydroxy benzophenone in refluxing THF gave the difluoro monomer **2** as illustrated in scheme 4.2. The elemental analysis was compatible with proposed structure of **2**. The ^{1}H NMR spectrum of **2** in $CDCl_3$ shows that a multiplet peak corresponding to eight aromatic protons ortho to C=O groups appears at 7.7-7.9 ppm. Another multiplet peak assigned to eight aromatic protons meta to C=O groups was observed at 7.0-7.2 ppm. The dioxybiphenyl aromatic protons were seen as two multiplets at 7.29- 7.43 (8H) and 7.49-7.55 ppm (8H), respectively. The integration of dioxybiphenyl aromatic protons to 4'-fluorobenzoylphenoxy aromatic protons was obtained in a ratio of 1:1, confirming the structure of **2** as seen in Appendix 4.3. Also ^{31}P NMR spectrum of difluoro compound exhibited AB_2 type pattern with a coupling constant of 93.8 Hz, indicating the presence of two types phosphorus in the cyclotriphosphazene ring, substituted with 4'- fluorobenzoylphenoxy and dioxybiphenyl groups as given in Appendix 4.4.

Melting point of **(2)** was measured as 144 °C by DSC as given in Appendix 4.5

4.3 A Typical Polymerization Procedure of Polymer I



Scheme 4.3 A Typical Polymerization Procedure Polymer I

Polymerization reactions involving the novel difluoro monomer **2** and/or 4,4'difluoro benzophenone **3** were carried out with bisphenols (**4a** and **b**) and K_2CO_3 in DMAc is given in Scheme 4.3. The reaction conditions and the properties of two series of polymers (**5a** and **b**) are presented in Tables 4.1 and 4.2. The gradually decrease in the contents of cyclotriphosphazene units in the polymer backbone brought about an increase in the solubility in organic polar solvents such as THF. This could be attributed to the bulky bis-spiro dioxybiphenyl groups attached to the cyclotriphosphazene ring in the PEK backbone. In the first polymerization system, **5a**, the THF soluble polymer was first obtained in mol ratio of 0.3. However, in the second case, **5b**, it was attained at 0.6 (Tables 4.1 and 4.2). The incorporation of CF_3 groups into the polymer backbone enhances the polymer solubility [42].

The apparent molecular weights of the polymers as determined by GPC are given in Tables 4.1 and 4.2. The GPC traces of the THF soluble polymers display a unimodal distribution with the moderately high molecular weight (M_w) values ranging from 49,000- 13,000. The polymers partly soluble in THF showed large poly dispersity values, e.g. 7-8, as a result of their low molecular weight fraction. The GPC traces belonging to the Polymers I, II, VII and VIII are presented in the Appendixes 4.6, 4.7, 4.8, 4.9 respectively.

The gradually decrease in the contents of cyclotriphosphazene units in the polymer backbone also reflected in the decrease of T_g values, measured by DSC at a heating rate of 10°C/min under nitrogen, for both polymerization systems (Tables 4.1 and 4.2). This could be the result of reduced flexibility of the dioxybiphenylyl spiro seven membered ring in a cyclotriphosphazene unit . All polymers obtained are amorphous and displayed T_gs in the range of 170 to 190°C. T_g values of the polymers in **5b** series are slightly higher than those of the corresponding polymers in **5a** series, due to CF_3 groups, which inhibit free rotation of the polymer backbone to a greater extent than CH_3 groups. Higher T_gs for both polymer series are also an evidence of the incorporation of cyclotriphosphazene units into PEK backbone, since the T_g values of aromatic PEKs derived from 4,4'-difluoro benzophenone **3** and bisphenols **4a** or **b** are at 153 and 164°C, respectively. T_g values of the polymers numbered as I, II, VII, and VIII, are shown correspondingly in the Appendixes 4.10, 4.11, 4.12, 4.13.

The thermal stabilities of the polymers were studied by TGA in nitrogen atmosphere at a heating rate of 10°C/min. The PEKs of two series, **5a** and **b**, demonstrated polymer decomposition temperatures ranging from 416 to 458°C at 10% weight loss (Tables 4.1 and 4.2). When comparing the thermal stabilities, it was seen that **5b** series polymers would have slightly higher TGA values than those of corresponding polymers in **5a**. This is because that the CF_3 groups between ether linkages in the polymer backbone are resistant to attack by free radicals or oxidation. In both of polymer series, the highest TGA values were obtained for polymers I and VII. It should be taken into account that PEKs obtained in this work have rather higher T_g and TGA values than PEKs containing arylenoxy-substituted cyclotriphosphazene units. All of the polymers displayed char yields of approximately 50% in nitrogen at 650°C. TGA values related to the polymers I, II, VII and VIII are given in the Appendixes 4.14, 4.15, 4.17, 4.18 correspondingly.

Clear and brittle films of polymers VI and IX -XII have been obtained by solution casting from $CHCl_3$.

Table 4.1 Synthesis and properties of PEKs, **5a**

					Polymer				
Polymer Sample	**2 (mmol)**	**3 (mmol)**	**4a (mmol)**	**2 / (2+3) mol ratio**	**Yield (%)**	**M_w[a]**	**M_n[a]**	**T_g[c] (°C)**	**TGA[d] (10%)**
I	1.195	-	1.195	1	94	16,500[b]	5,200[b]	188	444
II	0.8365	0.3585	1.195	0.7	95	31,200[b]	7,600[b]	181	429
III	0.717	0.478	1.195	0.6	90	61,300[b]	7,200[b]	179	438
IV	0.5975	0.5975	1.195	0.5	97	62,000[b]	9,400[b]	177	437
V	0.478	0.717	1.195	0.4	89	68,000[b]	19,100[b]	173	419
VI	0.3585	0.8365	1.195	0.3	93	34,200	15,000	167	416

[a]Determined by GPC based on polystyrene standards.
[b]THF soluble fraction was measured due to incomplete solubility in THF.
[c]From second heating run at midpoint in the transition at a heating rate of 10°C/min.
[d]At a heating rate of 10°C/min under nitrogen atmosphere.

Table 4.2 Synthesis and properties of PEKs, **5b**

Polymer Sample	2 (mmol)	3 (mmol)	4b (mmol)	2 / (2+3) mol ratio	Polymer				
					Yield (%)	M_w[a]	M_n[a]	T_g[c] (°C)	TGA[d] (10%)
VII	1.195	-	1.195	1	90	53,400[b]	11,500[b]	190	458
VIII	0.8365	0.3585	1.195	0.7	80	39,300[b]	15,200[b]	184	439
IX	0.717	0.478	1.195	0.6	80	13,100	8,200	182	435
X	0.5975	0.5975	1.195	0.5	80	49,200	17,500	179	431
XI	0.478	0.717	1.195	0.4	99	19,300	11,000	176	430
XII	0.3585	0.8365	1.195	0.3	85	18,200	11,300	173	434

[a]Determined by GPC based on polystyrene standards.
[b]THF soluble fraction was measured due to incomplete solubility in THF.
[c]From second heating run at midpoint in the transition at a heating rate of 10°C/min.
[d]At a heating rate of 10°C/min under nitrogen atmosphere.

CONCLUSIONS

A novel difluoro monomer containing bis-spiro dioxybiphenyl groups attached to the cyclotriphosphazene ring was prepared and reacted with 4,4'-difluoro benzophenone as a comonomer and bisphenols to produce PEK. Gradually decreasing the amount of cyclotriphosphazene monomer in polymerization reaction resulted in PEKs soluble in THF. The PEKs obtained herein displayed lower thermal stabilities and similar T_g values compared to those of wholly aromatic PEK.

These studies are expected to contribute to the development of the polymerization techniques, in a good way, of the different polymers containing cyclophosphazene units and then enable the manufacturing of the advanced technologic materials with better mechanical and physical properties.

