High performance polymers are commonly and widely used in advanced technologies and cover large varieties of applications such as micro and nanoelectronics, civil and military transportation, defense, etc. It is important for these technologies to design tailor-made high tech materials by focusing on molecular structure/processability/properties relationships of high performance polymers such as heterocyclic polymers known for their outstanding thermal properties and their good mechanical behaviour or even functionalized polymers or inorganic polymers. Nowadays, there is a strong demand of such resins since the development of composites and recently nanocomposite materials. Of the high temperature polymers commercially available, one can cite poly(arylene ethers), polybenzimidazoles, resins from cyanates, resin from bis-maleimides, organofluoro polymers, certain silicones and liquid crystalline polyesters. Polyimides and poly(arylene ether)s have attracted the attention of scientists and engineers more than other polymers. This attention is not only due to the attractive combination of properties but also because polyimides and poly(arylene ether)s can be readily tailor-made for specific applications. This article gives an account of developments in high temperature organic polymers during the last 5 years with major emphasis on linear, hyperbranched or dendritic structures concerning polyimides family, polyphenylquinoxalines and end-capped polymers such as bis-maleimides, PMR-15 and acetylene-terminated resins, highlighting the chemical structure with their ultimate physico-mechanical properties and focusing on the parameters which govern their processability. Processability and different applications will be presented as films (membranes for fuel cell), photosensitive products (microelectronics) or prepregs.

**ABSTRACT**

High performance polymers are commonly and widely used in advanced technologies and cover large varieties of applications such as micro and nanoelectronics, civil and military transportation, defense, etc. It is important for these technologies to design tailor-made high tech materials by focusing on molecular structure/processability/properties relationships of high performance polymers such as heterocyclic polymers known for their outstanding thermal properties and their good mechanical behaviour or even functionalized polymers or inorganic polymers. Nowadays, there is a strong demand of such resins since the development of composites and recently nanocomposite materials. Of the high temperature polymers commercially available, one can cite poly(arylene ethers), polybenzimidazoles, resins from cyanates, resin from bis-maleimides, organofluoro polymers, certain silicones and liquid crystalline polyesters. Polyimides and poly(arylene ether)s have attracted the attention of scientists and engineers more than other polymers. This attention is not only due to the attractive combination of properties but also because polyimides and poly(arylene ether)s can be readily tailor-made for specific applications. This article gives an account of developments in high temperature organic polymers during the last 5 years with major emphasis on linear, hyperbranched or dendritic structures concerning polyimides family, polyphenylquinoxalines and end-capped polymers such as bis-maleimides, PMR-15 and acetylene-terminated resins, highlighting the chemical structure with their ultimate physico-mechanical properties and focusing on the parameters which govern their processability. Processability and different applications will be presented as films (membranes for fuel cell), photosensitive products (microelectronics) or prepregs.

**Key Words:**
- polycyclic polymers;
- functional polymers;
- high-temperature polymers;
- linear and thermoset structures.

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  - Polyphenylquinoxalines
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INTRODUCTION

The quest for high temperature organic polymers, materials that perform at 200°C or higher, began in the late 1950s, to meet the demands primarily of the aerospace and microelectronics industries. Heterocyclic and aromatic polymers were introduced during the 1960s in order to match the thermal stability requirements of the aerospace industry. Aromatic and heterocyclic rings offer conjugated rigid structures with high transition temperature and strong linkage, allowing good resistance in harsh environments. Since then, many families of high temperature polymers have been reported and several of them have reached commercialization.

Therefore, aromatic polyimides play an important role in the field of high temperature polymers and are important classes of polymers that have found application as high performance polymers due to their thermooxidative stability, electrical properties, high radiation and solvent resistance and high mechanical strength [1-5].

