

Advances in synthetic optically active condensation polymers – A review

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Abstract. The study of optically active polymers is a very active research field, and these materials have exhibited a number of interesting properties. Much of the attention in chiral polymers results from the potential of these materials for several specialized utilizations that are chiral matrices for asymmetric synthesis, chiral stationary phases for the separation of racemic mixtures, synthetic molecular receptors and chiral liquid crystals for ferroelectric and nonlinear optical applications. Recently, highly efficient methodologies and catalysts have been developed to synthesize various kinds of optically active compounds. Some of them can be applied to chiral polymer synthesis. In a few synthetic approaches for optically active polymers, chiral monomer polymerization has essential advantages in applicability of monomer, apart from both asymmetric polymerization of achiral or prochiral monomers and enantioselective polymerization of a racemic monomer mixture. The following are the up to date successful approaches to the chiral synthetic polymers by condensation polymerization reaction of chiral monomers.

Keywords: biodegradable polymers, optically active polymers, polycondensation reaction, amino acids, chiral monomer

1. Introduction

Chiral phenomena play significant roles in nature. The synthesis and application of optically active polymers are topics currently attracting much consideration in recent times, due to the wealthy and multifaceted architecture of macromolecular chirality as compared to that of small molecules. Because of unique chiral arrays, nature produces numerous smaller chiral, optically active compounds. Most of the naturally occurring molecules/macromolecules, such as nucleic acids, proteins, and polysaccharides are chiral and optically active. Chirality is essential for life. This situation can be very obviously seen if we look at the chirality of nearly 800 drugs (about 97%) derived from natural sources. Only 2% are racemates and only 1% is achiral. In the past

30 years, the development of chiral drugs with a single enantiomer (optical isomer) has attracted great attention in drug industries, and the market for chiral drugs has tremendously grown. We are undoubtedly living in a chiral world, because of this fact that our life results from homochiral biosubstances [1–3]. Deoxyribonucleic acid (DNA) is a typical example of a homochiral biopolymer whose chirality derives from two features: (i) the incorporation of enantiopure chiral sugars connecting the achiral chromophoric bases such as adenine, guanine, cytosine and thymine and (ii) the double-stranded, stiff helical conformation arising from complementary base pairing and base stacking in water [4]. Optically active polymers often play important functions as key basic materials for well-

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defined high-performance polymers [5]. Recent advances in asymmetric reactions and catalysis as well as in chiral separations have afforded a rapid increase in the number of commercially available optically active compounds and reagents. Both naturally occurring and synthetic chiral polymers and supramolecules have found prosperous applications in chiral chromatographic separations and shown potential uses in chiral catalytic systems, liquid crystals in ferroelectric and nonlinear optical (NLO) devices, electrodes for enantioselective recognition for performing bioelectro synthesis, microwave absorbents, membrane separation technology, optical switches, biomedical equipments and optoelectronics application. A direct and efficient approach for synthesizing chiral polymers is to introduce chiral elements into the macromolecule backbone or the side chains [6–14].

In the history of synthetic polymer chemistry, it seems that one of the most challenging tasks is to construct functional polymeric systems and optically active synthetic polymers that will be as effective as those in living systems [15–18]. Specially, the synthesis of chiral polymers containing amino acids is a subject of much interest, since a high degree of amino acid functionality can lead to polymers with increased solubility and the ability to form secondary structures. The synthetic chiral polymers that have been reported may be categorized into two parts: the first category represents polymers that adopt helical conformations. Such polymers do not contain any chiral center in the main chain or side chain. If a right-handed or left-handed helical conformation is generated in excess, the polymer can show chiroptical properties. However, the helical conformation is responsible for their optical activity. Helical polymers existing in genes, proteins (α -helix), DNA (double helices), collagen (triple helices), enzymes, and polypeptides are frequently found in nature. They are easily denaturalized by certain physical factors such as heat, ultraviolet irradiation, and high pressure and by other chemical factors such as organic solvents. In contrast, synthetic polymers represent much better stability. Various helical polymers have been synthesized, which include polyisocyanates, polyisocyanides, polychloral, polymethacrylates, polysilanes, polythiophenes, poly(p-phenylene)s, poly(1-methylpropargyl-ester)s, poly(phenylacetylene)s

and poly(α,β -unsaturated ketone) [19–30]. The second one is polymers whose optical activity is derived from main chain or side chain chirality such as: amino-acid-based polymers. Because the amino acids are naturally occurring compounds, synthetic polymers based on amino acids are anticipated to be nontoxic, biocompatible, and biodegradable. On the other hand, synthetic polymers containing amino acid residues in the main chain or in the side chain can be employed for biomedical applications. Possible applications include dentistry, temporary artificial skin substrates, polymer carriers for protein conjugates, drug delivery, gene therapy, tissue engineering, chiral recognition stationary phases, asymmetric catalysts, metal ion absorbents, and biomaterials [31–33]. Chiral recognition of optically active polymers has been utilized in various forms of catalytic and separation chemistry. For example, one of the generally function of chiral polymers is the use as chiral stationary phase in high-performance liquid chromatography (HPLC) for the separation of racemic mixtures [2, 34–38].

Optically active polymers were divided to three types: biopolymers, polymers prepared by almost completely isotactic polymerization by modification of naturally occurring polymer backbones such as polysaccharides and synthetic polymers [2]. Chiral synthetic polymers can be classified as: addition polymers, condensation polymers and cross-linked gels. Addition polymers are including vinyl, aldehyde, isocyanide and acetylene polymers that were prepared via addition polymerization reaction such as poly(acryl amide)s, polyolephynes, polystyrene derivatives, polyazulenes, poly(vinyl ether)s, polymethacrylate, polymethacryloylamine, polychloral, polyisocyanides, polyisocyanates, polyacetylene and polyethers [39–45]. Condensation polymerization continues to receive intense academic and industrial attention for the preparation of polymeric materials used in a vast array of applications [46]. One of application is synthesis of chiral polymers. For this purpose, monomer must be optically active. Cross-linked gels possessing chiral cavities have been prepared and their chiral recognition ability has been studied. The synthesis of gels is based on molecular imprinting technique. Two distinctive methods have been independently developed, that is, (i) polymerizing a monomer having a removable chiral template moiety with a cross-linking agent

and removing the template groups from the products or (ii) polymerizing a monomer with a cross-linking agent in the presence of a non-polymerizable template molecule and removing the template [2]. This article reviews the synthesis of optically active polymers via polycondensation reaction of chiral monomers.

2. Synthetic optically active condensation polymers

2.1. Polyamides

Historically, the first study of optically active polymers has been of those available i.e. natural polymers such as proteins, polypeptides, polynucleotides and so on. These polymers are remarkable for their high structural regularity, their ability to take on secondary ordered structures, even in solution, and to undergo order disorder conformational transitions by changes in external conditions (solvent, temperature, pH, etc.). Progress in polymer chemistry has allowed the synthesis of entirely different condensation polymers which one of them is optically active polyamides (PA)s [47].

Many studies concerned with the synthesis and characterization of optically active PAs have been undertaken [48–55], mainly polypeptides and proteins which have been extensively investigated. Synthesis and optical properties of asymmetric PAs derived from composed of optically active cyclic dicarboxylic acids, (+)-(S)- and (-)-(R)-trans-1,2-cyclopropanedicarboxylic acids, (-)-(R)-trans-1,2-cyclobutanedicarboxylic acids, (+)-and (-)-trans-1,3-cyclopentanedicarboxylic acids and secondary diamines such as trans-2,5-piperazine, piperazine or N,N'-dimethylethylenediamine was reported by Overberger and Shimokawa [56]. Overberger *et al.* [57] also prepared optically active PAs by interfacial polycondensation reactions of (+)-(S)-trans-2-

methylcyclopropanedicarboxylic acid or (+)-and (-)-trans-1,2-cyclohexanedicarboxylic acids with rigid spirodiamine, 2,6-diazaspiro[3,3]heptane. They prepared several model compounds, too. These model compounds were (\pm)-trans-1,2-cyclopropanedicarboxylic acid azetidide, (+)-trans-2-methylcyclopropanedicarboxylic acid diazetidide, 2,6-di[(\pm)-trans-2-methylcyclopropanecarboxyl]-2,6-diazaspiro[3,3] heptane and (+)-trans-1,2-cyclohexanedicarboxylic acid dipiperidide for studying the conformation of the polymers. The conformations of the polymers and the model compounds were investigated by means of optical rotatory dispersion, circular dichroism (CD) and by hydrodynamic methods.

A series of chiral PAs containing optically active thymine groups as pendants were synthesized from N-acylation of an active diester of N-hydroxy-5-norborene-2,3-dicarboxamide, N,N'-(isophthaloyldioxy)-bis(5-norbornene-2,3-dicarboximide), with 1,3-diamino-2-hydroxypropane by Overberger's group [58]. Overberger *et al.* [59] prepared optically active PAs based on the polycondensation of two new active diesters: the active diesters of 4-chloro-1 hydroxybenzotriazole, such as 1,1'-(terephthaloyldioxy)bis(4-chloro-benzotriazole), and 1,1'-(isophthaloyldioxy)bis(4-chlorobenzotriazole), with optically active isomers of 2,4-diaminopentane. Dipolar aprotic solvents such as N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were used as reaction solvents. The solution polycondensation carried out in solution at room temperature afforded optically active PAs. The aminolysis of the two active diesters was carried out as a model reaction study.

Synthesis of optically active PAs derived from L or D-tartaric acid have been also reported in some cases [60–65] (Figure 1).

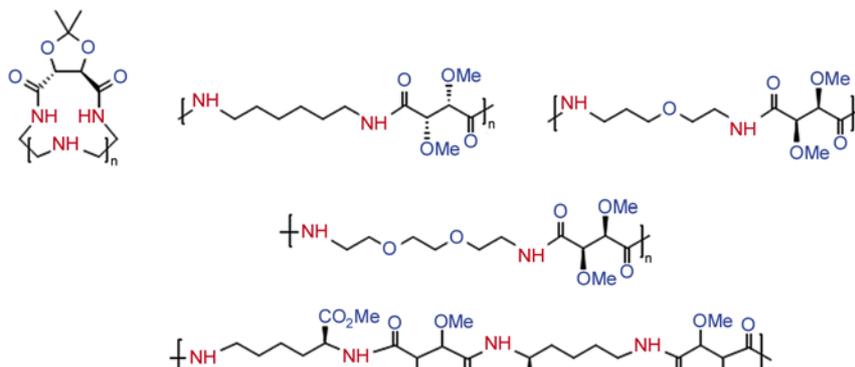


Figure 1. Chemical structures of PAs derived from tartaric acid [60–65]

A number of optically active PAs containing α -amino acids have been prepared. In the case of the synthetic PAs, only those containing the naturally occurring (L)- α -amino acids, being structurally close to the natural polypeptides, possess potentially degradable linkages that make them suitable as biomaterials [66–70].

A new polyamidation reaction between N,N'-bis(trimethylsilylated) diamines and 2,2'-p-phenylenebisazalactones in N,N-dimethylacetamide (DMAc) was investigated by Katsarava *et al.* [71]. By the interaction of bisazalactones with N^α,N^ε-bis(trimethylsilylated) L-lysyl alkyl ester, PAs were obtained containing dipeptide links in the main chain. It was shown that these can be transformed into water-soluble polyacids upon saponification of ester side groups.

PAs derived from carbohydrates are the object of current attention, because they are not only optically active, but also for its potential as biodegradable and biocompatible materials [72–77].

Mallakpour and coworkers [78–80] have investigated the synthesis of PAs from the polycondensation reaction of chiral 5-(4-methyl-2-phthalimidylpentanoylamino)isophthalic acid, (2S)-5-(3-phenyl-2-phthalimidylpropanoylamino)iso-phthalic acid and 5-(3-methyl-2-phthalimidylpentanoylamino)isophthalic acid with several aromatic and aliphatic diisocyanates such as 4,4'-diphenylmethane diisocyanate (MDI), toluylene-2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI) under microwave irradiation as well as conventional technique (Figure 2). The resulting aromatic PAs were optically active and soluble in various organic solvents and have good

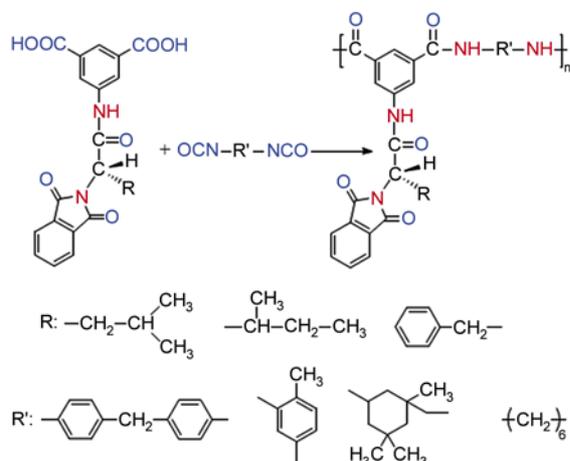


Figure 2. Synthesis of optically active and thermally stable PAs [78–80]

thermal stability. Microwave-assisted step-growth polymerization reactions proceeded rapidly compared to conventional solution polycondensation and it was almost complete within a short period of time. The reactions were carried out in the presence of a small amount of dibutyltin dilaurate (DBTDL), pyridine (Py) or triethylamine (TEA) as catalysts and/or under no catalyst conditions. The use of such an organic medium was necessary to induce effective homogeneous heating of the monomers. They obtained comparable results from the viewpoint of yield and inherent viscosity of the polymers with lower reaction time by several orders of magnitude under microwave conditions and straightforward procedure. The polymerization reactions were also carried out in the presence of tetrabutylammonium bromide (TBAB) as a molten ionic liquid (IL) or traditional solvent like 1-methyl-2-pyrrolidone (NMP) under microwave irradiation as well as conventional heating conditions by Mallakpour and coworkers [81–83]. In recent years, Mallakpour and coworkers reported on the synthesis and characterization of a new class of wholly aromatic and optically active PAs containing phthalimide and L-leucine pendant groups by condensation polymerization of a bulky diacid, (2S)-5-[4-(4-methyl-2-phthalimidylpentanoyl-amino)benzoylamino]isophthalic acid, and several diisocyanates (Figure 3) [84]. Polymerization reactions were performed in the presence of DBTDL as a catalyst and without catalyst in molten TBAB as a green solvent and were compared with polymerization in NMP as a conventional solvent. The resulting polymers were obtained in good yields and inherent viscosities ranging between 0.26 and 0.96 dL·g⁻¹. Amalgamation of the bulky side chain in the PAs, cause an

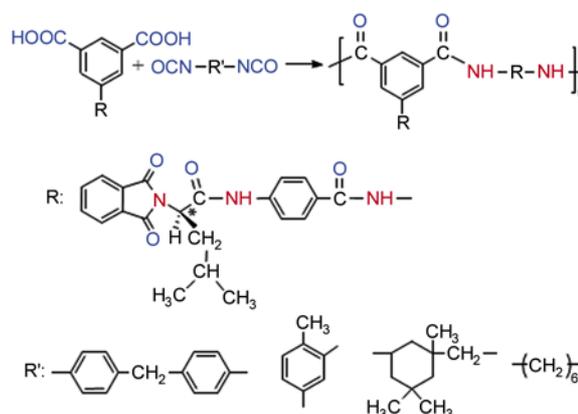


Figure 3. Synthesis of optically active PAs containing phthalimide and L-leucine pendant groups [84]

increase in the solubility, while maintaining good thermal stability.

