

Novel High-performance Poly(benzoxazole-co-imide) Resins with Low Dielectric Constants and Superior Thermal Stabilities Derived from Thermal Rearrangement of *Ortho*-hydroxy Polyimide Oligomers

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Abstract: Unsatisfied dielectric property and insufficient thermal stability are major obstacles for the commercialization of polyimide resins in the future ultralarge scale integration (ULSI) or radar-wave-transparent composite applications[1]. The incorporation of *ortho*-hydroxy diamine into a common phenylethynyl terminated oligoimides, aiming to subsequently form additional rigid benzoxazole units by the thermal rearrangement (TR), were prepared. Evolution of the thermal conversion was effectively monitored by the TGA-FTIR, ¹³C NMR and WAXD measurements. The effects of TR-able codiamine on the processing ability of oligoimides, thermal rearrangement and cross-linking reaction, molecular packing and properties, including thermal stability, dielectric property and bonding ability to reinforcing fibers, for the resulting poly(imide-co-benzoxazole) resins have examined in detail. These resultant PI-co-PBOs derived from the thermal rearrangement of *ortho*-hydroxy and imide groups exhibit the combined excellent properties of easy processibility, low dielectric constant, high thermal stability, and excellent bonding ability to a reinforcing glass fiber, indicating them a great potentials as the new low-dielectric constant polymer resins in microelectronic industries or advanced composites.

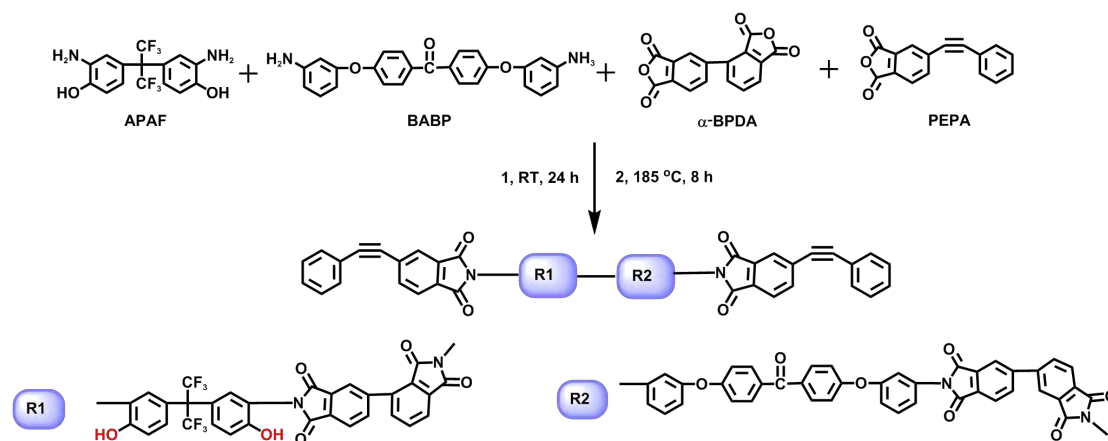
Keywords: poly(benzoxazole-co-imide) resins, thermal rearrangement, low dielectric constant, superior thermal stabilities, bonding ability

1. INTRODUCTION

Aromatic polyimide resins are attractive for their fascinating characteristics of superb thermal stability, flame retardancy, and good chemical resistance as well as satisfied mechanical performance^[1]. Polybenzoxazoles (PBOs), another class of heterocyclic polymers, are ranked as materials of the most superb thermal stability, the highest tensile strength and good chemical resistance among aromatic polymers^[2]. Recently, Mathias and *co*-workers^[3] reported a new way to synthesize polybenzoxazoles by *in-situ* thermal conversion of *ortho*-hydroxy polyimides (HPI) upon heating above 350 °C. The thermal rearrangement of a HPI into polybenzoxazole is expected to significantly reduces the polarizability and increase the free volume of polymer chains, which is advantageous from the low-dielectric point of view. Additionally, the rigid benzoxazole moieties are beneficial for reinforcing the thermal stability and mechanical properties of the resultant materials. All above mentioned features motivate us to incorporate the thermally rearranged benzoxazole moieties by *ortho*-hydroxy polyimide resins to decrease the dielectric constant and improve other properties of the resultant materials.

2. EXPERIMENTAL

As shown in Scheme 1, we prepared a series of *o*-hydroxy functional phenylethynyl-terminated polyimide oligomers containing a commercially available thermal rearrangeable(TR-able) diamine, 2,2'-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (APAF), a common non-TR-able diamine, 4,4'-bis(3-aminophenoxy) benzophenone (BABP) and an asymmetrical dianhydride, 2,3,3',4'-biphenyltetracarboxylic dianhydride (α -BPDA). Thermal rearrangement occurred simultaneously in the cross-linking process of HPI oligomers forming poly(benzoxazole-co-imide) (PI-co-PBO) resins.