Of the high temperature polymers commercially available, one can cite poly(arylene ethers), polybenzimidazoles, resins from cyanates, resin from bis maleimides, organofluoro polymers, certain silicones and liquid crystalline polyesters. Polyimides and poly(arylene ether)s have attracted the attention of scientists and engineers more than other polymers. This attention is not only due to the attractive combination of properties but also because polimides and poly(arylene ether)s can be readily tailor-made for specific applications. Within certain limits, properties such as chemical inertness, dielectric constant, color, glass transition (T_g) or crystalline melt (T_m) temperature, coefficient of thermal expansion (CTE), oxidative stability and solubility can be controlled by the chemical structure of the polymer. A recent book [6] offers the possibility of calculating some physical properties of polymers on the basis of the chemical structure of the repeat unit using simulation program CHEOPS. Mechanical manipulation can also improve certain properties such as tensile strength, modulus and CTE, for example of films and fibres. In addition, molecular weight and molecular weight distribution control and end-capping can alter properties such as viscosity and toughness.

For the past decades, increasing need in the high technology industries such as microelectronics, aerospace, defense, membranes, consumer sports, electronics, electrical, automotives and life science/medical industry etc., has been the driving force for the development of new polymeric systems combining thermal stability with specific functional properties.

The feature of polyimides and other heterocyclic polymers are now well recognized and used for long term temperature durability in the range 200-300°C.

This article presents a review of different classes of heterocyclic polymers including polyimides family, polyphenylquinoxalines and end-capped structures such as PMR-15, bis-maleimides and acetylene-terminated resin (ATR), linear and hyperbranched structures and dendrimers, highlighting the chemical structure with their ultimate physico-mechanical properties and focusing on the parameters which govern their processability.

LINEAR STRUCTURES

Polyimides

The most common technique for the fabrication of polyimides (PI) is forming the soluble precursor, a poly(amic-acid) PAA, casting films and then thermally dehydrating into the final imide form [7]. One of the best examples is the formation of Kapton from DuPont de Nemours, which results from a polycondensation reaction of a dianhydride, pyromellitic dianhydride PMDA and a diamine, oxidianiline ODA (PMDA/ODA polyimide) (Scheme I).

However, it suffers from insolubility and high softening temperatures that makes its processing impossible or expensive. This process leads to other problems such as inefficient cyclization, difficult removal of water and the formation of microvoids in the final material.

The key reasons for insolubility and the non-melting character of the wholly aromatic polyimides are the lack of flexibility and strong interchain interaction due to high symmetry and highly polar groups and also sometime hydrogen bonding [8]. In polyimides, strong interactions originate from intra- and interchain charge transfer complex (CTC) formation and electronic polarization which is supported by the strong electron acceptor character of imides and electron donor charac-
ter of amine segments. These interactions can be weakened by the disruption of the coplanarity and conjugation, by reduction of the symmetry and by alteration of electronic character of each segment.

In the last few decades, many studies have been conducted to control these interactions in order to produce more tractable polyimides which can be processed by conventional techniques such as melt processing or casting from volatile organic solvents while maintaining thermooxidative stability. The majority of these studies involved three main structure modifications to tailor the properties:

- Incorporation of thermally stable but flexible or non-symmetrical linkages in the backbone.
- Introduction of large polar and non-polar substituents pendant from the polymer backbone.
- Disruption of symmetry and recurrence of regularity through copolymerization [9].

Incorporation of flexible linkages such as -O-, -CH2-, -SO2- and hexafluoroisopropylidene groups (6F) into the backbone introduces kinks to the main chain which decrease the rigidity of the polymer backbone and inhibit packing, thus reducing the interchain interaction and H-bonding and leading to enhanced solubility [10]. Ultem® from GE is a good example with good mouldability and mechanical properties along with reasonable thermal properties.

Isomeric structures also distort linearity of the chain and increase the interchain distance which lowers the energy necessary for rotation. This lowers the Tg and the softening and or Tm and increases solvent penetration and solubilization of polymer [11]. For example, going from the all para structure of Kevlar® to meta-linked Nomex®, solubility improves drastically along with ca 100°C decrease in the melting point (from ca 530°C to ca 435°C).