The same researchers also synthesized novel thermally stable and optically active PAs with flame retardant properties which were prepared via an oil bath heating method using a mixture of 1,3-dipropylimidazolium bromide (as IL) and triphenyl phosphite (TPP) both as reaction media and activator [85]. The main advantage of this polycondensation reaction is that this procedure is a one-pot reaction and use of diacid chloride is not needed. These polymers presented high thermal stability, with the decomposition temperature being above 400°C, although slightly diminished compared with those of related aromatic PAs which do not contain any pendant groups (Figure 4). The reaction proceeded efficiently with IL/TPP as condensing agent without the need of any additional promoters, which are necessary upon utilizing of traditional organic solvents like NMP. The incorporation of tetrabromophthalimide, and L-phenylalanine groups into PAs backbone gave polymers with good solubility in common organic solvents.

In another study, Mallakpour and Rafiee [86] synthesized novel optically active aromatic PAs from the reaction of new diacid monomer, 5-[3-phenyl-2-(9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboximido) propanoylamino]isophthalic acid that was successfully synthesized starting from *cis*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid anhydride and L-phenylalanine and different aromatic diamines by two diverse methods such as: microwave-assisted and conventional heating polyamidation (Figure 5). A highly effective, very fast microwave method was described to syn-

thesize optically active aromatic PAs under microwave heating for only 3 min. Generally, better yields are obtained under faster and cleaner reactions when compared to those from conventional heating. All of these polymers having bulky anthracenic and amino acid functionality in the side chain showed excellent solubility and readily dissolved in various organic solvents. PAs were thermally stable, with 10% weight loss recorded at 385°C in the nitrogen atmosphere, and char yields at 800°C higher than 50% and glass transition temperature (T_g) above 180°C.

Because of importance of optically active materials and polymers with amino acid, Mallakpour and Taghavi [87] prepared a series of novel optically active PAs by direct polycondensation of novel chiral dicarboxylic acid, containing a rigid naphthalimide and flexible S-valine pendant group, 5-[3-methyl-2-(1,8-naphthalimidyl)-butanoylamino]isophthalic acid with different diisocyanates in the

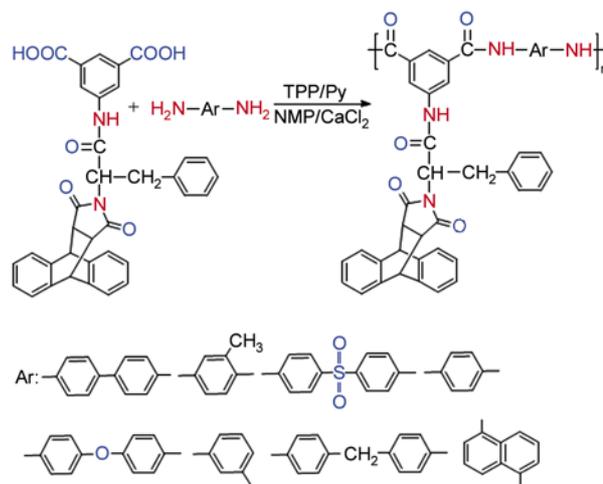


Figure 5. Polycondensation reactions of chiral monomer with aromatic diamines [86]

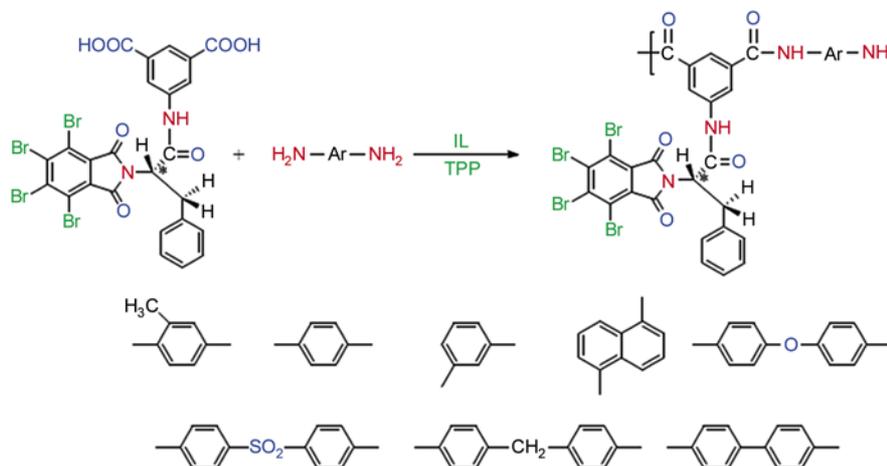


Figure 4. Synthesis of optically active flame retardant PAs [85]

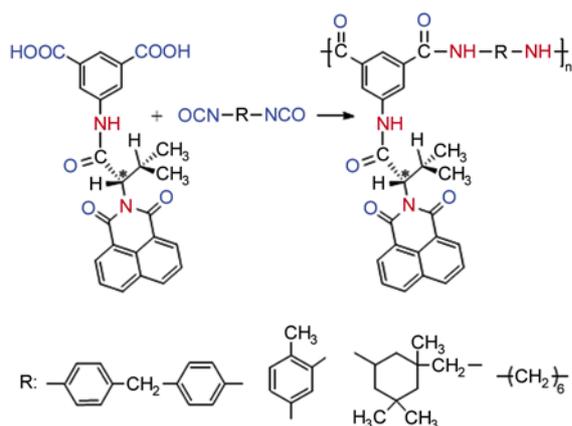


Figure 6. Synthesis of optically active flame retardant PAs [87]

presence of a small amount of ILs that act as a primary microwave absorber as well as conventional heating was carried out (Figure 6). Incorporation of the naphthalimide group into the polymer side chain as well as combination of the aromatic backbone and aliphatic pendant group in the presence of several functional groups remarkably enhanced the solubility while maintaining good thermal stability of the new polymers. The choice of 1,8-naphthalenedicarboxylic anhydride was due to the many derivatives of 1,8-naphthalic anhydride exhibit strong fluorescence emission and serve for this reason as fluorescent dyes and fluorescent whitening agents. They reported for the first time an electrochemical oxidation method based on the adsorptive stripping cyclic voltammetry technique on the multi-walled carbon nanotube-modified glassy carbon electrode for the investigation of electrochemical stability of the resulting polymers in aqueous solution at various pH values. The resulting polymers have many applications as photoactive materials which can be used in solar energy collectors as electro-optically sensitive materials and for laser activity.

Optically active PAs with asymmetric structure and dipole groups can easily form strong hydrogen bonds between amide groups along the molecular chain and hence can yield crystalline structures with asymmetric modality; as such, they should possess considerable ferroelectric properties. Liu *et al.* [88] synthesized a series of optically active PAs by polycondensation of various diamines and diacetyl chlorides and studied the dielectric properties of the resulting polymers. They found that these polymers formed a chiral tilted smectic phase and

therefore should have ferroelectric properties. This implies that the polymers have asymmetric liquid crystalline structures. Chen *et al.* [89] reported on the synthesis of a variety of optically active PAs and *o*-methylated PAs, derived from (–)-anti head-to-head coumarin dimer component. Polymers were absorbed on macroporous silica gel particles and used as chiral stationary phases for direct resolution of racemates having aromatic moiety by HPLC. Preparation and properties of aromatic PAs from 2,2'-bis(*p*-carboxyphenoxy) biphenyl or 2,2'-bis(*p*-carboxyphenoxy)-1,1'-binaphthyl and aromatic diamines was investigated by Liou *et al.* [90]. 2,2'-bis(*p*-aminophenoxy)biphenyl and 2,2'-bis(*p*-aminophenoxy)-1,1'-binaphthyl, were synthesized by the reaction of *p*-fluoronitrobenzene with biphenyl-2,2'-diol and 2,2'-dihydroxy-1,1'-binaphthyl, respectively, followed by catalytic reduction. Biphenyl-2,2'-diyl- and 1,1'-binaphthyl-2,2'-diyl-containing aromatic PAs having inherent viscosities of 0.44–1.18 and 0.26–0.88 dl/g, respectively, were obtained either by the direct polycondensation or low-temperature solution polycondensation of the diamines with aromatic dicarboxylic acids (or diacid chlorides). These aromatic PAs containing biphenyl and binaphthyl units had T_g s in the range of 215–255 and 266–303°C, respectively. This group also prepared [91] new aromatic dicarboxylic acids having 2,2'-bis(*p*-carboxyphenoxy) biphenyl and 2,2'-bis(*p*-carboxyphenoxy)-1,1'-binaphthyl by the reaction of *p*-fluorobenzonitrile with biphenyl-2,2'-diol and 2,2'-dihydroxy-1,1'-binaphthyl, respectively, followed by hydrolysis. Biphenyl-2,2'-diyl- and 1,1'-binaphthyl-2,2'-diyl containing aromatic PAs were obtained with inherent viscosities in the range of 0.58–1.46 and 0.63–1.30 dl/g, respectively via solution polycondensation of the corresponding diacid chlorides with aromatic diamines. Nozaki *et al.* [92] prepared two cyclic PAs from glycine and 1,1'-binaphthyls, and their structures were determined by single-crystal X-ray analysis. Conformations of these two cyclic PAs in organic solvents and their interaction with other organic molecules were also studied. Hsiao *et al.* [93] synthesized two series of novel fluorinated aromatic PAs from 2,2'-bis(4-amino-2-trifluoromethylphenoxy) biphenyl and 2,2'-bis(4-amino-2-trifluoromethylphenoxy)-1,1'-binaphthyl with various aromatic dicarboxylic acids via phosphorylation polycondensation tech-

nique and using TPP and Py as condensing agents in the NMP solution containing dissolved calcium chloride (CaCl_2). All polymerization reactions proceeded homogeneously throughout the reaction and gave clear and viscous polymer solutions. All of the resulting PAs could be cast to transparent, light-colored, and flexible films with moderately high T_g s and thermal stability. A series of optically active helical PAs were synthesized by Agata *et al.* [94] via polycondensation of (R)- or (S)-6,6'-diamino-2,2'-dimethylbiphenyl with various aromatic dicarbonyl chlorides with an optically active axially dissymmetric diaminobiphenyl compound. The molecular weights of the PAs obtained with the same type of (R)- or (S)-linkages were similar to each other, and also had very similar specific rotation values, with opposite signs. The resulting wholly aromatic PAs were soluble in common organic solvents, and excellent conformational stability of their helical structures was observed at higher temperatures. Liou *et al.* [95] prepared a series of novel aromatic PAs having noncoplanar biphenylene units in the main chain and bulky naphthyl or phenyl pendant

group at 2,2'-disubstituted position from phenyl and naphthyl-substituted rigid-rod aromatic dicarboxylic acids, 2,2'-diphenylbiphenyl-4,4'-dicarboxylic acid and 2,2'-dinaphthylbiphenyl-4,4'-dicarboxylic acid, and various aromatic diamines via direct phosphorylation polycondensation (Figure 7). The introduction of the bulky phenyl and naphthyl-substituted group could increase the solubility and disrupt the coplanarity of aromatic units in chain packing and exhibited excellent thin-film-forming ability and thermal stability.

