

Synthesis of Poly (2-aminothiazole) Using Chemical Oxidation Method

Xia Wang¹, Lu Wang^{1, a, *}, Hua Zou¹, Wei Qian¹, and Yaozu Liao²

¹School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai, China

²School of Chemistry, University of Bristol, Bristol, England BS8 1TS, UK, China

^awanglu1390636@163.com

Keywords: Poly (2-aminothiazole), chemical oxidation, oxidation Method.

Abstract. Poly (2-aminothiazole) was synthesized by chemical oxidative polymerization of 2-aminothiazole, through selecting the appropriate reaction medium and simply modulating reaction parameters such as reaction time, temperature and oxidant concentrations, the chemical structure, product yield and the thermal stability of PAT are facilely optimized. Structural analysis of the polymer was carried out by FT-IR and UV-VIS spectroscopies. Yield was calculated using gravimetric method. Thermal properties were studied by TGA.

Introduction

Polymers with conjugated structure have attracted considerable interest in the past few decades. Because of their actual and potential applications in different technical fields, such as lithium ion battery, electro chromic materials, corrosion protection and sensors [1-4]. Some conventional polymers, such as polythiophene [5], polypyrrole [6] and polyaniline [4] have been extensively studied. Synthesis and characterization of novel conductive polymer material can enlarge the diversity with special properties.

Thiazole is a five-membered heteroaromatic compound, containing nitrogen, sulfur heteroatoms. It was favored by the majority of researchers because of its thermal stability and excellent conductivity properties, 2-aminothiazole (AT), since the introduction of the amino group, it had a lower oxidation potential and higher chemical reactivity, chemical oxidative polymerization is easier to conduct compared to thiazide. Due to its special chemical, electronic structure, AT can be involved in a variety of biochemical reactions, it has good functions such as bactericidal, anti-inflammatory, anti-viral, anti-corrosion, heavy metal ion adsorption and so on[7]. It can be anticipated, these superior performance of AT can be improved through functional group content increased after the polymerization. Apart from this, Poly (2-aminothiazole) (PAT) will has superior optical, electrical properties with the formation of a large π -conjugated structure. So PAT will become a kind of new organic polymer material transcend traditional conductive polymers.

PAT can be synthesized by chemical and electrochemical method [8-9]. The chemical polymerization technique is very useful for obtaining large amounts of the polymer, while the electrochemical synthesis technique is more suitable for gaining smooth polymers. It has been reported dehydrogenation synthesis of poly (2-aminothiazole) by the electrochemical oxidation polymerization method. However, the product is entirely dependent on the electrode area and the yield is low so that large-scale synthesis is difficult. Compared with the electrochemical oxidation, chemical oxidation method is simple, mild, high yield, low energy consumption, easy to promote mass production, more effective to avoiding the shortcomings of electrochemical polymerization.

Experimental

AT monomer was dissolved in 10 ml solvents. FeCl₃ as an oxidant was dissolved in corresponding solvents. The amount of the FeCl₃ was added drop wise to the monomer solution. Control the reaction temperature, the reaction was stirred for a certain time. The resulting product was filtered, washed, and dried.

FT-IR spectra were recorded on a Spectrum 100 FT-IR spectrometer using KBr pellets. Absorption spectra were measured using a Lambda 750 UV-vis spectrophotometer in DMSO. Thermogravimetric analyses (TGA) of the samples were conducted in N₂ at a heating rate of 10 °C/min from room temperature to 600 °C using a Perkin-Elmer Pyris 1 TGA apparatus.

Results and Discussion

Several representative oxidant species potentials (ORPs) was reported to be selected to optimize the polymerization with different standard oxidation reduction, including NaClO (1.63V), H₂O₂ (1.77V), H₂O₂/FeCl₂ (2.80V), (NH₄)₂S₂O₈ (2.01V), FeCl₃ (0.77V).

This article select oxidant with minimum ORPs for exploratory. In order to select a suitable solvent serves as the reaction medium, the solubility of the monomers and oxidant in different solvents were test. In methanol, ethanol, acetone, nitromethane, both monomer and oxidant can dissolve simultaneously. It means that with the help of these solvents, contacting of oxidants and monomer in the molecular level can be achieved to ensure that the reaction proceed sufficiently, so that these solvents meet the necessary conditions of the reaction medium.

