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POLYIMIDES

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Polyimides

Preface

The last twenty years or so have seen a flurry of activity in the synthesis of new polymer systems. This interest has developed largely as a result of the increased need for advanced materials.

Despite the emergence of a number of outstanding polymers, it is the polyimides that have captured the imagination of scientists and engineers alike as materials that offer outstanding promise for the high technology applications of the future.

The reputation of the polyimide has been established on the bases of outstanding thermal stability, excellent mechanical properties and the ability to be fabricated into useful articles.

Polyimides offer a versatility unparalleled in most other classes of macromolecules. Polymers can be prepared from a variety of starting materials, by a variety of synthetic routes. They can be tailor-made to suit specific applications. By judicious choice of starting materials, polymers can be made that offer variations in such properties as glass transition temperature, oxidative stability, toughness, adhesion, and permeability.

It is this versatility that has led to the use of polyimides in a wide variety of applications. The electronics industry makes extensive use of polyimide films in, for example, semiconductor applications. The leading polymer matrices for high temperature advanced composites are polyimides. High temperature adhesive systems for the bonding of metals or composites are often based on polyimides. In addition, polyimides are now finding use as fibres, foams, sealants and even membranes for the low energy separation of industrial gases.

Despite the widespread interest in polyimides and the amount of published papers, reviews and books, there are very few comprehensive reference works on the subject.

In this book, the chemistry and applications of this versatile class of polymers will be brought together for the first time. A detailed description of the main types of polyimide, their chemistry, production, properties and their most important end uses will be given. The book is written for materials scientists, polymer technologists and engineers, especially those in the electronics, aerospace, automotive and chemical industries. It is authored by an international group of scientists and technologists from the USA, Europe and Japan.

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1 Synthesis of aromatic polyimides from dianhydrides and diamines

F.W. HARRIS

1.1 Introduction

Although the first synthesis of an aromatic polyimide was carried out in 1908 [1] it was not until the late 1950s that high molecular weight polymers were prepared [2–4]. Perhaps more surprising is that even today the most common method for their synthesis, i.e. the treatment of an aromatic diamine with an aromatic tetracarboxylic acid dianhydride, is still not completely understood. This is because the course of the reaction, which is carried out by both two- and one-step methods, is dramatically affected by the reaction conditions [5]. Even the mode of monomer addition can affect the molecular weight of the polymer obtained [6, 7]. In the following paragraphs the complexities of the sequence of events leading to the polyimide structure will be thoroughly examined.

1.2 Two-step method for polyimide synthesis

In the classic method of polyimide synthesis, a tetracarboxylic acid dianhydride is added to a solution of diamine in a polar aprotic solvent, such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAC), and N-methylpyrrolidone (NMP) at 15 to 75°C [2–11]. The generated poly(amic acid) is then cyclodehydrated to the corresponding polyimide by extended heating at elevated temperatures or by treatment with chemical dehydrating agents (Scheme 1.1). Since the polyimide is often insoluble and infusible, the polymer is usually processed in the form of the poly(amic acid), which is thermally imidised in place.

1.2.1 Mechanism of poly(amic acid) formation

A mechanism that accurately describes the formation of the polyimide precursor is shown in Scheme 1.2.



This is not to imply that the equilibrium constants are independent of the

monomers' structures. Considerable differences appear when polymerisations are carried out in ether or hydrocarbon solvents [12,16]. In such solvents, the equilibrium constant strongly depends upon the amine's basicity and the acidity or electrophilicity of the dianhydride. In polar aprotic solvents, although very unreactive diamines ($pK_a < 4$) and dianhydrides can lower the equilibrium constant, the primary result of differences in monomer structure is differences in the rate at which the polymerisation occurs.

Another important observation to be made concerning the equilibrium is that the forward reaction is exothermic at ambient temperature [12]. The magnitude of the heat of reaction depends on the solvent's basicity. Thus, the equilibrium is shifted to the left and the product's molecular weight is lowered when the reaction temperature is increased [17]. Conversely, decreasing the reaction temperature results in a shift of equilibrium to the right and an increase in the molecular weight. In basic aprotic solvents, however, the equilibrium already lies so far to the right at ambient temperature that the increase upon cooling is usually not detectable.