Among PAs there is a large group of polymers which differ from other PAs in their properties and methods of preparation. This group, called polypeptides or Poly(amino acid)s (PAA)s, is very close in its composition and structure to one of the most important classes of polymeric substances-proteins [96]. PAA)s are of substantial commercial interest. As biodegradable polyanionic materials their applications range from slow release agents in agriculture, to detergents, surfactant, metal adsorbents, and cosmetics [97]. PAA)s may offer numerous advantages in biomedical applications such as in diagnos-

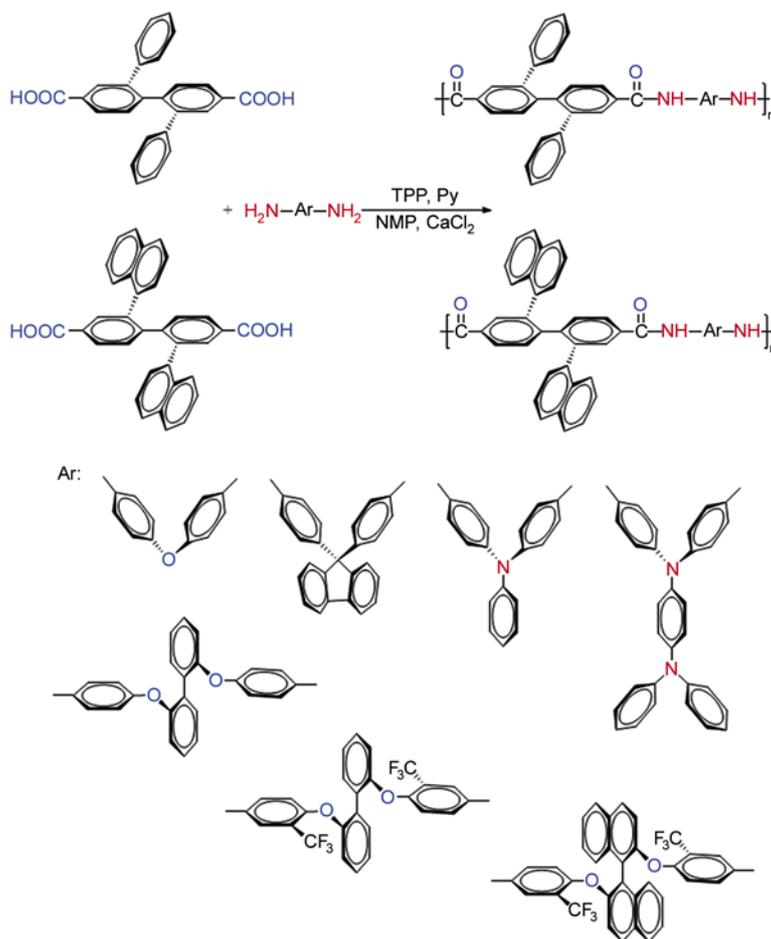


Figure 7. Synthesis of noncoplanar aromatic PAs [95]

tics, sustained release matrices, microencapsulation, for plasma membrane isolation and chromosomal preparations, carriers for therapeutic protein conjugates and drug delivery systems [98, 99]. PAAs are obtained by the polymerization of amino acids or their suitable derivatives, serving as monomers, and like other synthetic polymers they represent a mixture of macromolecules of varying chain lengths. Recent refinements in the chemical technique of polymerization and the development of new physical methods in polymer chemistry have led to a renewal of interest in the polymers of amino acids. Most of the polymers described in the literature are composed of a single amino acid. A number of copolymers have also been prepared [100]. Many attempts were made to prepare PAAs and much considerable progress has been achieved in the synthesis and study of them. Several studies were carried out in polycondensation of α -amino acid derivatives by Frankel and coworkers [101–105]. Fasman and Blout [106] studied the synthesis and the conformation of poly-L-serine and poly-*o*-acetyl-L-serine. These materials were synthesized with degrees of polymerization (DP) slightly above 100. Novel derivatives of poly(aspartic acid) conjugated with various amino acids such as γ -amino butyric acid, leucine, serine, valine, glycine and β -alanine and their amphiphilic copolymers were synthesized and characterized by Kim *et al.* [107]. The resulting polymers exhibited biocompatibility by in-vitro cytotoxicity test. These amino acid-conjugated biocompatible polymers had potential applications in pharmaceutical and cosmetic fields as base materials for drug-carrier systems. Yuki *et al.* [108] prepared a series of poly(β -amino acids), poly[(RS)- β -proline] and poly[(R)- β -proline], by the polycondensation reaction of the *p*-nitrophenyl esters. They studied conformational properties of polymers.

2.2. Polyimides

As polyimides (PI)s possess many desirable attributes, so this class of materials has found applications in many technologies. They have inherently high mechanical properties, good chemical resistance, low dielectric constant and high thermal stability. The high processing temperature of these materials requires dopant molecules to have high thermal decomposition temperatures. Currently,

high performance PIs are being widely used for several primary applications in the electronics area as: (1) Fabrication aids such as photoresists, planarization layers and in implant masks; (2) Passivation overcoats and interlevel insulators; (3) Adhesives and underfill materials for micro BGA (μ BGA) packaging and flip chip technology; (4) Substrate components. Some of other applications include aerospace, automotive and general engineering. In the aerospace and automotive industry they are used in structural composites and as high temperature adhesives. General engineering applications include high temperature bearings and seals [109, 110].

More recently, optically active PIs have been developed. The synthesis of optically active PIs derived from binaphthyl compounds and dianhydrides was reported [111–113]. Binaphthyls are very important chiral compounds which have been used in polymer systems. The chirality of them is arising from the restricted rotation along the carbon-carbon single bond of the two naphthalene rings. The resulting polymers showed good chiral recognition ability when used as a chiral packing material for HPLC. In 1996 Mi *et al.* [114] reported on the first synthesis of a type of thermally stable and optically active aromatic PIs possessing (R)-(+)- or (S)-(–)-1,1'-bi-2-naphthalene units in the main chain, along with some of their important properties. The key monomers, optically active (R)-(+)- or (S)-(–)-2,2'-bis(3,4-dicarboxyphenoxy)-1,1'-binaphthalene dianhydrides (5R and 5S), were prepared by the reactions of optically active (R)-(+)- or (S)-(amic acid)s and subsequent chemical imidization with acetic anhydride-triethylamine (Figure 8). The solubility of resulting PIs was greatly improved by the incorporation of noncoplanarity in axially dissymmetric 1,1'-bi-2-naphthalene units into the polymer backbone. The optical stability at high temperatures could be expected because the racemization resulting from the rotation around the axis of the two binaphthalene rings would be highly hindered by the long chain stretching out on both sides. This group [115] also prepared new optically active aromatic PIs from (R)-(+)-2,2'-bis(2-trifluoro-4-aminophenoxy)-1,1'-binaphthyl monomer with 4,4'-oxydianhydride by one step method. The same researchers [116] performed the similar reaction for the preparation of thermally stable chiral PIs. They

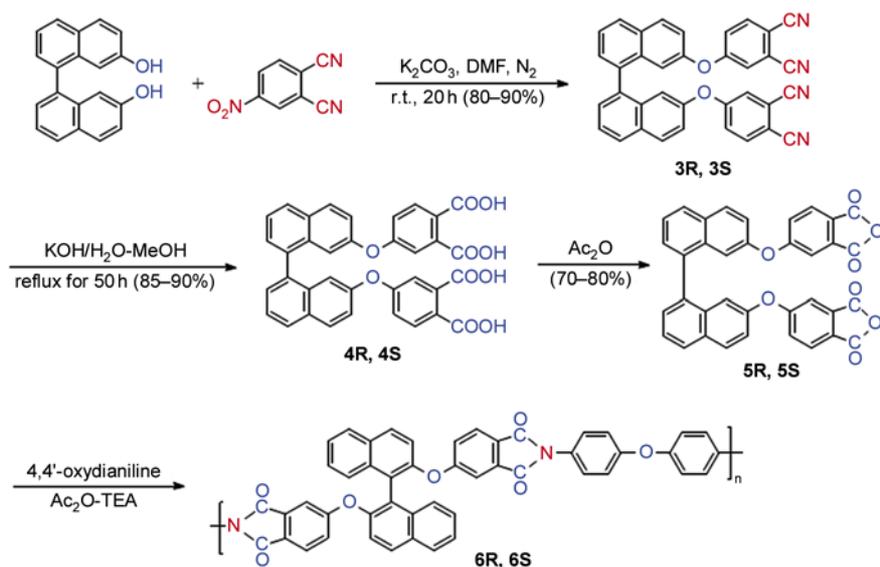


Figure 8. Synthesis of optically active twisted PIs containing 1,1'-bi-2-naphthalene unit [114]

synthesized polymers from condensation of aforementioned monomer with various dianhydrides by using the one-step method. These polymers had glass-transition temperatures of 256–278°C and were optically active with specific rotations ranged from 167–258° and their chiroptical properties also were studied.

Liou [117] reported on the synthesis of organosoluble aromatic chiral PIs from 2,2'-bis(3,4-dicarboxyphenoxy)-1,1'-binaphthyl dianhydride. The dianhydride monomer was subjected to the one-step polycondensation with various aromatic diamines, giving moderate molecular weight PIs with inherent viscosities up to 0.67 dl/g. The introduction of bulky, cranked, and twisted noncoplanar binaphthyl-2,2'-diyl unit into the polymer backbone highly improved solubility of the PIs in organic solvents. All the PIs showed typical amorphous diffraction patterns and had T_g s in the range of 280–350°C, depending on the nature of the diamine moiety. All polymers were stable up to 400°C, with 10% weight loss being recorded above 485°C in air.

Yigit *et al.* [118] described chiral synthetic functionalized PIs containing a chiral (R,R) or (S,S) 1,3-bis(p-N,N'-dimethylaminobenzyl)-perhydrobenzimidazol-2-thion unit in the backbone. The reactions were performed between an optically active aromatic dimethylamine and various dianhydrides such as: pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BPDA), 4,4'-oxydiphthalic anhydride (ODPA) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BTDA) in the

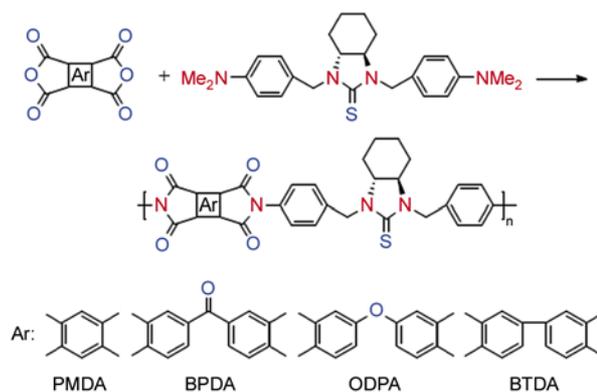


Figure 9. Synthesis route for PIs [118]

presence of the solvent NMP (Figure 9). PIs were soluble in some polar aprotic solvents such as NMP, DMF, DMAc and DMSO and insoluble in apolar solvents such as ether and hexane. The inclusion of chiral groups containing perhydrobenzimidazole groups in the polymer backbone makes the polymer thermally stable with increased solubility. The improved solubility may be attributed to the bulky structure of the monomers, which decreases the interchain interaction owing to the rigid aromatic repeating units. The PIs prepared exhibit excellent properties, with a high potential for optically active polymers.

Kudo and coworkers [119] have reported on the synthesis of constitutionally isomeric head-to-head, head-to-tail and random PIs using an unsymmetric alicyclic tetracarboxylic dianhydride. They reported on a first example for the structurally isomeric PIs that show a different physical property (Figure 10). They also prepared optically active alicyclic PIs via

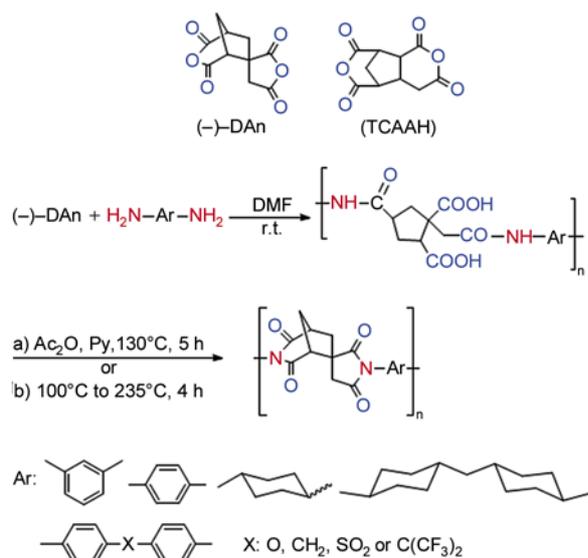


Figure 10. Synthesis of optically active coPIs derived from DAN [119–123]

polycondensation of (–)-[1S*,5R*,6S*]-3-oxabicyclo[3.2.1]octane-2,4-dione-6-spiro-3'-(tetrahydrofuran-2',5'-dione) [(–)-DAN] with diamines and subsequent chemical or thermal imidization (Figure 10). The dianhydride (–)-DAN was synthesized by an asymmetric Diels-Alder reaction of a chiral itaconic acid derivative as a key step. Colorless or slightly yellow flexible films were obtained for the (–)-DAN-derived PIs. The resulting polymers showed good solubility toward dipolar aprotic solvents and Py [120]. Kudo's group also successfully synthesized a series of optically active and soluble PIs having a spiro alicyclic unit in the main chain by the reactions of DAN with several diamines through a general two-step polymerization method [121–122]. In another research, they reported on a systematic investigation of the physical properties of coPIs of DAN [123]. The comonomer used in their study was c-3-carboxymethyl-r-1,c-2,c-4-cyclopentane tricarboxylic acid 1,4:2,3-dianhydride (TCAAH), a structural isomer of DAN, which is unsymmetric but does not have a spiro unit (see Figure 10). The refractive indices of coPIs were also studied. They showed the DAN content in the backbone affects various properties of coPI, which might be attributed to its unsymmetric spiro-alicyclic structure. The structure property relationships found here should be universal in principle, and might be applicable to the design and modification of other polymers.

