High-Performance Polymers
Chemistry and Applications 2

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HIGH-PERFORMANCE POLYMERS

2 Polyquinoxalines and Polyimides

CHEMISTRY AND APPLICATIONS

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Polyquinoxalines and Polyimides

CHEMISTRY AND APPLICATIONS

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Preface

Forty years ago, Sroog at Du Pont de Nemours proposed the concept of "convertible polymers"to synthesize virtually intractable polymers via intermediate macromolecules exhibiting good solubility in organic solvents. Following an extensive research and development program including various tetracarboxylic acid dianhydrides and aromatic diamines, Du Pont's team concentrated its efforts on the most promising polymer based on the reaction of pyromellitic acid dianhydride with oxydianiline. This heterocyclic polymer of the isoindoledione family, universally known as the "PMDA-ODA polyimide", was the first member of an impressive series of new *high performance polymers* based on alternate aromatic homocyclic and heterocyclic rings. In 1958, IFP created a laboratory within a research centre of the French atomic energy commission to study the effect of nuclear radiations on organic molecules. A few years later, it was obvious that the organic materials resistant to α-, β-, γ- and X-rays also exhibited excellent heat stability. In conjunction with the activity on organic coolants for nuclear reactors offering poor market opportunities, researchers explored the potential of heterocyclic polymers as sources of new heat resistant materials. Since that time, the concept of "polyheterocyclisation" has been taken in consideration worldwide in industry and universities. Four decade later, thousands of patents, scientific papers and technical communications have been published and their volume is expanding every year. High performance adhesives, composites, coatings, films, fibres and foams are now commercially available for the aerospace, automotive, electrical and electronic industries. Even though practically all possible heterocycles have been introduced into macromolecules, the number of remaining competitors is limited to five or six polymer families. At the highest level of thermal resistance, polyimides are leading before polyphenylene sulphide, followed by polybenzimidazole and polyphenylquinoxaline (PPQ). There have been numerous reviews, review symposia and books published worldwide on polyimides or other high performance polymers. However, information on polymers such as polyphenylquinoxalines, polybenzhydrolimides or cardo polyimides is more scattered in the literature. So, we thought it was opportune to summarise the results published in this field as an introduction to the third volume of the present series which will focus on the applications of heterocyclic polymers in the electronic industry.

The first chapter deals with the chemistry of linear polymers containing quinoxaline rings, including unsubstituted and phenyl-substituted polyquinoxalines, polyquinoxalinones, poly(ether-quinoxalines), fluorinated polyphenylquinoxalines and ladder polymers. Thermosetting polyphenylquinoxalines carrying reactive substituents are then concisely reviewed with a particular attention to ethynyl-substituted macromolecules which were evaluated as adhesives or composite matrices. Finally, the experimental approach developed at IFP to produce polyphenylquinoxalines by an interfacial process is described. This method made it possible the production of "electronic grade" polymers.

Polyphenylquinoxalines (PPQs) were the first heterocyclic polymers soluble in organic solvents in the form of precyclised macromolecules. This allowed researchers to study both reaction kinetics and molecular properties in solution. The results obtained in the USA, in the former Soviet Union and in our laboratory are compared and discussed in chapter 2. Molecular weight measurements in chloroform solutions show unusually high polydispersity values for step polycondensation products. Even if interfacial polycondensation results in dispersity higher than two, light scattering analysis clearly indicates the formation of super-molecular structures which survive in very dilute solutions.

Chapter 3 provides an overview of the mechanical and electrical properties of polyphenylquinoxaline films. There exists relatively strong acid-base interactions between PPQ and the phenolic solvents used to prepare the polymer. As a result, the drying schedule must include a final stage at 400–450°C to produce films with the optimum electrical characteristics. Isothermal ageing tests in air show that polyphenylquinoxaline exhibits often better than that of most polyimides although some pyrolytic cross-linking is perceptible at temperatures upper than 350°C. In contrast with polyimides, PPQs do not possess strong dipoles so as they have excellent dielectric properties. All factors that can affect both the relative permittivity and the dielectric losses are discussed in this chapter.

