Synthetic Routes for Polyimides, Aramids and Benzimidazoles (PBI)

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Introduction

This essay is only intended to be a light survey of some of the basic chemical aspects associated with these three polymer families and is not designed to be an exhaustive resource or provide any kind of in-depth treatment of the subject. Over the last few decades, a multitude of improved and alternative synthetic approaches has evolved in each of these polymer fields, and each class has expanded immensely as it has grown in numerous directions utilizing a variety of pathways and innovative schemes, most of which cannot be covered in a short paper such as this. However, it is hoped that some of the more fundamental elements associated with the synthesis and properties of these three important polymer families can be briefly introduced in an appropriate manner. There are several important chemical and physical aspects that tie the three polymer families together. For example, the ideas associated with inter-chain interactions, liquid crystalline behavior and the associated processing challenges apply similarly to all three polymer classes. Obviously, it would be redundant to discuss the stacking nature of these polymers in all three sections since they all exhibit this effect to varying degrees, and so each section sequentially supports the discussion in the other sections. Thus, it is recommended that the entire paper be reviewed in order to acquire a complete picture for any one of the three polymer types which may of particular interest to the reader.

Polyimides, aramids and benzimidazoles are often classified as high performance thermoplastics. While the specific processing requirements, mechanical properties and ultimate user forms associated with each of these three material families do not always coincide, they all have some very important attributes in common. For instance, they are all highly aromatic structures containing nitrogen which are synthesized via step growth or condensation polymerization-type mechanisms. More importantly, they provide exceptionally high mechanical and thermal properties when compared to traditional thermoplastic materials. Indeed, they rival and surpass the thermosets in many regards. There are other polymer types which could fall into this series, but only these three polymer families were chosen as the subject matter for this paper.

One of the most unique properties exhibited by these polymer systems is their tendency for form highly oriented, rod-like liquid crystal particles within the reaction solution (a sort of ‘mesophase’) during the polymerization process. Formation of this liquid crystal (LC) mesophase is due to enhanced stacking interactions between adjacent polymer chains coupled with π orbital interactions between the adjacent (planar) aromatic rings which become the primary mesogenic structures along the polymer backbone in these molecules. This is not unlike the LC mesophase formed when highly aromatic carbonaceous pitch mixtures are heated (prior to carbonization), except that the organic pitch mesogens evolve into disc-shaped LC particles whose alignment becomes ‘discotic’, whereas the specialized polymers under study in this paper condense into rod-like structures whose mesogenic orientations become ‘nematic’ (the rods align longitudinally but their centers do not necessarily coincide). Undoubtedly, LC behavior is responsible for the extraordinary mechanical and thermal properties that products made from these polymers are known so well for. Geometrically, the rod-like structures exhibit high aspect ratios and the interparticle alignment strengthens substantially when the LC mesophase is subjected to flowing and shearing forces during processing.

Moreover, it is the LC behavior of the aramids and benzimidazoles that plays a most prominent role in their use as high strength, high temperature fibers. However, the strong tendency for these polymers to agglomerate or associate into LC arrays also makes the polymerization process difficult to carry out and this imposes undesirable restrictions on the manufacturability of end-products and constituents, such as fibers. For instance, it is difficult to solvate these polymers with most of the more common organic solvents, and since they have no discernable melting point, they cannot be melt-processed either. Aprotic solvents such as N-methyl pyrrolidone (NMP) and dimethyl acetamide (DMAc) have been successfully used to process these polymers. Throughout the industry, these solvents are frequently used for the most difficult fiber spinning processes (DMF dimethyl formamide and DMSO dimethyl sulfoxide may also be acceptable solvents). Unfortunately, polymer concentrations obtained in these solvents are not very high – often less than 4 or 5%. Processing in 100% sulfuric acid permits concentrations close to 20%. Sulfuric acid is actually one of the more classical solvent systems for such polymerizations but the processing and equipment challenges associated with large scale production operations involving 100% H_2SO_4 are undesirable, to say the least.

Today, the most prevalent method for generating fibers from liquid crystal solutions, particularly the aramids and PBI, is dry-jet wet spinning (or gel spinning) which contains elements of both the dry and wet spinning processes. In this method, the filaments leave the spinneret head and pass through a gaseous space or air gap before entering the coagulation bath. In a typical sulfuric acid process, the fiber precipitates in the air gap and the acid is removed as the filament passes through the bath. The process can be performed at moderate temperatures (< 100°C) where the specific gap spacing and gap atmosphere can be adjusted and used as control parameters to impart certain properties to the fibers. The process of channeling the spinning dope through the spinneret and the gap space greatly enhances nematic alignment of the liquid crystal particles to produce solid fibers that are highly oriented in the longitudinal fiber direction. Additionally, the transverse inter-polymer interactions which are responsible for the LC behavior (to be discussed later) provide a substantial level of lateral cohesion that makes these polymer products quite unique.

Polyimides can be prepared in low concentration solutions (NMP, DMAc), or by vapor phase polymerization, and even by melt processing techniques. Solution concentrations as high as 25-30% are possible. Polyimides also exhibit planar aromatic ring stacking and can be formed into liquid crystal structures (particularly when synthesized with highly aromatic ester and ester/amide co-monomers), though not as robustly as the aramids and benzimidazoles. Modified polyimide resins (or more appropriately, polyimide resin precursors based on polyamic acid) are now available for various production and developmental processes including compression and injection molding, coatings, films, adhesives, composite matrix resins and even fibers. While dry-jet wet spinning is a likely method for the formation of polyimide fibers, it is conceivable they could also be produced via *reaction* spinning in which the polyamic acid intermediate is converted into the final polyimide after the spinning step. An emerging developmental approach involves the *electro*-spinning of fibers which can be optimized for all three of these polymer families to produce non-woven mats, continuous high surface area nano-fibers and surface deposition webs.

Some of the more prominent polyimide brands available today include the well known Kapton® which has been produced by Dupont de Nemours for over 40 years, Norton's TH series (now Saint Gobain), Upilex® from Ube Industries and Apical® from Kenecka Corporation. Dupont is also famous for its para-oriented polyaramid known as Kevlar® and meta-aramid Nomex® (there are some interesting differences between the para and meta aramids which will be considered shortly) Aramids can be synthesized with various co-monomers to modify their handling and performance properties. An example is Teijin's Technora® which combines the attributes of para and meta aramids into a single product. While there may be new producers of PBI on the horizon, Hoechst Celanese Corporation was the original developer and domestic producer for PBI since the early 1980's (the Celazole® brand is now owned and operated by PBI Performance Products).

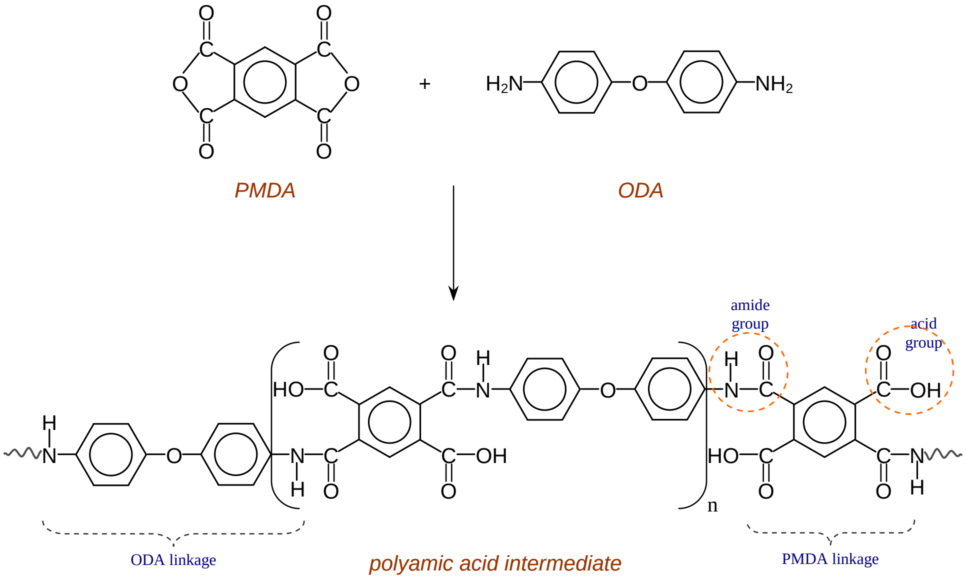
The polyimides, polyaramids and polybenzimidazoles are stable in pyrolytic (oxygen-free) environments at continuous operating temperatures exceeding 200°-300°C with excursions as high as 400°-450° and above. These polymers will eventually break down after longer exposures beyond about 500°. In contrast, essentially all other organic polymer forms are incapable of withstanding more than about 300°-325° before thermal degradation commences (~325°-375°C generally marks the beginning of pyrolytic conversion or carbonization in which organic carbon is transformed into inorganic carbon char). This includes the well known classes of highly cross-linked thermosets in the epoxy, phenolic and polyester families.