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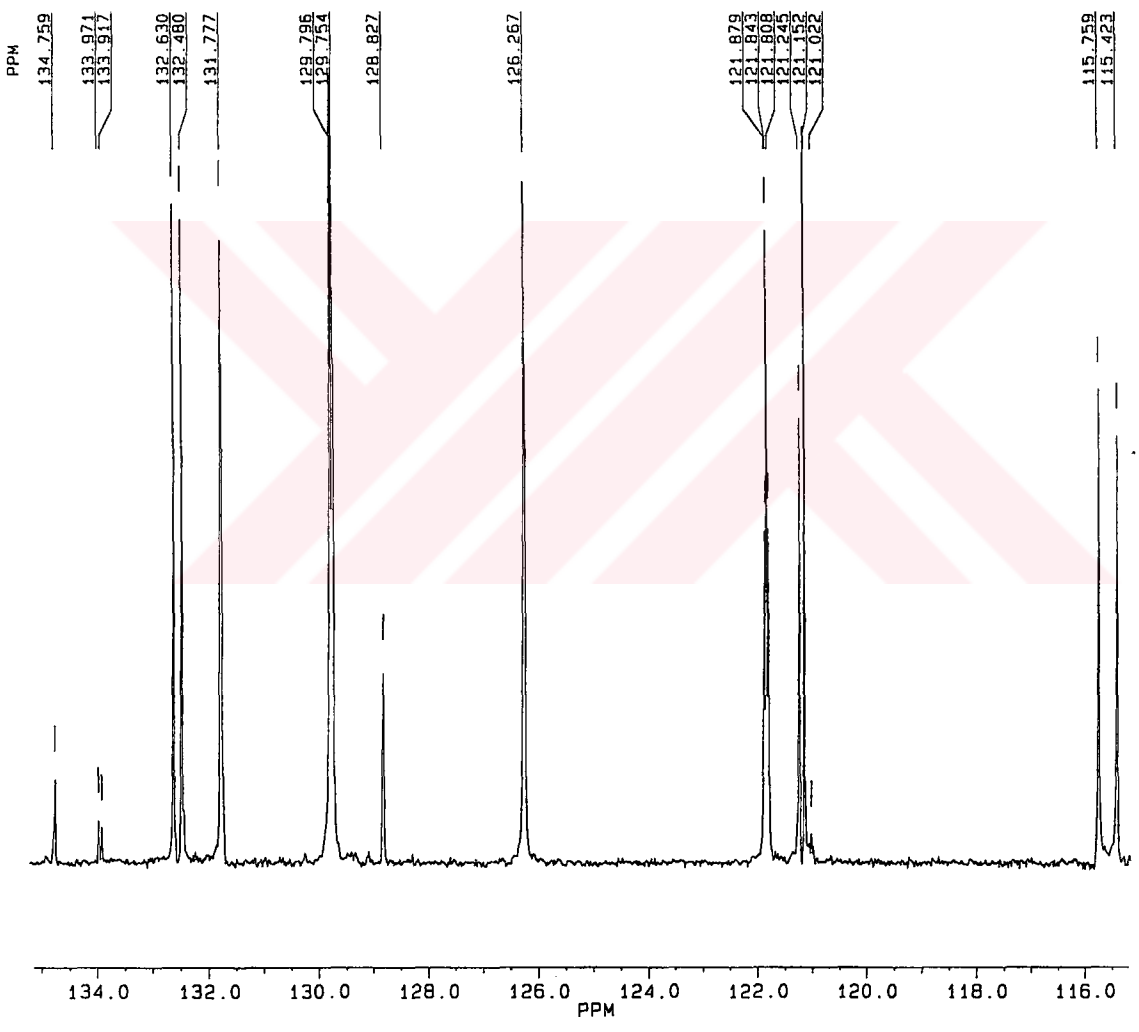
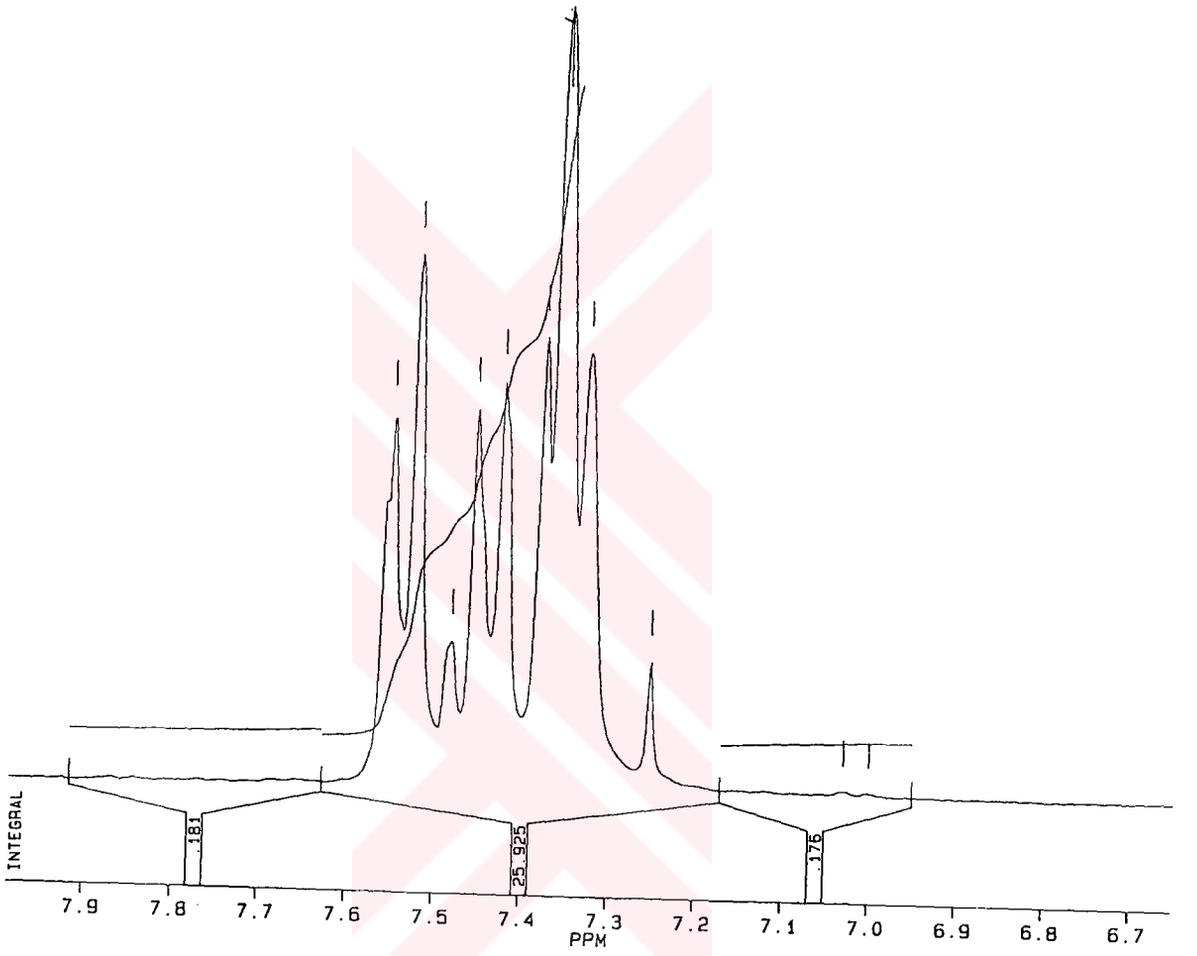
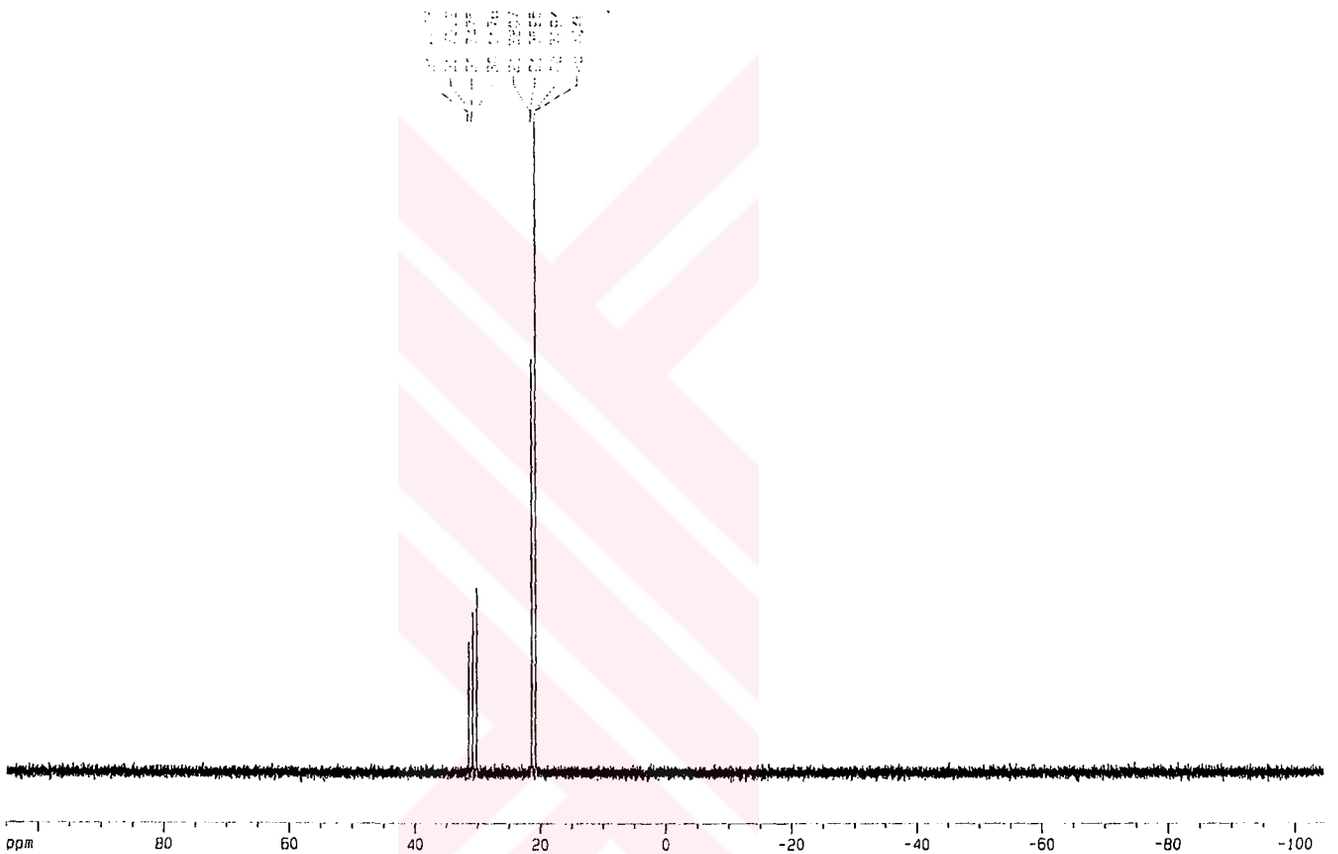
APPENDIXES



