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A SHORT REVIEW ON TRANSPARENT AND COLORLESS POLYIMIDES

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Abstract. Polyimides are known as high performance polymers that are widely used in opto-electronic devices as well as other high engineering applications. Among polyimides, in particular transparent and colorless polyimides (CPIs) are recently in high demand in opto-electronic industries because of their transparency as well as balanced thermo-mechanical properties. It is known that the charge transfer complex (CTC) formation in aromatic polyimides provides them to have brownish-yellow colors as well as optical opaqueness, for which their application in optoelectronic devices are limited, while the CTC also donates a high glass transition temperature (Tg) by restricting their segmental mobility. In this short review, recent trends to prepare CPIs with balanced thermo-mechanical properties were overviewed, which have been reported mainly by our group for years, with expecting to be a useful guideline to the synthesis and design of CPIs. Main efforts to synthesize CPIs have been generally oriented toward to the reduction of the intra- or inter charge transfer interactions between diamines and dianydrides in the aromatic polyimides through the design conceptions including the incorporation of bulky substituents, non-coplanar segments, fluorine atoms, and alicyclic diamines and dianhydrides, etc. to prepare PIs. Thus prepared CPIs possess good transparency and colorlessness with high Tg's.

Keywords: Polyimides, transparent, colorless

Classification numbers: 2.9.3., 2.1.3.

1. INTRODUCTION

Aromatic polyimides (PIs) have been widely used in various microelectronic and electric industries due to their easy processing, good electric insulation property and excellent high thermal and mechanical properties due to their high glass transition temperature (Tg), i.e. over 200 °C or even much higher [1], which is mainly attributed to their imide groups on the backbone. The diamine (electron donating) and dianhydride (electron accepting) of the PIs lead to the formation of the charge transfer complex (CTC) in between molecules (intra- and inter-), which provides a high Tg by restricting their segmental mobility.

Paradoxically, however, the CTC let aromatic PIs have brownish-yellow colors as well as optical opaqueness, for which their application in optoelectronic devices are limited, where optical transparency and colorlessness are needed [2 - 5] Figure 1 illustrates the CT interactions of a typical PI, i.e. poly(p-phenylene pyromellitimide).

Thus, there have been many research attempts to improve the optical transparency of PIs' with maintaining their thermo-mechanical properties via a variety of syntheses approaches to inhibit the CTC formation[1], such as introducing bulky substituents [6, 7], asymmetric segments [8, 9], fluorine atoms [10, 11], and alicyclic dianhydrides or diamines [12 - 15].

This short review overviews briefly typical examples of the transparent and coloress PIs (CPIs) mainly based on our previous works for years.

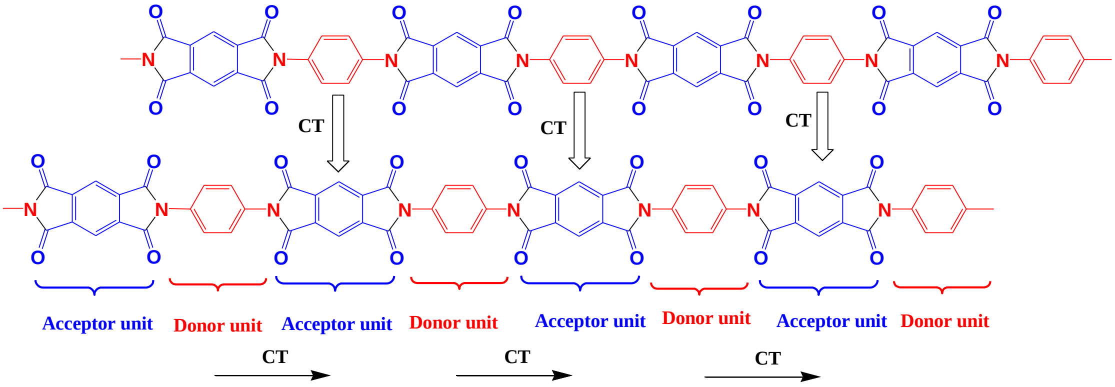


Figure 1. Intra- and intermolecular CT interactions in poly(p-phenylene pyromellitimide [1].

