Synthesis and characterization of novel transparent aromatic polyimides derived from ester-containing dianhydrides

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Aromatic polyimides (PIs) have been widely utilized in a variety of electronic and microelectronic applications for their reliable and excellent properties, i.e., considerably high glass transition temperatures (T_g), high resistance to chemicals, good dielectric and mechanical properties.[1] However, the widespread applications of polyimides in optical fields are often limited because of deep coloration which is caused by the strong intra- and intermolecular charge transfer (CT) interactions.[2] So far, much effort has been devoted to development of transparent polyimide films based on structural design. The most effective approach for inhibiting CT interactions is to use non-aromatic (cycloaliphatic) monomers either in diamines or tetracarboxylic dianhydrides.[3] Unfortunately, this approach somewhat sacrifices high-temperature stability. For fully aromatic polyimides, the best way is incorporation of trifluoromethyl group in the monomers, such as 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 2,2'-bis(trifluoromethyl)biphenyl-4,4'-diamine (TFDB), which are commercially available but expensive. Another strategy for obtaining transparent polyimides is to use dianhydrides with low electron-acceptability and diamines with low electron-donatability as monomers for weakening both intra- and intermolecular CT interactions. For example, the polyimide films derived from bis(ether anhydride)s with electron-donating atom "O" in phthalic anhydride, which decreased the electron affinity (E_a) of dianhydride, showed good transparency.[4] However, poly(ether imide)s (PEIs) based on bis(ether anhydride)s decrease the T_g due to the introduction of flexible ether linkage.

Recently, our group are more interested in semi-aromatic or fully aromatic transparent PIs.[5-11] Here, we will show the results of some novel transparent aromatic polyimides derived from ester-containing dianhydrides. Note that the poly(ester imide)s (PEsIs) derived from trimellitic acid anhydride achieved higher T_g and lower water absorption (W_A) etc, which was widely used in electronic devices such as integrated circuits.[12] However, as far as we know, only few reports are available on the comparative study of transparent PEIs and PEsIs derived from bis(ether anhydride)s and bis(ester anhydride)s. Therefore, two series of PIs were prepared by solution polycondensation of different bis(ether anhydride)s and bis(ester anhydride)s with TFDB (**Fig. 1**). The solubility, thermal, mechanical, and optical properties of these PIs as well as the different imidization methods were comparatively well investigated.[10]

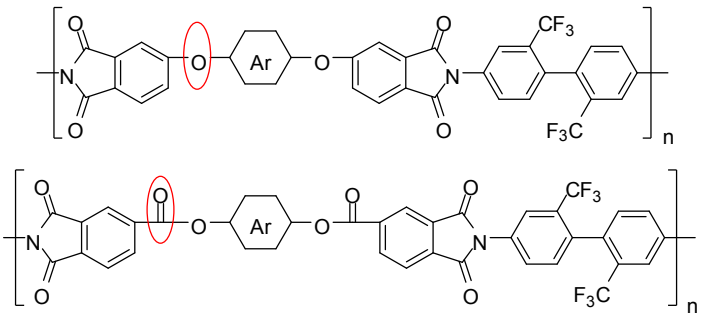

Fig. 1 PEIs and PEsIs derived from bis(ether anhydride)s and bis(ester anhydride)s

Furthermore, the introduction of polar ester linkage in the polymer chain, increased the intermolecular interaction, which was beneficial to improve T_g and lower water absorption, but also increased the electron

affinity of dianhydride due to the electron-withdrawing C=O group directly substituted at phthalic anhydride, which enhanced the electron-acceptability of dianhydride leading to increase the coloration of resulting polyimides at the same time.

Therefore, PEsIs derived from hydroxyl phthalic anhydride would be a best strategy to obtain combined excellent properties. The existence of ester group would remain the excellent properties of poly(ester imide)s, such as high T_g and low W_A, while using electron-donating atom "O" linked with phthalic anhydride would decrease the electron affinity of dianhydride to improve the transparency of films (Fig. 1). To the best of our knowledge, there is no report on the isomeric effect of such linkage on the polyimides. Herein, two series of PEsIs were prepared from two dianhydrides with different electron affinities, bis(trimellitic acid anhydride) phenyl ester (TAHQ) and bis[(3,4-dicarboxylic anhydride) phenyl] terephthalate (PAHP), with various aromatic diamines via solution polycondensation. The thermal stability, solubility, water absorption, coefficient of thermal expansion (CTE), mechanical and optical properties of these polyimides as well as the different properties caused by the different ester linkages were well investigated. The polyimides derived from hydroquinone diphthalic anhydride (HQDPA) were also prepared and investigated for comparison.[11]

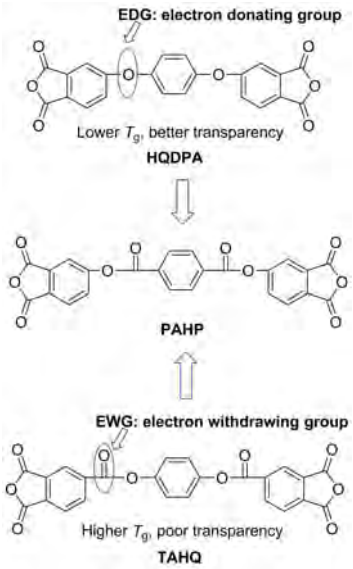

Fig. 2 Chemical structures of HQDPA, PAHP and TAHQ.

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