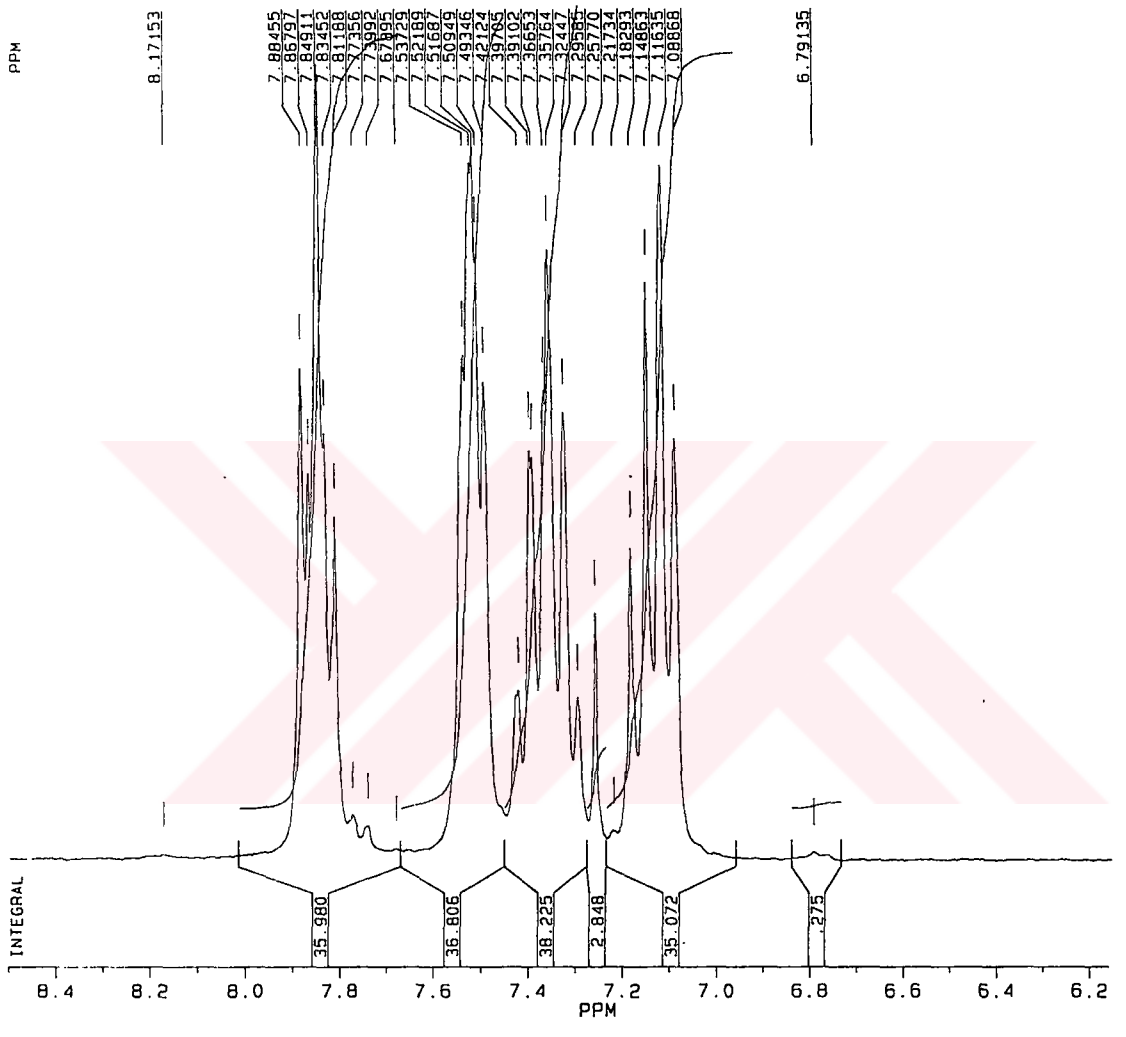
Appendix 3.1 The ^{13}C-NMR spectra of the monomer, **(2)**, 2,2-bis (4'-fluorobenzoylphenoxy)-4,4,6,6-bis [spiro (2',2''-dioxy-1',1''-biphenylyl)] cyclotriphosphazene



