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Thermally induced structural transformation of polytriazoleimide to polyindoleimide

Yan Peng E, Li Qiang Wan, Yu Jing Li, Fa Rong Huang *, Lei Du

Key Laboratory for Specially Functional Polymeric Materials and Related Technology of the Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

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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_2.

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_2–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-triazaole-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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* Corresponding author.
E-mail address: fhuanglab@ecust.edu.cn (F.R. Huang).

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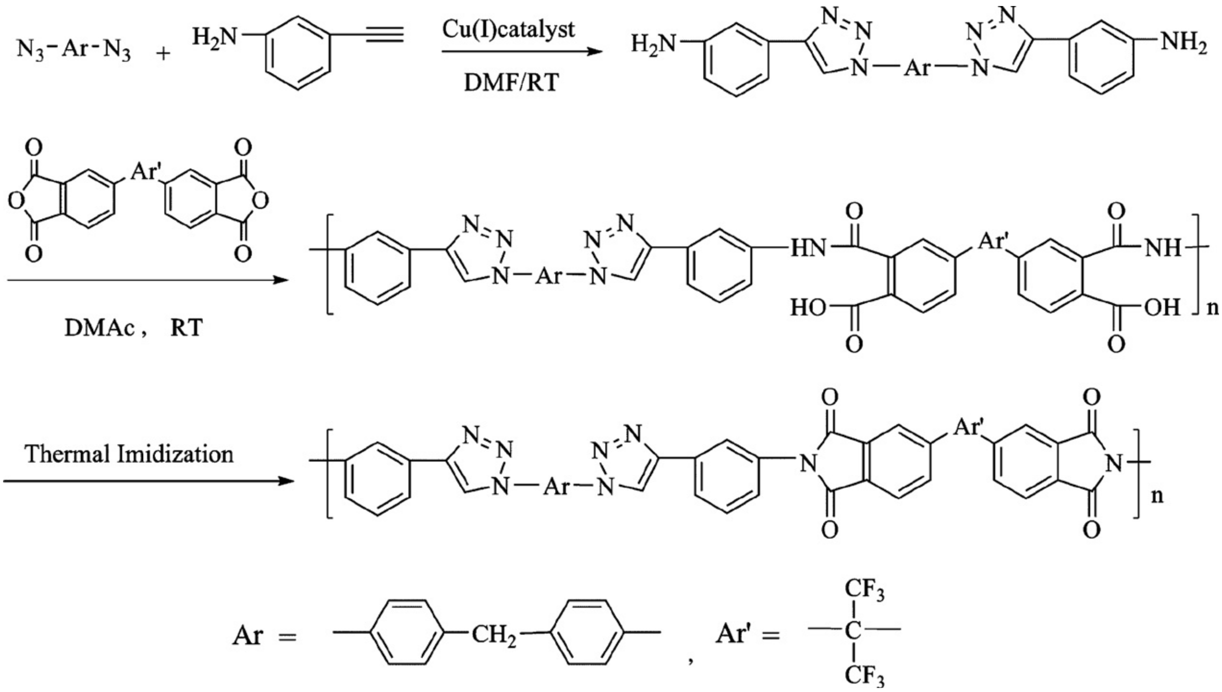


Scheme 1. Synthetic route for diamine and polytriazoleimide.

3-aminophenylethyne were connected by CuAAC in DMF, using sodium ascorbate and $CuSO_4 \cdot 5H_2O$. 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 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 N_2. The treated polytriazoleimide film is designed as PTAI-t.

