Chapter 1

POLYIMIDES: chemistry & structure-property relationships – literature review

1.1 Introduction

Polyimides are a class of thermally stable polymers that are often based on stiff aromatic backbones. The chemistry of polyimides is in itself a vast area with a large variety of monomers available and several methodologies available for synthesis. However, there has been considerable debate on the various reaction mechanisms involved in different synthesis methods. This review however, covers only the important fundamentals regarding the polyimide synthesis. The focus in this review will rest only on 'aromatic' polyimides as they constitute the major category of such materials. Secondly, the properties of polyimides can be dramatically altered by minor variations in the structure. The subtle variations in the structures of the dianhydride and diamine components have a tremendous effect on the properties of the final polyimide. This chapter reviews several such features that are important towards understanding these structure-property relationships.   Specifically, the effects of changing the diamines, dianhydrides or the overall flexibility of the chain on the basic parameters like T_g and T_m are also examined.

1.2 Two step method for polyimide synthesis

The most widely practiced procedure in polyimide synthesis is the two-step poly(amic acid) process. It involves reacting a dianhydride and a diamine at ambient conditions in a dipolar aprotic solvent such as N,N-dimethylacetamide (DMAc) or N-methylpyrrolidinone (NMP) to yield the corresponding poly(amic acid), which is then

cyclized into the final polyimide. This process involving a soluble polymer precursor was pioneered by workers at Dupont[1] in 1950's, and to this day, continues to be the primary route by which most polyimides are made. Most polyimides are infusible and insoluble due to their planar aromatic and hetero-aromatic structures and thus usually need to be processed from the solvent route. This method provided the first such solvent based route to process these polyimides. The process also enabled the first polyimide of significant commercial importance-'Kapton[TM]', to enter the market. The process for most extensively developed Kapton[TM] polyimide utilizes the monomer pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) and is illustrated in Figure 1.1.

However, the seemingly simple process involves several elementary reactions that are interrelated in a complex scheme[2]. The course of these reactions can be tremendously effected by a large number of factors that include reaction conditions[3] and even the mode of monomer addition[4]. The success of the overall reaction to yield high molecular weight polymers is critically dependent on seemingly subtle details. The ensuing discussion will address several parameters which govern these interrelations with respect to dependence of the synthesis on choice of monomers, solvents, reaction conditions and the importance of various side reactions involved in the synthesis.
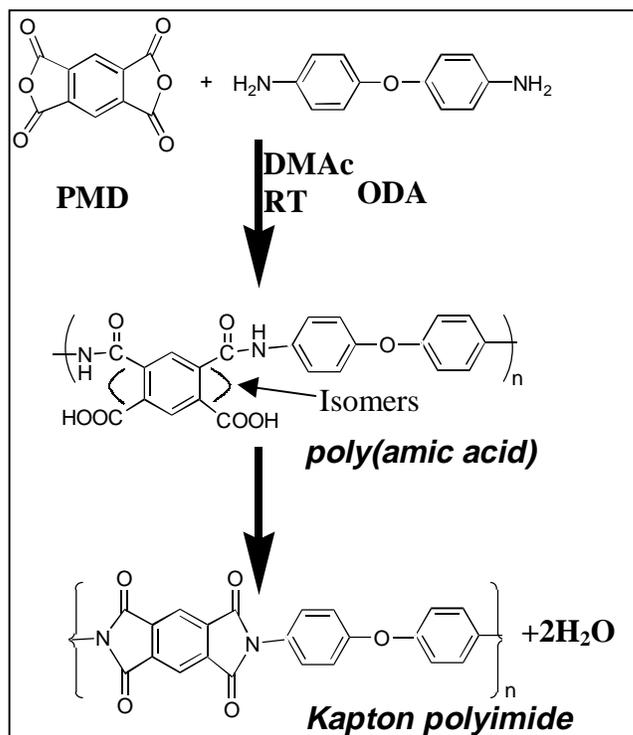
Figure 1.1   Reaction scheme for the preparation of kapton[TM] polyimide (ref 2)

1.2.1 Formation of poly(amic acids)

Addition of a dianhydride to a diamine in a dipolar aprotic solvent such as DMAc or NMP at ambient temperatures leads to the formation of the intermediate poly(amic acid) due to the nucleophilic attack of the amino group on the carbonyl carbon of the anhydride group. The scheme that is illustrated in Figure 1.2 involves a reversible reaction leading to opening of the anhydride ring to form an amic acid group[5]. However, the forward rate constant for the reaction is several orders of magnitude larger than the reverse reaction[6] and thus the reaction often appears irreversible if pure reagents are utilized. The formation of high molecular weight product is also dependent on this large difference in the reaction rate constants and thus it becomes important to examine the driving forces favoring the forward reaction. For the reverse reaction to take place, the carboxyl proton needs to attack the adjacent poly(amic aid) group[2]. Thus any reagent, that hinders this reaction can decrease the rate of backward reaction and thus can shift the equilibrium to the right.
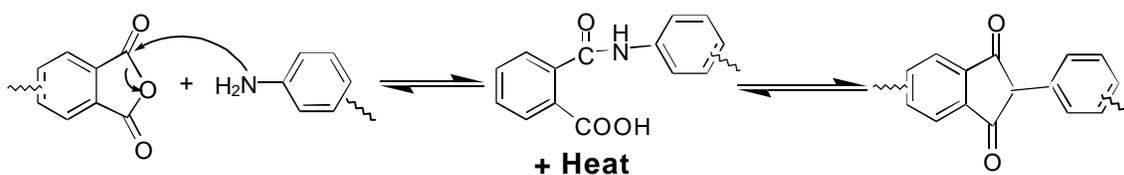
Figure 1.2   Generalized reaction mechanism of aromatic imide formation[2]