Barikani *et al.* [124] investigated a new optically active diisocyanate containing methylene groups and a preformed imide ring using the Curtius rearrangement of corresponding diacylazides. The diisocyanate was polycondensed with PMDA, benzophenone tetracarboxylic dianhydride, and hexafluoroisopropylidene diphthalic anhydride to provide three optically active PIs. The introduction of methylene moieties as well as the presence of a preformed imide ring in the polymer backbone improved the solubility of the polymers without too much thermal stability being sacrificed. Synthesis and characterization of new optically active PIs containing L-leucine amino acid residue are reported by Yeganeh *et al.* [125]. They prepared a new optically active diisocyanate from the reaction of L-leucine and PMDA and subsequent transformation of intermediate imide-containing diacid to diisocyanate via Weinstock modification of Curtius rearrangement using TEA, ethylchloroformate and sodium azide reagents. The solution polycondensation using DMF solvent and appropriate duration and temperature programming which optimized via study of model compound was applied successfully for preparation of PIs from this diisocyanate and three different dianhydrides such as PMDA, 3,3,4,4-benzophenonetetracarboxylic dianhydride, and hexafluoroisopropylidene 2,2-bis(phthalic anhydride). Two different optically active dianhydrides were also prepared by them [126] from the reaction of L-aspartic acid with either PMDA or benzophenone tetracarboxylic dianhydride and subsequent transformation of tetraacids to dianhydrides using thionyl chloride. Twelve novel optically active and soluble PIs having inherent viscosities of 0.18–0.55 dl/g were synthesized from the reaction of optically active dianhydrides with different aromatic and aliphatic diisocyanates. These polymers showed acceptable physical properties as well as optical activity.

2.3. Polyesters

Recently, Mallakpour and coworkers [127–131] synthesized optically active thermally stable aromatic polyesters (PE)s containing phthalimide group from the reaction of two different diacid monomer with several aromatic diols via direct polyesterification with tosyl chloride (TsCl)/Py/

DMF system as condensing agent. The resulting polymers were obtained in good yields with inherent viscosities ranging between 0.21 and 0.61 dL/g. Thermal gravimetric analysis (TGA) showed that the 10% weight loss temperature in a nitrogen atmosphere was more than 360°C, which indicates that the resulting PEs have a good thermal stability. From the chemical point of view the ester group imparts to the polymer's structure increased sensibility to hydrolysis that can cause chain breaking. In addition because of the existence of amino acids in the polymer pendant group these polymers were expected to be biodegradable and were therefore classified under environmentally friendly polymers. More recently this group also synthesized optically active and photoactive aromatic PEs by step-growth polymerization of a chiral diacid containing naphthalimidyl and flexible chiral groups with different diols via direct polyesterification reaction. The resulting polymers show excellent solubility due to bulky pendant groups, good thermal stability with glass transition temperature around 200°C, and fluorescence emission phenomena [132].

A series of coPEs based on 2-[(S)-(+)-methyl-1-butoxy]hydroquinone as the chiral monomer with several nonchiral hydroquinones was synthesized by Fujishiro and Lenz [133] to form a new family of main-chain cholesteric liquid crystalline polymers containing a flexible spacer. Copolymers containing unsubstituted hydroquinone units formed two liquid crystalline phases, one of which was a cholesteric phase, but the other may have been a cybotactic nematic phase. Copolymers with nonchiral substituted hydroquinone units formed only a cholesteric phase. Schwartz *et al.* [134] reported on the polycondensation of silylated 2,3-isopropylidene D-threitol with a dicarboxylic acid dichloride in *o*-dichlorobenzene or 1-chloronaphthalene at 180–230°C and ten cholesteric coPEs were prepared by polycondensation of mixtures of silylated methylhydroquinone and *cis*- or *trans*-1,4:3,6-dianhydro-D-sorbitol (*trans*: isosorbide, *cis*: isomannide), or 2,3-isopropylidene threitol with the dichloride of 1,10-bis(4'-carboxyphenoxy)decane. The polymers containing isosorbide units are optically active. The resulting coPEs form a broad cholesteric phase above 200°C. This approach is also useful for the synthesis of coPEs from diols and diphenols, and thus, allows the preparation of cholesteric

PEs with interesting optical properties. For the first time, Kricheldorf's group [135] investigated a process for the production of optically active PEs based on the polycondensation of 4-carboxycinnamic acid in the form of its acid chloride with chiral spacers in the presence of Py. Difunctional cinnamic acids such as 4-hydroxy- or 4-aminocinnamic acid are useful and interesting components of photoreactive polycondensation. Chiral spacer was synthesized from (R)-3-bromo-2-methyl-1-propanol and 4-mercaptophenol. Three homoPEs were also prepared via polycondensation of 4,4'-dihydroxybiphenyl and 2,5-bis(*n*-octyloxy)-2,5-bis(dodecyloxy)- or 2,5-(hexadecyloxy) terephthaloyl-chloride by this group [136]. Furthermore, several coPEs were synthesized from 4,4'-dihydroxybiphenyl and mixtures of 2,5-bis-(hexadecyloxy) terephthaloylchloride and 2,5-bis((S)isopentyloxy)terephthaloylchloride. All PEs were characterized by inherent viscosities, elemental analyses, ¹H NMR spectroscopy, differential scanning calorimetry (DSC) measurements, dynamic mechanical analyses (DMA), wide-angle X-ray diffraction (WAXD) powder patterns at various temperatures and optical microscopy. Two liquid crystalline phases were detected for the homoPEs and most coPEs: a viscous sanidic (biaxial nematic) phase and, at higher temperatures, a mobile nematic phase. Sanidic PEs are PEs forming a layered supramolecular structure with the layer planes parallel to the main chain in contrast to the smectic systems where the layer planes are more or less perpendicular. Kricheldorf and coworkers [137] also synthesized a series of chiral PEs by polycondensation of silylated 4,4'-dihydroxybiphenyl and mixtures of 2,5-bis(dodecylthio)terephthaloyl chloride and 2,5-bis((S)-2-methylbutylthio)terephthaloyl chloride. The resulting coPEs were characterized by elemental analyses, viscosity, DSC and X-ray measurements, and optical microscopy. Depending on the reaction conditions low and high molecular weights were obtained. Bahulayan and Sreekumar [138] investigated chiral PEs with azobenzene moieties in the main chain by the polycondensation of terephthaloyl chloride with isosorbide, which acts as the chiral building unit, and an azobiphenol, bis(4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane or bis(4-hydroxyphenylazo)-2,2'-dinitro-3,5,3',5'-tetramethyldiphenylmethane in a solvent mixture of DMAc and 1,2-

dichlorobenzene (1:4 v/v). These polymers exhibited good thermal properties, had high T_g values and TGA studied showed they were stable up to 400°C. The polymer chains characterized by helical structures were non-centrosymmetric at the molecular level. But in randomly oriented polymer films obtained by solvent evaporation, non-centrosymmetry may be lost. This group [139] prepared a series of optically active PEs with π -conjugated donor-acceptor segments was synthesized by the condensation of azobenzene-4,4'-dicarbonylchloride with 1,4:3,6-dianhydro-D-sorbitol ($[\alpha]_D^{25} = 42.5^\circ$) and biphenolic chromophores, bis(4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane and bis(4-hydroxyphenylazo)-2,2'-dinitrodiphenylsulfone. The second-harmonic generation (SHG) efficiency of the polymers was experimentally verified by a powder-reflection technique with 2-methyl-4-nitroaniline as a reference. The SHG efficiencies of the polymers were compared to those of the chromophores and explained as a function of the percentage of chiral composition. WAXD scans showed that with the increase in the percentage of the chiral unit, the packing order in the polymers increased. They also synthesized [140] several chiral PEs containing donor-acceptor substituted π -conjugated segments in the main chain by high-temperature polycondensation of biphenolic chromophores, bis(4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane and bis(4-hydroxyphenylazo)-2,2'-dinitrodiphenylsulfone with (2R,3R)-(+)-diethyl tartrate and terephthaloyl chloride. Results showed that the optical rotation increased with the increase in the composition of diethyl tartrate units. The temporal stability showed that the chiral organization and, hence, the dipole orientation are stable in these systems. The high T_g value of the polymers also supported the thermal stability of the orientation. Thus, chiral polymers incorporating donor-acceptor substituted π -conjugated segments can offer themselves as promising materials in the field of nonlinear optics. The same researchers reported on [141] the synthesis, characterization and solvatochromic behavior of a new series of optically active PEs. These polymers were prepared from polycondensation of diacid chlorides with biphenolic azo chromophores such as bis(4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane and bis(4-hydroxyphenylazo)-2,2'-dinitrodiphenylsulfone with Λ -shaped

conformation and isosorbide compound. The polymerizations were carried in different highly polar solvents like DMF and DMAc with Py as acid acceptor. The PEs were obtained with higher dipole moment in excited state than in ground state so that they were stabilized more in the excited state by an increase in solvent polarity. This shows that in all respects these PEs are suitable for NLO studies.

Nemoto *et al.* [142] prepared new types of PEs containing containing second-order NLO active chromophores with high density by the condensation polymerization between the isophthalic acid derivatives and the N-substituted diethanolamines using TPP and diethyl azodicarboxylate as the condensing agents in DMSO or NMP. The obtained amorphous PEs exhibited good solubility in common organic solvents and provided optical-quality films by spin-coating. The weight average molecular weights of PEs estimated from gel permeation chromatography (GPC) were the magnitude of thousand, which indicates the DP was ca. 10–15. Mehl *et al.* [143] investigated a series of optically active PEs containing chiral groups in the main chain by polycondensation of chiral diol with several aromatic diacids. The DP for all the polymers lay between 13 and 15 repeat units. The polydispersity of the samples was more or less similar, and therefore comparisons between different polymers were possible. The comparatively low polydispersity was a result of the good solubility of the monomers and low molar mass oligomers in methanol. Synthesis and characterization of novel optically active biodegradable network PEs from L- and D-malic acid and various glycols with different number of methylene groups ($\text{HO}(\text{CH}_2)_n\text{OH}$, nG, n = 2–6, 8–10, and 12) was studied by Nagata *et al.* [144]. The biodegradation experiments for the network PE films were carried out in enzymatic solution with *Rhizopus delemar* lipase and in an activated sludge. The stereochemistry between the L- and D-isomer of network PE films gave rise to the small differences in biodegradation rate: the rate of biodegradation for the network PE with L-isomer is higher than that with D-isomer. Bai *et al.* [145] synthesized a series of new liquid-crystalline PEs having the chiral centers and dipolar groups isoregically arranged along the polymer backbones. The physical properties such as molecular weights, intrinsic viscosities, elemental analyses, and thermal analy-

ses of polymers were studied. The thermal stability for polymers was similar regardless the difference in spacer length and molecular weight, because they have same functional groups and linkages. Srinivasan and Radhakrishnan [146] reported on the synthesis, characterization, and examination of liquid-crystalline properties of thermotropic main-chain random coPEs based on 4,4'-biphenol using twin spacers-chiral and achiral-revealed that chiral spacers were able to transmit the twist direction and a tilt angle to the molecule (their ferroelectric properties were investigated). The number average molecular weights measured by GPC were between 6000 and 8000 with polydispersities ranging from 1 to 1.1. Liquid-crystalline PEs based on hexanediol or butanediol, dimethyl 4,4'-biphenyldicarboxylate, and a sugar-based diol, and various levels of isosorbide or isomanide (Figure 11), were organized with conventional melt polycondensation by Lin *et al.* [147]. Modest molecular weights were obtained, although they were typically lower than those of PE analogues that did not include sugar-based diols. TGA confirmed that the insertion of isosorbide or isomanide units did not reduce the thermal stability in a nitrogen atmosphere.

Hilker *et al.* [148] reported on the examination of a novel concept for the synthesis of chiral PEs (Figure 12), a lipase-catalyzed dynamic kinetic resolution (DKR) polymerization of racemic monomers. In their investigation, a mixture of stereoisomers of a secondary diol is enzymatically polymerized with a difunctional acyl donor (dicarboxylic acid derivative) in the presence the Noyori-type ruthenium catalyst A and an immobilized *Candida Antarctica* Lipase B (Novozym 435). Because of its enantioselectivity the Lipase B converts only the hydroxy

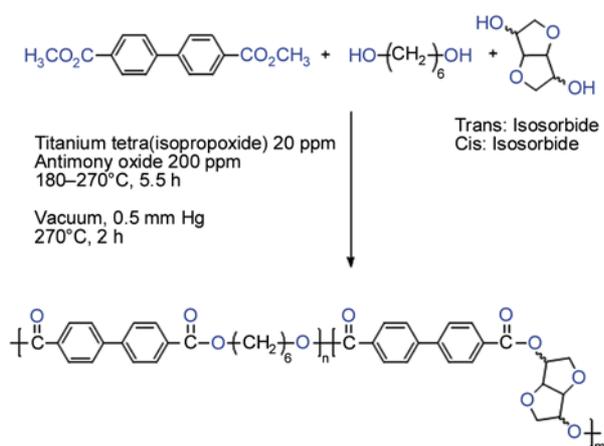


Figure 11. Synthesis of chiral liquid-crystalline PEs [147]

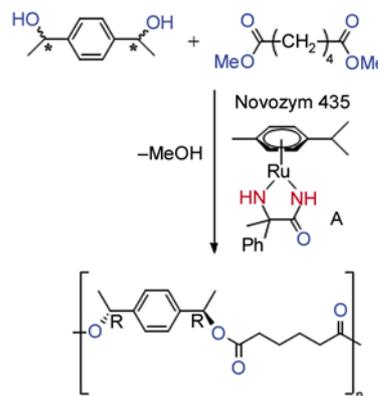


Figure 12. Reaction sequence for the one-pot DKR polymerization [148]

groups at the R-configured centers. In situ racemization of the hydroxysubstituted stereocenters from the S to the R configuration allows the polymerization to proceed to high conversion. They showed that DKR can be combined with enzymatic polymerization for the preparation of chiral PE from racemic secondary diols. This notion offers an efficient method for the one-pot synthesis of chiral polymers from nonnatural monomers.