Polyphenylquinoxalines have been evaluated for the last three decades in virtually all applications needing high performance polymers. Chapter 4 summarises the results obtained with PPQ adhesives, composite materials, membranes, enamelling varnishes, film capacitors and interlayer dielectrics for semiconductors and high density interconnect substrates. Samples of IP 200 PPQ® have been provided worldwide to many customers and, when available, their results are presented here. This is the case for wire coatings intended to be used in military applications as well as for the thin and thick films employed for the fabrication of electronic devices.

Chapter 5 gives a deeper insight into the mechanism of adhesion of polyphenylquinoxalines to silicon, silicon dioxide and metallic substrates. Peel tests are correlated with the processing conditions to determine the most significant parameters acting on the adhesion strength. The locus of failure is then studied by means of Fourier transform infrared analysis, X-ray photoelectron spectroscopy, contact angle measurements and transmission electron microscopy. These analytical techniques show the paramount effect of the aminosilane used as adhesion promoter, especially in high humidity conditions. In addition, it is demonstrated that the locus of failure is within the polyphenylquinoxaline film but very close to the interfacial region.

Polyimides are the topics of chapter 6 which summarises the chemistry used to make these polymers with a particular attention given to the commercial materials. Polyimides are classified according to four main categories: polyimides prepared via linear precursors, precyclised polyimides, condensation oligomers and thermosetting polyimides. Reaction mechanisms are not taken into account because the subject is covered in several excellent books. However, condensation oligomers are more extensively discussed to complete the rather scarce information available in the literature.

Chapter 7 focus on cardo polyimides which were discovered and patented in 1964 by Vinogradova and Vygodskii working in Korshak's team at the Moscow Institute of Element-Organic Compounds. The presence of cardo groups endows polyimides with very specific properties such as high glass transition temperature together with excellent solubility. Cardo polyimides were the first precyclised polymers exhibiting solubility in many organic solvents, thus allowing the development of the "one-step" synthesis in solution. A new way was opened to investigate kinetics and reaction mechanisms which could not be studied with the other polyimides. Although cardo polyimides have not been developed yet for commercial applications, they are considered as unique macromolecules for modelling polyimide synthesis and reactions. Chapter 7 also summarises the results of theoretical analyses conducted by Russian researchers to calculate various molecular parameters, such as the elastic modulus, polymer density and dielectric constant.

The main industrial applications for aromatic polyimides are listed in the last chapter, which, however, excludes electronics and microelectronics. This is a voluntary step because polyimides have found widespread use in the manufacture of electronic devices and are employed in increasingly diverse areas of electronics and photonics. As stated earlier, the structure-property relationship and the technological problems related to electronic applications are treated in Volume 3 of *High Performance Polymers*. Chapter 8 deals with heat resistant adhesives, composites, moulding resins, films, gas separation membranes, coatings for wire insulation and high-strength, high-modulus polyimide fibres.

The basic purpose of this book is to review the present status of two important classes of high performance polymers, i.e., polyimides and polyphenylquinoxalines. Information retrieval indicated that many sources exist which deal with the different aspects of polyimides: monomer production, chemistry, polymer synthesis, physical properties and industrial applications. Few books, however, offer a global image of the multiple polyimide facets. The figure is somewhat different for polyphenylquinoxalines because we were for approximately 20 years the unique supplier of PPQ. Within this period, we spent a lot of time to improve our production techniques and quality control tools. Thanks to my colleagues who worked for years in the field of polyphenylquinoxalines, cardo polyimides and other specialty polymers. I have to especially acknowledge Paul Mariaggi who was my collaborator for 20 years and developed in particular PPQ wire coatings. I am also grateful to Serge Gonzalez who devised the interfacial process for the production of IP 200 PPQ®. Many additional thanks to Frédérique Hauviller, Dominique Audigier and Pierre Panzarella who helped me in our research and development programs dealing with the production of new high performance polymers.