Polar aprotic solvents form strongly hydrogen bonded complexes with the free carboxyl groups and thus lead to equilibrium constants in excess of 10^5 l/mol at ambient conditions[6]. However, if the polymerization reaction is carried out in ether or hydrocarbon solvents, considerable differences in equilibrium constant are observed depending upon the amine's basicity and the dianhydride's electrophilicity[7].

It is also important to note that the poly(amic acid) formation is exothermic and the equilibrium is favored at lower temperatures[8]. However, the equilibrium is shifted

so far to the right at ambient that further lowering of the temperature usually does not show any detectable effect on the reaction. Another important factor effecting the reaction equilibrium is the monomer concentration. As the forward reaction is bimolecular and the reverse reaction unimolecular, increasing the monomer concentration favors high molecular weight products[8]. For the case of very dilute solutions this feature becomes especially important and leads to decreased molecular weight of the poly(amic acid).

1.2.2 Effect of monomer reactivity

As stated earlier, the mechanism of poly(amic acid) formation involves a nucleophilic substitution reaction at the carbonyl carbon atom of the dianhydride with a diamine. Hence the reaction is expected to depend upon the electrophilicity of the carbonyl groups of the dianhydride and the nucleophilicity of the amino nitrogen atom of the diamine. Electrophilicity of the dianhydride is usually gauged in terms of electron affinity (E_a) of the molecule measured by polarographic measurement techniques. PMDA that has the highest E_a, of the common aromatic diamines also usually demonstrates the highest reactivity when reacted with different diamines[2]. For dianhydrides with bridged bisphthalic anhydride structure (i.e. dianhydrides 2,3 and 5 in Table 1), electrophilicity is strongly influenced by the bridging group. In comparison to BPDA, which lacks a bridging group, the electron-withdrawing groups such as SO_2 and C=O increases the E_a value substantially whereas electron donating groups such as ethers decrease the E_a value. Due to this difference in reactivity, while ether-containing dianhydrides are not readily effected by atmospheric moisture, PMDA and BTDA have to be handled in strictly moisture free environments at all times.

Attempts at correlating the reactivity of the aromatic diamines with their nucleophilicity have been less successful. However, the reaction rates of the diamines with a given dianhydride usually increase with increasing ionization potential[2]. Also, considerable success has been achieved in quantitatively correlating the diamine basicity with reactivity, with the rate constants increasing with increasing value of pK_a[9].

Table 1.1 Electron affinity of common aromatic dianhydrides[2]

Dianhydride Structure	Name	Electron Affinity (eV)
	PMDA	1.90
	DSDA	1.57
	BTDA	1.55
	BPDA	1.38
	ODPA	1.30
	HQDA	1.19
	BPADA	1.12

The structure of the diamines effects the reaction rate significantly more than the changes in the dianhydride structure. It is often observed that the rate constant differs by four orders of magnitude between diamines with electron-withdrawing substituents and those with electron-donating ones[8].

1.2.3 Effect of reaction conditions and solvents on polyimide synthesis

Early workers found that using higher concentration of monomers could produce higher molecular weight poly(amic acids)[10]. It was also found that the order and the mode of the monomer addition strongly influenced the final molecular weight with the highest molecular weights obtained when solid dianhydrides were added to a solution of diamines[4,10]. It was reasoned earlier on, that this increase in molecular weights was entirely due to the avoidance of the side reactions[10]. Aromatic dianhydrides were known to react with water and other impurities in the amide solvents. However, the reactions with diamines were considerably faster. It was then correctly reasoned[1] that the solid mode of addition of dianhydride reduced its availability for competing reactions with water and other impurities, thus leading to higher molecular weights. Also a slight stoichiometric excess of dianhydride was found to increase the molecular weight. Similar reasoning is also offered to explain the dependence of molecular weight on concentration of monomers. A lower amount of solvent would result in a lower amount of impurities that interfere with the build-up in molecular weight[8].