Introducing aromatic and non-aromatic but thermally stable cardo-, spiro- or multicyclic structure as fluorene or adamantyl into the polymer backbone is also a promising method for property modification in polyimides [12].

Bulky substituents can impart a significant increase in both Tg and thermooxidative stability while providing good solubility, especially with non-symmetrical or flexible units in the backbone [13]. Basically, bulky substituents decrease crystallinity and packing efficiency by distortion of backbone symmetry and also restrict segmental mobility. The severity of the effect depends on the number, size and polarity of the substituents.

An interesting approach to overcome a trade-off between thermal properties and the solubility and processability since the same structural feature that enhances one decreases the other was to control chain flexibility and segmental mobility through the incorporation of diamines shown in Scheme II:

These are highly substituted (hindered) diamines
which reduce C-N bond rotation or extended bis(ether amine)s which combine flexible ether linkages and ortho-substituents (methyl, tert-butyl) that hinder internal C-O bond rotation or break the full aromaticity and planarity with a cardo-cyclohexene unit. Polyimides with enhanced solubility along with high $T_g$ and thermal stability have been synthesized from these sterically hindered diamines. Substitution at the ortho position of C-N bonds leads to this unique property combination which is very desirable for new application areas and fabrication opportunities that are not available for insoluble polyimides. Ortho-substitution at the C-N site is proposed to prevent coplanarity of the donor and acceptor units, weakening the intra- and interchain interactions and the packing, rendering these polymers soluble. High glass transition temperatures were therefore obtained as the segmental mobility was hindered dramatically by the ortho substituents to the nitrogens. [14].

A few years ago, an original way for obtaining new type of polyimides was initiated by using TNT derivatives in the framework of NATO program so-called Science for Peace (SfP) [15]. A wide range of amines was obtained containing fluoride, sulphur, particularly hydroxyl-containing diamines (HDA)s such as 3,5-diamino-4'-hydroxydiphenyl ether. This product was prepared using a 3-stage process: TNT dimethylation (oxidation/decarboxylation), substitution of one nitro group in 1,3,5-trinitrobenzene (TNB) formed with
hydroquinone and reduction of 3,5-dinitro-4'-hydroxydiphenylether thus obtained (Scheme III). These were used for the preparation of new organo-soluble hydroxylated polyimides (HPI)s [15], new fluorinated [16] and sulphur [17] polyimides based on TNT derivatives.

Hydroxylated polyimides are of great interest because of the presence of phenolic hydroxyl groups in these polymers results in interesting and potentially useful properties, e.g. high glass transition temperature, good solubility in organic solvents, high degree of water uptake due to hydrogen bonding. In addition, phenolic hydroxyl groups may be used for the introduction of unsaturated groups into the polyimide macro-molecules and as a result, for the preparation of photoactive polymers like negative photoresists [18].

An interesting approach was developed to reinforce domestic plastics by grafting polyimides and developing new polymer systems by additional thermal polymerization of different acrylates containing polyimides. Different systems of polyimide have been dissolved in methyl methacrylate or styrene and have been successfully copolymerized either by thermal or UV radical process [19-21].

Polyphenylquinoxalines

Polyphenylquinoxalines (PPQs) are a family of aromatic condensation polymers known for their outstanding thermal and chemical stability. The most known method for the PPQs preparation is the interaction of bis(o-phenylenediamines) with bis(α-diketones) in protogenic solvents [22,23].

The pendant phenyl groups and chains isomerism improve the solubility and processing characteristics of these polymers over the unsubstituted polymers. These polymers have also been shown to possess excellent thermooxidative stability and thermohydrolytic stability [24].

The most known PPQ commercialized in the USA and France is polymer based on 3,3’- dianimobenzidine (DAB) and 1,4-bis(phenylglyoxalyl)benzene (BPGB). In Russia, the main attention was paid to the PPQ’s based on 3,3’;4’,4-tetraaminodiphenyl ether (TADE). This monomer, which was firstly described by Stille et al. [25] and commercialized in pilot scale in Russia is more nucleophilic and less toxic when compared with DAB. In addition, incorporation of the ether groups in the PPQ’s macromolecules leads to the improved flexibility of the target polymers. As comonomers of TADE there were used 4,4’-bis(phenylglyoxalyl)diphenyl ether (BPGDPE) [26] and especially BPGB [27,28].