Interestingly, most inorganic carbon allotropes are capable of withstanding several thousand degrees before any phase changes occur – as long as oxygen is not present. A couple of the more prominent inorganic carbon forms include carbon fibers, bulk hexagonal graphite and glassy (amorphous) carbons. (Note: All crosslinked polymer thermosets become glassy hard carbons upon pyrolysis. Also, pre-carb oxidative stabilization procedures are generally required for PAN, rayon and pitch fiber precursors in order to convert their soft structures into infusible hard carbons that can be carbonized in the solid state.). While carbon and graphite articles are capable of withstanding several thousand degrees of pyrolytic heat, in oxidative environments, exposed carbon substrates and surfaces will begin to degrade as low 300°-325°C. However, special techniques can be incorporated to raise the survivability level of certain carbon forms up to the 525°-550° range. If these unprotected carbonaceous forms are rendered oxidation protective, such as by ceramicization, their thermal limits become governed primarily by the particular ceramic or oxidation protection mechanism applied, which can result in phenomenal protection to several thousand degrees in continuous thermooxidative environments. However, these treatments and processes are expensive, time-consuming and unnecessary for less rigorous (lower temperature) applications. They are often limited to components and articles requiring extraordinary thermal and oxidative resistance, as well as those which need to have (or at least can tolerate) the high modulus and brittleness that accompanies these materials.

On the other hand, the polyimides, aramids and benzimidazoles offer exceptional capabilities for moderate thermal and oxidation protection in physical forms that maintain their plastic behavior and are often elastic. With the incorporation of crosslinking groups into the polymer chains, these materials can sometimes attain the properties of thermosets which include enhanced mechanical strengths and potentially higher temperature capabilities before ultimately converting into glassy carbon char. However, in many applications, crosslinked versions of these polymers may not be desired since their more common thermoplastic forms appear to undergo a unique thermal degradation process leading to a softer, green char product that is almost flexible and self-extinguishing but without the rigid crosslinks and glassy brittleness.

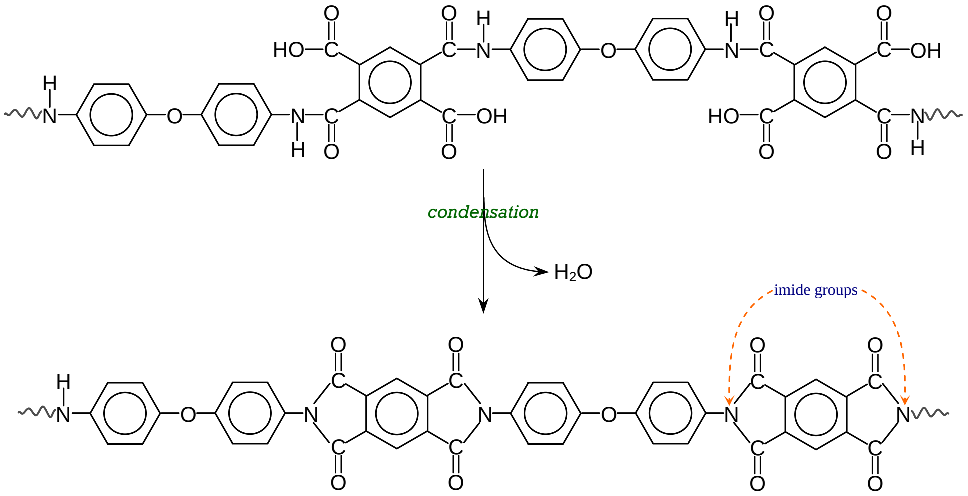
Polyimides

The chemistry of aromatic polyimides and the physical properties attained have undergone significant improvements and variations over the last three or four decades. Minor variations in the dianhydride and diamine monomer structures can have substantial effects on the properties of the final polyimide product, especially in terms of chain stiffness and the glass transition temperature T_g. Polyimide products that are soluble in the particular solvent utilized can be prepared in a single step process. However, the classical two step scenario is more prominent in the industry and is most relevant to the end-products of industrial interest (prepreg resins, adhesives and coatings). The second stage is actually a curing process imparted and completely controlled by the end user or fabricator. The two stage approach is also the method utilized for the formation of Kapton-like products which are made from the monomers pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA). The reaction can be carried out in NMP or DMAc. The first step involves the ring-opening reaction between the dianhydride and the diamine to form poly(amic) acid . . .



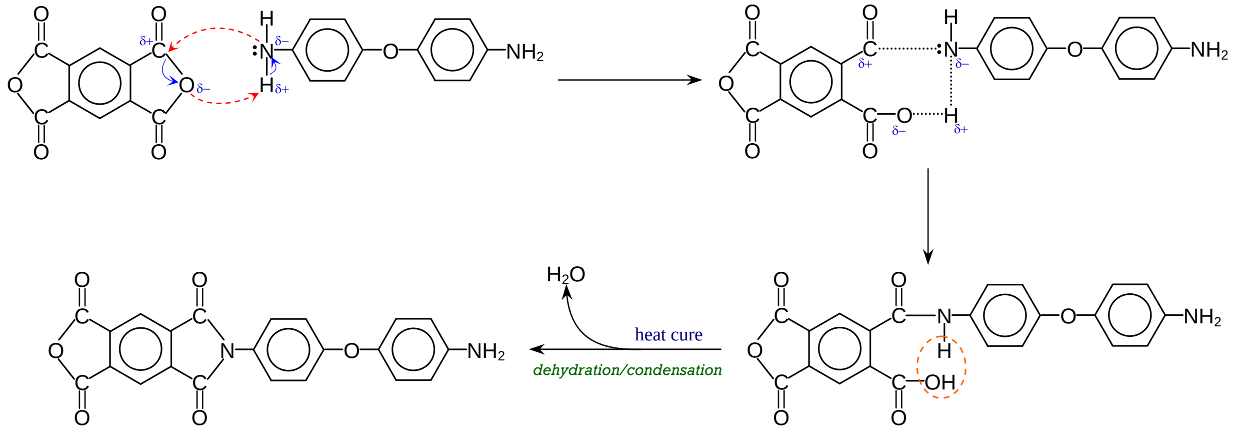
Polyamic acid is considered as an intermediate 'resin' which can then be used to cast or extrude films and coatings, prepare uncured liquid adhesive products and pre-impregnate composite reinforcement fabrics, all prior to the second phase of the process which involves heat curing of the resin to a hardened state. Prior to curing, the resin is often subjected to lower levels of heat (well below the gel temperature) for pre-optimized time intervals over specific time/temperature profiles either by the broad goods manufacturer and/or the fabricator/applicator. This procedure is referred as 'B-staging' as it increases the viscosity of the resin leading to enhanced handling properties during pre-cure assembly operations as well as more uniform and controlled heat distributions throughout the polymer body during the final curing process.

It is the second stage heat curing process that actually produces the polyimide. Pressurized autoclave curing to the 300°-350°C range is common for many industrial grade polyimides. Since the polyimides are condensation polymers, autoclave pressures can be optimized to control pore interconnectivity, resin bleed-out, solvent release and cured mechanical properties. The curing reactions convert the amic acid into the corresponding cyclic imide in ring-closing condensation reactions between associated carboxyl and amide groups which produces water as a by-product and leads to the final insoluble polyimide matrix . . .



cured polyimide chain

The mechanism for the first step likely involves nucleophilic attack on the carbonyl carbon of the anhydride group by the electron-rich nitrogen atom in the amino group which opens the anhydride ring leading to the formation of the amic acid group. In this scenario, the lone electron pair on the nitrogen atom exemplifies the Lewis base character of the amine group . . .

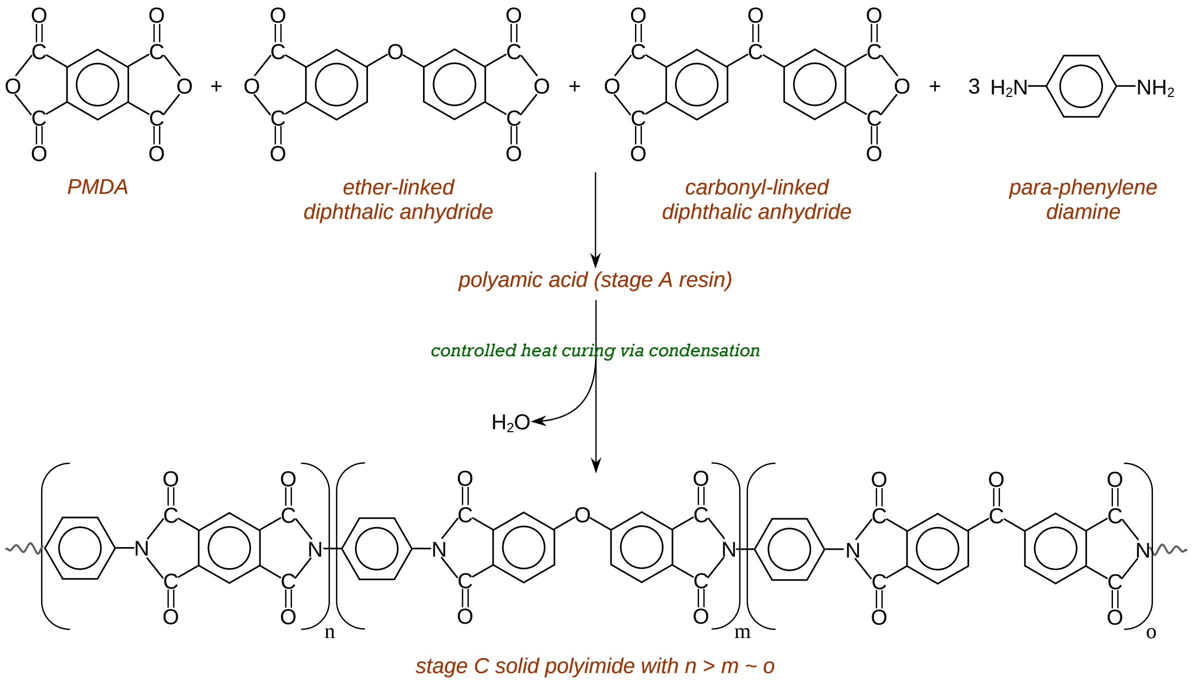


cyclic imide (step 2)