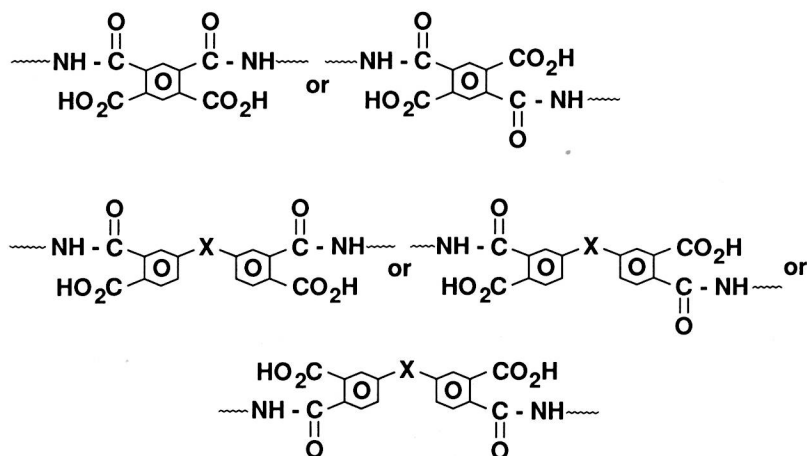
Some exceptions to the above generalisations are found with very unreactive monomers that do not react exothermically at ambient temperature. In these cases, the molecular weight of the poly(amic acid) increases as the temperature is increased. Although the effect is often obscured by the onset of imidisation, the polyimide produced usually has a higher molecular weight than that of its precursor [18–20].

Still another feature of the equilibrium that should be pointed out is that the forward reaction is bimolecular and the reverse is unimolecular. Thus, increases in the monomers' concentrations should shift the equilibrium to the right and *vice versa*. Although the molecular weight of poly(amic acids) has been found to be dependent upon monomer concentration [7], it is not clear how much of this effect can be attributed to equilibrium considerations, especially as the equilibrium constant is so large in polar aprotic solvents. This equilibrium effect, however, undoubtedly plays a role in the rapid decrease in molecular weight experienced by poly(amic acids) in very dilute solutions [10].

Equilibrium effects also help to explain the early observation that the addition of excess dianhydride or diamine to a poly(amic acid) solution results in a dramatic decrease in its viscosity [6]. Since the polymer is in equilibrium with the dianhydride and the diamine, the addition of an excess of either monomer results in an effective offset in stoichiometry that limits the molecular weight of the polymer.

Since the amine can attack either of the anhydride carbonyl groups, chain propagation results in the generation of isomeric repeat units. For example, in polymerisations involving pyromellitic dianhydride (PMDA) propagation results in both *meta*- and *para*-catenation. In the case of bridged dianhydrides, three different repeat unit isomers are formed during polymerisation. The situation can be simplified by considering only one half of the repeat unit

structure. Thus, propagation can occur at the carbonyl carbon in the *meta*- or *para*-position to the linking unit (Scheme 1.3).



Scheme 1.3

^{13}C NMR has been used [21] to determine the percentage of *meta*- and *para*-isomers in a series of poly(amic acids) prepared from various dianhydrides and *p*-phenylenediamine and benzidine (Table 1.1). The polymers compositions were found to be independent of the diamine used. Quantum chemical calculations did show that the isomeric ratios qualitatively correlate with the frontier electron densities f of the anhydrides carbonyl carbons.