Another very important factor to consider is that dianhydrides are usually added as solids to the reaction mixture. This solid mode of addition does not lead to immediate dissolution of the dianhydride[10]. The rate of dissolution itself depends on the concentration of monomers and is slow. If both the dianhydride solubility and monomer reactivities are low, then above a certain critical concentration, the process becomes diffusion controlled much like solid-liquid interfacial polymerization[11,12]. This leads to formation of very high molecular weight product at the beginning of the reaction, long before the dianhydride has completely dissolved and the stoichiometric balance has been

obtained. This kind of reaction can often lead (temporarily) to a polymer with a broad and often binodal distribution of molecular weight[8].

Early workers in the field also found that the viscosities of poly(amic acids) rapidly decreased when they were stored in a solution after preparation[4,10]. This was first attributed to the sensitivity of the amic acids to hydrolysis. Later work, however, showed that the phenomenon was associated with the reversibility of the propagation reaction[11]. Although the rate constants for such reactions are very small, the few such reactions that may take place can have a dramatic effect on the M_w of the polymer.

Solvents utilized in the poly(amic acid) synthesis also play a very important role. Common dipolar aprotic amide solvents utilized are DMF, DMAc, NMP and TMU. All these solvents share a common feature, as they are all Lewis' bases. Interestingly, while the starting reagents for the reaction are weakly basic aromatic amines and nonprotic anhydrides, yet the final product is an acid. Thus, while the starting mixture is basic, the product is acidic. The strong acid-base interaction of this resulting acid with the basic solvent medium is exothermic and one of most important driving forces for the reaction. It is thus expected that the rate of the reaction will be faster for more basic and more polar solvents. This was indeed found to be the case for reaction of phthalic anhydride with 4-phenoxyaniline with the reaction rate increasing in order of the solvent utilized as THF< acetonitrile< DMAc[13].

1.2.4 Side reactions and other factors involved in polyimide synthesis

There are several side-reactions involved in the poly(amic acid) synthesis, which accompany the main chain reaction. These side-reactions not only lead to undesired side-products, they can also have a tremendous effect on the molecular weight (both M_w and M_n) and the polydispersity of the final product. It is thus desirable to keep these side-reactions to a minimum if suitably high enough molecular weights are to be achieved.

One side reaction that cannot be completely eliminated is the reverse propagation reaction of the poly(amic acid) to yield the dianhydride and the diamine[8]. This intramolecular acidolysis which yields a anhydride is a result of the pendant carboxylic

groups at the ortho-positions[2]. In contrast, the acylation reaction of an amine with benzoic dianhydride is a irreversible reaction. However the former reversible reaction does not prevent the formation of high molecular weight product as the magnitude of the equilibrium constant (K_{eq}) is still very high. In fact, if this was the only side reaction involved, then the expected X_n for most poly(amic acids) would be over 300 ($X_n \sim K_{eq}^{1/2}$)[14]. In practice, the values of the X_n of the poly(amic acids) falls in the range of 25 to 275 that corresponds to a M_n in the range of 10,000 to 100,000[8].

An important side reaction often taking place is that of the dianhydride with water, which also competes, with the propagation reaction. This reaction has been stated to have a dramatic effect on the molecular weight of the poly(amic acid) as it removes the dianhydride from the equilibrium and upsets the monomer stoichiometry[8]. The reaction between dianhydride and water may be primarily driven by the enhanced nucleophilicity of the water in the polar aprotic medium. Also, some authors have speculated (with little or no evidence) that the ortho-dicarboxylic group that is formed is highly stabilized due to the acid-base interaction with the dipolar solvent and thus exists as one of the end groups of the poly(amic acid), thus effectively lowering the molecular weight[3]. As the anhydride group is consumed more is regenerated by the backward reaction to maintain the equilibrium. The above-discussed factors have lead to some widely practiced methods during the synthesis, namely

1) Higher concentrations of the monomers are favored in the poly(amic acid) synthesis.

2) The amine is added first and the dianhydride second (the dianhydride that is added second reacts faster with the diamine than with the existing water).

3) Sometimes a slight excess of dianhydride is found to be useful in attaining higher molecular weights.

It is important to remember that while the water may be present as an impurity in the monomers or the solvents, it is not the only source of water. While the conversion of a poly(amic acid) to a polyimide is slow at ambient temperatures, some water may form as a side product due to reactions occurring at ambient conditions if poly(amic acid) is left at these conditions for a long time[15]. Other solvent impurities like monofunctional 'amines' which may be present in the amide solvents can also have a devastating effect

on the main chain synthesis reaction[8]. These monofunctional impurities if present, would compete with the monomeric diamines throughout the polymerization reaction. These reactions can upset the monomer stoichiometry and lead to unreactive chain ends. Another side reaction speculated to have an important effect is the cyclic conversion of the o-carboxycarboxamide groups to an isoimide[16].

The excess dianhydride that sometimes has to be used to give high molecular weight products can also lead to several damaging side reactions. This is more so the case when highly reactive dianhydrides like PMDA are used as these are strongly dehydrating agents. The excess dianhydride groups attack the amic acid group leading to formation of a diacid and an imide. The ortho-dicarboxylic acid group, which remains as a chain end group, limits the molecular weight of the resulting poly(amic acid).