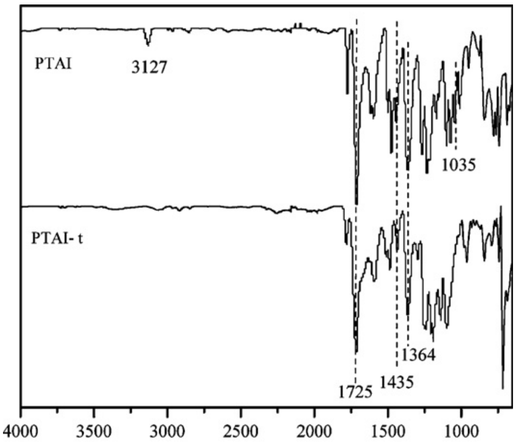


Fig. 1. FT-IR spectra of PTAI and PTAI-t.

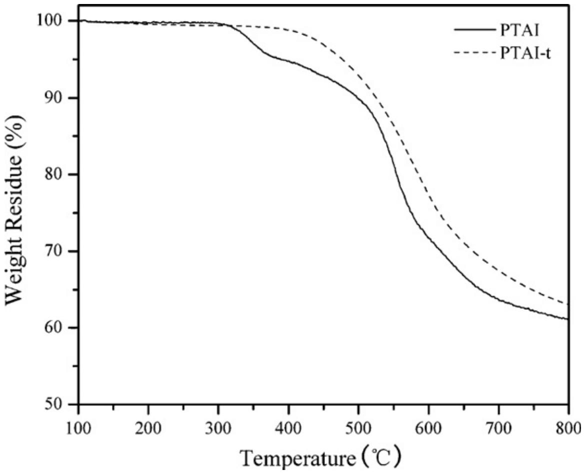


Fig. 2. TGA thermograms of PTAI and PTAI-t.

2. Results and discussion

Fig. 1 shows FT-IR spectra of PTAI and PTAI-t. The characteristic imide absorption bands at 1778 cm^{-1} (asymmetrical C═O stretch), 1725 cm^{-1} (symmetrical C═O stretch) and 1364 cm^{-1} (C–N stretch) are present. Meanwhile, the characteristic absorption peaks of the triazole ring at 3127 cm^{-1} and 1035 cm^{-1} are also present. The characterization by FT-IR and elemental analysis demonstrates that PTAI has been successfully synthesized. In the IR spectra of PTAI-t, triazole signals at 3127 cm^{-1} and 1035 cm^{-1} noticeably disappear, indicating the structure of PTAI changes after heat treatment. New absorption peak at 1435 cm^{-1} (phenylindole skeletal vibrations) appears, reflecting the triazole rings have transformed to phenylindole groups. In addition, the characteristic absorption bands of imide are still present, indicating the imide structure has not changed.

Thermogravimetric analysis (TGA) in N_2 was performed to provide an insight into the thermal stability of the polytriazoleimide [6,7]. Fig. 2 shows TGA thermograms of PTAI and PTAI-t. As shown in the figure, the decomposition process of PTAI is performed in two stages, whereas there is only one stage on TGA curve of PTAI-t. The decomposition weight loss of PTAI is 6% at the first stage (300–400 °C). If the 1,2,3-triazole ring opens and 2 nitrogen atoms are lost, the weight loss of the polytriazoleimide would be just 6%. Therefore, the weight loss of the first stage would be related with the 1,2,3-triazole ring-opening reaction resulting in release of N_2, and the second stage would be related with the decomposition of imide ring groups, etc. The decomposition temperatures at 5% weight loss (T_{d5}) for PTAI and PTAI-t are 389 °C and 477 °C, respectively.