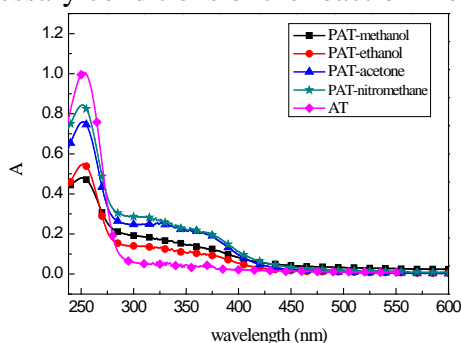


Fig.1. UV-VIS absorption spectra of AT and PAT in different solvent

The UV-VIS absorption spectra of PAT dissolved in DMSO displayed the formation of conjugated structure in Figure1. The peak at 265 nm could be ascribed to the $\pi \rightarrow \pi^*$ transition of thiazide ring of 2AT. The broad absorption bands at 350 nm with a long tail extending to 500 nm could be attributed to $\pi \rightarrow \pi^*$ transition of the conjugated polymers.

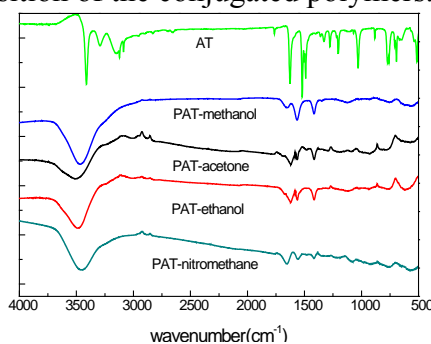


Fig.2. FT-IR spectra of AT and PAT reaction in different solvent

The FT-IR spectra of the 2AT monomer and PAT are shown in Figure 2. the bands at 3414 cm⁻¹ and 3297cm⁻¹ are attributed to the asymmetric and symmetric N–H stretching of the –NH₂ group in AT, respectively. These two bands turned to a single broad band at 3476, 3502, 3486, 3468cm⁻¹ in methanol, acetone, ethanol, and nitromethane respectively, assigned to N–H stretching. It indicated the oxidation of –NH₂ and formation of –N(H)– linkages between the 2AT rings.

System color and products shape changed during the reaction as shown in Table1. In nitromethane, the amounts of the product is more and the color is darker, it also intensely precipitate in the bottom of the bottle. This shows that it is more beneficial to polymerization and separate when nitromethane is the solvent.

The reaction time and temperature are two important parameters for the synthesis of PAT, they closely related to the performance of the reaction product. In general, as the reaction temperature increased, the reaction time will be shortened, but it is not conducive to the improvement of the

molecular weight and distribution. However, reducing the temperature is not beneficial to improve the yield of the polymerization, and if the reaction time was too long, the molecular chain has been formed will be degraded in the oxidizing environment. In addition, the amount of the oxidant also affect the progress of the reaction.

Table 1 Reaction phenomenon

solvent	Color of AT	Color of PAT	Feature of products
methanol	faint yellow	red	small amount of black solid
ethanol	faint yellow	red brown	small amount of black precipitate
acetone	faint yellow	brownness	large number of black floccules
nitromethane	faint yellow	puce	large number of black solid precipitation

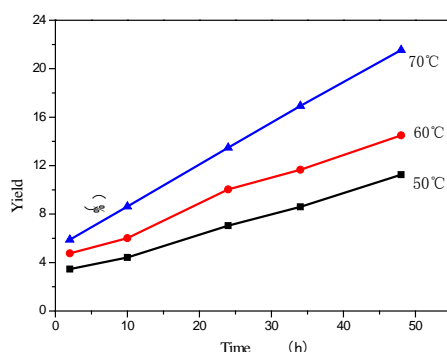


Fig.3. effect of reaction time and temperature on the yield of PAT

In this section, the yield of polymerization as shown in Figure 3, with the increasing of reaction time and temperature, the yield was increased. It suggested that, a suitable increasing of the reaction temperature and the time will be beneficial to the synthesis of the polymer. Considering the safety of solvent in high temperature and description of Figure 3, the study extended reaction times when the reaction condition is 70°C.