1.2.5 Thermal imidization of a poly(amic acid)

The intermediate poly(amic acid) is usually converted to the final polyimide by the thermal imidization route. This process is especially useful when the final product is desired in a film or a coating form. Films are first cast on a substrate and then undertaken through a thermal cycle with temperatures ranging from 100°C to 350°C. There has been considerable debate in the literature regarding the exact thermal cycle to be utilized for achieving close to 100% imidization of the poly(amic acids). While the types of thermal cycles utilized are many, they can essentially be divided into two different types

1)   Heating gradually to 250°C-350°C, depending on the stability and T_g of the polyimide[2,8,17].

2)   Heating the poly(amic acid) mixture to 100°C and holding for one hour, heating from 100°C to 200°C and holding for one hour, heating from 200°C to 300°C and holding for one hour and slow cooling to room temperature from 300°C[18,19,20,21].

However, irrespective of the type of thermal cycle utilized, it is important to recognize that there are several complicating factors involved in these seemingly simple thermal imidization processes, which finally determine the degree of imidization of the polyimide product. It needs to be emphasized that the imidization reactions take place in a very

concentrated viscous solution (during initial and intermediate stages) and the presence of residual solvent plays a very important role during imidization at the later stages of the reaction. In this regard, the imidization proceeds faster in the presence of dipolar amide solvents due to several reasons, some of which are;

1) Specific solvation allows the favorable conformation of the amic acid group to cyclize[22].

2) Plasticizing effect of the solvent to increase the mobility of the reacting functional groups[8].

3) The basicity of the amide solvent allows it to accept protons and may be responsible for the specific effect[2].

A simple kinetic expression for the imidization reaction is often not possible as the overall process involves several interrelated elementary reactions and dynamically changing physical properties such as diffusion rate, chain mobility, solvation and acidity. The rate of imidization is usually faster during the initial stages due to the presence of solvent and shorter chain sizes resulting in increased chain mobility. However, during the later stages of the reaction the rate tapers off due to primarily the reasons listed below:

1) Loss of residual solvent which occurs due to the extended heating[23].

2) The T_g of the polymer increases as the degree of imidization reaction proceeds and as the T_g approaches the reaction temperature, the imidization rate slows down markedly due to the decreased chain mobility.

Lastly, the rate of imidization may be dependent upon the availability of suitable conformations for the amic acid group to decyclohydrate in to an imide[3]. The slower rate of imidization during the later stages of imidization is attributed to unfavorable conformations, which have to rearrange to favorable conformations before imidization can take place[23]. Such a conformational rearrangement is only possible if the rotation of the adjoining polymer chain and strongly bound solvent molecules takes place.

1.2.5.1 Determination of the degree of imidization:

Infrared spectroscopy continues to be the prominent tool in determining the degree of imidization despite limited agreement on its sensitivity to chemical changes

taking place. The bands most frequently utilized are imide absorption bands near 1780 cm^{-1} (C=O asymmetrical stretching), 1380 cm^{-1} (C-N stretching) and 725 cm^{-1} (C=O bending). The strongest band that occurs at 1720 cm^{-1} (C=O symmetrical stretching) also overlaps with strong carboxylic acid band (1700 cm^{-1}, C=O) of the poly(amic acid). Some overlap of the 1780 and 725 cm^{-1} imide bands is also possible with absorption of anhydrides occurring at 1780 cm^{-1} and 720 cm^{-1}. The carboxylic acid bands of 1700 cm^{-1} (C=O) and 2800-3200 cm^{-1} (OH) and amide bands at 1660 cm^{-1} (C=O), 1550 cm^{-1} (C-NH) and 3200-3300 cm^{-1} (N-H) which often appear as broad peaks are also useful for qualitative assessment during imidization process.

1.2.5.2 Changes in mechanical properties & molecular weight during thermal imidization:

Dramatic changes in the mechanical properties occur as the poly(amic acid) sample is converted to the final polyimide. This phenomenon was covered qualitatively in a very early study[10] of thermal imidization and was later confirmed by other workers. The magnitude of the change that occurred depends upon the molecular weight of the starting poly(amic acid). For example, films prepared from polymers with inherent viscosity of less than 0.2 were brittle and remained brittle throughout the curing cycle. Poly(amic acids) with inherent viscosities in the range of 0.2-1.0 produced tough, creasable films that became brittle between 150°C and 200°C and tough and creasable again when heated above 275°C. Films prepared from samples with inherent viscosities greater than 1.0 were also tough and creasable and suffered only a minor and temporary loss in these properties during the cure cycle[8]. These fluctuations in mechanical properties have been attributed to fluctuations in molecular weight. These occur due to a small number of the amic acid groups that cyclize to regenerate anhydride and amine moieties at temperatures in the vicinity of 100°C. As the chains are broken at these points, the molecular weights and the resulting mechanical properties are reduced. As the temperature is increased, the terminal functional groups react and the mechanical properties improve due to increased molecular weight.