Under similar conditions DKR of secondary alcohols and esters was extended to secondary diols and diesters to afford chiral PE by Van As *et al.* [149]. With these conditions, chiral polymers were obtained with peak molecular weights up to 15 kDa, enantiomeric excess (ee) values up to 99%. At most, an ee of 46% was obtained with low molecular weights in the range of 3.3–3.7 kDa. This process is an example of iterative tandem catalysis, an effective method for synthesis of chiral polymers from a variety of optically inactive monomers. Gómez *et al.* [150] reported on the first synthesis of optically active PE containing 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ) as an efficient electron acceptor in the main chain by polycondensation reaction of (S)-2,2'-bis(dodecyloxy)-1,1'-binaphthyl-6,6'-dicarboxylic acid chloride with 2,6-dihydroxy-TCAQ. The reaction was carried out at moderate temperature in an aprotic solvent and in the presence of TEA. Cyclic voltammetry investigations showed that TCAQ preserved its acceptor ability in the polymer system and preliminary photophysical investigations showed fluorescence quenching in mixtures containing the acceptor polymer and fluorescent conjugated polymers.

2.4. Poly(amide-imide)s

Synthesis and characterization of a number of optically active poly(amide-imide)s (PAIs) were investigated by Mallakpour's group [151–154]. The polymerization reactions were carried out via polycondensation reaction of N-trimellitylimido-leucine, N-trimellitylimidoisoleucine, N-trimellitylimido-phenylalanine and N-trimellitylimido-DL and L-alanine with several diamines in the presence of TPP, NMP, Py, and CaCl₂ under various conditions for different periods of time, and in another method (Figure 13). These aromatic PAIs showed optical rotations, were readily soluble in various organic solvents, and had moderate thermal stability. This could be due to the formation of some cyclic polymers instead of linear polymers.

Mallakpour and coworkers [155, 156] reported on some of preparation of chiral PAIs via direct solution polycondensation of different aliphatic and aromatic diisocyanates with a chiral diacid monomer. The optically active N-trimellitylimido-L-isoleucine as a monomer was reacted with some aromatic as well as aliphatic diisocyanates according to isocyanate route. This method was a convenient technique for the preparation of novel optically active PAIs. In addition, in this method use of diamines was eliminated and there was no need to activate diacid monomer. Mallakpour *et al.* [157–159] have also investigated the synthesis of PAIs from the polycondensation reaction of N,N'-(pyromellitoyl)-bis-L- α -amino diacid chloride such as: L-phenylalanine, L-alanine and L-leucine with several aromatic diamines in o-cresol or DMAc (Figure 14). Polymerization reactions were carried out using microwave irradiation and conventional solution polycondensation. The polycondensation proceeded rapidly, compared with the conventional melt polycondensation and solution polycondensation giving a series of PAIs with inherent viscosities about 0.22–0.85 dl/g. All aromatic PAIs were optically active and readily soluble in various organic solvents and had good thermal stability. The inherent viscosities obtained from microwave assisted polycondensation reactions are much higher than those polymers obtained from solution polymerization. Furthermore, the above

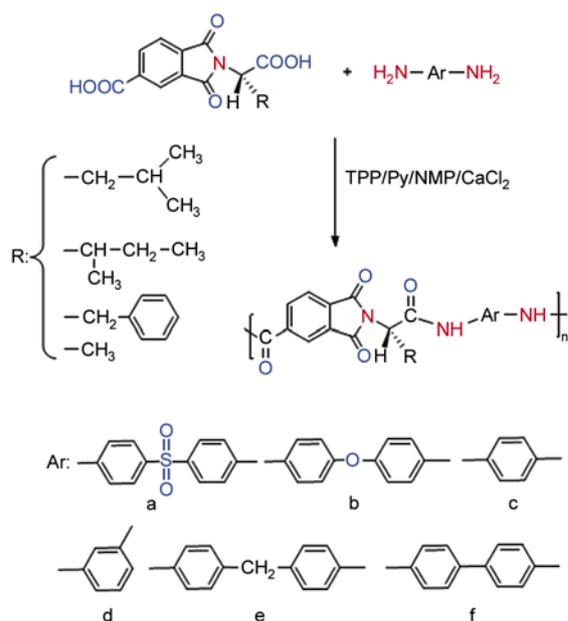


Figure 13. Synthesis route for optically active PAIs [151–154]

(pyromellitoyl)-bis-L- α -amino diacid chloride such as: L-leucine, L-isoleucine and L-valine with different aromatic diamines under microwave heating in a porcelain dish and the results were compared with those polymers obtained by conventional heating (Figure 14). The obtained aromatic PAIs were optically active and soluble in various organic solvents and have good thermal stability. Microwave-assisted step-growth polymerization reactions proceeded rapidly compared to conventional solution polycondensation and it was almost completed within a short period of time. Several types of optically active PAIs were prepared by Mallakpour *et al.* [160–163] from polycondensation reaction of N,N'-(4,4'-carbonyldipthaloyl)-bis α -amino diacid chloride such as: L-phenylalanine, L-alanine and L-leucine with several aromatic diamines in o-cresol or DMAc (Figure 15). Polymerization reactions were carried out using microwave irradiation and conventional solution polycondensation. The polycondensation proceeded rapidly, compared with the conventional melt polycondensation and solution polycondensation giving a series of PAIs with inherent viscosities about 0.22–0.85 dl/g. All aromatic PAIs were optically active and readily soluble in various organic solvents and had good thermal stability. The inherent viscosities obtained from microwave assisted polycondensation reactions are much higher than those polymers obtained from solution polymerization. Furthermore, the above

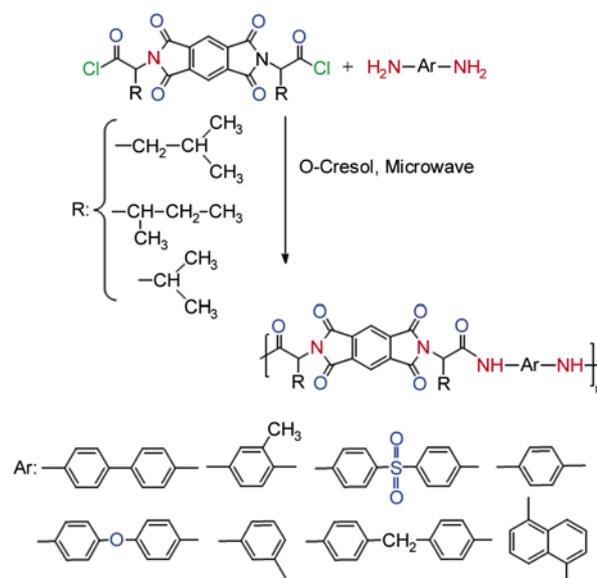


Figure 14. Synthesis of chiral PAIs by reaction of different N,N'-(pyromellitoyl)-bis-L- α -amino diacid chloride with aromatic diamines [157–159]

were also synthesized by both low and high temperature solution step-growth polymerization reaction. The polyamidation reaction of 4,4'-carbonyl-bis(phthaloylalanine) diacid chloride with six different derivatives of tetrahydropyrimidinone and tetrahydro-2-thioxopyrimidine compounds were discussed earlier in the work of Mallakpour *et al.* [180] in the presence of a small amount of *o*-cresol. Under microwave irradiation power of 900 W, a

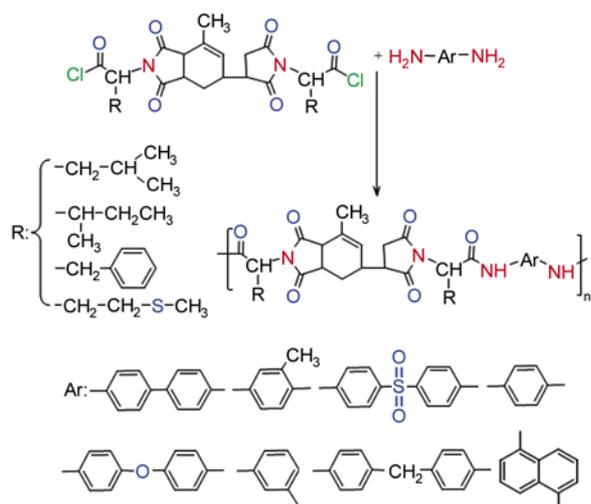


Figure 16. Synthesis of optically active PAIs containing epiclone and several amino acids [181–185]

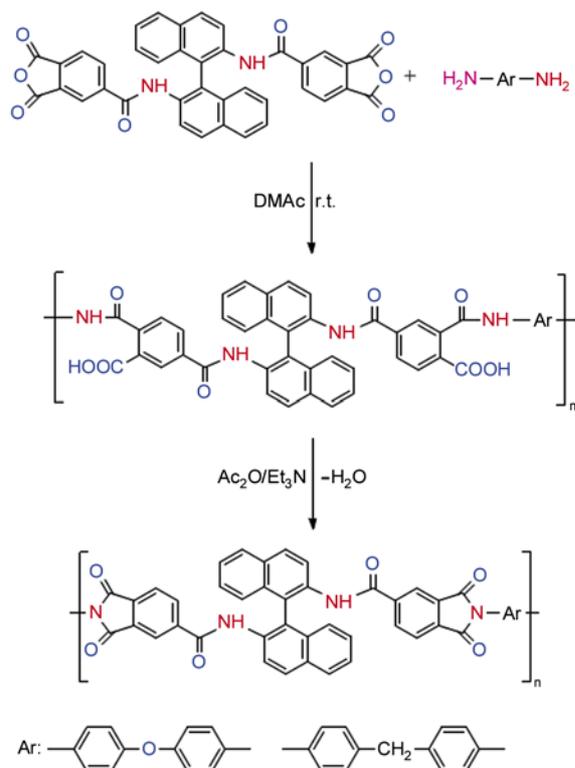


Figure 17. Synthesis of optically active PAIs derived from new chiral dianhydride and diamines [189]

series of optically active and thermally stable PAIs were produced within 10 min with inherent viscosities in the range of about 0.25–0.45 dL/g and high yields. The syntheses and characterization of optically active PAIs derived from diacid chloride containing epiclone and several amino acids such as L-phenylalanine, L-isoleucine, L-methionine, L-valine or L-Leucine with different aromatic diamines in the presence of a small amount of a polar organic medium such as NMP under microwave irradiation (Figure 16) was studied by Mallakpour and coworkers [181–185]. To compare microwave irradiation polymerization with solution polymerization methods PAIs were also synthesized by both low temperature and high temperature classical solution polymerization. The results of these methods were comparable with the microwave method. But the microwave heating is a more efficient method for these step-growth polymerization reactions.

Faghihi *et al.* [186–188] studied synthesis and characterization of optically active PAIs with hydantoin and thiohydantoin derivatives in the main chain via polycondensation reaction of *N,N'*-(pyromellitoyl)-bis-1-phenylalanine diacid chloride and six different derivatives of 5,5-disubstituted hydantoin compounds in the presence of a small amount of *o*-cresol as a polar organic media. Polymers were synthesized via two different methods: Classical heating and microwave irradiation method. The results showed that microwave heating is an efficient method for the polycondensation reactions. These PAIs exhibited excellent solubility in the organic solvents at room temperature.

Song *et al.* [189] prepared newly optically active aromatic PAIs from polycondensation reaction of 2,2'-bis(3,4-dicarboxybenzamido)-1,1'-binaphthyl dianhydride and different diamines in DMAC (Figure 17). Polymers with different ee% were investigated with respect to their structures and chiroptical properties. The results suggested that optically active PAIs possessed regular chiral conformations. They showed high glass transition temperatures of 287–290°C and 5% weight loss temperatures of 450–465°C in nitrogen.

2.5. Poly(ester-amide)s

Poly(ester-amide)s (PEA)s are emerging as promising materials for a wide range of biomedical applications due to their potential for both hydrolytic and

enzymatic degradation as well as the ease with which their properties can be tuned by the choice of monomers. The architecture of the PEA polymers is a blend of PA and PE polymer character. This leads to a blend of the characteristic behavior and properties of these two distinct polymers as well. The thermal properties of PEAs include higher melt transitions and increased thermal stability versus PEs. Conversely, the characteristic thermal properties are lower for PEAs than for PAs. PAs tend to be high melting and thermally stable. These characteristics make PAs difficult to process. PAs also generally display better mechanical endurance than the corresponding PEs, thanks to the formation of strong hydrogen bonding between the amide linkages of individual chains. PEs, on the other hand, is generally superior in flexibility, solubility, and hydrolytic susceptibility, and can thus be designed to degrade within a reasonable time-scale. PEAs represent a mixture of PE and PA character and therefore the corresponding thermal properties are a blend of the two homopolymers. The lower melt transitions versus PAs mean that molding, shaping and extruding are all possible. As a consequence, it is preferentially cleaved by enzymes. In PEAs, the combination of the bonding from two parent polymer families can be used to tailor the final thermal and enzymatic properties of the synthesized PEA polymer. The blend of characteristics is accomplished by varying the ratio of amide to ester bonds in the final polymer. This can be accomplished via co-polymerization of monomers containing both types of bonds, but more frequently by the condensation of monomers with terminal amines and terminal acids. The biological degradation behavior for PEAs is generally less complete than for PEs but much more complete than PAs. This is due to the ester bond being more readily hydrolyzed than the corresponding amide bond. The structure of the PEA polymer backbone, in particular, provides a straightforward route to biodegradable materials because of the possibility of incorporating biologically related molecules. The incorporation of pendant functional handles along the PEA backbone has the potential to further expand their applications by allowing the charge and hydrophilicity of the polymers to be altered, and facilitating the conjugation of active molecules such as drugs, targeting groups, and cell signaling molecules [190–193].