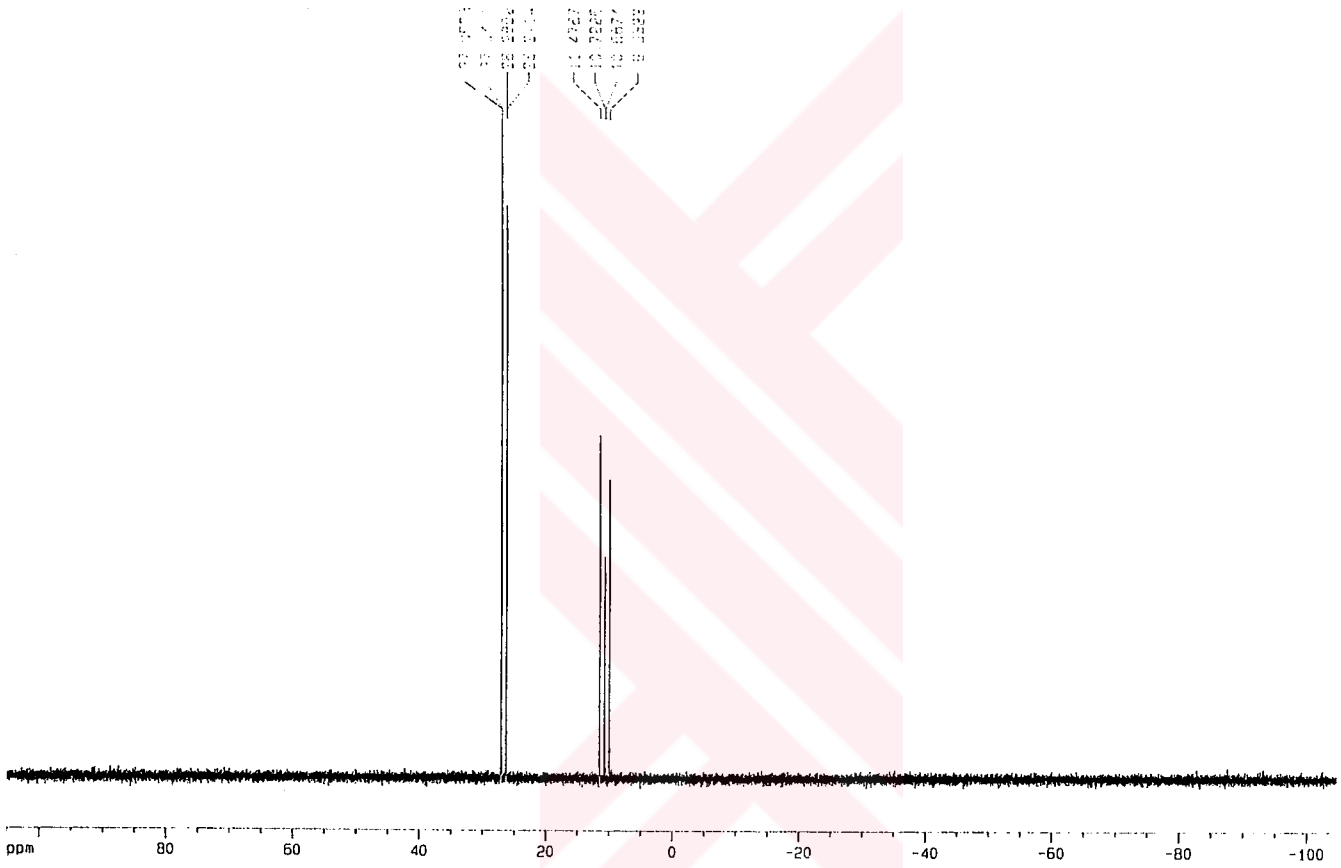
Appendix 4.1 The ^{1}H-NMR spectra of the bis-spiro compound, **(1)**, 2,2-dichloro-4,4,6,6-bis [spiro (2,2'-dioxy-1,1''-biphenylyl)]cyclotriphosphazene



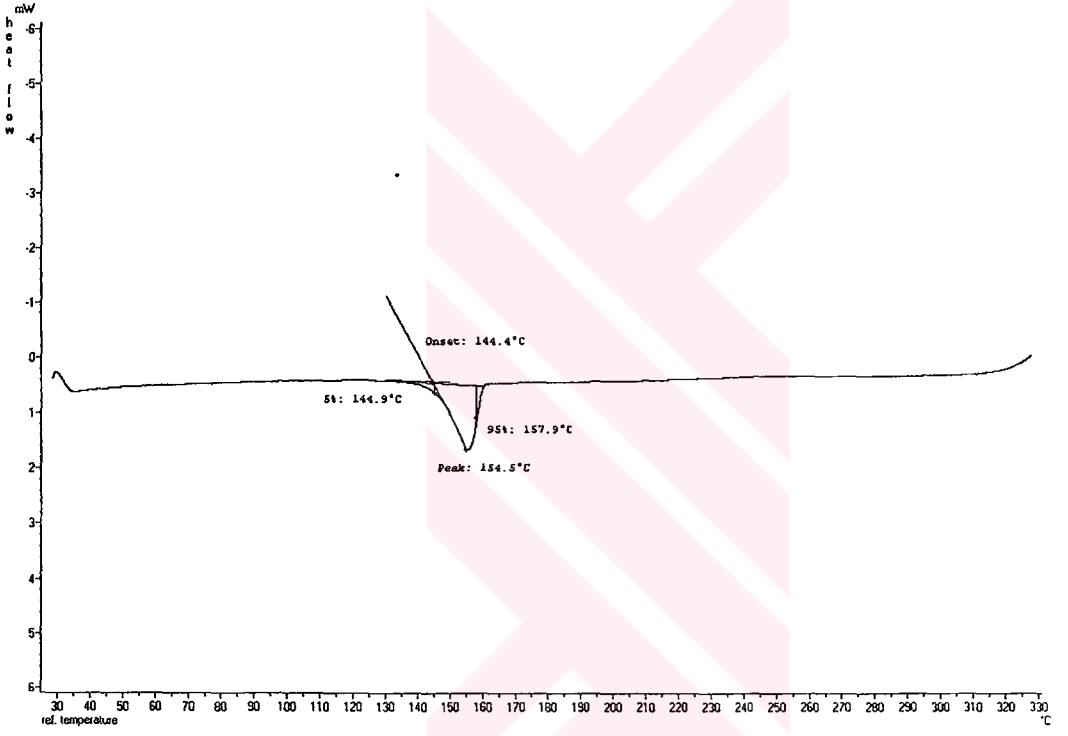
Appendix 4.2 The ^{31}P-NMR spectra of the bis-spiro compound, **(1)**, 2,2-dichloro-4,4,6,6-bis [spiro (2,2'-dioxy-1,1''-biphenylyl)]cyclotriphosphazene



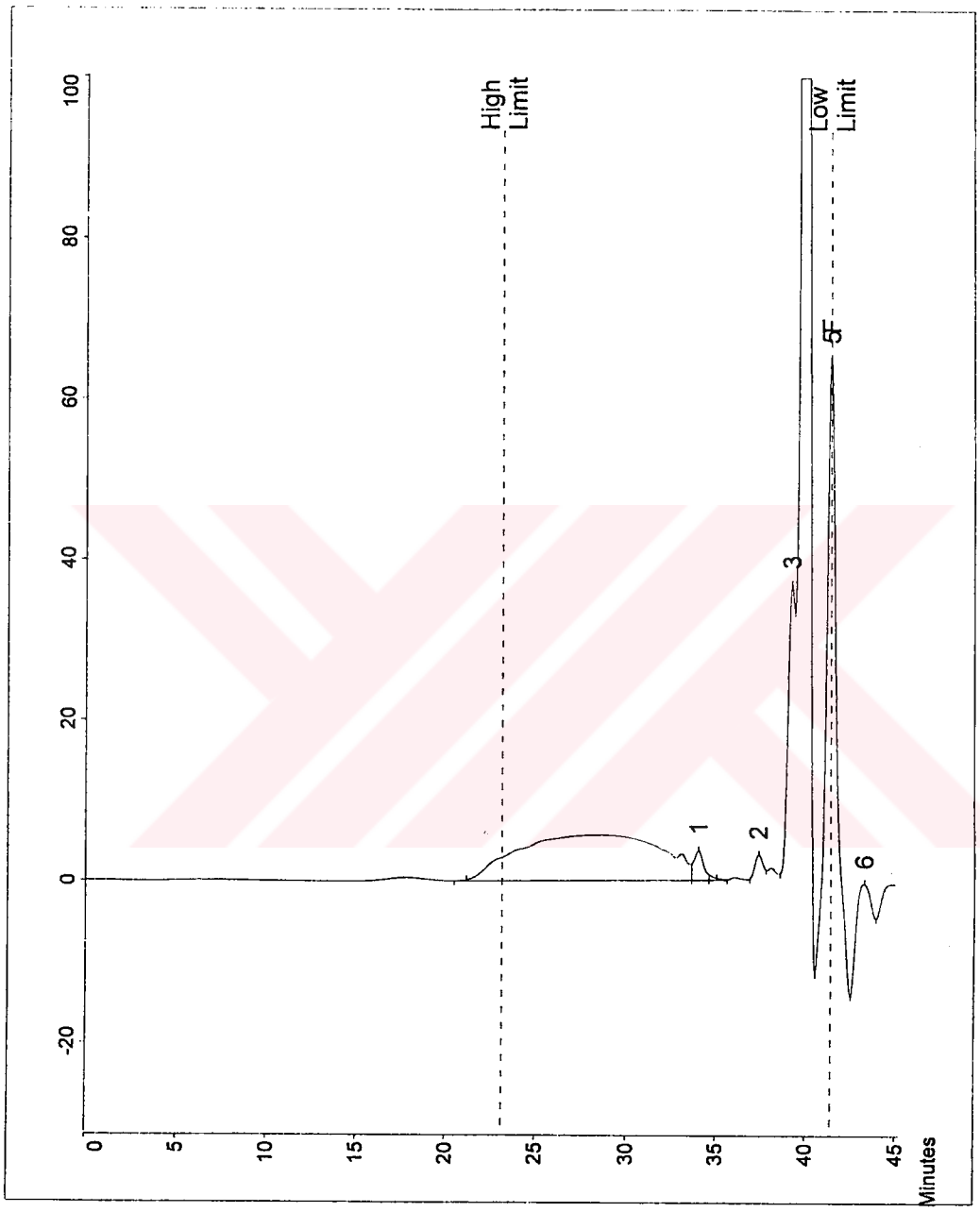
Appendix 4.3 The ^{1}H-NMR spectra of the monomer, **(2)**, 2,2-bis (4'-fluorobenzoylphenoxy)-4,4,6,6-bis [spiro (2',2''-dioxy-1',1''-biphenylyl)] cyclotriphosphazene