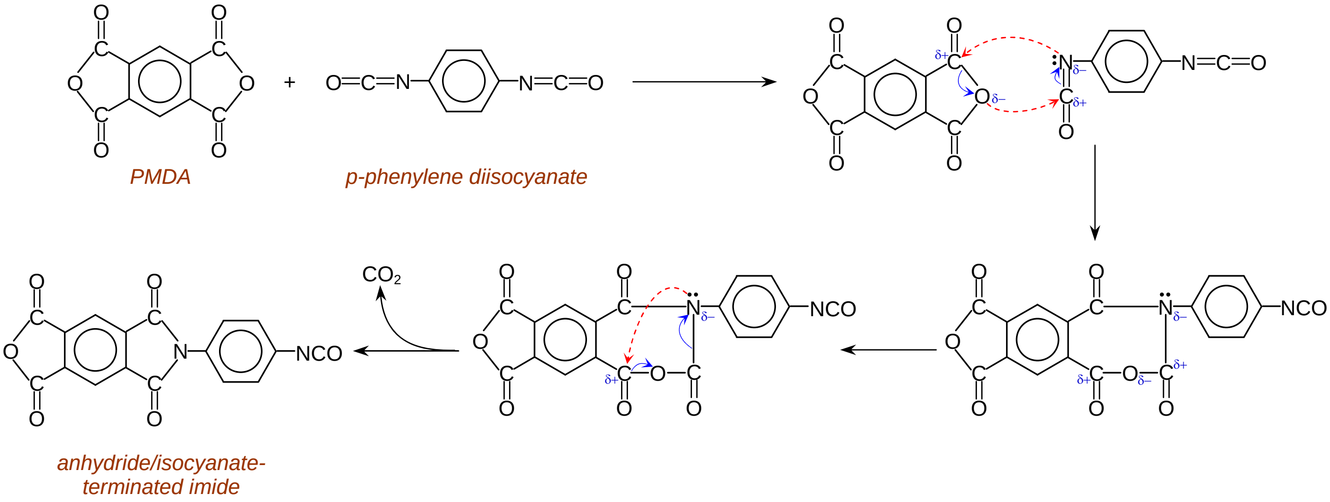
amid acid (end of step 1)

The second step is a condensation reaction in which water is extracted from the amic acid group as the ring is closed. The first step is probably better represented as an equilibrium. However, equilibrium is shifted strongly to the right in this reaction for at least a couple of reasons. The use of the aprotic solvents NMP or DMAc tend to form hydrogen bonded complexes with the carboxyl groups in the newly generated amic acid chain which drives the reaction to the right. Additionally, higher monomer concentrations, the basicity of the diamine and the heat generated during the reaction all favor formation of the amic acid (Note: The formation of polyamic acid is exothermic.). In all cases, the reaction is expected to be highly influenced by the respective nucleophilic and electrophillic strengths of the particular amine monomer used and the carbonyl groups on the anhydride.

Now the electron affinity of the anhydride plays a prominent role in controlling the primary reaction as well as undesirable side reactions. For instance, the reactivity of dianhydride monomers formed by two phthalate rings joined together can be strongly influenced by the nature of the linking group connecting the two rings together, specifically, whether the group is more activating (electron-withdrawing) or deactivating (electron-donating). Strongly activating groups increase the electrophilicity (and the electron affinity) of the anhydride group which equates to a monomer with higher reactivity. These connecting groups also play a dominating role in the ultimate physical/chemical properties achieved for the polyimide product, such as polymer flexibility, solubility, mechanical and thermal properties, stacking and crystallinity. A variety of anhydride monomers is now available for such property modifications with ring-connecting entities containing ethers, carbonyls, alkyls, arenes, sulfones and even bisphenol A. While the activating properties of PMDA are hard to beat, some of these other anhydride co-monomers can be used to create tailored polyimides for highly specialized applications. Phthalic anhydride groups linked together with simple ethers and carbonyls (both activating groups) can effect changes in solubility, chain stacking and crystallinity (thus improving processability and flexibility), but they may also cause reductions in mechanical strengths, modulii and some of the thermal properties. The trade-offs may be warranted or desired for particular applications. Processing of such composite systems would likely include tightly controlled levels and feed rates for the monomers . . .



In a similar manner, the structure and nucleophillicity of the diamine or nitrogen-containing co-reactant can also have substantial effects on the processability and ultimate physical/thermal properties of the polyimide product. Ionization potential might be reflective of this nucleophillicity, or perhaps the ability of the nitrogen to act as a base. Nitrogen compounds are generally Lewis bases, and the basicity of the amines is determined by the nature of the attached substituents which influence the ability of the nitrogen atom to donate its lone electron pair in such reactions. Amine structures which hybridize into sp^3 orbitals are more basic than those which form sp^2 orbitals, and *sp* structures are even less basic. That is, the lone pair tends to be more strongly held in orbitals with more *s* character. However, reaction rate is not necessarily the key factor in choosing the best monomers. Ease of processing, cost factors and the required physical properties are the principal drivers. Even though *sp* and *sp*^{2} hybridization reduces the relative basicities of the nitrile group and the isocyanates respectively, aromatic versions of these compounds can still be used as monomers for reaction with dianhydrides to form custom polyimides. Consider the reaction of something like para-phenylene diisocyanate with PMDA which forms the corresponding polyimide in a single stage process . . .

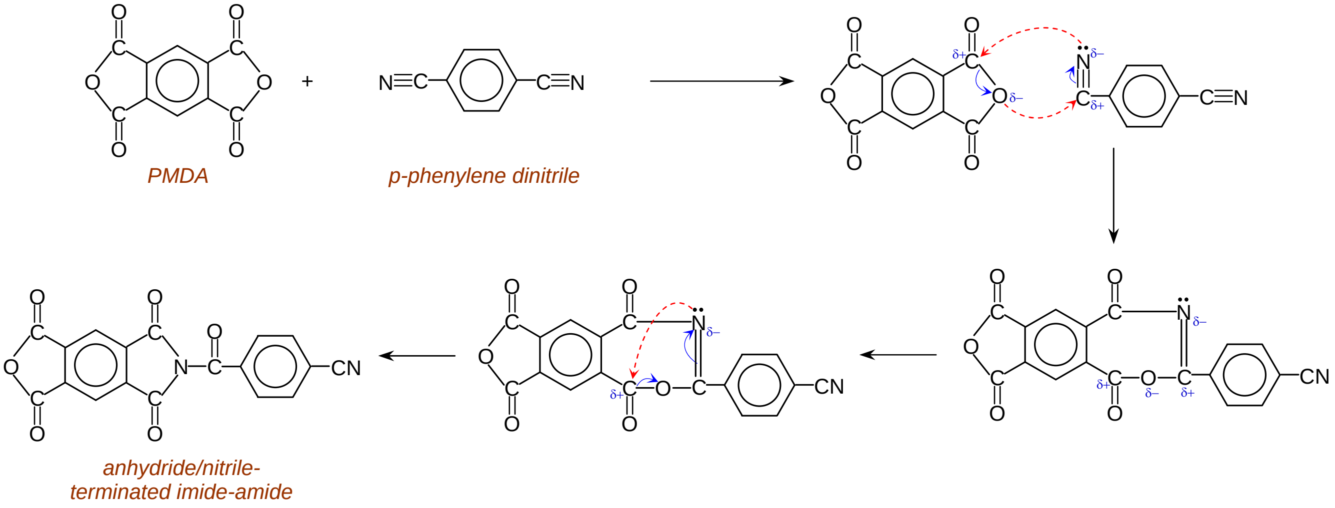


PMDA

p-phenylene diisocyanate

anhydride/isocyanate-terminated imide

. . . or the reaction with a nitrile group forming an intermediary imine to give a polyimide-amide . . .