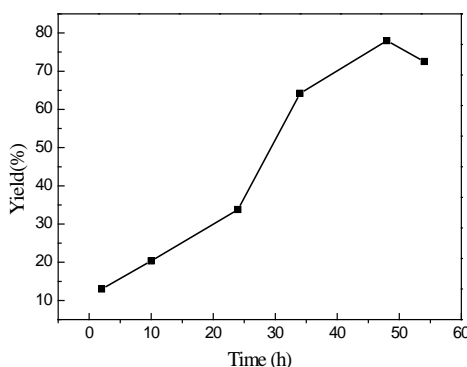


Fig.4 Effect of reaction time on the yield of PAT

Figure 4 shows the presence of automatic acceleration process. It is due to that the hindered the movement of long. However, monomer is relatively small, so the increase of the viscosity cannot hinder polymerization of the monomers. As the reaction continues, the presence of excess oxidant, and the oxygen in the air will cause over-oxidation, the long-chain structure is destroyed, cracked into smaller molecular, polymers will dissolve in the solvent and lost during filtration when the temperature is high.

Thermal stability of the product has a great influence on the application. As shown in figure5 and figure 6, relative to monomers, the thermal stability of polymers have significantly improved, and char yield are greatly enhanced. Furthermore, initial decomposition temperature was 282°C at 24h, it improved to 306 °C at 48h, it indicated that with the increasing of reaction time, the thermal stability of the polymer getting better (Fig.5).

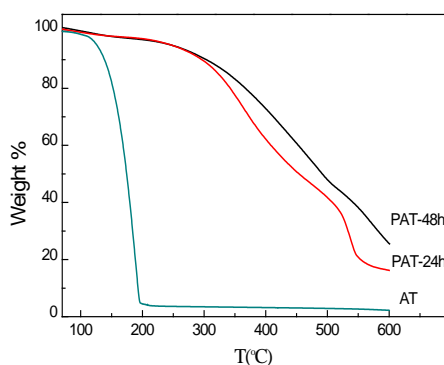


Fig.5 TG curves of PAT at different time

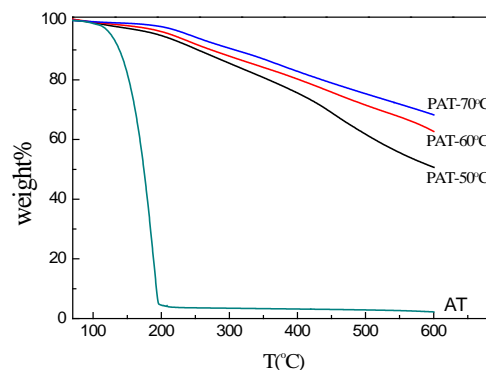


Fig.6 TG curves of PAT at different temperature

Initial decomposition temperature was 161 °C, 178 °C, 199 °C, and the char yield was 50.7%, 62.7%, 68.3% respectively when the reaction temperature was 50 °C, 60 °C, 70 °C (Fig.7). This suggests that increasing the reaction temperature is also conducive to improve the thermal stability of the product effectively.

Thus, through the rational design of experiments, the appropriate reaction conditions will severely affect the performance and efficiency of the polymeric products.

Conclusions

In summary, in this paper, PAT were successfully synthesized by chemical oxidative polymerization method using the FeCl₃ dissolved in nitromethane. The structures of the polymers were clarified by FT-IR, UV-VIS, when the reaction condition was 70 °C, 48h, the yield and thermal stability shows satisfactory results.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (51203090, Y.Z.L.), the Natural Science Foundation of Shanghai (12ZR1446700, Y.Z.L.), the Innovation Program of Shanghai Municipal Education Commission (13YZ074, Y.Z.L.) and the Hujiang Foundation of China (B14006, H.Z.).

References

- [1] Odaci D, Kayaham SK, Timur S, Toppare L. *Electrochim Acta* 53: p.4104–4108 (2008).
- [2] Retama JR, Mecerreyes D, Lopez-Ruiz B. *Colloids Surf a* 270: p.239–244 (2005)
- [3] Armelin E, Pla R, Liesa F, Ramis X, Iribarren JI, Aleman C. *Corros Sci* 50: p.721–728 (2008)
- [4] Rehan HH. *J Power Sources* 113: p.57–61 (2003)
- [5] Kabasakaloglu M, Talu M. *Appl Surf Sci* 218: p.84–96(2003)
- [6] Ahuja T, Mir IA, Kumar D, Rajesh D. *Sensors Actuators B* 134: p.140–145(2008)
- [7] Zhou X, Shao L, Jin Z, Liu JB, Dai H, Fang JX. *Heteroat Chem* 18(1): p.55–59 (2007)
- [8] Ciftci H, Testereci HN, Oktem Z. *Polym Bull* 66: p.747–760 (2011)
- [9] Yildırım M, Kaya I. *Synth Met* 162: p.436–443 (2012).