The results of this study can be rationalised in the following manner. The nucleophilic amine prefers to attack the most electron-deficient carbonyl carbon in the anhydride. This inherent preference is not changed by changes in the nucleophilicity of the amine. The major factor that determines the position

Table 1.1 Isomeric composition of poly(amic acids)⁽²¹⁾

Dianhydride	<i>Meta</i> -isomer ^a (%)	<i>Para</i> -isomer (%)
PMDA	60	40
ODPA ^b	63	37
BPDA ^c	50	50
BTDA ^d	45	55

a Compositions were determined by ^{13}C -NMR analysis.

b 4,4'-Oxydiphthalic anhydride.

c 3,3',4,4'-Biphenyltetracarboxylic dianhydride.

d 3,3',4,4'-Benzophenonetetracarboxylic dianhydride.

of attack is the relative difference in electrophilicities between the two carbonyl atoms. Strongly electron-withdrawing groups located in *ortho*- and *para*-positions to the carbonyl carbon will, therefore, increase its susceptibility for attack; electron-donating groups in these positions will decrease it.

Meta-catenation is slightly preferred in PMDA polymers because the incoming amine chooses between a carbonyl atom activated by an acid group and a carbonyl atom activated by a carboxamide group. (Acid groups are slightly stronger electron-withdrawing groups [22].) The preferred position of attack in bridged dianhydrides is determined by the electron-withdrawing ability of the bridge group. The stronger its electron-withdrawing abilities, the higher is the percentage of *para*-catenation.

1.2.2 Kinetics of poly(amic acid) formation

Although the kinetics of the propagation reaction have been studied extensively during the past 25 years, there is still some confusion over what kinetic law is followed. Several workers have reported that the reactions of various dianhydrides with aromatic diamines follow irreversible, second-order kinetics [23–26]. However, other workers claim that reversible, autocatalytic kinetics are followed [16, 27]. For example, a relatively recent study clearly showed that autocatalytic, reversible kinetics were followed in the formation of a poly(amic acid) in tetrahydrofuran (THF) [16]. It was also found that added carboxylic acid effectively catalysed the reaction, but produced polymers with low molecular weights.

Much of the confusion undoubtedly stems from the effect of the polymerisation solvent. Polymerisation carried out in amide solvents are apparently not subject to autocatalytic effects [28]. These basic solvents form such tight hydrogen-bonded complexes with the amic acid carboxyl groups that they are not free to catalyse further reactions. Interestingly, simple carboxylic acids, such as benzoic acid, do catalyse acylation reactions in amide solvents. These somewhat contradictory results suggest that the carboxamide moiety actively participates in complex formation between the *o*-carboxycarboxamide groups and the solvent. Since less basic solvents, such as THF, do not tie up the amic acid carboxyl group, they are free to function as a catalyst and participate in the reverse reaction.

The actual rate of polymerisation is also strongly dependent on the solvent. The rate generally increases as the solvent becomes more polar and more basic [12, 23]. For example, the results of one model compound study showed that the rate of acylation increases with solvent in the order THF < acetonitrile < DMAC < *m*-cresol [28]. The large rate constant obtained in *m*-cresol suggests that the solvent also functions as an acid catalyst.

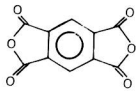
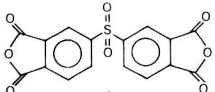
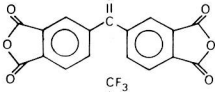
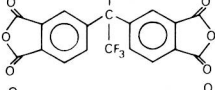
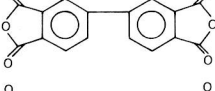
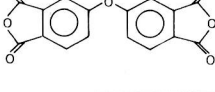
It should be pointed out that the majority of rate constants that appear in the literature have been determined in amide solvents using the assumptions that the propagation reaction follows second-order kinetics and is not reversible.

Although the latter assumption is not technically correct, it is a close approximation of the situation.