2. GENERAL TRENDS TO PREPARE CPI

There are three kinds of PIs as shown in Figure 2, i.e. fully aromatic PIs, semi aromatic PIs and fully aliphatic PIs depending on the monomers that were used for the syntheses of PIs [16]. Aromatic PIs are synthesized using an aromatic diamine and dianhydride. For semi-aromatic PIs, one monomer is aromatic, while the other one is aliphatic. The fully aliphatic PIs are synthesized using aliphatic dianhydride and diamine. Either of or both nonaromatic diamines or dianhydrides are used for the synthesis of CPIs [1, 17, 18]. The aliphatic polyimides (APIs) generally exhibit better transparency and solubilities than aromatic PIs, whereas they possess lower dimensional properties than that of aromatic PIs. Typical examples of monomers to be used to synthesize APIs are displayed in Figure 3 [16]. Alicyclic PIs also exhibit high transparency due to their low CT interaction and can be used in optoelectronic devices and interlayer dielectrics [21, 22]. For example, aliphatic PIs (APIs) using bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride with several alicyclic and aliphatic diamines were reported to be optically transparent and soluble in several organic solvents [21]. We found that the use of adamantane (tricycle[3.3.3.1.1]decane) group in the APIs lead to excellent thermal stability and low dielectric constant in addition to high transparency and solubility [22].

It is interesting to note that the properties of alicyclic PIs can be further improved by introducing siloxane groups in the backbone of the APIs. Figure 4 illustrates the copolymers of APIs and siloxane groups, e.g. APISiOs. The copolymers exhibited both high thermo-mechanical properties of PIs and ductility and low moisture absorption of siloxanes as well as excellent solubility in organic solvents [16, 19, 20, 23].

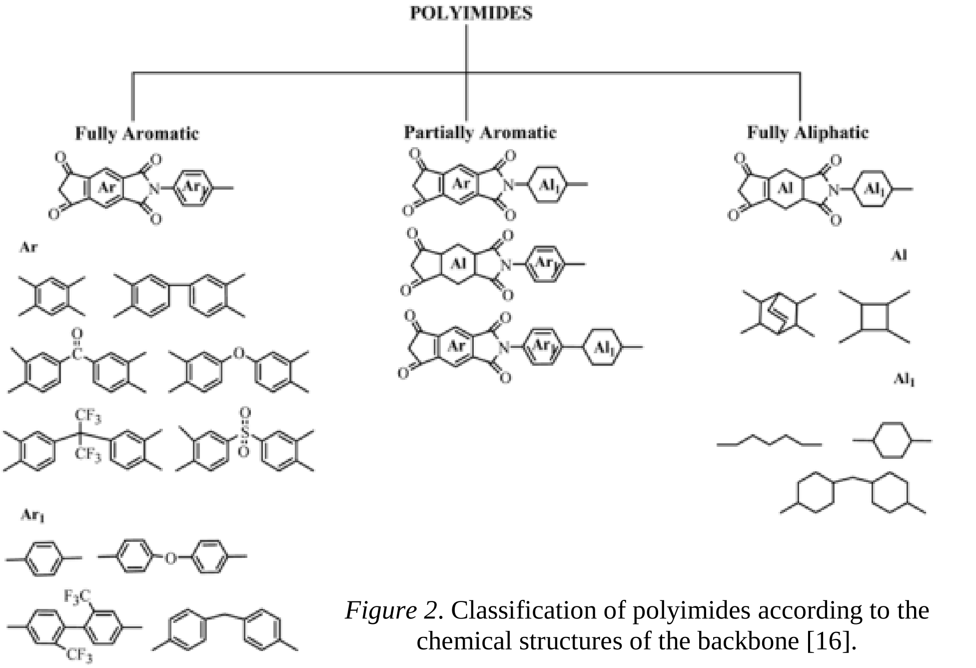


Figure 2. Classification of polyimides according to the chemical structures of the backbone [16].