1.2.6 Chemical imidization of the poly(amic acids):

The chemical imidization of the poly(amic acids) is a useful technique for manufacturing molding powders[8]. Despite low energy requirements for such a process, it is rarely used for other applications due to the dangerous reagents involved. The process essentially consists of treating the poly(amic acid) with a mixture of aliphatic carboxylic acid dianhydride and tertiary amine at ambient temperatures[27-30]. The common reagents utilized are acetic anhydride, pyridine and triethylamine[24].

The mechanism of chemical imidization involves the reaction of the tertiary amine with an anhydride, which is more susceptible to nucleophilic attack. The final polyimide formed is insoluble in the imidization mixture and hence precipitates out. However, the possibility exists that precipitation occurs before all the amic acid groups have cyclized into an imide. The percentage of imidization achieved thus depends on the solubility of the polyimide in the imidization mixture with more soluble polyimides attaining higher degrees of imidization[3]. In general though, the chemical imidization technique requires a final treatment where the powder is heated briefly to temperatures near 300°C ($>T_g$) to complete the imidization and remove traces of any solvent[25]. It has been stated that the reverse propagation reaction characteristic of the thermal imidization process does not occur during chemical imidization, which means that the mechanical properties of the polymer do not change much during the conversion process[25]. This is an important factor in the imidization of films and fibers. However, chemical imidization may lead to substantially higher percentage of 'isoimide' moieties in the final product[8], which at higher temperatures converts to the more stable imide.

1.3   One step method- high temperature solution polymerization:

This technique is employed for polyimides that are soluble in organic solvents at polymerization temperatures[26]. The process involves heating a stoichiometric mixture of monomers in a high boiling solvent or a mixture of solvents at 180°C-220°C[2,3,8]. The imidization proceeds rapidly at these temperatures and water generated due to the reaction is distilled off continuously as an azeotrope along with the solvent. The commonly utilized solvents are nitrobenzene, m-cresol and dipolar aprotic amide solvents. The imidization still proceeds via the amic acid route although the concentration of amic acid at any time is very small. The amic acid group rapidly converts to an imide or reverts back to amine and dianhydride. The high temperature solution polymerization is often performed in the presence of catalysts such as quinoline, tertiary amines, alkali metals and zinc salts of carboxylic acids[27,28,29,30]. This process is especially useful for polymerization involving unreactive dianhydrides and diamines. An interesting feature of this method is that it often yields materials with a higher degree of crystallinity than can be obtained with two-step methods[8], which may be due to the increased solubility of the monomers in the solvent medium.

1.4   Structure property relationships in linear aromatic polyimides

1.4.1 T_g – structure relationships:

While the glass transition temperature of linear aromatic polyimides is strongly intertwined with the chemical structure of the polyimide, the exact nature of this relationship is complex due to several factors involved in determining the T_g of the final polyimide. While the chain stiffness is certainly the most important aspect, other factors like chain-chain interactions effect the T_g substantially. Isomeric attachments of the flexible/rigid groups and presence of bulky side groups can also effect both the chain-

stiffness and chain-chain interactions and thus are important in determining the T_g. Other traditional factors like presence of crystallinity and molecular weight (when below a certain critical molecular weight) can also contribute to influencing the T_g. The multitude of factors effecting T_g is certainly one of the reasons why not a single comprehensive study fundamentally addressing the exact T_g-structure relationship of polyimides exists in the literature. The large varieties of monomers used in the synthesis of polyimides have certainly raised the difficulty of any such analysis considerably. The extensive amount of experimental data existing in the literature may sometimes help in crudely predicting the approximate T_g of any new polyimide being developed depending upon the similarity of structure of the proposed polyimide with previously developed polyimides. However, several studies in the literature have addressed the various key features effecting the glass transition behavior of linear aromatic polyimides. The following section will briefly address some of these features:

1.4.2 Polyimide chain-chain interactions

The formation of a charge transfer complex (CTC) formation between the dianhydride and diamine groups in polypyromellitic diimides was first proposed by Kotov et al.[31] in 1977 using UV spectroscopy. They described the color changes in these materials by a cut-off of optical wavelengths, E_{opt}, which in turn were found to be inversely correlated with the ionization potential of the diamines. The authors attributed these changes to the formation of a CTC. Fryd[32] applied a similar reasoning in 1984 when proposing a CTC formation between dianhydride and diamine groups in polyimides being an important reason for high T_g's of polyimides. The increased inter-chain attractive forces due to such interactions were proposed as effectively increasing the chain rigidity and hence the T_g. It was also proposed that the presence of any bridging group in the dianhydride had a strong influence on the glass transition as it changed its electron affinity and hence promoted the possibility of CTC formation. Table 1.4 later in this report depicts such behavior for a series of polyimides based on ether diamines in which the dianhydrides with varying E_a were utilized.
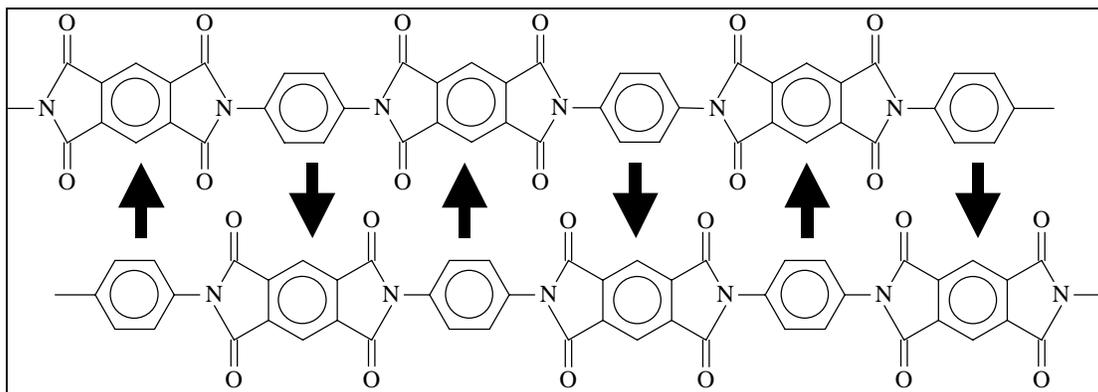
Figure 1.3 Idealized charge transfer complex formation in dianhydrides[31].

Figure 1.3 shows the idealized form of such an interaction between the dianhydride and diamine groups. However, such alignment of repeat units will not occur over more than a few repeat units. Though the values of E_a cannot be used directly to give a quantitative value for the measure for this interaction, it is clear that the more electron deficient PMDA will have a much larger affinity than ODPA for the electron rich amine-derived center. This type of interaction can also be looked as a Lewis acid-base kind of interaction[33]. It has been widely speculated in the literature[33] that the presence of such very strong electronic interactions in polyimides is responsible for their enhanced color[34]. Several researchers have worked on lessening these interactions in order to develop polyimides with reduced color, increase solubility and to lower the dielectric constant[35,36,37]. Although the CTC model successfully explains the *qualitative* nature of the relationship between the T_g's of the polyimides and the E_a's of the dianhydrides for several polyimides, the T_g seems to become insensitive to E_a of the dianhydride as the bridging group in the dianhydride becomes longer[33].

Another type of idealized chain-chain interaction visualized for polyimide is called the "*Preferred Layer Packing*" arrangement where the dianhydride and the diamine sections of the one chain are correspondingly packed alongside the dianhydride and diamine

sections of another chain[38]. This type of chain-chain interaction that may exist in the crystalline state is schematically shown in Figure 1.4.
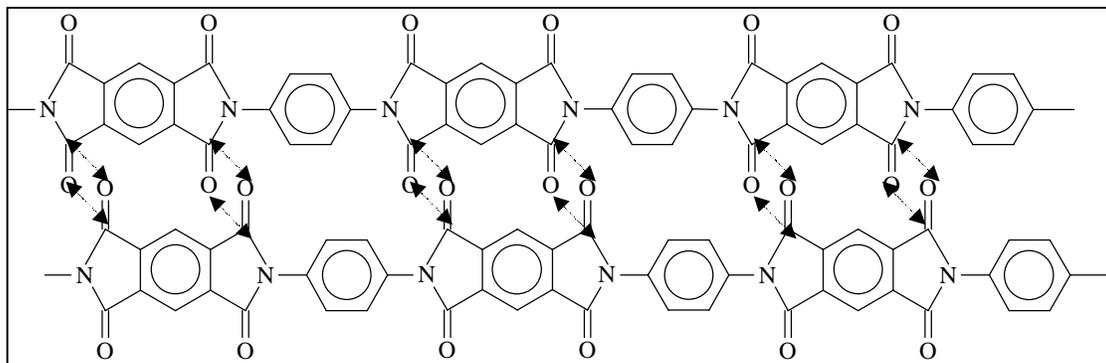
Figure 1.4   Idealized polymer chain-chain interaction in the crystalline state[38].