Very simple and inexpensive route for the preparation of BPGB developed by our group is based on the interaction of terephthalic acid dichloride with two-fold molar amount of styrene with subsequent oxidation of the 1,4-distyrylbenzene thus formed [27,28].

PPQs of general formula (Scheme IV) are soluble in CHCl₃, m-cresol and benzyl alcohol.

They demonstrate good film-forming properties, moderate glass transition temperatures (250-280°C), excellent thermooxidative and thermohydrolytic stability. This stability makes these polymers candidates for development as proton exchange membranes (PEMs) to be used in fuel cells [29]. In addition to thermohydrolytic stability, PEMs require high protonic conductivity and in order to achieve this they also require high water uptake. Aromatic condensation polymers do not possess these properties, but ionomers derived from them may have them.

Nanocomposites

The nano-scale technology is also an ongoing focus of intense research. It concerns a new emerging field of R & D where organic polymer/inorganic hybrid or nanocomposites materials (ceramer) would exhibit properties of combination of both ceramics (retention of mechanical properties at high temperature, low thermal expansion) and organic polymers (toughness, ductility and processability). Some recent results on polyimide/clay nanocomposite were recently presented at STEPI 6 and properties have been compared to commercial polyether-imide ULTEMfi 1000 (from GE) and
polyimide KAPTONf H (from DuPont) products [30].

HYPERBRANCHED AND DENDRITIC STRUCTURES

In 1941 Flory introduced the concept of hyperbranched macromolecules that still remains an area of intense research interest. Hyperbranched polymers and dendrimers, which are termed as "dendritic macromolecules" have received much attention in recent years [31]. Perfectly defined structures can be obtained only when monomer condensation are done step-by-step. At each step, the trifunctional molecule AB₃ reacts selectively via A with only one of the two B functions of another molecule because the second B function has been protected (Scheme V). When the B function that could not react is deprotected, the reaction can be continued and a structure without default, so-called dendrimer, can be obtained (Scheme VI). Condensation without protecting functions yields structures called hyperbranched.

One of the main interest of this class of structural polymer is that thermal properties (glass transition, heat stability) are unaffected by polymer architecture, but branched structures are more soluble than the linear structure [32]. Because of their unique architecture, these polymers show attractive properties such as low viscosity and excellent solubility in organic solvents, which make them as good candidate for impregnation of carbon fibres for producing laminate composites.

Publications dealing with hyperbranched polyimides are recent and not very numerous. Different systems have been investigated, ABₓ in one [33] or two step reaction [34], unsymmetrical BB′₂ monomer and an A₂ monomer (for which in situ AB′₂ intermediate formation during polymerization was suggested to resemble the AB2 polymerization) [35] or A₂ + B₃ [36, 37]. Although the A₂ + B₃ polymerization approach shows many advantages such as facile preparation and scaling up, easy to tailor structure, over the AB₂ polymerization approach, it has an intrinsic problem that gelation is unavoidable over a certain conversion in a 1:1 molar monomer feed ratio, as pointed out by Flory over 50 years ago.

THREE-DIMENSIONAL STRUCTURES

Initially developed linear systems were obtained by polycondensation reactions and exhibited very high glass transition temperature which presented problems in processing. In an attempt to overcome these difficulties, research has focused on reactive oligomers exhibiting the required Tₓ and flow characteristics.