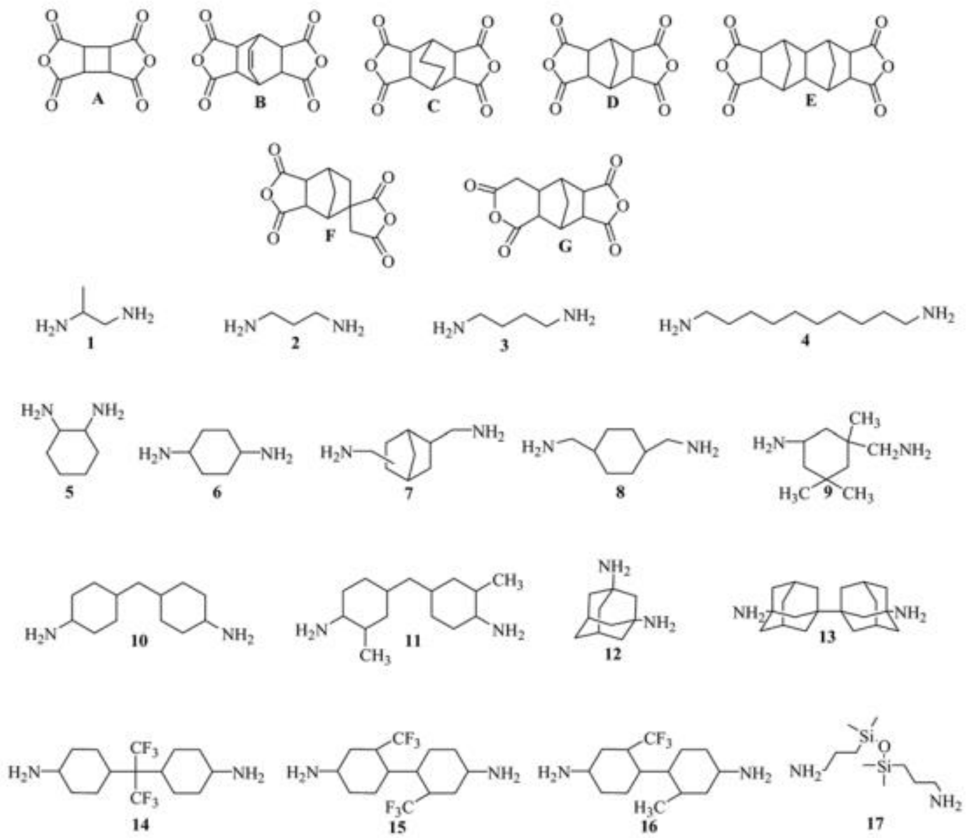


Figure 3. Typical monomers used to synthesize APIs[16].