Contents

Chapter 1
POLYPHENYLQUINOXALINES AND RELATED POLYMERS

Chapter 2
POLYPHENYLQUINOXALINE SOLUTION PROPERTIES

Chapter 3

POLYPHENYLQUINOXALINE FILM PROPERTIES

Chapter 4

APPLICATION OF POLYPHENYLQUINOXALINE FILMS

Chapter 5

ADHESION OF POLYPHENYLQUINOXALINES

Chapter 6

POLYIMIDE CHEMISTRY

Chapter 7

CARDO POLYIMIDES: CHEMISTRY AND PROPERTIES

Chapter 8

POLYIMIDES: PROPERTIES AND APPLICATIONS

Chapter 1

POLYPHENYLQUINOXALINES AND RELATED POLYMERS

1.1 INTRODUCTION

On a theoretical point of view, the highest achievable thermal stability of organic polymers should be attained with poly(1,4-phenylene). Its macromolecular backbone, represented in Figure 1.1, contains only carbocyclic aromatic rings connected at the 1,4-carbon atoms. However, there is no chemical way to prepare this polymer because it does not exhibit any melting point and solubility as soon as the degree of polymerisation *n* exceeds 5–6. This observation was the key factor to develop the "polyheterocyclisation" concept, involving alternate aromatic carbocyclic and heterocyclic rings. The former are carried out by the "monomers", whereas the latter are formed during either the polycondensation reaction or the processing stage. Some examples of heterocycles introduced in polymer repeating units are provided in Figure 1.1 to illustrate the versatility of the chemistry explored for the last decades. Many thermally stable heterocyclic polymers have been studied for more than thirty years but few of them have achieved commercial development. The main reason is not the unavailability of the starting reagents or monomers but the extreme conditions required to process these materials, generally related to the insolubility of most polymers in any solvents, except sometimes strong inorganic acids. Examples are the fully aromatic polybenzimidazoles, polybenzothiazoles, poly(imidazoquinazolinediones) and "ladder" polymers made of highly rigid fused polycyclic structures. In the literature, these polymers are described as "brick dust" materials because they are obtained only in the form of non-fusible orange, red or even black powders.

Obviously, heterocyclic polymers synthesized at high temperatures (350–450 °C) exhibit an outstanding thermal stability, up to 500 °C, when they are subjected to dynamic thermogravimetric analysis (TGA). This, however, can be misleading because the stringent conditions of polycondensation in solid or semi-solid phases are sometimes over the actual onset of thermal decomposition. This can be illustrated with the carborane chemistry, which is only evoked in a forthcoming paragraph. Carborane-containing macromolecules were, for a time, considered as the most thermally resistant polymers because they did not exhibit any weight loss below 700 °C. Studying poly(carboranylene-azomethines) [1] and poly(carboranylene-dihydrobenzothiazoles) [2], we paid a particular attention to the thermal behaviour of these materials. We clearly demonstrated that the apparent high thermal stability of carborane polymers is an artefact because the weight loss due to the degradation of the organic moieties is hidden by the gain in mass resulting from oxidation of the carborane cage into boron oxide and boric acid. During the 1960–1970 decade an impressive number of heterocycles were introduced in macromolecules without taking into account their processability. At the time being, a few heterocyclic polymers have found general acceptance in the industry as heat-resistant adhesives, dielectric and insulating films, high-modulus fibres, protecting overcoats, and matrices for composites.