Appendix 4.4 The ^{31}P-NMR spectra of the monomer, **(2)**, 2,2-bis (4'-fluorobenzoylphenoxy)-4,4,6,6-bis [spiro (2',2''-dioxy-1',1''-biphenylyl)] cyclotriphosphazene



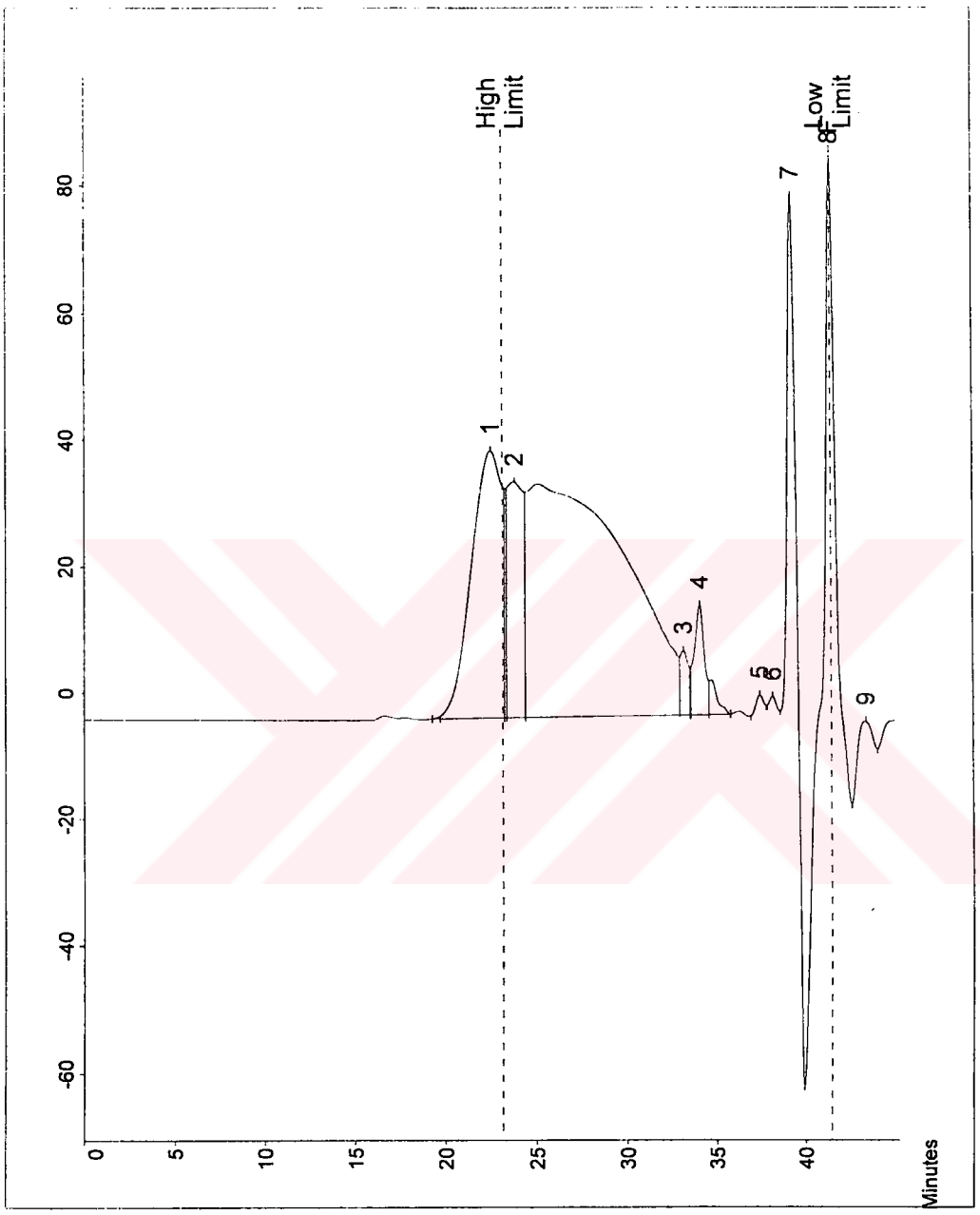
Appendix 4.4 The DSC thermogram of the monomer, (**2**), 2,2-bis (4'-fluorobenzoylphenoxy)-4,4,6,6-bis [spiro (2',2''-dioxy-1',1''-biphenylyl)] cyclotriphosphazene



Molecular Weight Averages

Mp =	8460	Mz =	36430
Mn =	5194	Mz+1 =	52616
Mw =	16525	Mv =	14139
Polydispersity =	3.181	Peak Area =	2706900