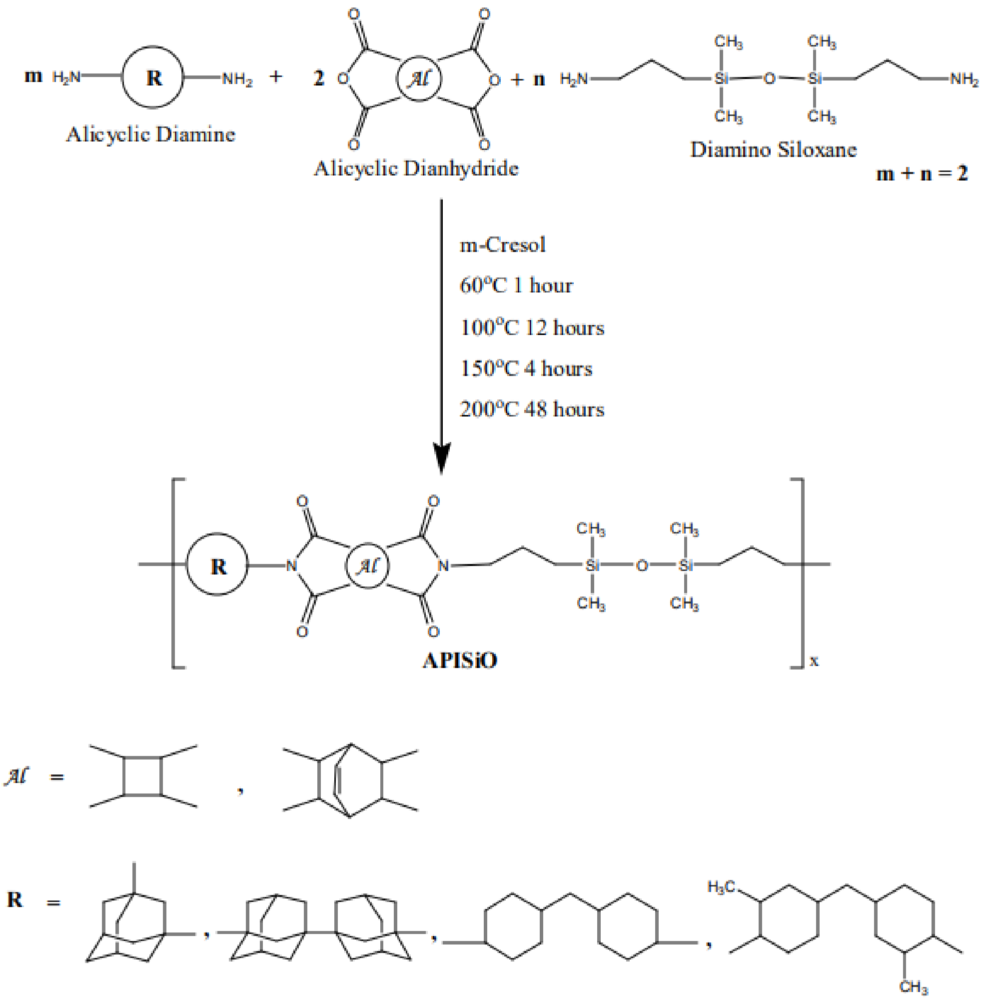


Figure 4. Scheme to synthesize fully APISiO [23].

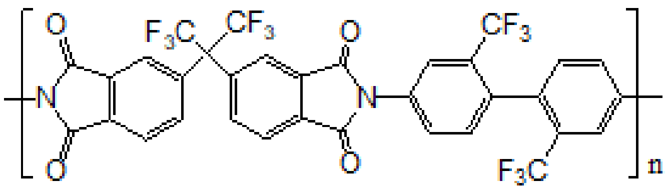


Figure 5. Chemical structures of 6FDA(1) and TFDB(2) [1].

Another example of aromatic CPIs is by introducing fluorinated one. The most famous CPIs till date were prepared from 2,2-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (6FDA) and 2,2-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) (2) [24, 25].

The fluorinated CPI is well known for its superior transparency and colorlessness as well as high thermal stability and good organo-solubility [1]. Many reports have also been made to develop new types of non-fluorinated CPIs. For instance, chlorinated PIs was reported by our group [26], as shown in Figure 5. The fully aromatic PI from TCDB (2,2',5,5'-tetrachlorobenzidine) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) PI was colorless and transparent. The transparency of the chlorinated PI was quite high, which is almost similar as that of 6FDA/TFDB PI.

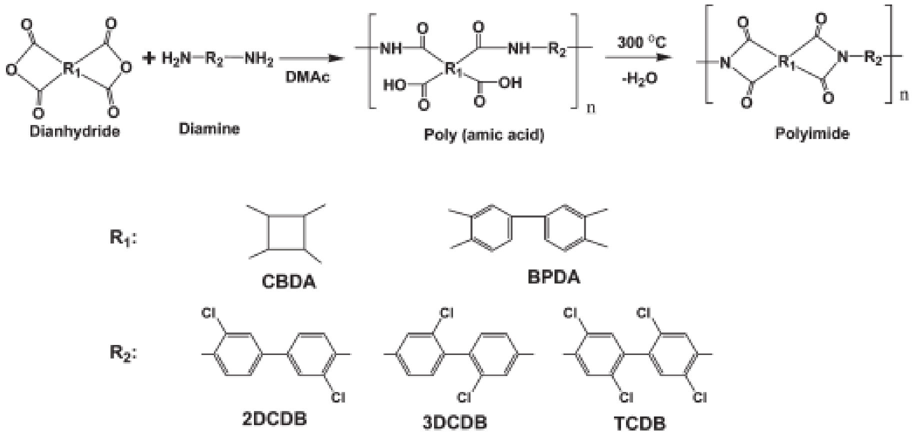


*Figure 6***.** Preparation procedure of chlorinated PIs [26].