Scheme 1. Synthesis of *ortho*-hydroxy polyimide oligomers. Molar ratios of R1:R2 are 60:40, 40:60, 20:80, 10:90, 5:95 and 0:100.

3. RESULTS AND DISCUSSION

TGA and first derivative thermogram (DTG) curves for each PI-*co*-HPI composition, as well as the reference PI oligomer precursor, are illustrated in Figure 1. Thus, all thermograms present a distinct weight loss in the range of 325-425 °C, prior to the generalized decomposition of the polymer backbone around 450-700 °C. Obviously, the weight loss corresponding to this evolution differs for different compositions and increases as the mole fraction of TR-able comonomer APAF increase, indicating the thermal rearrangement reacts to the fullest extent. Therefore, the process of thermal conversion from hydroxyimide oligomers to PI-*co*-PBOs can be optimized by fine-tuning the polymer chains rigidity or regulating the thermal rearrangement protocol.

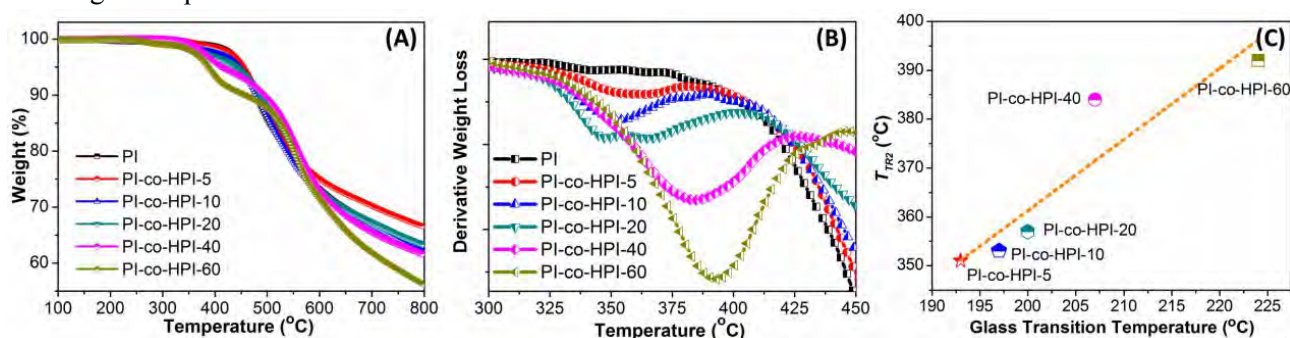


Fig. 1. (A) Thermogravimetric analysis, (B) derivative weight loss curves of *o*-hydroxy oligoimide precursors and (C) the rearrangement temperature T_{TR2} of different PI-*co*-HPI oligoimide precursors as a function of their T_g .

Thermal behaviors of products obtained by thermal rearrangement and cross-linking polymerization of PI-*co*-HPI oligoimides were also studied by DSC and DMA. As shown in Figure 2(A), the prepared thermosets exhibit gradually increased glass transition temperatures with increasing APAF content, which are in accordance with the increased rigidity of polymer chains. In detail, T_g s for the cured PI and PI-*co*-PBOs are 230, 248, 264, 284, 297 and 313 °C, respectively. However, in Figure 10(B), T_g s determined as the peak temperatures of $\tan \delta$ curves in DMA are 20-40 °C higher than the values obtained in DSC analysis. Of particular case is the PI-*co*-PBO-60 containing abundant rigid benzoxazole units, it is difficult to measure the glass transition behavior in DMA measurement due to high fragility of this sample^[4].

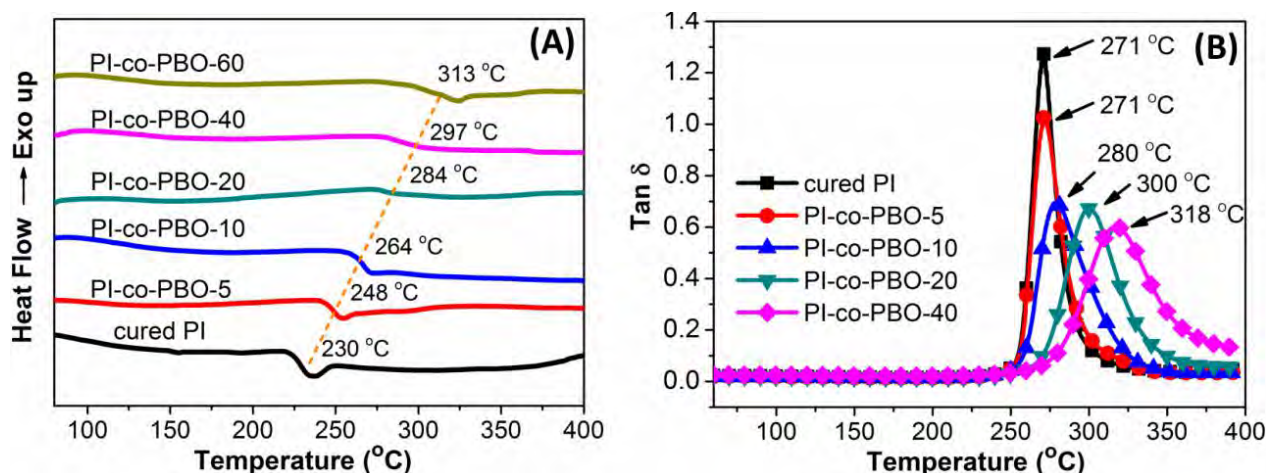


Figure 2. (A) DSC thermograms and (B) DMA curves of cross-linked PI and PI-co-PBO resins.