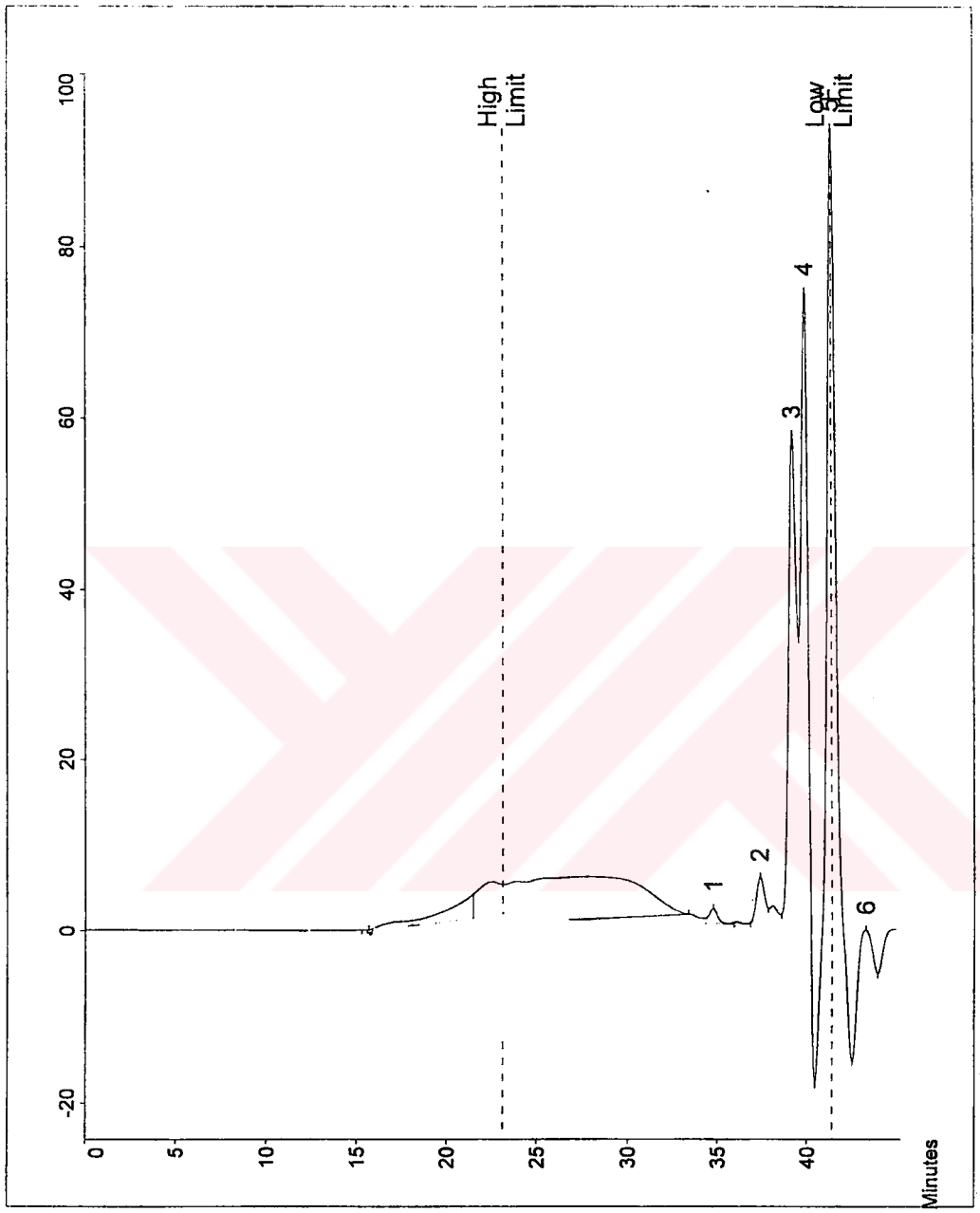
Appendix 4.6 The GPC chromatogram of the polymer I



Molecular Weight Averages

Mp =	70248	Mz =	62737
Mn =	7630	Mz+1 =	83791
Mw =	31160	Mv =	26800
Polydispersity =	4.084	Peak Area =	18875968

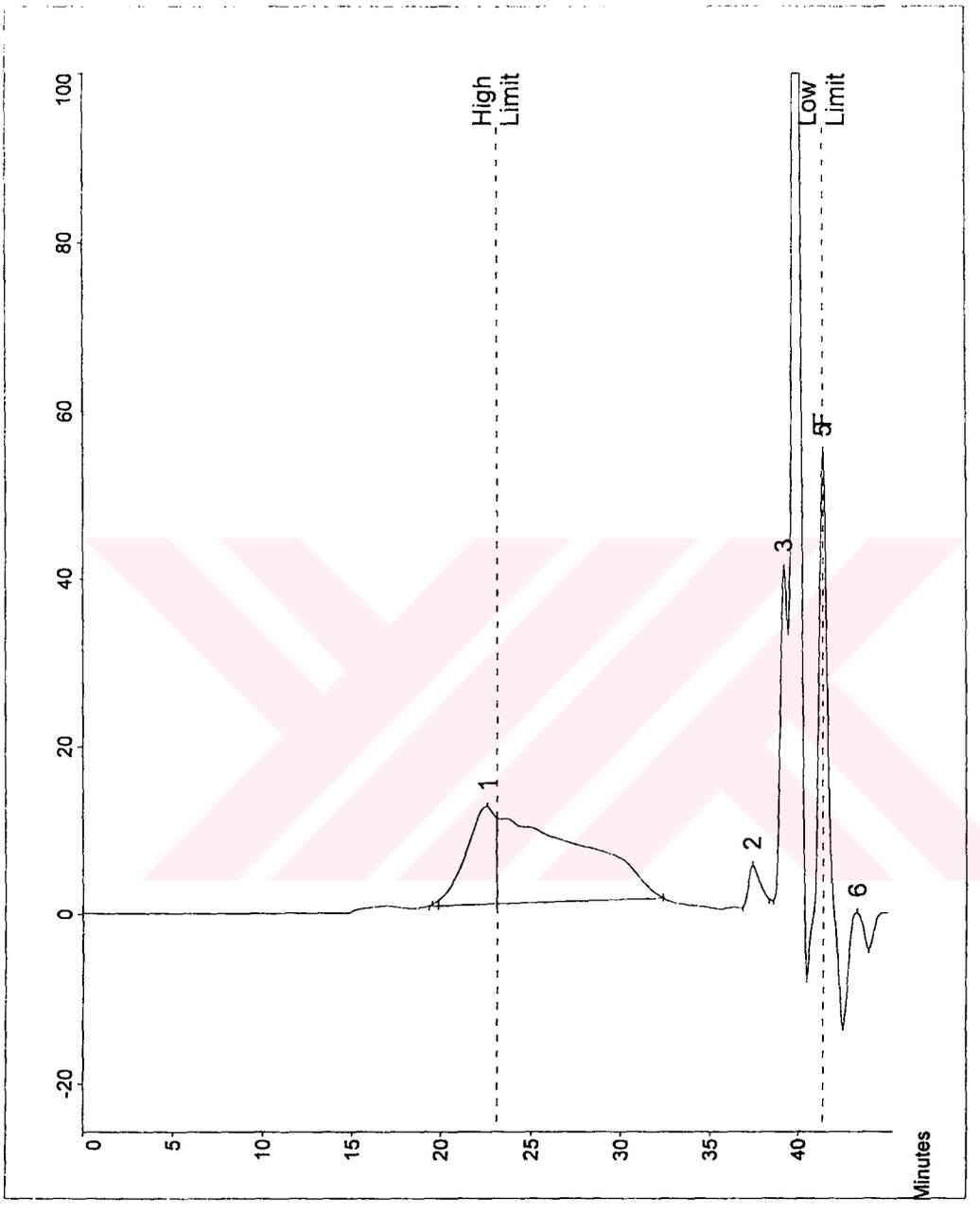
Appendix 4.7 The GPC chromatogram of the polymer II



Molecular Weight Averages

Mp =	24916	Mz =	193725
Mn =	11563	Mz+1 =	357618
Mw =	53429	Mv =	42029
Polydispersity =	4.620	Peak Area =	2740131

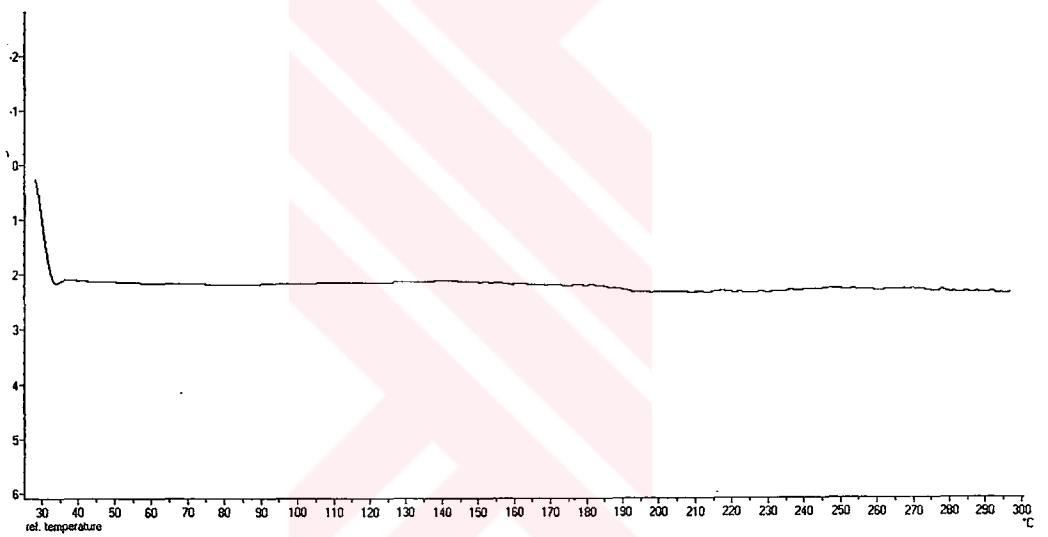
Appendix 4.8 The GPC chromatogram of the polymer VII