PIs are generally synthesized by mixing diamine and dianhydride monomers in a polar high -boiling-point solvent, which is carried out by conventional polycondensation method via poly(amic acid) solution. Though dimethylacetamide (DMAc) and N-methyl-2-pyrrolidone (NMP, preferred for its lower toxicity) are normally used as a solvent, other solvents are also used such s N,N-dimethylforamide (DMF), dimethyl sulfoxide (DMSO), *meta*-cresol, and γ-butyrrolactone (GBL) [1]. Special care should be taken to prepare PI films with high transparency during polymerizations. In particular, the use of highly purified monomers is desirable in order to avoid contamination in the polymerization media.

3. RECENT EFFORTS TO SYNTHESIZE NEW MONOMERS TO PREPARE CPI

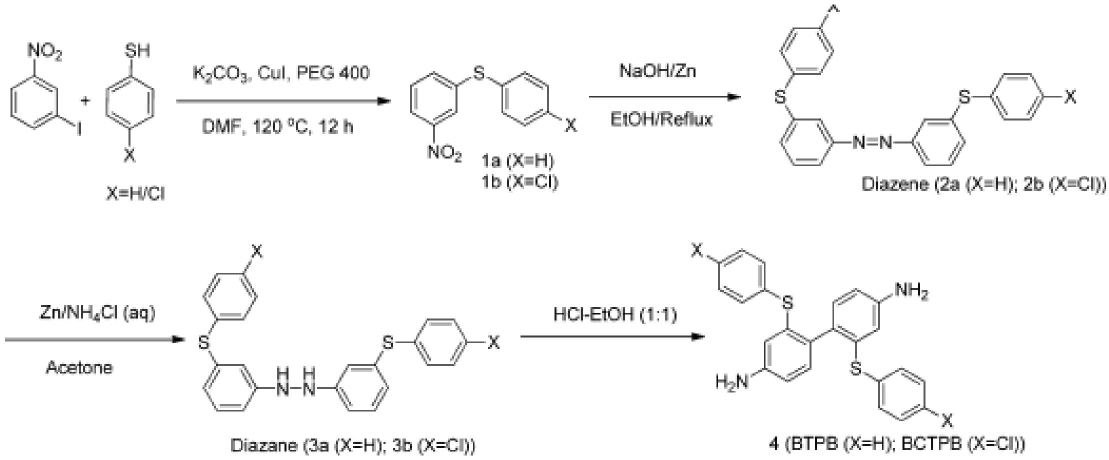
A general overview of design concepts of new monomers for CPIs was well reviewed in our work [1]. Thus it is recommended for readers to refer the review article. Here are just some of typical examples that were reported in my laboratory.

As stated in the Introduction, the transparency and solubility of PIs can be improved with restricting the CTC formation if bulky units are introduced in the main chain or as side groups. For this, many new monomers based on previous reports that introduced fluorinated, perfluoro or halogenated groups and so on have been reported.

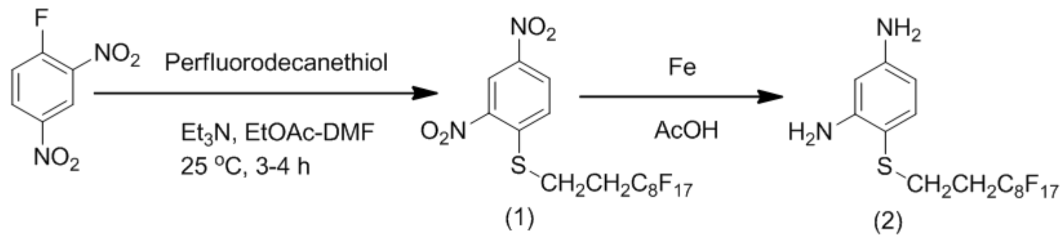
For example, our group prepared 2,2′-bis(4-chlorothiophenyl)benzidine (BCTPB) and 2,2′-bis(thiophenyl)benzidine (BTPB) (Scheme 1) [27]. We reduced (3-nitrophenyl)(phenyl)sulfane and (4-chlorophenyl)(3-nitrophenyl)sulfane, followed by a benzidine rearrangement of the hydrazobenzene derivatives. All the sulfur-containing non-fluorinated aromatic PIs thus obtained showed excellent transparency.