As was mentioned earlier, propagation proceeds via a nucleophilic substitution reaction at one of the carbonyl carbons of the anhydride. The more electrophilic the dianhydride, the more susceptible it is to nucleophilic attack. An excellent measure of an anhydride's electron acceptor properties is provided by its electron affinity (E_a), which can be obtained from polarographic reduction data [15]. In fact, direct monotonic relationships between acylation rate constants and the values of E_a have been found to exist. A quantum-chemical basis for these relationships has been found by molecular orbital calculations [29]. Thus, the energies of the lowest unoccupied molecular orbital of a series of dianhydrides have been shown to be directly proportional to the experimental values of E_a and the logarithm of the rate constant. (The acylation reaction is presumed to involve the formation of a chemical bond through the interaction of the highest occupied molecular orbital of the diamine, which contains an unshared electron pair, and the lowest unoccupied molecular orbital of the anhydride.)

As shown in Table 1.2, PMDA displays the highest E_a of the commercially available dianhydrides. The strong electron-withdrawing anhydride moieties in this molecule activate each other towards nucleophilic attack. Even after

Table 1.2 Commercially available dianhydrides

Dianhydride	Abbreviation	$E_a(\text{eV})^{[15]}$	Sources ^a
	PMDA	1.90	Allco Chemical Corporation, Pittsburg, KS
	DSDA	1.57	New Japan Chemical Co., Kyoto, Japan
	BTDA	1.55	Allco Chemical Corporation, Pittsburg, KS
	6FDA	NA	Hoechst Celanese, Coventry, RI
	BPDA	1.38	Ube Industries, Ltd., Tokyo, Japan
	ODPA	1.30	Occidental Chemical Corp., Grand Island, New York

^a All the dianhydrides may also be purchased from Chriskev Company, Leawood, Kansas.

one side of the molecule has undergone reaction, the generated carboxyl and carboxamide groups strongly activate the second anhydride group because of their own electron-withdrawing abilities. The E_a values of the bridged monomers are strongly dependent upon the electron withdrawing ability of their bridge group [15]. These values and the corresponding rate constants decrease as the ability of the bridge group to withdraw electrons decreases.

Attempts to correlate the reactivity of aromatic diamines with their ionisation potential (I), i.e. their electron-donating ability, have been less successful [5]. Although the rate constants for the reactions of diamines with a given dianhydride generally decrease as the diamines ionisation potential decreases, no quantitative relationships have been established [30]. Only qualitative correlations have been found between the energies of the highest occupied molecular orbitals of the diamines, the experimental values of I and the logarithm of the rate constant. Interestingly, qualitative correlations have also been made between the calculated charges on the diamine nitrogen atoms and these parameters [30]. This indicates that there are substantial electrostatic interactions between the reactive sites during the propagation reaction.

Considerable success has been achieved in quantitatively correlating diamine basicity with reactivity. Well-defined linear relationships exist between the pK_a values of diamines and the logarithm of their acylation rate constants [25, 26]. As shown in Table 1.3, the rate constants increase as the pK_a increases. In bridged diamines with the general formula $H_2N-C_6H_4X-C_6H_4-NH_2$, the values of pK_a and acylation rate constant decrease as the electron-withdrawing ability of the bridge group increases. Kinetic studies have also shown that structural changes in the diamine affect the reaction rate more significantly than changes in the dianhydride [30].

1.2.3 *Effect of reaction conditions on the preparation of poly(amic acids)*

Early workers in the field of polyimide chemistry found that higher molecular weight poly(amic acids) could be produced by using higher concentrations of monomers [7]. It was also discovered that the molecular weight of the products was influenced by the order and mode of monomer addition, with the highest molecular weights being obtained when solid dianhydrides were added to solutions of diamines [6, 7]. In fact, a slight stoichiometric excess of dianhydride was used to enhance the molecular weight. Temperature was also found to be critical, with the best results being obtained when polymerisations were run between -20 and 70°C [6, 10]. It is important to note that these early studies used dilute solution viscosity measurements alone as a means of assessing molecular weight. Thus, the molecular weight average that was being followed was the viscosity-average molecular weight, \bar{M}_v , which is very close to the weight-average molecular weight, \bar{M}_w [31]. Changes in \bar{M}_w produce much larger changes in intrinsic viscosity than do changes in the number-average molecular weight \bar{M}_n .