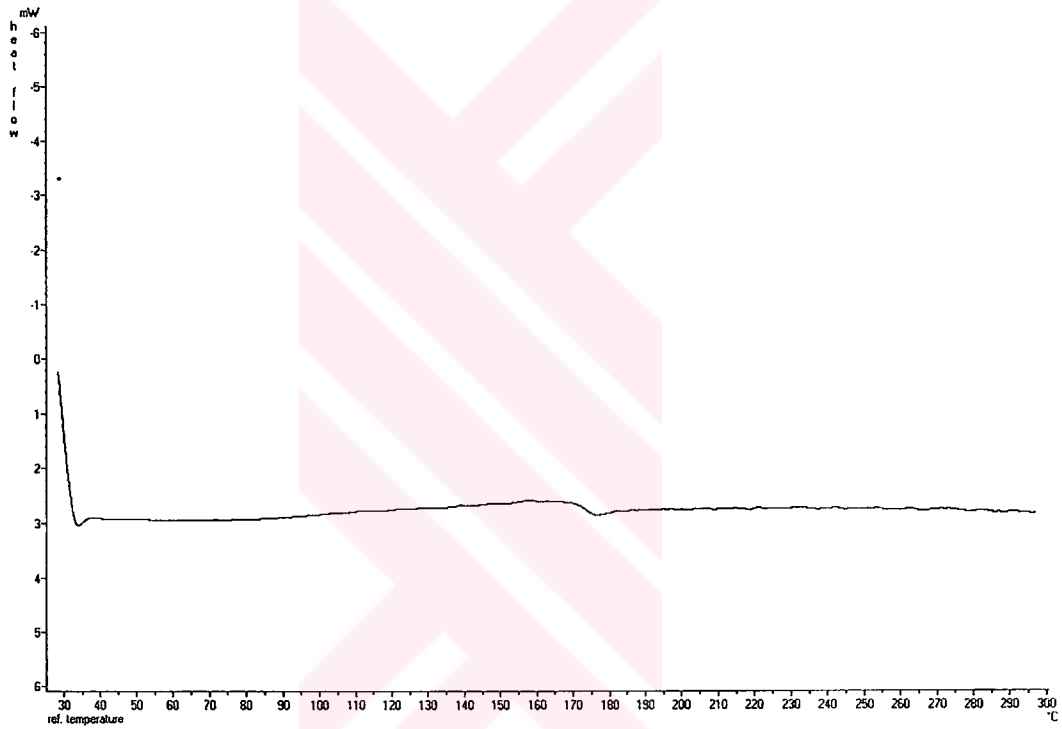
Molecular Weight Averages

Mp =	69912	Mz =	68657
Mn =	15176	Mz+1 =	90272
Mw =	39286	Mv =	35106
Polydispersity =	2.589	Peak Area =	3997661

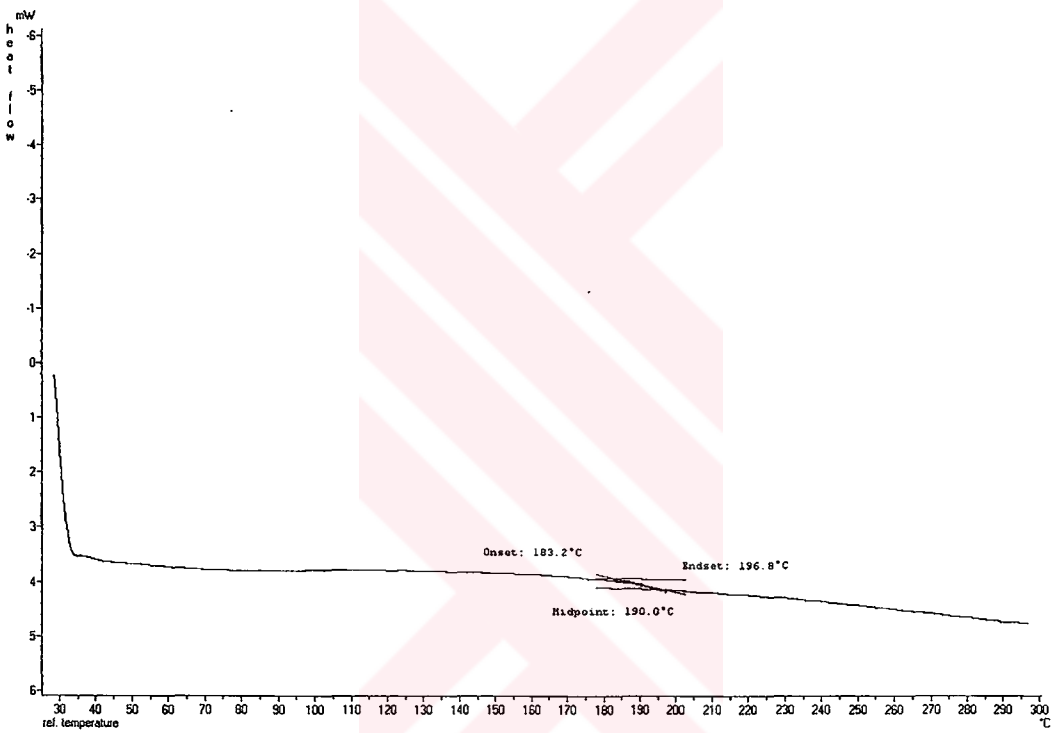
Appendix 4.9 The GPC chromatogram of the polymer VIII



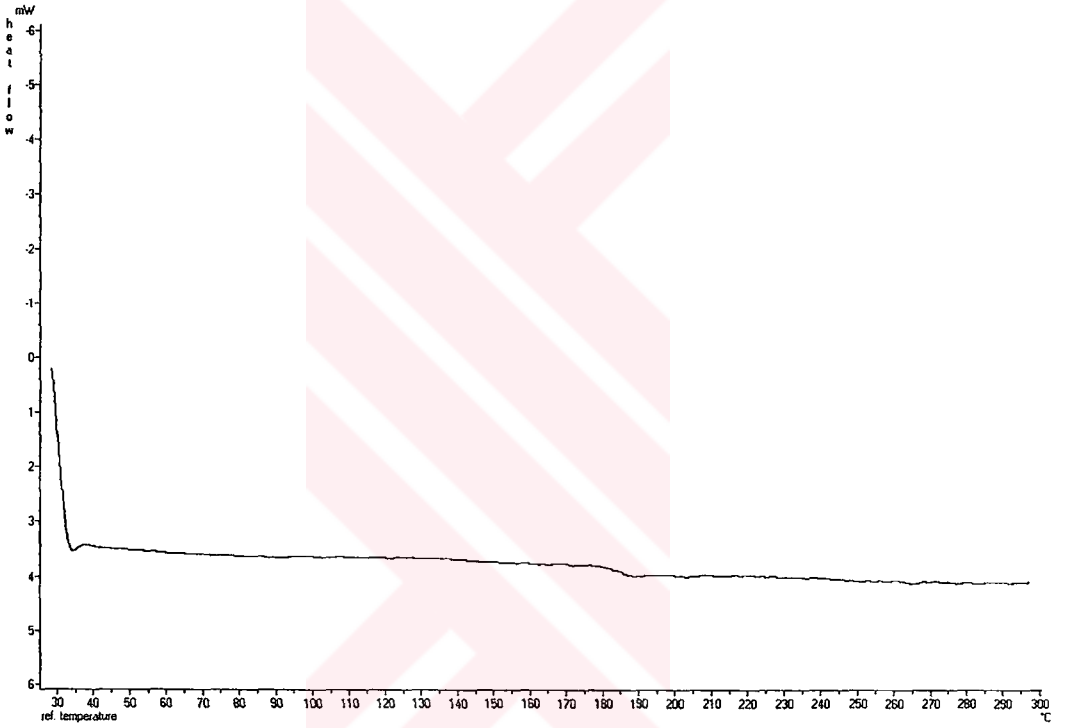
Appendix 4.10 The DSC thermogram of the polymer I



