

# Thermally induced structural transformation of polytriazoleimide to polyindoleimide

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## Abstract

A new kind of polytriazoleimide containing bisphenyl-1,2,3-triazole (BPT) was synthesized by copper-catalyzed 1,3-dipolar cycloaddition of azides and alkynes (CuAAC) and polycondensation. The thermal stability and degradation mechanism of the polytriazoleimide were investigated. The results show that the structure of BPT in polytriazoleimide transforms to phenylindole after thermal treatment, accompanying the release of N<sub>2</sub>.

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**Keywords:** Polytriazoleimide; Structural transformation; Phenylindole; Thermal stability

The copper-catalyzed 1,3-dipolar cycloaddition of azides and alkynes (CuAAC) has been used as a powerful tool in polymer chemistry for designing a variety of molecular architectures and functionalizing synthetic polymer [1]. Recently, we have successfully synthesized a series of 1,2,3-triazole-containing polyimides (PTAIs) derived from dianhydrides and diamines which are prepared by CuAAC. PTAIs possess good solubility in organic solvents, mechanical property, adhesion property [2,3], as well as gas preselectivity [4], which indicates that there are potential applications as high-performance metal adhesives, gas separation membranes and matrix of advanced polymer composites. However, the decomposition temperatures at 5% weight losses of these polyimides (360–400 °C) are lower than many commercial polyimides [2]. The thermal stability is related to the breakage of CH<sub>2</sub>–N bonds in the main molecular chains [5]. To prove the conclusion, it is necessary to study the relationship between the structures and degradation stability of these polyimides.

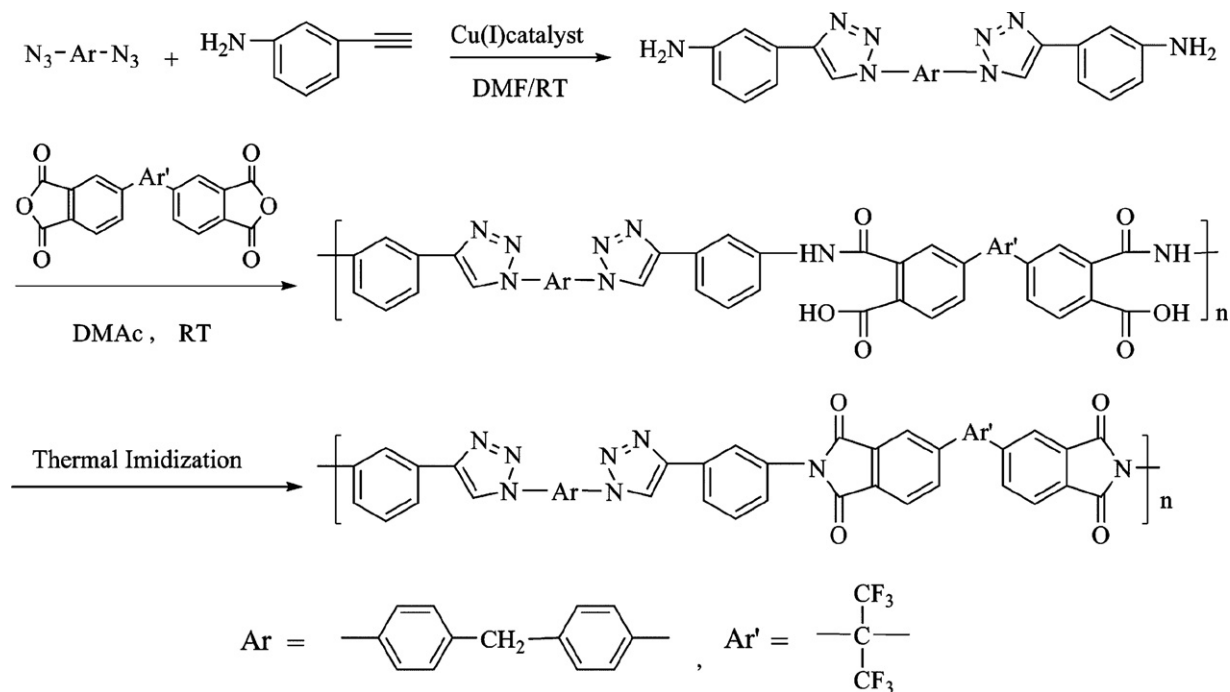
In this work, a new kind of a diamine containing bisphenyl-1,2,3-triazole (BPT) was synthesized by CuAAC, and then a novel polytriazoleimide was prepared by polycondensation of the diamine and aromatic tetracarboxylic dianhydride. The structure and degradation stability of the polytriazoleimide are characterized. Meanwhile, the structural transformation of the polytriazoleimide is investigated.

## 1. Experimental

The synthetic route of 3,3'-(1,1'-(4,4'-methylenebis(4,1-phenylene))bis(1,2,3-triazole-4,1-diyl))diamine (MPBTA) and the structure of a polytriazoleimide are shown in Scheme 1. Bis(4-azidophenyl) methane and

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Scheme 1. Synthetic route for diamine and polytriazoleimide.

3-aminophenylethyne were connected by CuAAC in DMF, using sodium ascorbate and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The solution was stirred for 24 h and washed with deionized water for three times, and a pale gray solid diamine product was obtained.

The synthesis of the polytriazoleimide was carried out in two steps. 5.0 mmol of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) was added to a stirred solution of 5.0 mmol diamine made above in DMAc. The mixture was stirred at room temperature for 12 h under  $\text{N}_2$ , forming a viscous solution of poly(amic acid) (PAA). The PAA solution was cast uniformly on a glass plate, followed by thermal treatment with a programmed procedure (80 °C/2 h, 120 °C/1 h, 150 °C/1 h, 180 °C/1 h, 220 °C/1 h, 250 °C/1 h, 280 °C/1 h) to produce a fully imidized polytriazoleimide film (PTAI). The PTAI film was treated at 350 °C for 1 h under  $\text{N}_2$ . The treated polytriazoleimide film is designed as PTAI-t.

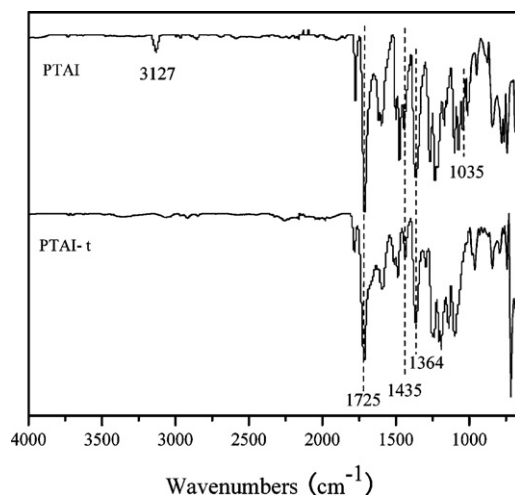


Fig. 1. FT-IR spectra of PTAI and PTAI-t.

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