The dependence of dielectric constant and dielectric loss ($\tan \delta$) of cured PI and cross-linked PI-co-PBO thermosets on the frequency of the applied field was investigated. As shown in Figure 3(A), all cross-linked PI-co-PBOs exhibit very good stabilities of dielectric constant over a high frequency range of 0.1 to 1 GHz as the cured PI doses. The dielectric constant of PI-co-PBOs expectedly decreases with an increase of APAF fraction, which is observed to vary from 2.56 to 3.40 for PI-co-PBOs at $f=0.1$ GHz under an ambient condition, lower than the cured PI with a dielectric constant of 3.55^[5]. Firstly, the introduction of bulky -CF₃ group in APAF into PI-co-PBOs is beneficial for reducing the dielectric constant of the resultant materials by decreasing the polarizability and increasing the free volume. Figure 3(B) displays the dielectric loss of the cured PI and PI-co-PBOs. It can be found that the dielectric factors ($f=0.1$ GHz) for these materials are at a very low scale between 1.2×10^{-2} and 3.0×10^{-2} , and it is difficult to identify any clear trend linking dielectric loss to the content of APAF in cross-linked PI-co-PBOs.

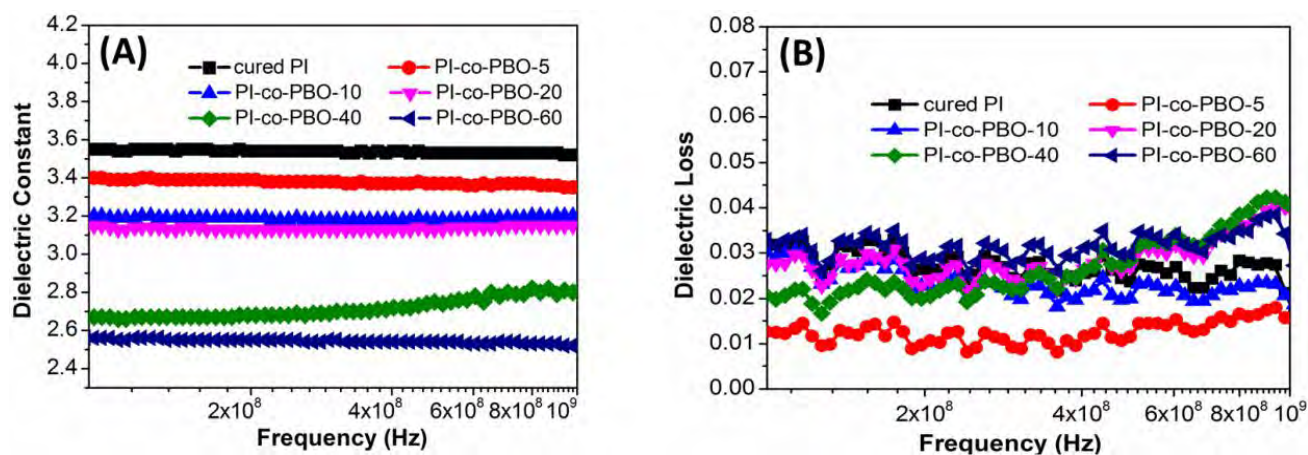


Figure 3. (A) Dielectric constant and (B) dielectric loss versus frequency of cross-linked PI and PI-co-PBO thermosets at room temperature.

4. CONCLUSIONS

In summary, aiming at achieving high-performance polyimide resin with both low-dielectric constant and high thermal stability, the rigid benzoxazole unit derived from thermally ranged *ortho*-hydroxy imide ring was introduced into the oligoimide backbone, resulting in series of PI-co-PBO resins containing various benzoxazole molar fractions. Such a design endows the PI-co-PBO resins with excellent combinational performances with low dielectric constants and simultaneous excellent thermal stabilities as compared to most other polymer resins so far. For instance, the PI-co-PBO-40 exhibits a dielectric constant of 2.7 at $f=0.1$

GHz under an ambient condition, 30 % and 63% lower than that of commercial epoxy and cyanate ester resins, and its T_g still reaches over 310 °C. As a result, we anticipate that this simple approach might be applicable for synthesizing polyimides with low dielectric constants and good thermal stabilities as high performance resins.

References

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