Atkins *et al.* [190] described a simple and versatile approach based on orthogonal protecting groups, by which L-lysine and L-aspartic acid could be incorporated into several families of PEAs based on monomers including the diacids succinic and terephthalic acid, the diols 1,4-butanediol and 1,8-octanediol, and the amino acids L-alanine and L-phenylalanine. Molina Pinilla *et al.* [194] reported on the synthesis and stereoregular high intrinsic viscosity chiral PEA derived from L-arabinose and succinic anhydride by using the active ester polycondensation method. The polymerization reaction was carried out in different polar solvents. The TGA thermogram indicated that this PEA was stable up to 250°C under nitrogen. Fan *et al.* [195] prepared several optically active PEAs derived from L-isoleucine. Polymers were synthesized from the p-toluenesulfonic acid salt of o,o'-bis(leucyl)-hexanediol (TS+LHD+TS-) and p-phthaloyl chloride and styrene-2,5-dicarbonyl chloride styrene by interfacial polymerization. The resulting polymers were soluble in strong acids (formic, dichloroacetic and trifluoroacetic acid) and chlorinated polar solvents such as chloroform and dichloromethane. The synthesis of PEAs from the reaction of p-nitrophenyl esters of sebacic or adipic acids and diamines containing α -amino acid ester groups was studied by Fan *et al.* [196] (Figure 18). The biodegradability of the resulting polymers was investigated by *in vitro* hydrolysis with proteases and a lipase as catalysts in borate buffer solutions. The results indicated that the polymers containing L-phenylalanine were hydrolyzed most effectively by α -chymotrypsin (α -CT), subtilisin Carlsberg, and subtilisin BPN'. The PEAs containing other amino acid residues also underwent hydrolysis to different extents, reflecting the substrate specificity of the proteases. Lipase had almost no effect on the hydrolytic degradation of these PEAs. The polymers containing glycine residues were hardly decomposed by any of the enzymes used.

Several optically active PEAs were synthesized by interfacial polycondensation of the mixture of 1,6-hexanediol diester of L- and D-alanine with sebacoyl chloride or terephthaloyl chloride by Nagata [197]. The enzymatic degradation of the PEAs was followed by the weight loss in a buffer solution (pH 7.2) of proteolytic enzymes (proteinase-K, papain and α -CT) and lipase enzymes (R. delemar, P. cepa-

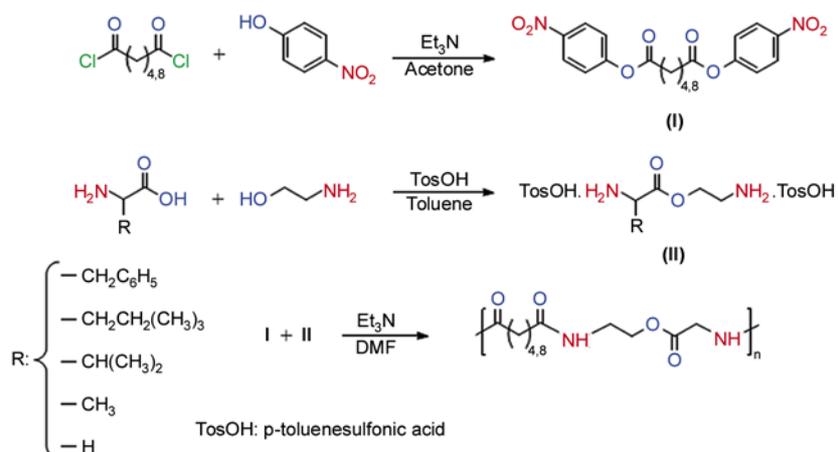


Figure 18. Synthesis of the optically active and biodegradable PEAs from amino acids, 2-aminoethanol, and dicarboxylic acid [196]

cia and *C. rugosa*) at 37°C. It was found that the degradation with the proteolytic enzymes is not caused by hydrolysis of the semi-peptide linkage but of the ester linkage. The synthesis and characterization of a new series of chiral PEAs was reported by Philip and Sreekumar [198]. These PEAs were prepared by solution polycondensation of diacid chlorides of bismaleamic acid with biphenolic azo chromophores and optically active isosorbide in DMAc at 100°C. The resulting polymers showed T_g between 100 and 190°C and were stable up to 400°C.

Asin *et al.* [199] synthesized sequential chiral PEAs derived from glycine by a two-steps method, involving a final thermal polyesterification. They compared this method in detail with their previous reported on the basis of interfacial polymerization. Thermal synthesis of the indicated glycine derivatives was carried out with high yield and generally provided polymers with the right molecular weight (M_w) to render fiber- and film-forming properties. Thermal synthesis seems to be useful for preparing polymers derived from diacid chlorides such as oxaloyl or succinoyl chlorides and diols such as 1,4-butanediol because the interfacial synthesis of these polymers is highly deficient. Furthermore, the intrinsic viscosities of the other studied polymers with aliphatic or aromatic components were generally higher when thermal synthesis was used. The resulting PEAs appear to be susceptible to the proteolytic enzymatic attack with papain as a result of the presence of glycine units. Degradable polymers may still be obtained when oxaloyl or terephthaloyl units were incorporated. In another study by Pare-

des *et al.* [200], a new kind of PEA derived from L-alanine was synthesized and the biodegradation and biocompatibility of the resulted polymer were investigated by them. The obtained polymer had good fiber and film-forming properties, as well as other characteristics like thermal stability and solubility in chloroform, which enhanced its processing facilities. Degradation studies showed that both pH and temperature influenced in the hydrolysis rate that took mainly place through the ester linkages. Degradation was also studied using different enzymes. Results indicated that papain was the most efficient of these, and that the hydrolysis to water-soluble products could be attained in a few days. The biocompatibility of the obtained polymer was investigated using cell culture techniques, because in vitro assessment of biocompatibility with permanent cell lines is a good screening method for detecting adverse effects.

Amino alcohols are easily obtained by the reduction of amino acids, which serve as useful chiral building blocks in organic synthesis. Step-growth polymerization of dicarboxylic acids with diols having amide moieties derived from optically active amino alcohols were carried out by Koyama *et al.* [201]. Polymers were obtained by the polycondensations using of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride in DMF at room temperature for 8 h in satisfactory yields. The T_g of the polymer rose with decrease of the methylene chain length of the dicarboxylic acid. Currently available synthetic biodegradable elastomers are primarily composed of crosslinked aliphatic PEs, which suffer from deficiencies including (1) high crosslink

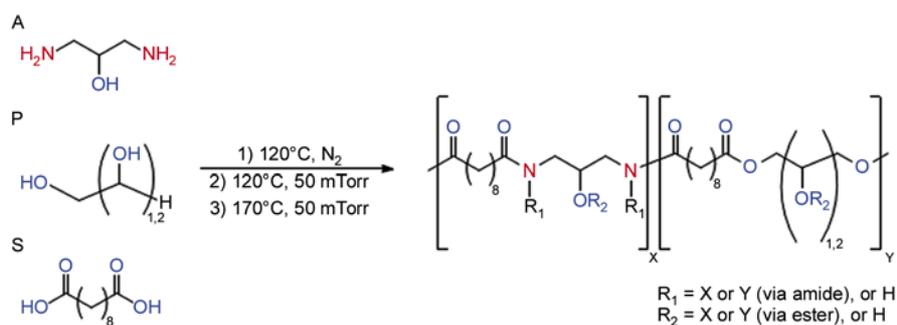


Figure 19. Synthesis scheme of APS polymers [202].

densities, which results in exceedingly high stiffness, (2) rapid degradation upon implantation, or (3) limited chemical moieties for chemical modification. Bettinger *et al.* [202] developed a new class of synthetic, biodegradable and chiral elastomeric PEAs, poly(1,3-diamino-2-hydroxypropane-copolyol sebacate)s, composed of crosslinked networks based on an amino alcohol (Figure 19). These crosslinked networks featured tensile Young's modulus on the order of 1 MPa and reversible elongations up to 92%. These polymers showed *in vitro* and *in vivo* biocompatibility and were projected degradation half-lives up to 20 months *in vivo*.

Kobayashi *et al.* [203] prepared several optically active PEAs from polycondensation of ester-containing chiral dicarboxylic acid and different aromatic diamines in the presence of TPP, Py, and CaCl_2 in NMP. The resulting optically active polymers were obtained with inherent viscosities of 0.44–0.79 dl/g, and specific rotations from -43.6 to -78.5° . The T_g s of the polymers were in the range from 129 to 169°C, and their decomposition started at a temperature from 231 to 249°C to afford bis-crotonamide and terephthalic acid.

A new class of optically active and biodegradable PEAs was prepared by Gomurashvili *et al.* [204]. Polymers were synthesized by two step method. At first isosorbide or isomannide were esterified with α -amino acids in the presence of *p*-toluenesulfonic acid, and the resulting esters bisammonium tosylates were isolated. Second, the amino groups were liberated and polycondensed with *p*-nitrophenyl esters of aliphatic dicarboxylic acids. Biodegradation of resulting polymers was studied by chymotrypsin or lipase.

Poly(lactic acid) (PLA) and its copolymers have received great interest in industrial and medical applications. It can be used in plastic and fiber

grade. Some of applications of PLA are resorbable sutures, drug delivery systems, artificial skin, implants for orthopedics, surgical materials, thermoforms, injection-molded or blow-molded containers, oriented and blown films, nonwovens, scaffold for tissue engineering and renewable plastics [205, 206]. To extend the use of LA-based polymers, functional group such as amide was introduced in the main chain. Most of the reports focus on the linear polymer, because they are easy to process, shape and manufacture. On the other hand, the attention was paid to the cross-linked polymers for enhancing the mechanical and thermal properties. A novel LA-based cross-linked PEA (LCPEA) with different cross-linking density was synthesized via polycondensation reaction of a dicarboxylic-terminated oligoester ELDA, a diacid derived from LA, TDI by Yue Ying *et al.* [205]. The tensile strength, elastic modulus and bend strength of the LCPEA of 65% gel fraction were 4.65, 136.55 and 39.63 MPa, respectively. The thermal decomposition temperature (50 wt%) of the LCPEA was around 410°C.

Although a number of PEAs of different compositions have been reported, there is a significant need for the incorporation of amino acids with functional side chains. This will allow for the conjugation of drugs or cell signaling molecules in tissue engineering scaffolds, thus expanding the potential applications of these materials. De Wit *et al.* [207] studied the synthesis, characterization and functionalization of novel PEAs. They reported on the incorporation of L-lysine into PEAs comprised of succinic acid, 1,4-butanediol, and L-phenylalanine to provide pendant amine functional groups for the first time in PEAs. The degradation of thin films of polymers was studied using scanning electron microscopy and the incorporation of lysine was found to signif-

icantly accelerate both the hydrolytic and enzymatic degradation.

2.6. Poly(ester-imide)s

A series of optically active Poly(ester-imide)s (PEIs) were prepared through a facile and rapid polycondensation reaction of chiral *N,N*-(pyromellitoyl)-bis-*L*-leucine diacid chloride and *N,N*-(pyromellitoyl)-bis-*L*-phenylalanine diacid chloride with several aromatic diols such as phenol phthalein, bisphenol-A, 4,4'-hydroquinone, 1,8-dihydroxyanthraquinone, 1,5-dihydroxy naphthalene, 4,4'-dihydroxy biphenyl, and 2,4-dihydroxyacetophenone using a domestic microwave oven in the presence of a small amount of a polar organic medium such as *o*-cresol by Mallakpour *et al.* [208, 209] (Figure 20). The polymerization reactions proceeded rapidly and were completed within 10–20 min, producing a series of optically active PEIs with good yield and moderate inherent viscosity of 0.10–0.27 dl/g and were compare with polymerization reaction under solution condition but the resulting materials were soluble in methanol probably due to formation of oligomers. Therefore microwave technique in this case was superior to the conventional solution method. These aromatic PEIs showed optical rotation and were readily soluble in various organic solvents and had good thermal stability. Fluorine containing PEIs having different α -amino acid such as: *L*-leucine, *L*-isoleucine and *L*-methio-

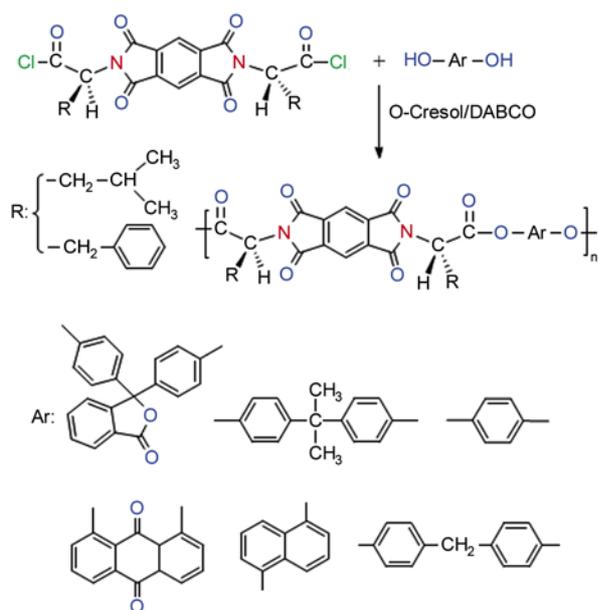


Figure 20. Polycondensation reaction of chiral *N,N*-(pyromellitoyl)-bis-*L*-amino acid chloride with several aromatic diols [208, 209]

nine in main chain were also prepared by Mallakpour and coworkers [210–213] (Figure 21).

The reactions with TsCl were significantly promoted by controlling alcoholysis with diols in the presence of the catalytic amounts of DMF to give a series of optically active PEIs with good yield, moderate to high inherent viscosity ranging 0.35–1.12 dL/g and also showed optical rotation. Thermal stability of the PEIs with fluorine containing linkage was higher than a related polymer having non-fluorinated. Furthermore, the resulting optically active PEIs containing amino acid linkages so could be biocompatible and biodegradable.