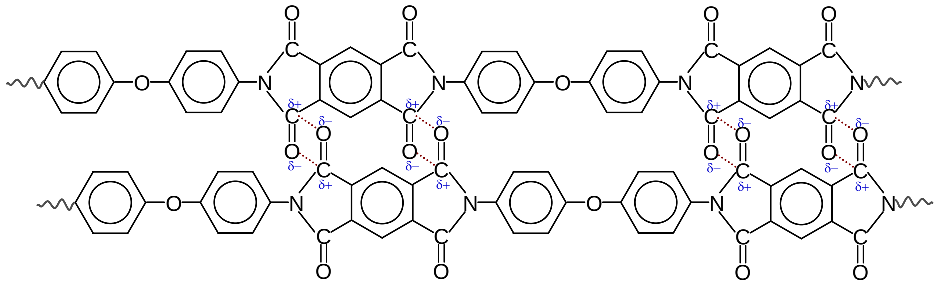
PMDA

p-phenylene dinitrile

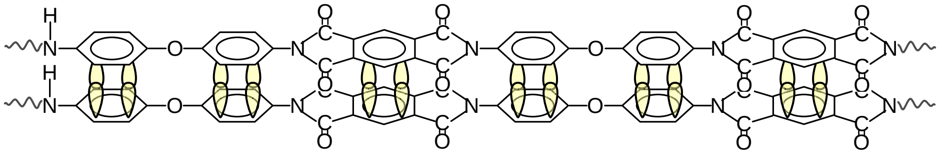
anhydride/nitrile-terminated imide-amide

Reactions of aromatic dianhydrides with these other nitrogen-bearing monomers imply the feasibility of combining polyimides with polyurethanes and perhaps even acrylonitriles (PAN) leading to the possible formation of a new sub-class of synergistic high performance copolymers. For strong LC properties, these illustrations may be oversimplified since more complex di-, tri- and poly-nuclear isocynates and nitriles are often required effectively bring out the LC behavior in the polymer chain.

Solubility and processability can also be improved by using *meta*-substituted diamines instead of the classical para-oriented monomers. However, meta units tend to retard chain stacking and inter-polymer interactions (see below), leading to reductions in LC orientation, higher fractions of amorphisity and ultimately, degradation in the mechanical properties of the polymer. Intermolecular (inter-chain) interactions are responsible for some the most unusual mechanical properties exhibited by these materials as well as their propensity to transform into LC mesophase solutions during the polymerization process. These interaction fields actually hold the chains together in a 3-D network that leads to planes or sheets of associated polymer chains with exceptional anisotropic behavior. There are at least a couple of such interaction fields that are known to exist and others could be suggested. One involves electrostatic interactions between the carbonyl groups of adjacent chains . . .



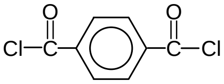
As with the polarization effect characteristic of the typical $^{\delta+}$C=O$^{\delta-}$ carbonyl group, these interactions are driven by the electronegativity difference between the oxygen and the associated carbon atom. More importantly however, mesogenic (LC) inter-chain interactions are most pronounced and quite predominant in these polymer systems. Because of the planar nature of the chains, π orbital overlaps or interactions are established in the z-direction between adjacent (stacked) benzene rings which have become essentially indexed on top of one another, facilitating stacking of the electron clouds. The greater the density of aromatic rings along the polymer chain, the more extensive the mesogenic effects . . .



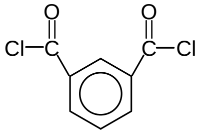
Obviously, these types of alignments and interactions will likely not traverse the entire length of the polymer chains, and not all the mesogenic segments of neighboring chains will necessarily be able to align effectively with one another. However, even a limited number of interacting segments will have profound effects on the behavior of the material. Along with hydrogen bonding (illustrated on page 10), collectively, these inter-chain interactions are the driving forces leading to the unique inter-molecular alignment, liquid crystalline behavior, mechanical and thermal properties exhibited by all three of the polymer groups under study in this project. Each family can be defined by the various types of interactions established throughout the respective polymer networks and without a doubt, the choice of monomers used fabricate a given polymer control the nature, range and intensity of these inter-molecular force fields.

Polyaramids

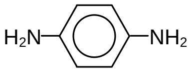
Aramids are a unique subclass of polyamides which also includes the extensive family of nylons. They are unique to nylons and other polyamides because their monomers are comprised exclusively of aromatic rings, whereas most polyamides contain an abundance of aliphatic units along the chain. As a matter of fact, the term ‘aramid’ is actually truncated from the words ‘aromatic’ and ‘polyamide’ (so the term ‘polyaramid’ may be redundant). Nevertheless, classical synthetic approaches to the formation of amides is accomplished by the condensation reaction between two aromatic monomers – a diamine and a diacid (or the corresponding diacid chloride). As with the polyimides, polyamides are formed by the step-wise addition of monomers along the growing polymer chain. These mechanisms also apply to the aramids. Monomer-wise, the only basic difference between the polyimides and the aramids is the use of diacid chlorides instead of dianhydrides. The most common aramids are formed from terephthaloyl chloride or isophthaloyl chloride, and p-phenylene diamine (recall the use of p-phenylene diamine in the previous section on polyimides) . . .



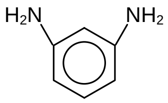
terephthaloyl chloride (TPC)



isophthaloyl chloride (IPC)

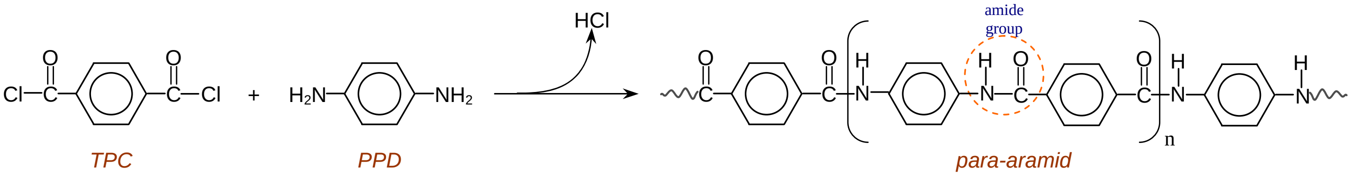


para-phenylene diamine (PPD)

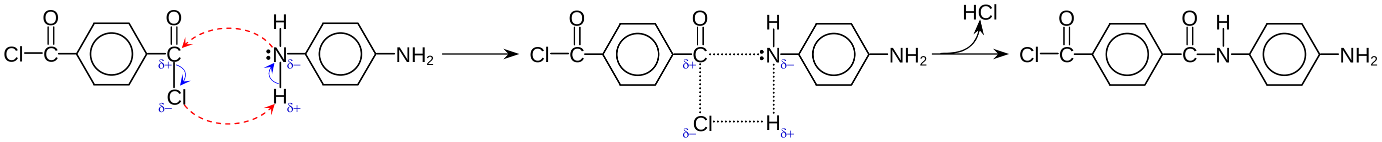


meta-phenylene diamine (MPD)

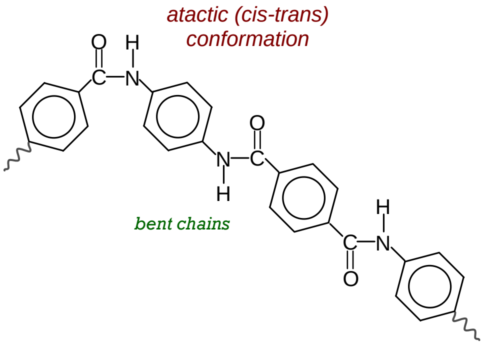
Note that in structures TPC and PPD, the functional groups are attached to the ring at the 1,4 (para) positions while in structures IPC and MPD, they are attached at the 1,3 (meta) positions. There are two basic subclasses of the aramids based on the predominance of the para-configuration or the meta-configuration along the polymer chains, the so-called para-aramids and meta-aramids respectively. Reactions exclusive between para-monomers such as TPC and PPD give para-aramid polymers analogous to Kevlar® . . .

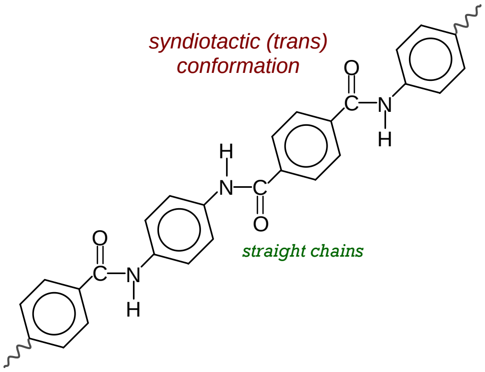


The mechanism of this single stage process is the same as that for all amides and involves nucleophillic attack by the nitrogen on the electrophillic carbonyl carbon atom in the acid chloride group which leads to the expulsion of HCl to form the aramid. . .

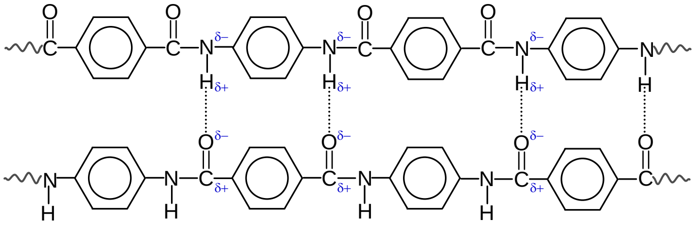


For the para-aramids, the structure indicated above is not exactly correct since it indicates that the link has formed in the *cis* configuration. One of the unique features associated with the reaction between para-monomers is the tendency for these links to form in the *trans* position leading to syndiotactic conformations. The predominance of *trans* over *cis* bonding in these polymers has enormous consequences on the ultimate physical properties attained. Consider a couple of possible arrangements for comparison, one with mixed *cis*-*trans* bonding (atactic) and another with only *trans* (syndiotactic) orientations . . .