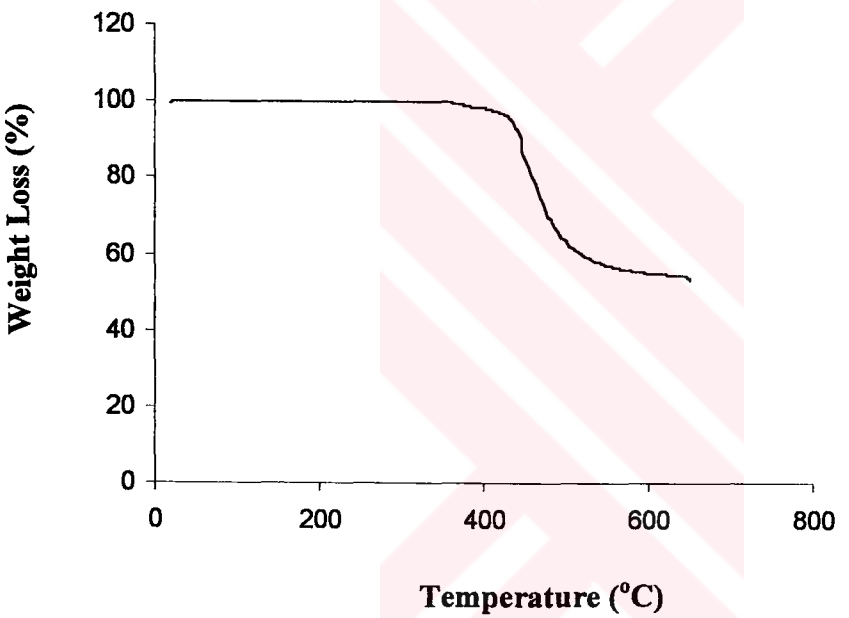
Appendix 4.11 The DSC thermogram of the polymer II



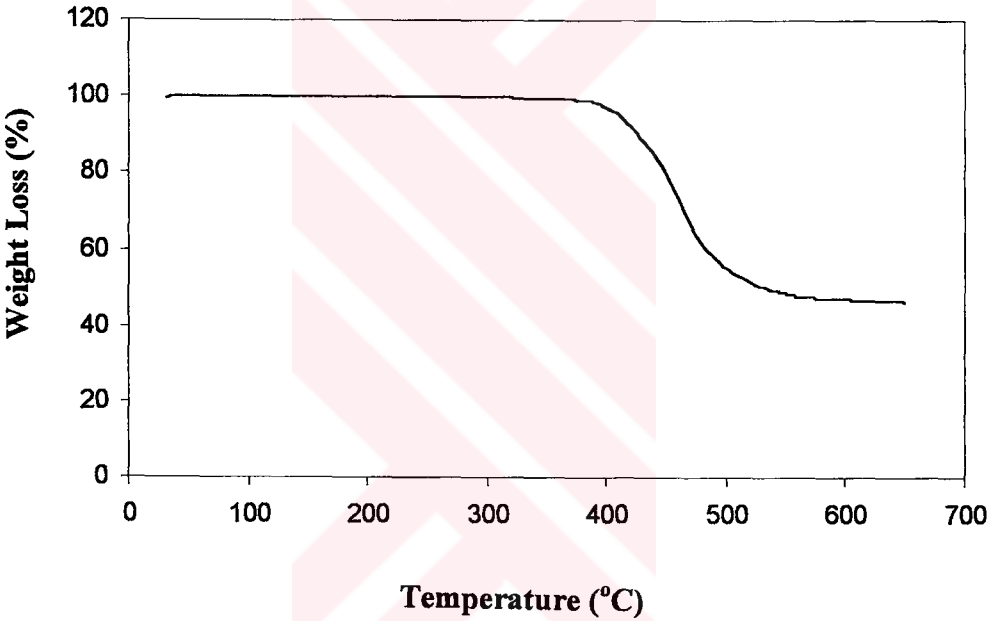
Appendix 4.12 The DSC thermogram of the polymer VII



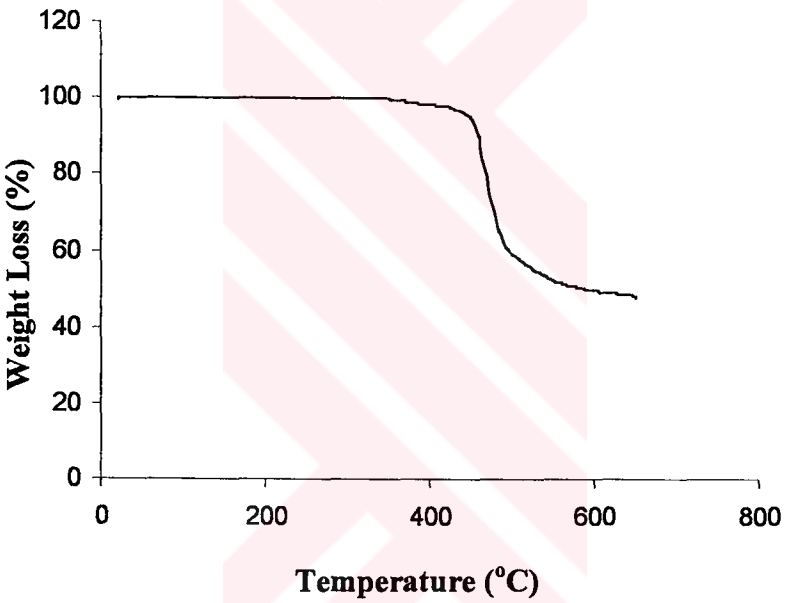
Appendix 4.13 The DSC thermogram of the polymer VIII



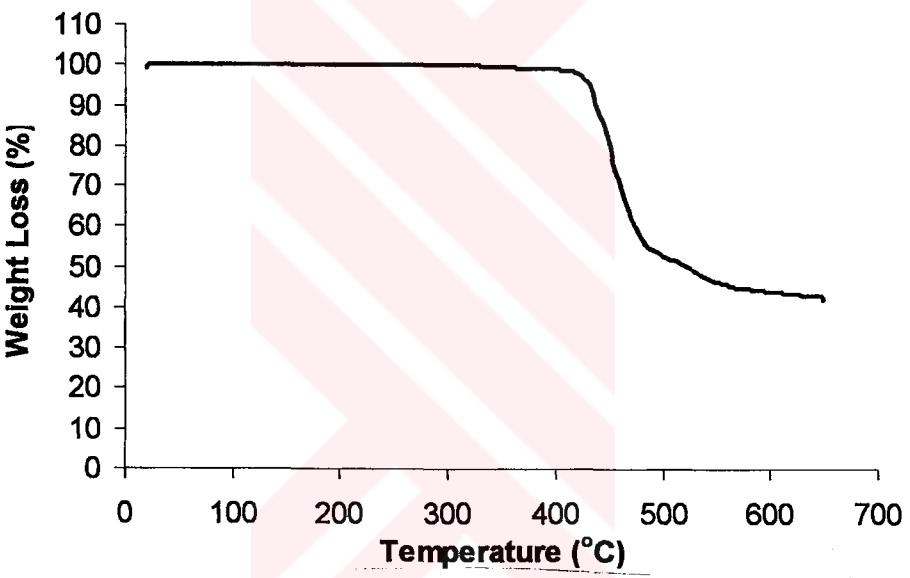
Appendix 4.14 The TGA thermogram of the polymer I



Appendix 4.15 The TGA thermogram of the polymer II



Appendix 4.16 The TGA thermogram of the polymer VII



Appendix 4.17 The TGA thermogram of the polymer VIII

AUTOBIOGRAPHY

He was born in 1975 in Istanbul. In 1993, He graduated from Istanbul Kabatas Erkek High School and attempted to the Chemistry Department of 19 Mayıs University in the same year.

After graduating from 19 Mayıs University in 1997, he was accepted as a master student to Istanbul Technical University, Polymer Science and Technology Programme of the Institute of Science and Technology in which he is about to graduate at the moment.