Such chain packing models have also been utilized to qualitatively explain the predominating effect of any bridging groups present in the dianhydride, which then may disrupt the packing arrangement by inhibiting the carbonyl-carbonyl dipolar attractions. The presence of such bridging groups in the diamine has been proposed to only reduce the packing density and thus exerts lesser influence on the final T_g[38]. While such explanations provide some degree of qualitative explanation of T_g behavior, they cannot be utilized for any convenient quantification to predict the T_g. Although such ideal chain-chain interactions have been hypothesized, the structural arrangements within any polyimide should be governed by minimum energy conformations. Interestingly the crystal structure determinations of some polyimides have shown the packing arrangement to be dissimilar to any of the packing arrangements shown in Figure 1.3 or Figure 1.4. Figure 1.5 illustrates the crystal packing arrangement for New-TPI as proposed by Okuyama et al[39] which does not lends itself to comparison between the two different kind of arrangements but rather seems to be intermediate between the two kinds.
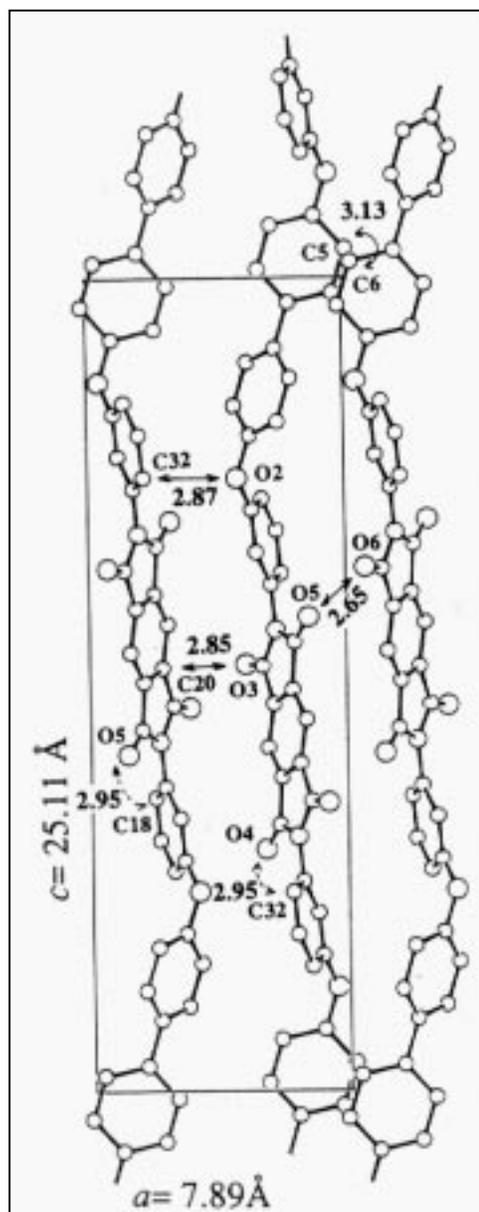
Figure 1.5   Packing structure of New-TPI viewed along the b-axis as proposed by okuyama et al[39].

1.4.3 Effect of chain length of the ether diamine on the glass transition:

Tamai et al.[40] studied the effect on T_g of ODPA based polyimides due to the chain length of the diamine by introducing ether linkages in the diamine component. The inherent viscosity's of the initial poly(amic acids) were kept constant at 0.5 dl/g and the chain ends were endcapped with phthalic anhydride. The results are shown in Table 1.2. It is clear that the chain length of the diamine component can significantly effect the glass transition of the final polyimide significantly. This effect is primarily due to introduction of additional flexible linkages that in effect decreases the persistence length of the polyimide. These shorter and more flexible ether linkages require lesser "kT" for the motion to set in. Another feature illustrated in Table 1.2 is that the para-amino-substituted polyimides have a significantly higher T_g for all the polyimides with equal number of benzene rings [i.e. polyimide (b) & (f), (c) & (g), (d) & (h)]. However, the effect of number of benzene rings seems to be more important than the nature of amino substitution. It is also seen that no clear correlation seems to exist regarding the presence of crystallinity, or when it is present, regarding the melting point. The study also illustrates the range of glass transitions (from 181°C to 326°C) and the range of melting points (from 318°C to 491°C) that can be obtained by varying the number of benzene rings in the ether diamine while keeping the dianhydride the same.

Table 1.2   Dependence of glass transition on the chain length of diamines[40].
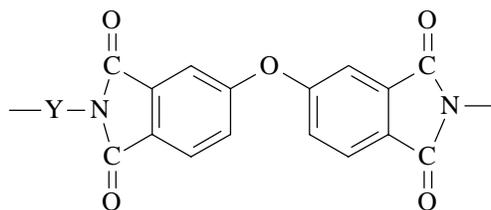
Polymer	Dianhydride	Y	T_g (°C)	T_m (°C)
(a)	ODPA		326	ND
(b)	ODPA		242	374
(c)	ODPA		222	428
(d)	ODPA		204	332
(e)	ODPA		261	491
(f)	ODPA		205	ND
(g)	ODPA		189	318
(h)	ODPA		181	ND

1.4.4 Effect of isomeric attachment of the diamine:

The effect of isomeric attachment on T_g is more clearly illustrated in Table 1.3, which shows a series of ether diamines with varying para-, and meta- linkages[40]. It is clear that as degree of para-substitution decreases and that of meta-substitution increases, the glass transition decreases tremendously. Also, it is clear that the nature of amino-substitution is far more important than the type (para- or meta-) of ether linkages inside the diamine. No clear correlation seems to exist for the crystallinity to exist. It is however, no surprise that more flexible chains yield lower melting points. However, as the position of the amino substitution changes to the ortho-position (which are expected to be even more flexible) this general rule is broken and the polyimides show considerably higher T_g's than just expected from the flexibility of the diamine. This phenomenon is shown in Figure 1.6 which illustrates the effect of isomeric attachment in diaminobenzophenone in a series of BTDA based polyimides[41] of similar molecular weight. The unusually higher T_g of ortho-substituted polyimides is in large part due to the strong dipolar attractions between the imide linkage and the closely placed carbonyl moiety on the diamine.