We also prepared 2,2'-Bis((1H,1H,2H,2H-perfluorodecyl)thio)[1,1'-biphenyl]4,4'-diamine (BPFBD) and 2,4-diamino-1-(1H,1H,2H,2H-perfluorodecathio) benzene (DAPFB), and next mixed the two perfluorodecylthio substituted aromatic diamines with 6FDA, followed by thermal imidization [1, 28].

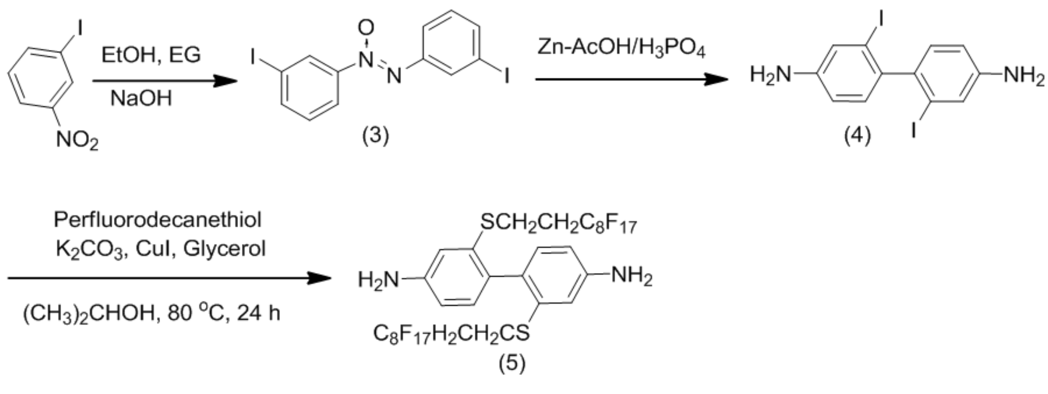
For the first step, S-arylation of perfluorodecanethiol (PFDT) was done with 2,4-dinitro-1-fluorobenzene to synthesize (1), where triethylamine (Et_3N) was used as a base. In the second step to obtain DAPFB(2), the dinitro compound (1) was reduced by Fe/AcOH. BPFBD was synthesized as in the Scheme 3. The cross-coupling reaction of DAIB (4) with PFDT using CuI as a catalyst was done to obtain the BPFBD. The two perfluorinated PI films showed excellent transparency and colorlessness.



Scheme 1. Scheme of syntheses of BTPB and BCTPB. Reproduced with permission [27] Copyright 2015, American Chemical Society.