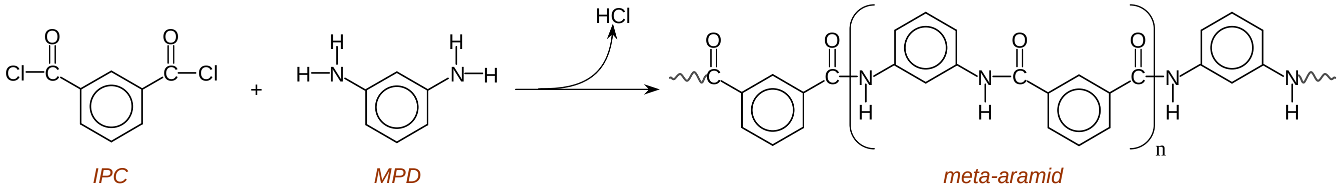


Since bond rotation is possible in these types of structures, a mixture of the two orientations is expected for most aliphatic nylons. However, in aramid structures, the *cis* conformation would lead to steric hindrance (over-crowding) between neighboring benzene rings and their hydrogens. This results almost exclusively in *trans*-oriented peptide links between monomer units and facilitates the formation of very long, straight polymer chains which makes the para-aramids exceptionally unique for the production of fibers. Additionally, the aramids are known to form strong liquid crystalline structures and will exhibit z-directional π orbital stacking between the rings as well as carbonyl-carbonyl interactions in the x-y plane as illustrated for the polyimides on page 8. However, due to the higher levels of benzene rings and amide links, these effects are expected to be even more pronounced in the para-aramids than in the polyimides. Yet another x-y interaction field established within aramid networks involves hydrogen bonding associations between the nitrogen atoms and carbonyl oxygens of adjacent chains . . .



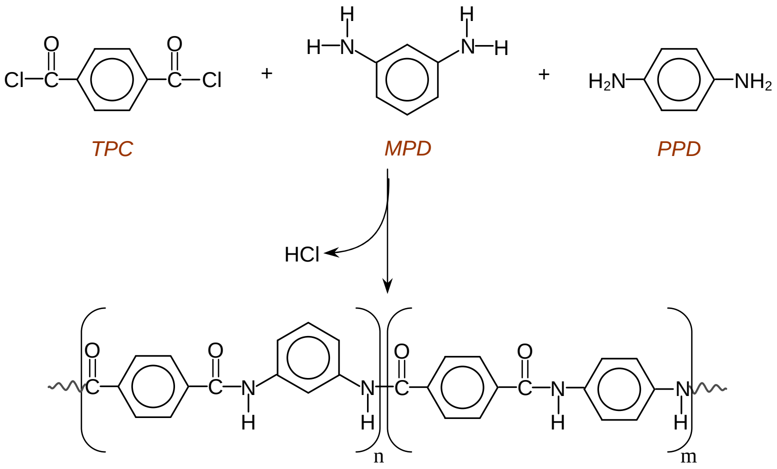
Hydrogen bonding is so pronounce in these systems that an ionic co-solvent (such as $CaCl_2$) must be used (within the NMP primary solvent) to tie up or occupy the H-bonds during processing. Thus, carbonyl-carbonyl interactions, π electron cloud stacking, *trans*-dominated bond configurations and extensive hydrogen bonding lead to a level of structural order in the para-aramids that is unlike other polymer types. The combination of all these interactions between the chains essentially forms a network and must lead to an incredible degree or structural orientation directly related to their LC behavior, exceptionally high mechanical and impact strengths, and their unusually high thermal properties. It would also explain their lack of solubility in solvents, their absence of melt-flow behavior and their extraordinary thermal stability at temperature levels well beyond those when most polymers begin to undergo degradative carbonization.

Now the meta-aramids, such as those analogous to Nomex®, are formed almost exclusively from meta-oriented monomers such as IPC and MPD (page 9). As with the para-amides, the same mechanism applies and progresses along the same pathway with the same side product (HCl) . . .



In contrast to the para-aramids, these configurations exhibit substantially reduced alignment tendencies and their LC behavior is greatly diminished along with their mechanical properties (para-aramids are generally 4 or 5 times stronger than meta-aramids). While carbonyl interactions, H-bonding and π cloud stacking are still at play, they are significantly lessened, and meta-aramid polymers generally do not achieve the same degree or orientation during fiber spinning. However, the meta-configuration has some desirable benefits that the para-aramids do not possess, namely, increased solubility, flexibility and processability. With reduced crystallinity and 3-D ordering, these polymers can be more easily processed in solution and woven into flexible textile fabrics. While these semi-elastomers still offer fairly high temperature resistance, lower mechanical and impact properties are the trade-offs for improved processability.

As an alternative to straight para and meta structures, some vendors have introduced composite polymers utilizing varying fractions of para and meta monomers in efforts to optimize the two extremes. Co-polymer formulations generated from proprietary levels of para and meta monomers are now readily available, such as the Technora® brand produced by Teijin. There are now a variety of monomers available for producing composite aramids – the number and complexity of linking groups and molecules between the reactive end-groups on the monomers are as vast as those available for the polyimides. These products can be tailored to exhibit a wide range of intermediate properties capturing the best of both worlds. A rudimentary example reaction might utilize a mixture of simple para and meta difunctional phenylenes and diamines . . .



para/meta-aramid composite co-polymer with n and m custom tailored to the application

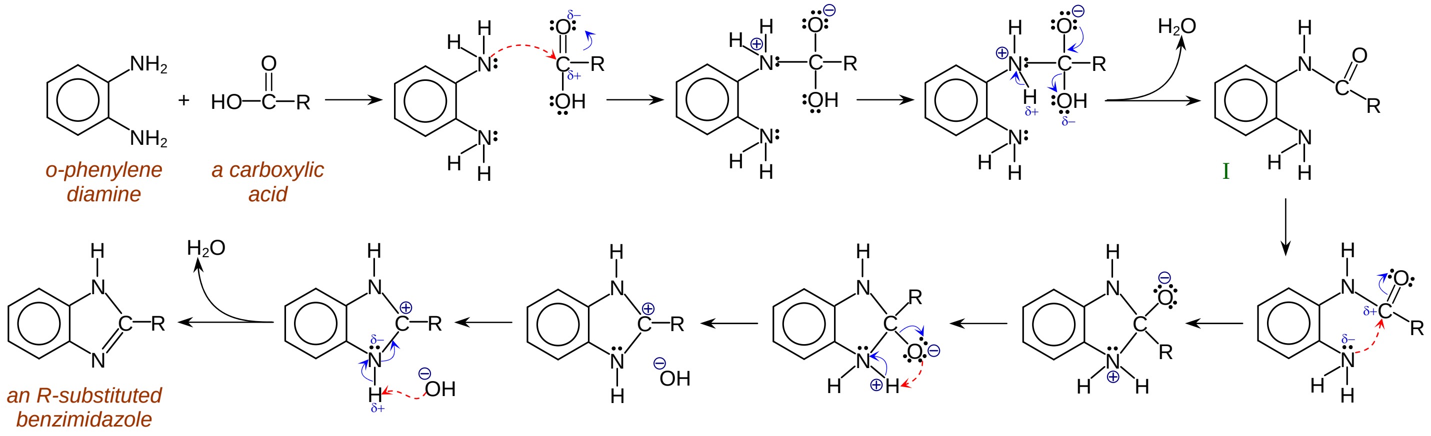
Solubility can also be greatly influenced by incorporating side group substituents at specific positions on the benzene rings, but these can also have negative effects on the LC properties, mechanical and thermal attributes. Aromatic side group substitution is generally not practiced in the industry for these polymer types.

Polybenzimidazoles

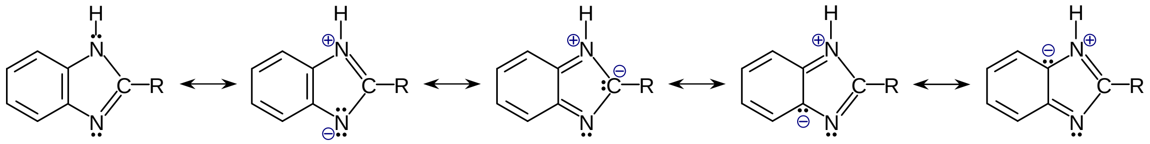
Structurally, polybenzimidazoles (PBI) bear some similarity to the polyimides. As with the imides and aramids, PBI-type polymers also exhibit similar difficulties in processing, leading to extremely low solubilities, low concentrations and the requirement for elevated processing temperatures. NMP and DMAc (as well as DMF, DMSO and concentrated H_2SO_4) are again some of the few solvent choices available. Linear, liquid crystalline, rod-like PBI structures comprise the strongest and most robust forms of this material, but these are also the least soluble – polymer concentrations of < 5% are typical (however, ranges up to ~20% are possible in hot 100% H_2SO_4 under pressure). To improve some of these shortcomings, the structural and handling properties of the polymer are controlled either by (a) the choice of monomers utilized (for example, the relative levels of para- and meta-oriented diacids can markedly influence the degree of chain linearity and hence liquid crystallinity), and/or by (b) introducing side chains or modifications to active sites along the chain *after* the polymer has been synthesized, especially the reactive imidazole nitrogens (these sites can provide substitution points to attach functional or plasticizing groups, or they can be used for crosslinking).