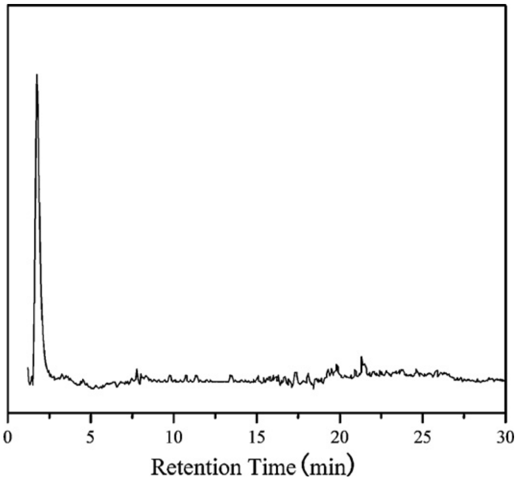
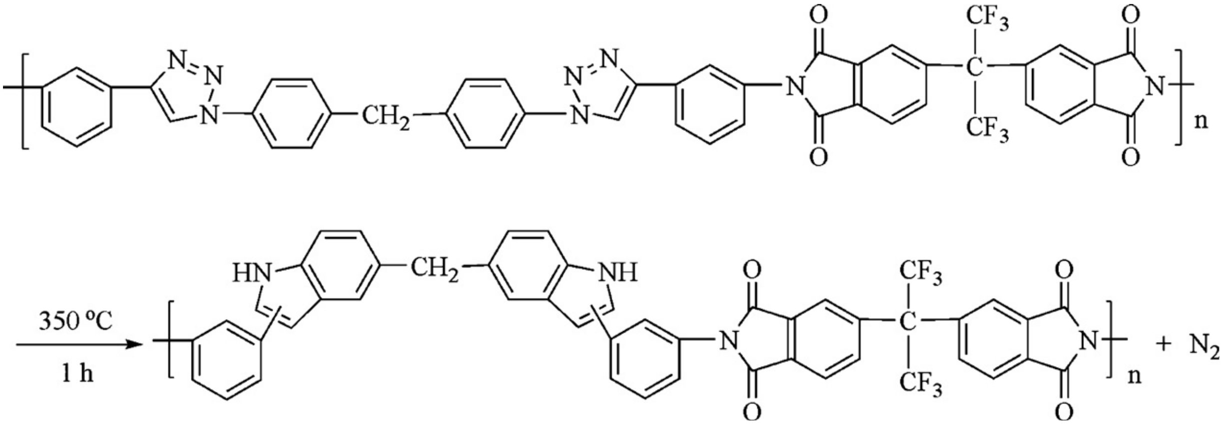


Fig. 3. The gas chromatogram of the pyrolysis product of PTAI.



Scheme 2. Thermal induced structural transformation route of PTAI.

The pyrolysis gas chromatography–mass spectrometry (Py/GC/MS) combined technique was utilized to trace thermal degradation of the polytriazoleimide [8]. Fig. 3 shows the gas chromatograms of the pyrolysis product of PTAI at 400 °C. The only pyrolysis product for PTAI pyrolyzed at 400 °C is N_2, confirming the thermally induced structural transformation from bisphenyl-1,2,3-triazole to phenylindole. It also demonstrates that phenylindole is stable at 400 °C.

In a weight-loss test, the original weight of PTAI is 0.2849 g. After treated at 350 °C for 1 h, the weight of PTAI-t is 0.2678 g. The weight loss is also 6%, which is the same as the analysis results of TGA. In addition, we recently take interest in the insights reported by Gilchrist and co-workers on the conversion of bisphenyl-1,2,3-triazoles to phenylindoles with release of nitrogen gas by flash vacuum pyrolysis [9,10]. Based on the above results and discussion, a new kind of polyindoleimide has been prepared and a thermal induced structural transformation route of PTAI is suggested as shown in Scheme 2.

3. Conclusion

In summary, we synthesized a novel polytriazoleimide (PTAI) containing bisphenyl-1,2,3-triazole by CuAAC and polycondensation and investigated thermal stability of PTAI and treated PTAI (PTAI-t). The results show that the decomposition temperatures at 5% weight loss of PTAI and PTAI-t are 389 °C and 477 °C, respectively. The PTAI undergoes ring-opening reaction with the release of N_2 and a polyindoleimide forms when it is heated at 350 °C for 1 h. The formed polyindoleimide is stable at 400 °C. At last, thermally induced structural transformation route of PTAI to the polyindoleimide is suggested.

Acknowledgments

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