Amine attachment	T_g (°C)
2,2'	289
2,3'	259
2,4'	289
3,3'	264
3,4'	282
4,4'	293
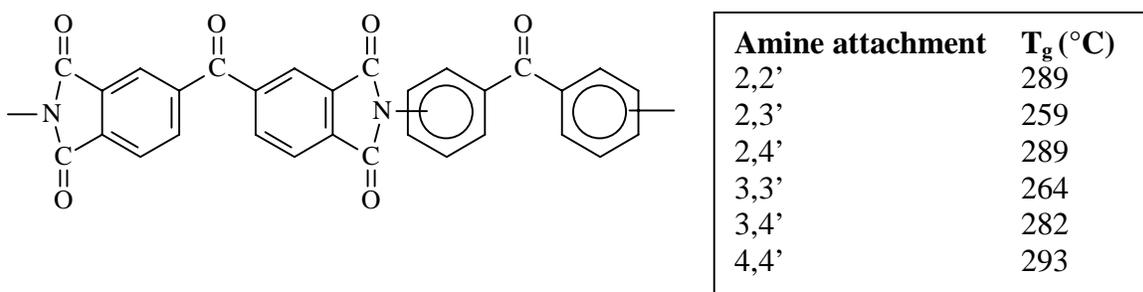
Figure 1.6   Effect of isomeric attachment of BTDA based polyimides[33].

Table 1.3 Effect of isomeric attachment of the diamine for ODPA based polyimides[40].
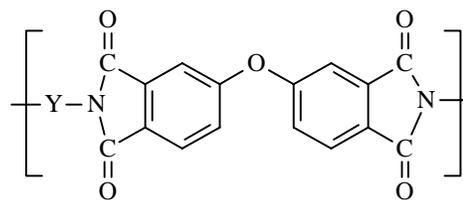
	Diamine Structure	$T_g(°C)$	$T_m(°C)$
A		242	374
B		219	325
C		205	ND
D		222	428
E		201	341
F		189	318
G		168	ND

1.4.5 Effect of the dianhydride structure on the glass transition:

The nature of the bridging group in the dianhydride strongly effects its electron affinity (see Table I) and also its T_g. As explained earlier, these factors have been correlated on the basis of the CTC model by many authors i.e. polymers with higher E_a have a much higher propensity for CTC formation and thus display a higher T_g. Although, this general relation seems to hold well for most short chain diamines, discrepancies are often observed for BTDA and BPDA based polyimides

Table 1.4 Effect of dianhydride on the T_g of the various ether diamine based polyimides[40].

X	PMDA	BPDA	BTDA	ODPA
—	250°C	221°C	216°C	199°C
$-\overset{O}{\underset{\parallel}{C}}-$	230°C	211°C	205°C	193°C
—O—	212°C	199°C	192°C	181°C

1.4.6 Effect of chain structure on the crystallinity:

Although many semicrystalline polyimides have been synthesized, the literature provides only little work on the crystallization behavior of these polyimides, once they are taken above their melt temperatures. While many crystalline polyimides have been reported, it has often been ignored that this initial presence of crystallinity is the result of solvent aided crystallization that occurs in parallel with the later stages of the synthesis reaction. This also has been due to the fact that most of these researchers were not concerned with developing melt-processable polyimides. It is thus difficult to properly ascribe the effects of structural changes on the crystallization behavior from the melt for most of these polyimides. However, few factors appear to be distinctly important for inducing crystallinity (initial) in polyimides. For a given dianhydride (Table 1.3), para-substitution polyimides appear to favor the crystallization while increasing meta-substitution seems to reduce the ability of the polymer to crystallize. Similar behavior is also observed in Table 1.2 where the ether diamines based with all para-substituted positions appear to be much more inclined to crystallization. Another feature related to the ability of the polyimides to crystallize is the nature of the dianhydride. For most polyimides using common dianhydrides, the ability to crystallize often goes with BTDA>PMDA>BPDA~ODPA, although some exceptions to this rule do exist. Also, while para and meta substituted ether linked diamines seem to be the best candidates for inducing crystallinity in the polyimides increasing the flexibility by introducing ortho-substitution often inhibits the presence of crystallinity. This is because the ortho-substitution often contorts the chain symmetry and thus makes it harder for the chain to pack into the crystal lattice. Introduction of bulky bridging groups or pendant side groups along the chain backbone also inhibits crystallinity and is actually often one of the means practiced when developing soluble polyimides[42]. The crystallization behavior from the melt for many crystalline polyimides will now be examined in the next chapter.

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