As with the polyimides and aramids, most of these kinds of alterations generally have negative effects on the strength of the polymer's liquid crystallinity, which directly controls the ultimate mechanical properties achieved. However, certain control measures are often deemed necessary for many applications, such as those requiring resinous-type solutions and (compression) moldable versions of PBI. For instance, by incorporating the slightly bent structure of meta-phthalate in place of the linear para-phthalate unit, material properties are moderately diminished – but this is accompanied by tremendous improvements in solubility and processability. That is, the occasional or regular occurrence of meta (or ortho) units along the main chain decreases the ability of the chains to stack and interact (see pages 8 and 10 for illustrations), thus lowering their ability to crystallize, but it also facilitates solvent infiltration into the polymer chains.

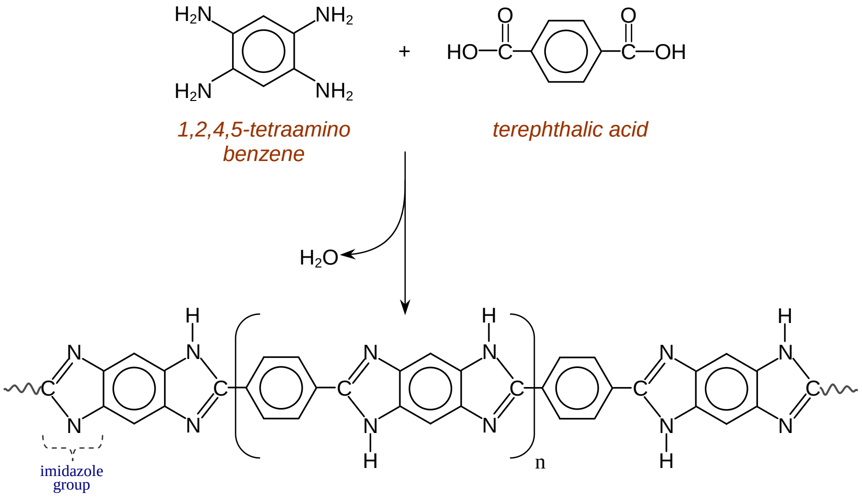
Simple heterocyclic benzimidazole compounds can be formed by the reaction of a carboxylic acid (or corresponding acid chloride) with an ortho-substituted diamine, such as o-phenylene diamine (recall the meta and para isomers of phenylene diamine considered earlier for the aramids and polyimides). With this reaction however, the close proximity of the two amine groups in the 1,2-ortho positions facilitates coupling with the carbonyl carbon of the acid group via ring closure when one of the nitrogens attacks the carbonyl. A hypothetical mechanism might have an amide formed in a condensation step producing water (I), and then ring closure ensues when the second nitrogen attacks the re-formed carbonyl group creating a zwitterion transition complex which produces the benzimidazole via condensation releasing a second water molecule . . .



The lone pair of electrons on the single bonded nitrogen atom actually become part of the π electron cloud as they participate in bonding resonance, strengthening the aromatic character of the benzimidazole ring system. However, the double bonded nitrogen (or imine) still has its electron pair available to instigate reactions and thus, this nitrogen is significantly more basic than the single bonded nitrogen whose lone electron pair is tied up in the π bond. The aromaticity of the imidazole ring can be understood by considering some of its possible resonance structures (note that the electron pair on one of the nitrogen atoms delocalizes around the ring and participates in the resonance while the electron pair on the other nitrogen remains fixed signifying the more basic nitrogen in the imidazole ring) . . .

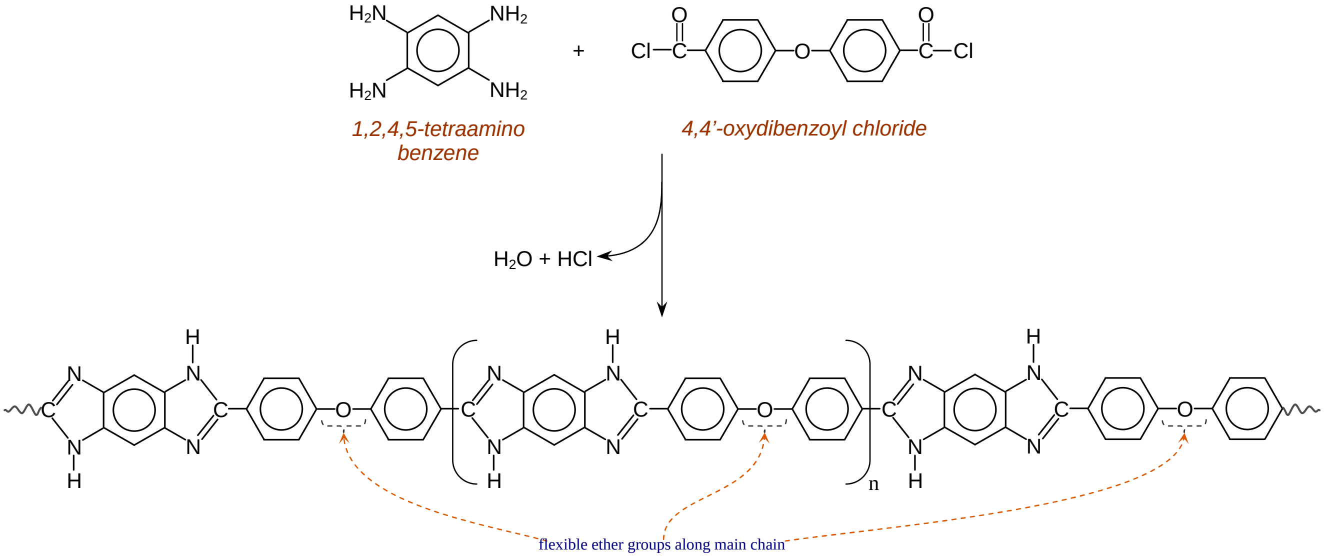


Additional resonance structures can be drawn. By itself however, benzimidazole is not a monomer for the production of any of the *poly*benzimidazoles. Recall that condensation polymers of the amides (nylons), polycarbonates and esters are generally formed by reactions between di-functional monomers, each containing two reactive sites per molecule, and where a single reactive site on one monomer couples with a single reactive site on the other monomer. However, for imidazole ring closure reactions, *two* amine groups situated at ortho (1,2) ring positions are required for each single reactive group on the other monomer in order to form the link. Thus, if the amine monomer contains two pairs of ortho-situated amine groups attached to a single ring system, then two sites become available for reaction with di-functional acids (diacids). Consider the condensation reaction between the symmetrical 1,2,4,5 tetraamino benzene and terephthalic acid to give a highly linear, but rudimentary PBI chain structure . . .



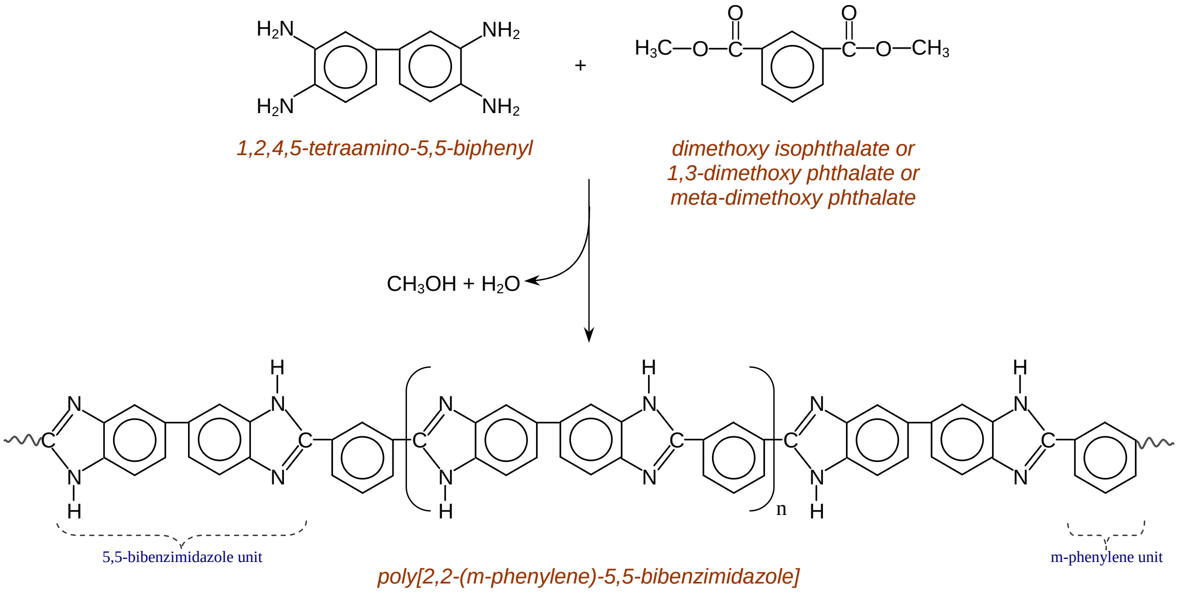
polybenzimidazole; poly(terephthalic acid)-benzene-1,2,4,5-tetraamine

Note that terephthalic acid is an analog to terephthaloyl chloride (TPC) introduced earlier for the aramids. Both structures are linear and contain a benzene ring with their two functional groups in the 1,4-(para) position. Again, linear monomers lead to strong liquid crystallinity along the main polymer chains accompanied by processability challenges directly associated with these strong mesogenic interactions that are extremely problematic. However, the solubility of a PBI structure can be moderately improved without substantially degrading its liquid crystalline properties by introducing a more flexible monomer into the chain in place of straight terephthalate. Consider a PBI chain formed from the same tetraamine as above but with something like 4,4'-oxydibenzoyl chloride (two benzoyl rings joined back-to-back by an ether group) . . .