Mallakpour's group reported on the direct polycondensation reactions of *N,N'*-(4,4'-oxydiphthaloyl)-bis-leucine diacid and *N,N'*-(4,4'-oxydiphthaloyl)-bis-methionine diacid with several aromatic diols in a system of TsCl, Py and DMF (method I) or thionyl chloride/Py (method II) [214–216] (Figure 21). The influence of aging time, amount of DMF, concentration of monomers and condensing agents and reaction time on the physical properties of the resulting polymers was investigated by this group. Direct polyesterification in method II showed a series of advantages including improved reaction yield and higher M_w of the resulting PEIs and is very efficient in terms of cost and energy. The

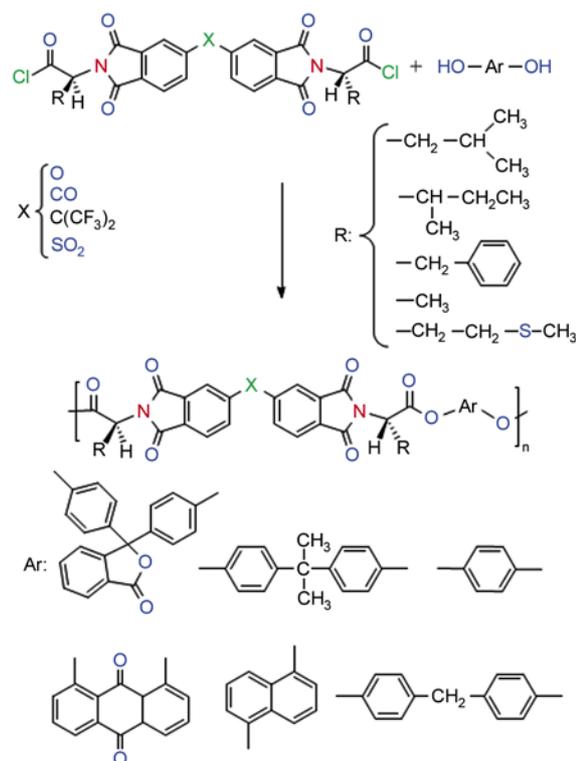


Figure 21. Preparation of different PEIs by reaction of several imide dicarboxylic acid and diols [210–219]

resulting PEIs had good yield and moderate inherent viscosity. The obtained polymers were thermally stable and were readily soluble in common organic solvents. Optically active PEIs containing benzophenone tetracarboxylic and L-phenylalanine or L-alanine moieties were synthesized from N,N'-(4,4'-carbonyldipthaloyl)-bisphenylalanine or L-alanine diacid chloride with several aromatic diols by low-temperature solution polycondensation in $\text{CHCl}_3/\text{Et}_3\text{N}$ solution and under microwave irradiation in the presence of a small amount of a polar organic medium such as *o*-cresol [217, 218] (Figure 21). These PEIs showed optical rotation and were readily soluble in various organic solvents and had moderate thermal stability. The same researchers also used L-isoleucine amino acid as a biocompatible material as well as optically active pure and chemical functional group in the polymer backbone for the formation of a series of new PEIs by direct polyesterification from aromatic diols and imide dicarboxylic acid which was prepared from trimellitic anhydride and L-isoleucine amino acid in a system of $\text{TsCl}/\text{Py}/\text{DMF}$ [219] (Figure 21). Mallakpour's group also reported on [220] the synthesis of optically active PEIs via direct polycondensation of N-trimellitylimido-L-methionine with various aromatic diols such as bisphenol A, phenolphthalein, 1,5-naphthalendiols, 2,6-dihydroxytoluene, hydroquinone, biphenyl-2,2'-diol, 1,4-dihydroxyanthraquinone. The resulting PEIs were obtained in good yields and exhibited low to moderate inherent viscosities ranging from 0.15 to 0.40 dL/g. All of the PEIs showed good solubility and readily dissolved in aprotic polar solvents. Recently, this group [221] synthesized several novel chiral and potentially biodegradable PEIs bearing natural amino acids in the main chain as well as in the side chain via direct polyesterification of N,N'-(pyromellitoyl)-bis-(L-tyrosine dimethyl ester) as a biodegradable optically active phenolic diol and synthesized diacids containing different amino acids and phthalimide group in the side chain in $\text{TsCl}/\text{Py}/\text{DMF}$ system as a condensing agent under conventional heating condition.

A series of axially chiral PEIs were prepared by the polycondensation reactions of new axially asymmetric dianhydrides, (R)-2,2'-bis(3,4-dicarboxybenzoyloxy)-1,1'-binaphthyl dianhydride and (S)-2,2'-bis(3,4-dicarboxybenzoyloxy)-1,1'-binaphthyl

dianhydride, and various diamines with aromatic, semiaromatic, and aliphatic structures by Song *et al.* [222]. The film-forming ability of PEIs was tested by the casting of 10% (w/v) solutions in DMAc onto a glass slide. All the polymers were able to form tough, flexible, and transparent films with 6–10 μm thick.

Kricheldorf's group [223] prepared a series of chiral PEIs by polycondensation of acid chloride of 4-aminocinnamic acid trimellitimide with various chiral diols at low or moderate temperature (0–60°C) in the presence of Py as HCl acceptor. They also synthesized [224] several cholesteric PEIs from (S)-pentoxyterephthalic acid or (S,S)-2,5-bis(pentoxyterephthalic acid and N-(4'-hydroxyphenyl)-4-hydroxyphthalimide. 2,5-bis(dodecyloxy)terephthalic acid and 2-(4'-chlorophenoxy)terephthalic acid were used as comonomer.

2.7. Poly(amide-ester-imide)s

A series of optically active poly(amide-ester-imide)s (PAEIs) based on bis(p-aminobenzoic acid)-N-trimellitylimido-S-valine or L-isoleucine were prepared via polyesterification reaction of synthetic chiral diacids and different aromatic diols using $\text{TsCl}/\text{Py}/(\text{DMF})$ as a condensing agent by Mallakpour and coworkers (Figure 22) [225, 226]. The effect of the amount of DMF, aging time, reaction temperature, and reaction time was studied on the reaction yields and polymer viscosities. The resulting novel optically active PAEIs with inherent viscosities ranging 0.10–0.71 dL/g were obtained in high yield.

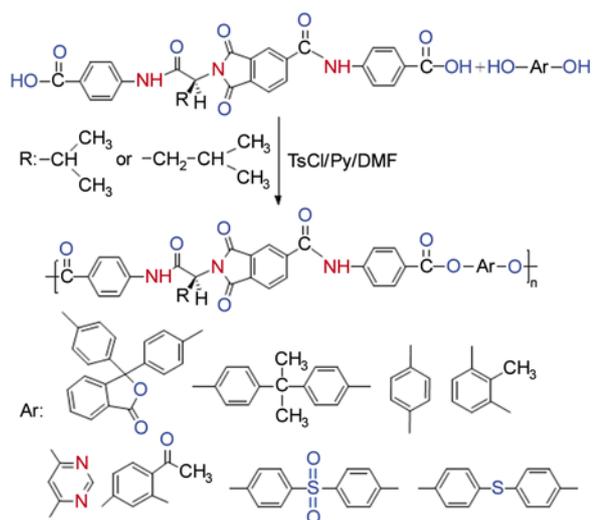


Figure 22. Preparation of optically active PAEIs [225, 226]

Li *et al.* [227] prepared PAEIs from amino acid (4-aminobenzoic acid, 3-aminobenzoic acid, or 6-aminohexanoic acid) and N-(4-hydroxyphenyl) phthalimide-4-carboxylic acid, N-(3-hydroxyphenyl) phthalimide-4-carboxylic acid, or N-(2-methyl-4-hydroxyphenyl) phthalimide-4-carboxylic acid in the presence of diphenylchlorophosphate and Py as direct condensation agents. The inherent viscosities of PAEIs were in the range of 0.13–0.95 dl/g. Thermotropic liquid crystalline behavior of these polymers was examined by DSC and optical polarizing microscopy. These PAEIs showed thermotropic liquid crystalline behavior in the range of 190–426°C.

2.8. Polyurethanes

Polyurethanes (PU)s, having a relatively short history, of slightly more than 65 years, became one of the most dynamic groups of polymers, and their use covers practically all the fields of polymer applications such as foams, elastomers, thermoplastics, thermorrigids, adhesives, coatings, sealants, fibres and so on. PUs are used in nearly every aspect of daily life, changing the quality of human life. Furniture, bedding, seating for cars, shoe soles, thermoinsulation for refrigerators and buildings, wood substitutes, packaging, and coatings, are only a few common examples of PU use in every day life [228]. Because of importance of PUs and optically active polymers, many studies have been performed in the synthesis of optically active PUs by researchers. Chen *et al.* [229] synthesized an optically active PU by the step-growth polymerization of (2R,3R)-(+)-diethyl L-tartrate, MDI and polyeth-

ylene glycol (PEG) with various molecular weights at 60°C in DMSO. Chirackal Varkey and Sreekumar [230] prepared the TDI based optically active PUs consist of chiral units (diethyl-(2R,3R)(+)-tartrate) and donor-acceptor building blocks in the main chain with a helical conformation in the macromolecular chain by using DBTDL catalyst by incorporating the amido diols which were obtained by the aminolysis of ϵ -caprolactone by using the diamines, diaminoethane, diaminobutane, and diaminohexane, respectively. The effect of incorporation of the chiral molecule diethyl-(2R,3R)-(+)-tartrate on the properties of PUs was studied by changing the chromophores and also by varying the chiral-chromophore composition. An azobenzene PU containing chiral units with high thermal stability was synthesized by Qiu *et al.* [231] via step-growth polymerization of a chiral diol derived from diethyl-(2R,3R)-(+)-tartrate and 4-(4'-nitrophenylazo) phenylamine with TDI in the presence of the catalyst T-12 (Figure 23). It was a levopolymer whose optical rotation and melting point were -18.06 and 302°C , respectively. They investigated optical parameters, including the refractive index (n) and thermo-optic coefficient (dn/dT); the dielectric constant (ϵ) and its variation with temperature; and the thermal volume expansion coefficient and its variation with temperature of PU. These parameters are of great significance for the optical application of the material, particularly for the development of optical materials because of the control of their n values. The results indicated that the PU could be used in the design of high-performance thermo-optic polymer devices. Nagai *et al.* [232]

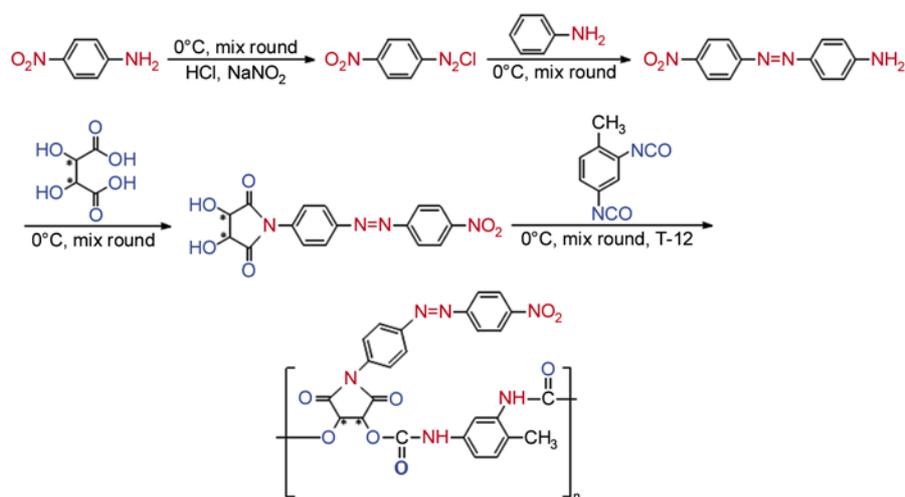


Figure 23. Synthesis of the chiral azobenzene PU containing [231]

reported on the synthesis and self-step-growth polymerization of optically active monomers having both isocyanate and hydroxyl groups derived from tyrosine. The resulting PUs had specific head-to-tail structures and some regulated, higher order structures such as helical conformation because of its asymmetric carbon. A series of optically active PUs were prepared by Chen *et al.* [233] from step-growth polymerization of chiral 1,1'-binaphthyl and TDI and the high-intensity ultrasonic was applied to the preparation of PU/TiO₂ nanocomposites. TGA studies indicated that thermal stability of the nanocomposites has improved with increasing nanoparticles content. Infrared emissivity study showed that the nanocomposites possessed lower emissivity value than those of PU and TiO₂, respectively. The ultrasonic method is a simple and inexpensive route to synthesize the polymer/nanoparticles, which can be extended to prepare a novel low infrared emissivity material. Zhou's group [234] also described the synthesis and the properties of novel optically active PUs based on chiral binaphthol via direct step-growth polymerization. The effect of optical purity on the specific rotation of the polymers was studied and results showed that the specific rotation of the polymer kept increasing with the optical purity, it may be explained that the increment of the optical purity caused a bigger chiral groups density. The resulting polymers displayed low infrared emissivity, which were expected to have potential application in the field of stealth materials.

2.9. Polyureas

Diamines are frequently used to cure diisocyanates, especially isocyanate prepolymers, to give polyureas. The reaction has the advantages that no by-products are produced and that it can be carried out at low temperatures. Optically active polyureas have been reported to be prepared from optically active diisocyanate (L-lysinediisocyanatemethyl ester) and optically inactive linear diamine H₂N(CH₂)_n, where $n = 2-6$ and 9. Polymerization reaction was carried out by step-growth polymerization method [235]. The values of optical rotation of obtained polyureas were dependent on the methylene number of diamines. Asymmetric selective polyaddition of L-lysinediisocyanatemethylester for racemic 1,2-diaminopropane was unsuccessful.

