Chinese Chemical Letters Vol. 10, No. 5, pp. 371–372, 1999

Synthesis of a Poly (amide-imide) from 5,6-Diphenyl-1-chloroformyl-3,4-benzenedicarboxylic Anhydride and Bis (4-aminophenyl)ether

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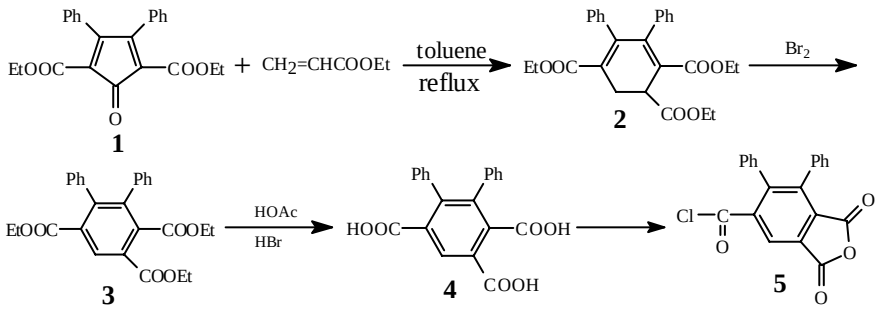
Abstract: A novel poly (amide-imide) was prepared from a novel monomer: 5,6-diphenyl-chloroformyl-3,4-benzenedicarboxylic anhydride and bis (4-aminophenyl) ether. The polymer was characterized by FTIR, ^{1}HNMR, DSC and TGA.

Keywords: Poly (amide-imide), 5,6-diphenyl-chloroformyl-3,4-benzenedicarboxylic anhydride.

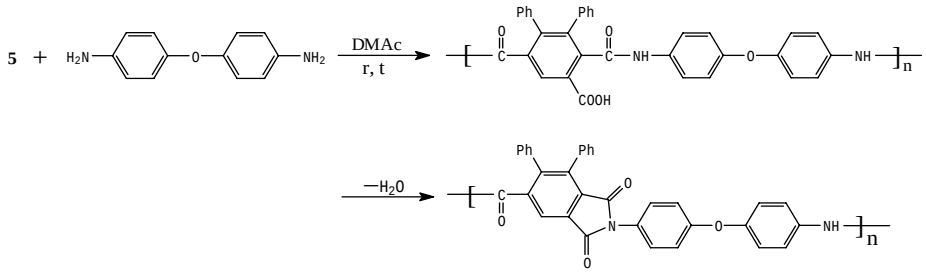
Polyimides are well known as one of the most important classes of high-performance polymers. However, their utilization is greatly limited due to their poor handling and processing characteristics[1]. A number of methods including incorporation flexible or nonsymmetrical linkages in polymer backbone or using monomers with bulky substituents, have been used to improve their solubility. Poly (amide-imide) s have also been provided a favorable balance between processability and performance[2].

Scheme 1.



In this letter. We synthesized a novel monomer **5** by introducing the two phenyl rings into the adjacent positions on the core benzene ring of trimellitic anhydride and poly (amide –imide) based on this novel monomer (**Scheme 1**). Monomer **5** was readily synthesized from the cyclone **1** and ethyl acrylate in high yields. The approach involved

Scheme 2.



the Diels-Alder reaction with ethyl acrylate, followed by aromatization with bromine, hydrolysis, dehydration and chloroformylation with thionyl chloride. The highly pure monomer was recrystallized from actone and hexane. Its structure was unambiguously confirmed by FTIR, NMR, MS and elemental analysis. The poly (amide-imide) was synthesized from **5** and bis (4-aminophenyl) ether by the two-step procedure involving the polymerization in DMAc at room temperature and subsequent thermal cyclodehydration (**Scheme 2**). The polymer was obtained in quantitative yield with inherent viscosity of 0.43dL/g in NMP at 25℃ . Spectroscopy confirmed the formation of poly (amide-imide). The FT–IR exhibited characteristic absorptions for the imide ring at 1780 and 1726 cm^{-1}, indicative of the asymmetrical and symmetrical C=O stretching vibration, 1100 and 740cm^{-1} due to ring deformation. Bands of amide groups appear at 3300,1668 and 1539 cm^{-1}. The ^{1}H–NMR of the polymer also confirmed the poly (amide-imide). The signal at 10.21 ppm was peculiar to the protons in the amide groups , 8.1ppm to the phenyl of the trimellitic units, 6.9-7.5 ppm to the phenyl groups. Their intensity ratio was 1:1:18, which show agreement with the calculated amount of the proposed structure. The T_g was 336℃. The temperature for 5% weight loss was 468℃ in air. Furthermore, the polymer was readily soluble in NMP, DMAc, DMSO, DMF and m-cresol.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (59473019).

References and Notes

1. Z. Y. Wang, Y. Qi, *Macromolecules* **1994**, *27*, 625.
2. M. Beltramo, *Engineering Plastic*, **1993**, *6*, 40.
3. Selected data of monomer **5**: pale-yellow crystal, mp: 195℃, Elemental anal: Calcd for $C_{21}H_{11}O_4Cl$ (362.76) (%): C: 69.53; H: 3; Cl: 9.77. Found: C: 69.48; H: 2.99; Cl: 9.72. ^{1}HNMR (δ, ppm, 90MHz DMSO-d_6): 8.3 (s, 1H), 7.5~6.8 (m, 10H). ^{13}CNMR (δ, ppm, 22.5MHz, DMSO-d_6): 166.82, 160.98, 160.37, 147.87, 143.69, 134.76,132.38, 130.58, 130.42, 129.68, 129.50, 128.68, 128.57, 128.36, 128.15, 127.76, 123.75. FT-IR (cm^{-1}): ~3030 (Aromatic: C–H), 1858.6, 1790.9 (anhydride), 1443,1330, 1268, 1213, 737.4 (C-Cl in formyl chloride).

Received 10 December 1998