PMR-15

Up to now composites based on epoxy resin matrices have dominated the technology. However, their application is limited to maximum use temperature of about 130 °C. There are many applications that require materials that may be used at temperatures substantially in excess of this, particularly in the aerospace industry. While the processing of thermoplastic polyimides is often difficult during composite fabrication, the use of oligomeric imides with reactive end-caps has greatly improved the processability of polyimide composites. A leading candidate for high temperature resin is the NASA developed polyimide "PMR-15". PMR stands for "Polymerization of Monomeric Reactants" and refers to the way in which carbon fibres are impregnated with a solution of the monomers which are then polymerized in-situ. Using the ester-acid route, the PMR approach ensures easy processing of imide oligomers. As a result, PMR-15, an addition curing polyimide based on 3,3′,4,4′-benzophenonetetracarboxylic acid dimethyl ester and methylene dianiline (MDA) with nadic ester as the endcap has been recognized as the state-of-the-art high temperature resin for composite application at 288°C (550 °F). The chemistry of the cure process is shown in Scheme VII:

PMR-15 is a processable, high-temperature polymer developed at the NASA Lewis Research Center in the 1970’s principally for aeropulsion applications. Use of fibre-reinforced polymer matrix composites in these applications can lead to substantial weight savings, thereby leading to improved fuel economy, increased passenger and payload capacity, and better maneuverability. PMR-15 is used fairly extensively in...
military and commercial aircraft engines components seeing service temperatures as high as 500 °F (260°C), such as the outer bypass duct for the F-404 engine. The current world-wide market for PMR-15 materials (resins, adhesives, and composites) is of the order of $6 to 10 million annually.

However, PMR-15 is prepared with a monomer, methylenedianiline (MDA), which is a known animal and suspect human carcinogen. The Occupational Safety and Health Administration (OSHA) and the Environmental Protection Agency (EPA) heavily regulate the use of MDA in the workplace and require certain engineering controls be used whenever MDA-containing materials (e.g., PMR-15) are being handled and processed. Implementation of these safety measures for the handling and disposal of PMR-15 materials costs the aircraft engine manufacturing industry millions of dollars annually.

Under the Advanced Subsonic Technology (AST) Program, researchers at NASA Lewis, General Electric, DuPont, Maverick Composites, and St. Norbert College have been working to develop and identify replacements for PMR-15 that do not rely upon the use of carcinogenic or mutagenic starting materials. This effort involves toxicological screening (Ames’ testing) of new monomers as well as an evaluation of the properties and high-temperature performance of polymers and composites prepared with these materials. A number of diamines have been screened for use in PMR-15 replacements. Three diamines, BAX, CO-BAX, and BAPP, passed the Ames’ testing (Scheme VIII).

Graphite-reinforced composites prepared with polyimides containing these diamines were evaluated against a PMR-15 control in terms of their high-temperature stability (weight loss after 125 h in air at 316°C and 5-atm pressure) and glass-transition temperature (an indication of high-temperature mechanical performance). Of these three materials systems, both the BAX and CO-BAX composites had stabilities and glass-transition temperatures comparable to those of PMR-15. Further evaluation of the processability of these materials as well as their long-term stability and mechanical performance at 288°C (550 F) is in progress (Figure 1).

By replacing methylene diamin (MDA) in PMR-15 ($T_g = 348°C$) with 2,2’-dimethylbenzidine (DMBZ, i.e. $m$-Toluidine), whose non-coplanar conformation is known to enhance the processability of addition polyimides, raises the glass transition temperature of the resulting polyimide (DMBZ-15) to $T_g = 414°C$ [38]. Apparently, the two methyl substituents on the biphenyl moiety of DMBZ impart a higher rotational
due to higher T_g, DMBZ-15 composites exhibited better mechanical properties than PMR-15 composites beyond 300-400°C for short excursion (Figure 2).

Acetylene-terminated Resin (ATR)

End-capped oligomers with acetylene functions polymerize without releasing volatile products. The resulting networks take up water to a relatively slight extent and have good thermal resistance. As in the case for all oligomers, mechanical properties are mainly controlled by the structure of groups located between acetylene functions. Even so, there are some disadvantages when using these oligomers:

- The synthesis of the reactant bearing the acetylene function is a multi-step synthesis and make the product costly. The most classical process uses a Palladium based catalyst that catalysis an oxidizing degradation even at low concentration in the polymerized network,
- The processing window is very narrow since polymerisation starts at low temperature (120°C), thus at the same time as oligomer melting,
- The polymerization enthalpy is relatively high (130 kJ per function).