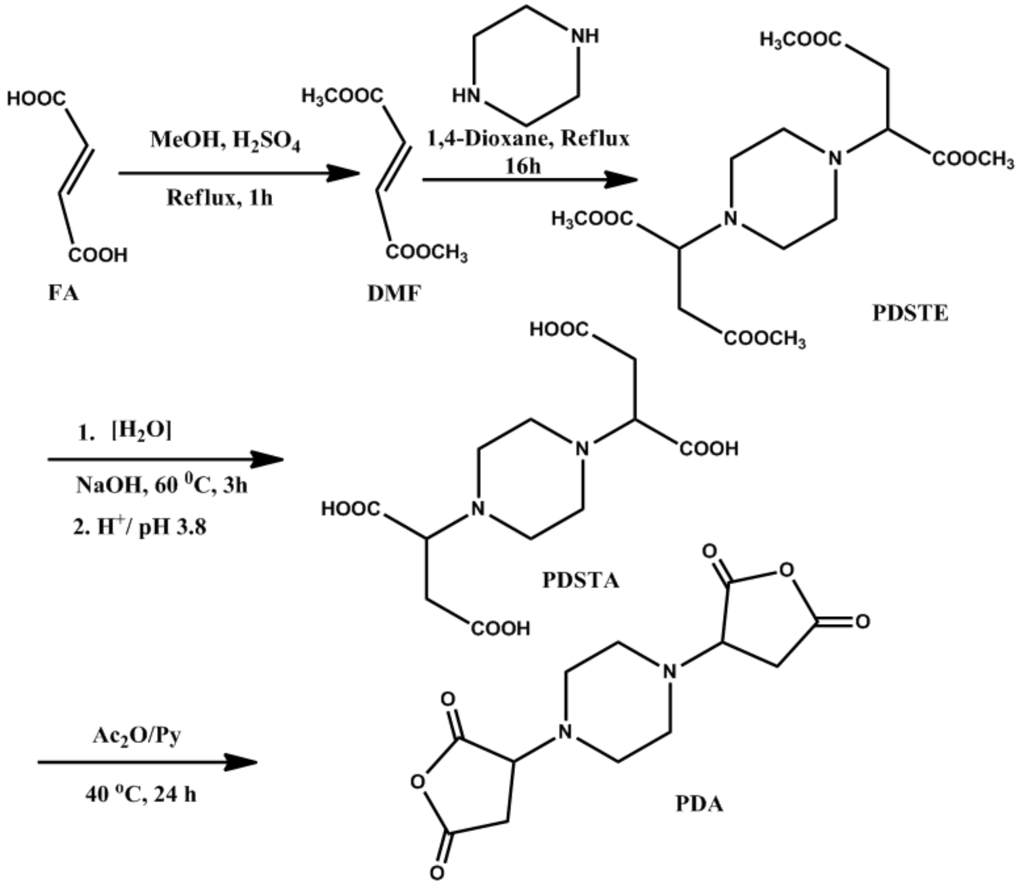


*Scheme 2***.** Synthetic route to prepare DAPFB. Reproduced with permission [28]. Copyright 2015, John Wiley & Sons, Inc.



Scheme 3. Synthetic route to prepare BPFBD. Reproduced with permission [28] Copyright 2015, John Wiley & Sons, Inc.

We also synthesized the piperazine based alicyclic dianhydride monomer (PDA)[1, 29] (Scheme 4). First, we synthesized 1,4-piperazinediyl-tetramethyldisuccinate (PDSTE) from dimethyl fumerate (DMF) and Michael addition reaction with piperazine. Then we prepared the corresponding disuccinic acid derivative hydrolysis of the PDSTE using NaOH catalysis, which were then acidified. Then, the dianhydride PDA was converted from PDSTA using Ac_2O/pyridine. Thus obtained MCA/PDA PI and MMCA/PDA PI films were almost colorless.



Scheme 4. Synthetic route of PDA. Reproduced with permission [29]. Copyright 2014, John Wiley & Sons, Inc.

Recently, it has also been reported that the transparency, solubility and thermal stability can be improved when monomers with noncoplanar (e.g. cardo, spiro, and kink) structures are incorporated into the polymer [1, 30], though we did not investigate this topic yet.

4. CONCLUSIONS

This review overviews recent research trends on the transparent and colorless PIs that were reported mainly by our group for years. Nowadays, colorless and transparent polymers with high thermo-mechanical properties are quite needed in electro-optic industries [1]. PIs are well known high performance polymers having high Tg over 300 °C. However, the deep color of the conventional aromatic PIs due to intra- or inter CT interactions between diamines and dianhydrides limited their application in optoelectronic devices, where colorlessness and transparence are quite essential pre-requisites. Thus many research attempts have been made for the design conceptions such as the incorporation of bulky substituents, non-coplanar segments, fluorine atoms, and alicyclic diamines and dianhydrides to prepare PIs with good transparency and colorlessness with high Tg as well. I hope this short review article could be one of useful guidelines to the synthesis and design of colorless and transparent PIs for readers.

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Declaration of competing interest. The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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