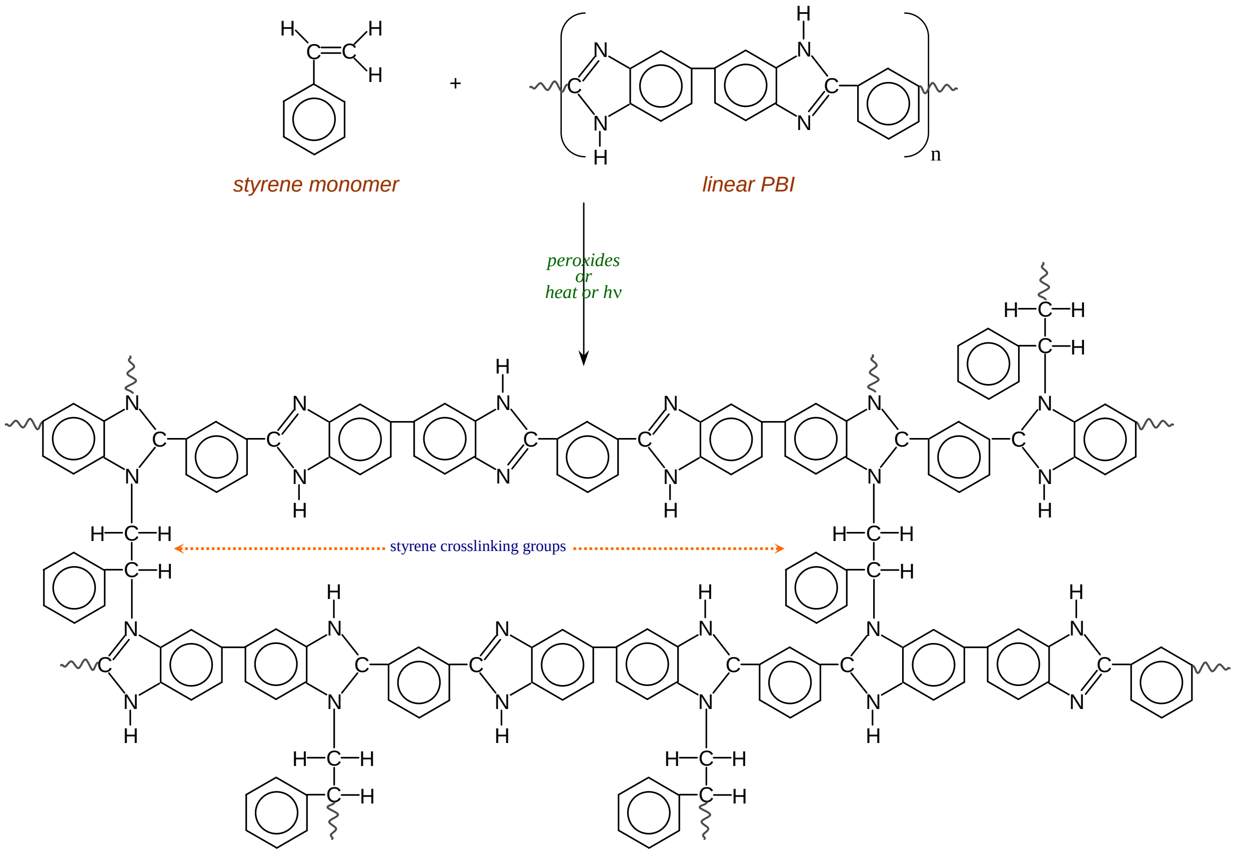
Thus, the 'softer' ether links add a certain degree of flexibility to the polymer back bone while maintaining high aromatic content *and* main chain linearity (retaining a substantial level of the LC behavior). Other ring-to-ring connecting groups can also be employed to achieve similar effects including methylene groups, carbonyls and ester linkages. Unfortunately however, in-line oxygen-containing groups also provide vulnerable sites for hydrolytic instability or solvent attack leading to premature cleavage of the polymer chains as well as polymer structures with poor resistance to chemicals. Additionally, for many applications, the degree of flexibility and/or processability imparted by this approach is still not quite adequate – the stout main chain liquid crystallinity must be disrupted or diminished somewhat in order to provide the necessary properties that can lead to higher solution concentrations, potential moldability and enhanced weaveability.

Undoubtedly, the highest performance PBI products are formed from the most linear aromatic monomers. However, the greater the (mechanical) performance properties desired, the more difficult it is to process/produce the material. Incorporation of specialized side groups into these types of molecules can have profound effects on solubility, processability and crystallinity, but in industry, comprises between the two extremes have often been implemented by introducing a controlled level of isophthalate co-monomers into the main chain (that is, 1,3-substituted monomers in which the functional groups are oriented at the meta position). Main chain flexibility can also be incorporated by varying the structure of the tetraamino monomer. As an example, consider the Celazole® brand of PBI polymers which appears to be synthesized exclusively from isophthalatic acid (or its chloride or suitable ester derivative) and tetraamino biphenyl (which contains a softer sigma bond symmetrically joining the two *o*-diamino phenyl rings together back-to-back) . . .



Again, such monomer configurations are implemented in industrial scale reaction schemes to improve polymer processability and product versatility by allowing higher solution concentrations and molding processability. These modifications open the door to an array of solid and liquid PBI-based powders, pellets, resinous solutions and potential injection molding precursors which have now become commercially available. The Celazole® PBI product brochure advertises a very high T_g that is very close to its heat deflection temperature (425°-435°C) and a CTE of 23 ppm (most hardened polymers exhibit CTE ranges much higher than this, approaching the 60-80 region and higher). Under high enough pressures, PBI structures fabricated into these types of configurations provide candidates with the potential to be compression molded into objects and articles containing complex shapes (analogous to injection molded plastics). Neat resin solutions and PBI-based adhesives may also be on the horizon.

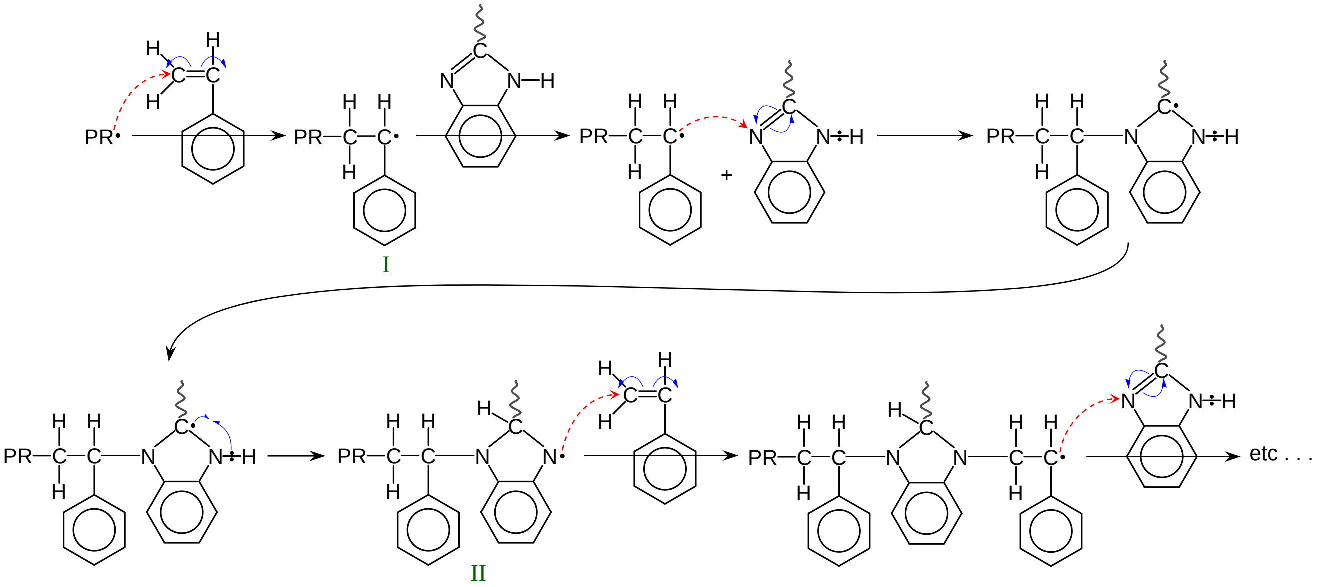
Another unique feature of PBI molecules is the presence of the unsaturated imidazole group which sets these polymers apart from the polyimides and aramids. The embedded N═C ring group expands the capabilities of these polymers by allowing reactions involving ionic mechanisms and free radical addition which can facilitate customized post-processing approaches such as the incorporation of tailored side groups and the formation of 3-D polymer thermoset networks via crosslinking. Free radical monomers initiated by peroxides or UV light may be feasible by employing simple and readily available monomers such as styrene and/or methyl methacrylate. While no specific references or published documentation were available for this study detailing the crosslinking of PBI molecules, a possible hypothetical scenario can be proposed in which an unsaturated monomer such as styrene is utilized as a crosslinker for PBI. Under conditions favorable to free radical generation, such a reaction might lead to styrene-crosslinked PBI networks of the form . . .