A series of chiral polyureas having chiral diamine unit as part of the backbone were synthesized via step-growth polymerization of two chiral diamines and several aromatic and aliphatic diisocyanates by Dunjic *et al.* [236]. The resulting polymers were complexed with rhodium and used as catalysts in asymmetric hydride transfer C=O bond reduction.

2.10. Poly(imide-urethane)s

A series of poly(imide-urethane)s (PIU)s derived from N,N'-(pyromellitoyl)-bis-(L-leucine) diisocyanate and aromatic diols were synthesized via solution polycondensation by Mallakpour and Shahmohammadi [237]. Polymers were obtained in good yield and moderate inherent viscosity in the range 0.18–0.28 dl/g. The resulting PIUs have potential to be used as packing materials in column chromatography. Wang *et al.* [238] reported on the synthesis and characterization of optically active helical PIU with optical activity based on R-1,1'-binaphthyl-2',2'-diol and racemic PIU based on racemic 1,1'-binaphthyl-2',2'-diol. The thermal stability of R-PIU was higher than that of racemic-PIU due to the higher degree of hydrogen bond for R-PIU. In another study, this group prepared [239] helical PIU@attapulgit composite based on the surface modification of attapulgit. The results indicated that helical PIU has been grafted onto the surfaces of the modified attapulgit without destroying the original crystalline structure of attapulgit. The infrared emissivity of result composite was also investigated. The infrared emissivity value of PIU@attapulgit composite (0.628) was lower than that of bare attapulgit (0.934) due to the interfacial interactions between organics and inorganics. This work opened up a possibility for the preparation of infrared low-emissive materials.

2.11. Poly(urea-urethane)s

The synthesis and characterization of five new optically active poly(urea-urethane)s (PUU)s by solution step-growth polymerization of (1S,2S)-(+)-2-amino-3-methoxy-1-phenyl-1-propanol with diisocyanates (MDI, TDI, HDI, IPDI, *m*-xylylene diisocyanate) was reported by Chen and Tseng [240]. The conformation of the polymers in film state was studied by CD spectra, by comparison with the corresponding model compounds which

were synthesized from (1S,2S)-(+)-2-amino-3-methoxy-1-phenyl-1-propanol and phenyl isocyanate or propyl isocyanate. Polymers derived from aromatic diisocyanates formed as ordered conformation in the film state, while those from aliphatic diisocyanates did not. After packing as chiral stationary phases of HPLC, the polymers showed selective resolution to trans-stilbene oxide and trans-1,2-cyclopentanedicarboxanilide. Wang *et al.* [241] prepared several helical R/S-PUUs with R/S-1,1'-binaphthyl-2',2'-diol, TDI, and 1,4-diaminobenzene by a simple step-growth polymerization reaction. R-PUU and S-PUU were two enantiomorphs with wonderful mirror-image symmetry. The optical rotation values were +54.7 and -60.7°, respectively. The left-handed rotation structure was more stimulative for thermal stability than the righthanded rotation below 250°C because of both conformation and interchain hydrogen bonds, and they were reversed above 250°C; this can be attributed to the breaking of hydrogen bonds. The crystallizability of S-PUU was better than that of R-PUU because of the more orderly hydrogen bonds resulting in the interchain effects of S-PUU. The interchain hydrogen bonds were the plane-bifurcated structures, which are more stable and interlocked to the helical structures. In another study, this group also synthesized an optically active helical PUU with single-handed helical conformation by step-growth polymerization of chiral binaphthyl compound with MDI [242]. The interchain hydrogen bonds were controlled and changed in the synthesized progress, and they were affected by the helical conformation and the optical activity.

2.12. Poly(amide-imide-urethane)s

A series of optically active poly(amide-imide-urethane)s (PAIUs) based on PEG and MDI were prepared by Mallakpour's group [243–247] by the chain extension reaction of NCO terminated oligoamide prepared from the reaction of a chiral amino acid based dicarboxylic acid having a preformed imide ring according to diisocyanate route, with different M_W of PEG polyols by the two-step methods. The synthetic procedure referred to as two-step method, is effective for the synthesis of the multiblock copolymers having high structural regularity. Systematic study of PAIUs based PEG-MDI obtained in the presence of different solvents

and catalysts under different reaction time and temperatures demonstrated the influence of reaction condition on the efficiency of the polymer chain growth, viscosity, solubility and therefore processability of PAIUs. Best condition for the preparation of these optically active PAIUs was NMP as a solvent in the absence of any catalyst. They also synthesized [248] a new class of optically active PAIUs via a two-step diisocyanate route. In the first step, MDI was reacted with different diacids to produce an isocyanate-terminated oligo(amide imide). The chain extension of the previous hard segment with PEG with a M_W of 400 dalton was the second step for furnishing a series of new PAIUs. N-Trimellitylimido-L-leucine was used as a diacid monomer for polycondensation reactions. Polymerization reactions were performed without any catalyst or with Py or DBTDL as a catalyst. The optimized reaction conditions were used for the reaction of N-trimellitylimidoisoleucine, N-trimellitylimidomethionine, N-trimellitylimido-S-valine, and N-trimellitylimidophenyl-alanine as diacid monomers with MDI. In another study by Mallakpour *et al.* [249], a new series of optically active PAIUs were synthesized via two-step reactions. In the first step, MDI reacted with several PEGs such as PEG-400, PEG-600, PEG-2000, PEG-4000, and PEG-6000 to produce the soft segment parts. On the other hand, 4,4'-(hexafluoroisopropylidene)-N,N'-bis(phthaloylleucine-p-amidobenzoic acid) was prepared from the reaction of 4,4-(hexafluoroisopropylidene)-N,N'-bis(phthaloylleucine) diacid chloride with p-aminobenzoic acid to produce hard segment part. The chain extension of the above soft segment with the amide-imide is the second step to give a homologue series of PAIUs.

2.13. Poly(amide-imide-ether-urethane)s

Mallakpour's researcher group [250] used mathematical method for the optimization of some of the reaction parameters, that can influence viscosity and polymer chain growth of thermally stable optically active poly(amide-imide-ether-urethane)s (PAIEU)s based on a reaction component, bis(p-amidobenzoic acid)-N-trimellitylimidoleucine. It was shown that, the temperature of 85°C and the reaction time of 2 h gives the highest viscosity for any PEG M_W . It means that, in spite of what they assumed, the constructed correlation in this study

showed there was no significant difference between the viscosities of polymers based on different M_w of PEGs. Another series of optically active PAIEUs based on polytetrahydrofuran (PTHF), of number-average molecular weights (M_n) = 1000 dalton as soft segment were synthesized by Mallakpour and Rafiemanzelat [251]. These copolymers were prepared via direct polycondensation reaction of an aromatic diacid based on L-leucine with preformed imide ring, MDI and PTHF-1000. The effect of the introduction of bis(p-amidobenzoic acid)-N-trimellitimidoleucine (BPABTL) into PU back-bone on their properties was also studied. It was shown that BPABTL is an interesting candidate to incorporate amide, imide and amino acid moieties into segmented PUs and prepare them with more thermal stability, induced more crystallinity as well as good solubility.

2.14. Poly(amide-imide-ether-urea)s

Mallakpour and Seyedjamali [252] have also investigated the synthesis and characterization of a new multifunctional diamine containing L-leucine moieties in the structure and its polymerization with various diisocyanates to afford corresponding optically active poly(amide-imide-ether-urea)s. These components supplied several functional groups which showed some regulation effects on the properties of final polymers. The incorporation of stiff functions (imide, amide and urea groups) and flexible functions (aliphatic and ether moieties) made polymer chains flexible enough to be soluble in the

common aprotic organic solvents as well as preservation of good thermal stability especially when aromatic diisocyanates were employed. The existence of isobutyl moieties in the structure of L-leucine may be the source of the increase of the free inter-chain volumes, suppressing the usual attraction of polymer chains as well as inducing the asymmetric character.

3. Synthesis of optically active polymers by Suzuki-Miyaura coupling reaction

The palladium-catalyzed cross-coupling reaction between organoboron compounds and organic halides or triflates provides a powerful and general methodology for the formation of carbon-carbon bonds. Recently, this reaction has been called the Suzuki coupling, Suzuki reaction, or Suzuki-Miyaura coupling [253]. Lately, many optically active conjugated polymers were synthesized by this reaction. Hu *et al.* [254] synthesized an optically active conjugated poly(arylenevinylene). They selected 1,1'-bi-2-naphthol, and its derivatives as building blocks in the construction of main chain chiral polymers because of their outstanding asymmetric differentiation properties. This polymer was soluble in common organic solvents and could be cast into self-standing films. This researcher group also prepared [255] an optically active polyarylene from the palladium-catalyzed Suzuki cross-coupling of an optically active binaphthyl molecule, 2'-bis(hexyloxy)-1,1'-binaphthyl-6,6'-diboronic acid, with 1,4-dibromobenzene. GPC analysis of this

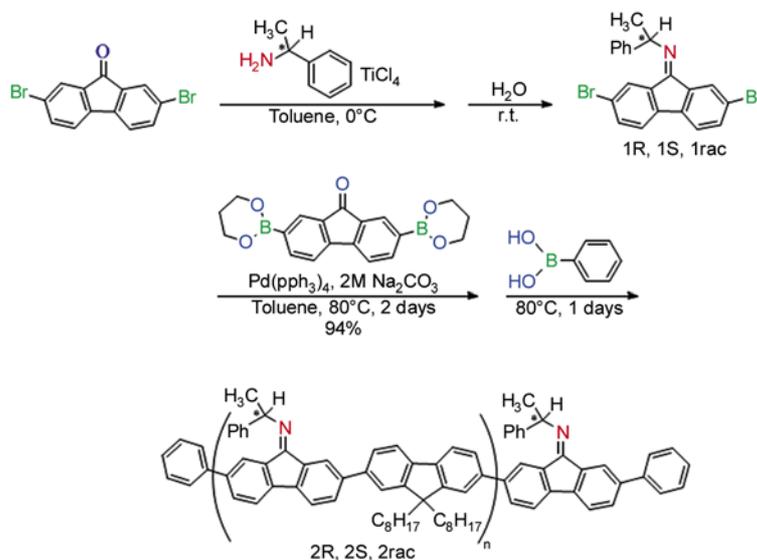


Figure 24. Synthesis of optically active polyfluorenes with chiral Schiff bases in the side chain by the palladium-catalyzed Suzuki-Miyaura coupling polymerization [258]

polymer showed $M_w = 41\,000$ and $M_n = 20\,000$. The specific optical rotation of resulting polymer was -289.4° . In another study Pu's group [256] synthesized a series of binaphthyl-based chiral poly(aryleneethynylene)s with different M_w by Suzuki coupling reaction of an optically active binaphthyl molecule, (R)-2,2'-bis(octadecyloxy)-6,6'-diethynyl-1,1'-binaphthyl, with 1,4-diodobenzene in the presence of tetrakis(triphenylphosphine)palladium(0) and cuprous iodide catalysts. The synthesis of the first optically active 1,1'-bi-2-naphthol and 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl copolymer by Suzuki coupling reaction was reported by Yu *et al.* [257]. The resulting polymer showed $M_w = 11\,600$ dalton and $M_n = 7500$ dalton as was measured by GPC relative to polystyrene standards. They utilized this polymer in a tandem catalytic asymmetric diethylzinc addition and asymmetric hydrogenation of p-acetylbenzaldehyde to generate a chiral diol.

The synthesis of optically active poly(fluorene-alt-chiral iminofluorene)s using 1-phenylethylamine as a chiral auxiliary was described by Asai *et al.* [258]. Optically active polyfluorenes were synthesized by the palladium-catalyzed Suzuki-Miyaura coupling polymerization of 9,9'-dioctylfluorene-2,7-bis(trimethyleneborate) with a chiral Schiff base monomer (imino group modified-fluorene) (Figure 24). The obtained polymers showed intense green emission with high quantum efficiency.

4. Synthesis of optically active polymers by Sonogashira reaction

In 1975, Sonogashira *et al.* reported [259] for the first time a coupling reaction of terminal alkynes with aryl or vinyl halides. Recently, this reaction has been used for the synthesis of different optically active polymers. Block and Hecht [260] used this reaction for the synthesis of a series of block copolymers composed of a highly isotactic and non-racemic poly(propylene oxide) segment joined to a poly(phenylene ethynylene) segment, with either meta or para connectivity. Two regioregular poly(p-phenyleneethynylene-alt-m-phenyleneethynylene)s bearing (–)-trans-myrtanoxyl side groups with different substitution patterns were designed and synthesized by Li *et al.* [261] via Sonogashira reaction. These two polymers have the same chemical com-

ponent and main chain structure, but the substitution pattern of the chiral groups was different from each other. The effects of annealing temperature and time on the properties of the films were investigated by ultraviolet-visible absorption, fluorescence and CD spectra. The observations indicated that the substitution pattern of the chiral side groups had significant effect on the chiroptical properties of chirally substituted conjugated polymers.

5. Conclusions

In this paper, synthesis of various optically active condensation polymers was reviewed. There is currently intense interest in the synthesis and control of optically active polymers. Many of the condensation polymers reviewed here are prepared by polycondensation reaction of chiral monomers, which is more versatile, inexpensive and generally poor in control than addition polymerization. Optically active polymers often play important roles as key fundamental materials for welldefined polymers with specific secondary and/or tertiary structures. Optically active polymers have stimulated wide interest from synthetic, structural, and functional viewpoints. They have been extensively studied aiming at the application in optoelectronic devices and chiral recognition materials including asymmetric catalyst, chiral stationary phase in HPLC, enantioselective permeation membrane, chiral adsorbent for separation of racemates and in liquid crystals. Nature uses chirality as one of the key structural factors to perform a series of complicated functionalities such as molecular recognition and catalytic activities and can be saying that chirality is important for life.

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