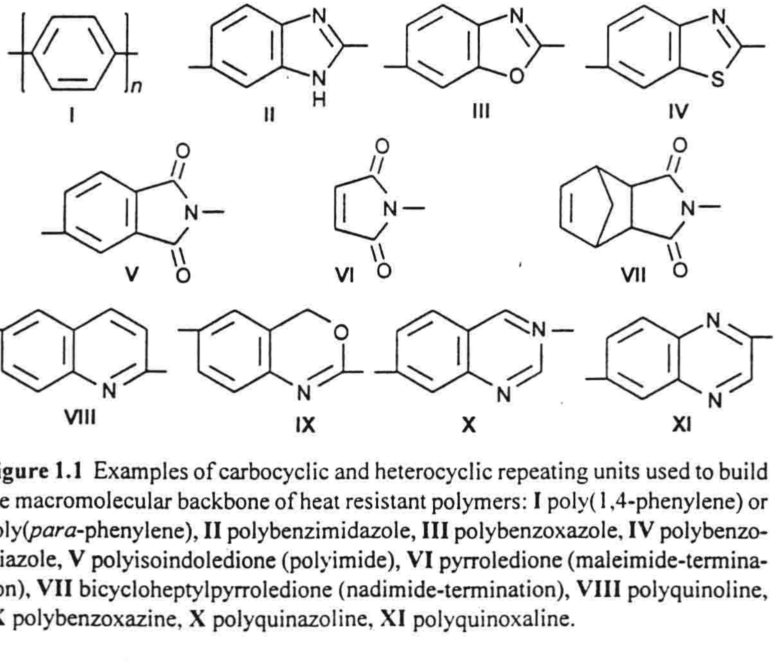

Figure 1.1 Examples of carbocyclic and heterocyclic repeating units used to build the macromolecular backbone of heat resistant polymers: **I** poly(1,4-phenylene) or poly(*para*-phenylene), **II** polybenzimidazole, **III** polybenzoxazole, **IV** polybenzothiazole, **V** polyisoindoledione (polyimide), **VI** pyrroledione (maleimide-termination), **VII** bicycloheptylpyrroledione (nadimide-termination), **VIII** polyquinoline, **IX** polybenzoxazine, **X** polyquinazoline, **XI** polyquinoxaline.

Aromatic polyimides, first patented by Edwards and Robinson [3], compose certainly the family of heat-resistant polymers which provides most of the existing high-performance organic materials. They are now available from many manufacturers in the form of both polyimide precursors, such as polyamic acids and polyamic esters, and as pre-cyclised soluble and meltable polyimides. Far behind this series, are commercially available one polybenzimidazole, produced by Hoechst-Celanese [4] to make heat resistant fibres and fabrics and one polyphenylquinoxaline developed at the Institut Français du Pétrole in the early 1980s. Extensive reviews of the chemistry and applications of heterocyclic polymers, particularly polyimides, can be found elsewhere [5–10]. The first chapters of this book are devoted to phenyl-substituted polyquinoxalines, often referred to as polyphenylquinoxalines or PPQs, because they possess some unique properties compared to the other heterocyclic polymers. Then, in chapter 6 and the followings, chemistry, structure-property relationships, and applications of polyimides are briefly reviewed. According to the intended use, dielectric properties, moisture absorption, solubility, thermoplasticity, glass transition temperature and thermal resistance have to be optimised by testing different chemical structures and choosing the best compromise between many conflicting requirements. The versatility of polyimides makes this possible, whereas polyphenylquinoxalines are more limited.

1.2 HISTORICAL BACKGROUND

The chemistry and applications of polyquinoxalines were extensively reviewed by a number of researchers considering this class of polymers as a whole or as a part of the heterocyclic polymer family [11–24]. Accordingly, we intend to provide hereafter only an overview of polymers containing quinoxaline rings with some emphasis on the series we studied in our laboratory for about 25 years.

1.2.1 Polyquinoxalines

Unsubstituted polyquinoxalines were independently patented and reported in 1964 by de Gaudemaris and co-workers [25–27] and Stille and Williamson [28, 29]. As shown in Figure 1.2, these polymers are prepared by reacting aromatic tetraamines **1** with bis(α-ketoaldehyde) dihydrates **2** using a two-step process. Tetraamines are generally synthesized from commercial aromatic diamines, which are successively subjected to reactions of acetylation, nitration, deacetylation and reduction of the nitro groups [30, 31]. Bis(α-ketoaldehyde) dihydrates are prepared by the selenium dioxide oxidation of methyl-aryl ketones or methylene-aryl ketones developed by Riley et al. [32]. Polycondensation can be carried out either in molten phase or by using polar solvents such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAC), *N,N*-dimethylaniline (DMA), hexamethylphosphotriamide (HMPT), dioxane, *meta*-cresol or polyphosphoric acid (PPA). In either cases, the first step produces a mixture of low-molecular weight polyquinoxaline oligomers **3**, which are statistically terminated by the two opposite reactive centres. At this stage, the degree of polycondensation (*m* in formula **3**) is small, as demonstrated by a value of 0.05 to 0.2 dl g^{-1} for the inherent viscosity (η_{inh}), determined at a concentration of 0.5% in concentrated sulphuric acid. These oligomers are no longer soluble in organic solvents and any increase in molecular weight can be only achieved by subjecting the powder to a high-temperature treatment ending at 375–400 °C. This results in the formation of deep brown coloured polymers **4** exhibiting reasonably good thermal stability up to 400 °C. Melt polycondensation is performed by mixing the starting reactants in a rotating flask and heating them first at 180 °C and then at 250 °C. The resulting prepolymer is ground, introduced again in the rotating flask with stainless steel balls (diameter 8 mm) and heated to 375 °C for 3 hours under a partial pressure of 0.1 mm Hg to produce high molecular weight polyquinoxalines **4**. When this cure cycle is completed, the inherent viscosity is of