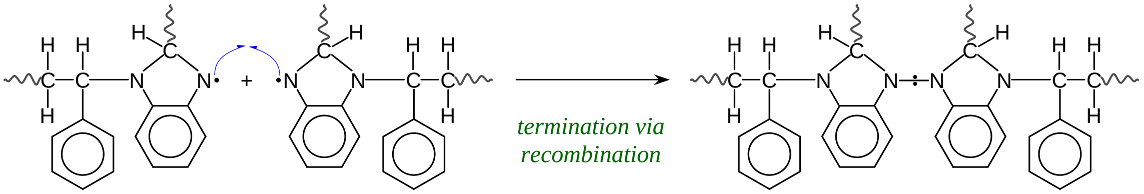
idealized crosslinked PBI network

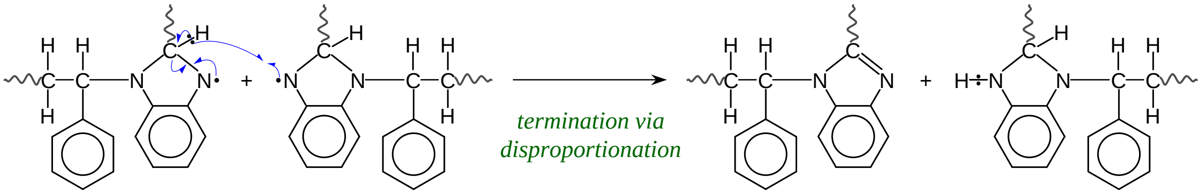
Obviously, this is an oversimplified representation of what the structure might look like. Some styrene molecules will dimerize or trimerize before reacting with main chain nitrogens (and the product mixture will undoubtedly contain fractions or regions of polymerized styrene as well). The nature of the chain links are governed by localized inter-chain distances which can vary from segment to segment and molecule to molecule (the representative structure given above shows only single styrene units connecting the chains). Also, it is almost certain that not all the imidazole groups will react (as illustrated). Reactivity of these groups will be influenced heavily by (a) the extent of mesogenic (LC) alignment between adjacent polymer main chains which tends to rigidize the chains, restricting segmental mobility and reducing the capability of local reaction sites to interact, and by (b) the bulky planar structure of these molecules, evitably leading to a certain degree of obstruction or steric hindrance which can block bulky monomers, such as styrene, from reaching the imidazole nitrogens. Both effects are expected to play big roles in the frequency, location and nature of the crosslinks established. Also, the radical electron may occasionally localize on the imidazole carbon during the transition state causing a few crosslinks to form at that point instead of the adjacent nitrogen (obviously, steric hindrance effects will diminish the likelihood of this reaction).

A possible (hypothetical) mechanism for this scheme might involve attack on styrene by a peroxide radical PR•, to generate a peroxide-styrene initiating radical (I) which then couples with an imidazole nitrogen and rearranges to form a propagating radical (II) that can react with more styrene monomer, and so on . . .



Termination can occur via recombination (coupling between two propagating radicals) and/or by disproportionation (involving hydrogen abstraction from one radical with the formation of two separate polymers). Either of these paths can involve styrene-propagating (front) groups, nitrogen front groups or a combination of both. The following reactions show how these two termination schemes might proceed using styrene-nitrogen radical front groups to illustrate the processes . . .





Recombination enhances the formation of high molecular weight products and is favored at lower reaction temperatures, while disproportionation increases the polydispersity index (molecular weight distribution) and becomes predominant at higher temperatures (it takes more energy to break bonds during the disproportionation process than during recombination). Since reactions of this type are generally accompanied by the production of heat at the onset of gelation, it is often difficult to maintain low reaction temperatures throughout the process (most free radical crosslinking processes generate quite substantial exotherms). In most cases, a mixture of the two termination processes is inevitable.

Using the appropriate synthetic methods, unsaturated side groups can also be introduced onto the chains (or the rings) of the polyimides and aramids, transforming these polymer systems into thermosetting networks in which the chains are interconnected with crosslinks. In another area, mesogenic (LC) side groups could be incorporated along the chains of certain elastomers, such as the silicones, ethylene-propylene (EPDM) or nitrile-butadiene-type rubbers (NBR), forming a specialized class of synergistic 'liquid crystal elastomers'. With flexible main chains and LC side groups, these materials would be expected to exhibit some very unique properties. The specifics of all these processes and concepts will not be dealt with here.

In polymeric carbonaceous pitch mesophase resins (graphite precursors), liquid crystal alignment is very pronounced and is controlled by the temperature as the LC macromolecules grow. This alignment is due to localized mesogenic interactions between the benzene rings on polymer chains while the pre-graphitic macrostructure condenses into LC 'particles' which eventually assume platelet or disc-like shapes. So the net LC alignment ultimately becomes 'discotic'. Thus, carbonaceous mesophases are dispersions of LC platelets in solution with smaller aromatic and aliphatic hydrocarbons. When heated, thermoplastic polymer movement is limited by mesogenic interactions which facilitate an almost seamless conversion into high temperature hexagonal graphite (the rings are essentially indexed on top of one another throughout the heating process).

All amorphous carbon-based materials which are graphitizable must pass through a liquid crystal mesophase state before they can convert into true 3-D graphite. Most sp^2-bonded organic (aromatic) carbon precursors form LC mesophase mixtures around 400°- 500°C and then carbonize (or char) into a green coke. These types of carbons are classified as 'soft' carbons (because they graphitize so easily). On the other hand, when chemical crosslinks are incorporated into the organic (pre-carbonized) structure, as with highly crosslinked thermoset polymers such as the phenolics, polyesters and epoxies, the amorphous (glassy) structure of the polymer network is stoutly reinforced by the crosslinks. When these materials are heated to graphitization temperatures (2300°- 3000°C), the crosslinks prevent molecular movements and rearrangements, eliminating their ability to align into liquid crystals or pass into any type of mesophase state.

The strength of these crosslinks is so pronounced that neighboring benzene rings are rigidly fixed in space and cannot index properly, so the structures remain in the glassy state across the entire temperature spectrum. These glassy materials are classified as 'hard' carbons because they will not undergo graphitization at any practical temperature. (Note: When speaking of the various carbon forms, the term 'amorphous' is not entirely accurate. It is used here with the understanding that most of these allotropes actually consist of hexagonally-bonded 2-D graphene layers, sheets or ribbons which exhibit no z indexing or '*d-spacing*' characteristic to true graphitic structures. So they are highly ordered in a 2-D sense but exhibit minimal, if any, 3-D organization. However, while soft carbons are pseudo-amorphous, hard glassy carbon structures derived from thermoset polymers approach a much greater degree of amorphicity.).

When thermoplastic PBI is subjected to increasing temperatures, mesogenic alignment between the polymer chains (along with the other interaction fields at play) imparts very high thermal resistance to the polymer system up to around 400°- 425°C when the T_g and heat deflection temperatures coincide. As the temperature continues to rise, nematic alignment of the rod-like LC particles strengthens and the particles begin to coalesce, forming larger LC agglomerates. When the material just begins to char, say around 500°-550°, the polymer chains begin to convert into a soft green coke as oxygen and hydrogen are debonded from the structure, followed by nitrogen, and expelled from the system throughout the pyrolysis process.

When thermosetting crosslinks are established in the PBI polymer network, movement of the mesogenic segments during the carbonization process is restricted by the crosslinks. As the material converts into the green coke state, the structure contains glassy (non-graphitizable) regions *and* crystalline regions. Since neighboring benzene ring layers are already stacked (essentially indexed) along the main chain, little movement is necessary within the non-crosslinked regions to form graphite-like structures at the very high temperatures. While standard PBI materials will undoubtedly undergo graphitization, as all non-crosslinked thermoplastics would, including the polyimides and aramids, it is not known with certainty whether these types of (partially) crosslinked networks will actually form true 3-D hexagonal microstructures. However, it might be surmised that charred crosslinked PBI would likely exhibit the characteristics of both glassy (hard) and green (soft) carbons, perhaps in a synergistic way.

References

No specific citations are noted within the discussion except where inferred. However, the following references have been used as educational resources, for correct terminology, nomenclature and for verification purposes. Many of the reactions and structures presented in this paper are the author's perception of principles which are already established and documented within the literature and vendor brochures, and some are proposed as conceptual artifacts to supplement the discussion. All reaction mechanisms are provided solely from the author's perspective and no guarantee is given as to their correctness. All illustrations and figures are strictly the author's perception and handiwork.

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