In spite of this, National Starch has marketed THERMIDfi 600, an oligoimide that could be used as a composite or adhesive matrix up to 315°C. The search for a broader processability window is the reason behind the study of different types of oligomers with phenyl acetylene groups [39], within the chain [40-42].

Figure 1. Comparison of the glass-transition temperature and thermal-oxidative stability of graphite-reinforced composites prepared with non-MDA PMR-15 replacements. Left: Weight loss after 125 h in air at 316°C and 5 atm. Right: Glass-transition temperature.

Figure 2. One hot-wet cycle = 93°C water soak to >1% weight gain, dry out at 288°C to <0.1% moisture.
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Scheme VII

4,4 - Methylene dianiline  \( \rightarrow \)  BTDE dimethyl ester  \( \rightarrow \)  NE monomethyl ester

\[
\begin{align*}
\text{Polyamide} & \quad \text{acid} \\
\text{Polyimide} & \quad \text{N} = 2.087 \\
\text{Crosslinked} & \quad \text{polymer} \quad \text{N} = 2.087
\end{align*}
\]

Scheme VIII

\[
\begin{align*}
\text{MDA (used in PMR-15)} & \quad \text{BAX} \\
\text{CO-BAX} & \\
\text{BAPP (used in AMB-21)} & \\
\end{align*}
\]
Scheme IX

\[
\text{2,2-Diallylphenol A (DABA)} \quad \text{N-Ar'-N-Ar''} \quad \text{H}_2\text{N-Ar-NH}_2
\]

\[
\text{N-Ar'-N-Ar''} \quad \text{Thermal polymerization} \quad \text{N-Ar'-N-Ar''}
\]

Cross-linked network

Scheme X

\[
\text{Diels-Alder} \quad \text{R} \quad \text{R'} \quad \text{R''}
\]
or at the extremities [43]. Example of this type of oligoimidates is PETITf 5 developed by Cytec Fiberite for composites and adhesive matrices (Scheme IX).

Bismaleimides

Bismaleimide resins are still of increasing interest to the aerospace and electronic industry as matrix resins for fiber composites. Bismaleimides chemistry was first introduced and developed by Rh ne-Poullenc - KERIMIDf 601 [44]. Bis-maleimide-based network polymers possess high glass transition temperatures and high thermal stability and rigidity. At the same time, these polymers are very brittle, and the processing of the bismaleimides as such to fabricate articles is strongly complicated by high curing temperatures and limited durability. To overcome these problems, it is common practice to use reactive diluents (reactive comonomers) to improve resin processability.

Consequently, the ideal comonomer would function both as a reactive diluent, i.e. liquid at room temperature, and as toughening agent. The key issue to use a comonomer is that the comonomer undergoes a linear chain extension reaction with the BMI to reduce the crosslinking density in the fully cured resin. Therefore, the use of 2,2’-diallylbisphenol-A (DABPA) as a comonomer capable of entering the Michael reaction with bis-maleimides. The technological properties of the system based on 4,4’-(N,N’-bismaleimide)diphenylmethane (BMDM) and DABPA turned to be excellent, but the different reactions involved are quite complex, i.e. -ene and -diene addition reaction, Michael reaction, Diels-Alder reaction, homopolymerisation, copolymerization, reverse Diels-Alder reaction, etc. [45]. The brittleness was also substantially reduced, with retaining the high heat resistance (Scheme X).

The bismaleimide systems can be cured thermally either in excess of bis-maleimides or diamines.

Recent works on BMDP/DABPA shown that it was possible to crosslink the system by electron-beam (EB) or by UV at room temperature [46].

CONCLUSION

Aromatic and heterocyclic rings offer conjugated rigid structures with high glass transition temperature and strong linkages, allowing good resistance in harsh environments. However, it is always a compromise to be made to match at the same time the thermal stability requirements and processability which is needed for industrial applications.

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