The synthesis and characterization of a new cross-linkable copolymerization poly(arylene ether sulfone) End-Capped with Phthalonitrile

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Abstract. A novel of cross-linkable copolymerization poly (Arlene ether sulfonic) end-capped with phthalonitrile had been firstly synthesized by nucleophile substitution reaction. The effects of crosslink reaction on thermal property of PES films were studied. The 1H NMR spectroscopy spectra have confirmed that the phthalonitrile group was connected to PES chain terminal. The fracture morphology was observed by SEM, the results suggested that the crosslink reaction of the films occurred during the heat treatment. DSC, TGA and gel content testing indicated the thermal stability getting better after high temperature treatment. The Tag and T5% reach 221.7 co. and 546.6 co. after the PES films treatment at 340 co. for 6 h.

Keywords. Poly (Arlene ether sulfonic), cross-linking, thermal property

1. Introduction
In recent years, poly (Arlene ether sulfonic) (PES) as a high-performance engineering thermoplastic has attracted extensive interest for excellent thermal property, mechanical property, easy process ability and ageing resistance [1-4]. However, with the development of science and technology, conventional thermoplastic PESs are difficult to meet the requirement of human beings. Meanwhile, the thermal stability of PES is not high enough than some thermal stabilities of thermoset resin and some special engineering thermoplastics, such as bisphthalonitrile[5], poly(Arlene ether nitrile) (PEN)[6] and poly(ether ketone)[7].

Phthalocyanine is a porphyrine ring, the π electron of carbon and nitrogen on the ring form the macro-conjugated system. Owing to the ring skeleton of phthalocyanine, phthalocyanine possesses excellent properties, especially the thermal stability[8]. Zhou et al [9] reported a cross-linkable PEN end-capped with phthalonitrile, which exhibited more excellent thermaland mechanical properties duo to the crosslinking of phthalonitrile. However, because the presence of cyanogroup at the side chain of PEN, the crosslink sites of PEN end-capped with phthalonitrile are difficult to control. In this study, we synthesis a novel of cross-linkable copolymerization poly (Arlene ether sulfonic) end-capped with phthalonitrile (PES-t-Ph.). The synthesis of this copolymer was according to the principle of nucleophilic substitution reaction.
2. Experimental section

2.1. Materials
N-methylpyrrolidone was purchased from Tianjin BODI chemicals, Tianjin, China. Biphenyl, hydroquinone, potassium carbonate (K2CO3) and 4, 4’-dichlorodiphenyl sulfonic were purchased from Kalong Reagent Co. Ltd., Chengdu, China. 4-nitrophalonitrile (99%) was purchased from Alpha chemicals (Deshaun) Co. Ltd.

2.2. Synthesis of poly (Arlene ether sulfonic) end-capped with phthalonitrile (PES-t-Ph.).
The synthesis of PES-t-Ph. was obtained by one-step method. Biphenyl (BP) (0.164 moll), hydroquinone (HQ) (0.041 moll), anhydrous K2CO3 (0.28 moll) and 4,4’-dichlorodiphenyl sulfonic (0.2 moll) added into a three-necked flask loading with 25 ml toluene and 75 ml NMP. The mixture was heated at 150 co. to reaction 2 h, then continue to increase the temperature 170-180 co. by released part of toluene to for 3 h. Then, 4-nitrophalonitrile (3 g) and 50 ml NMP were added into the mixture after the temperature cooling to 80-90 co. and maintained for 5 h (Scheme 1). Finally, the mixture was poured into 0.1 moll/L Hall solution to remove K2CO3, and then washed with seething de-ionized water several times. Finally, the PES-t-Ph. was obtained after decompression filtration and dried under vacuum oven.

2.3. Preparation of PES-t-Ph. film and it’s heat treatment
The PES-t-Ph. films were prepared by solution casting method. Firstly, PES-t-Ph. was dissolved in NMP. Then, the mixture was then cast on a clean glass plate, and dried in an oven with the procedure of 80, 100, 120 co. for 1 h, 160 and 200 co. for 2 h, respectively. Finally, put the glass plate to a hyper thermal oven with 340 co. for 0 h, 2 h, 4 h and 6h, respectively. After slowly cooling back to room temperature, the glass plate was immersed in water to get four films.

2.4. Characterization
The structure of PES-t-Ph. was verified by 1H NMR spectroscopy (400 MHz) under DMSO-d6. The thermally induced phase transition behaviors of the PES-t-Ph. film and treated PES-t-Ph. films were performed on a TA Instrument DSC-Q100 with a heating rate of 10 co. /min from room temperature to 360 co. and in a nitrogen atmosphere. Thermal gravimetric analysis of the PES-t-Ph. film and treated PES-t-Ph. films were carried out using a TA Instrument TGA-Q50 with a heating rate of 20 co. /min from room temperature to 800 co. under a nitrogen atmosphere.

3. Results and discussion
Scheme 1 was the synthesis and cure reaction schematic diagram of PES-t-Ph. The structure of the PES-t-Ph. was verified by 1H NMR spectroscopy spectra of PES-t-Ph., the peak sites were between 6.5 and 8.0 (ppm), it indicated that all the hydrogen at the chain were in the benzene ring. The strong resonance peak at 7.11 and 7.89 ppm were belonged to the two kinds of hydrogen of phenyl sulfone. Meanwhile, the small resonance peak at 7.45, 7.76 and 7.81 ppm indicated the phthalonitrile group was connected to PES chain terminal. These results showed that the PES-t-Ph. could be obtained via this method.

Fig. 2(a) and (c) show the fracture morphology of untreated PES-t-Ph. film and the film heated at 340 co. for 4 h, respectively. From the images we can found that compared with untreated PES-t-Ph. film the fracture of PES-t-Ph. film after 340 co. treated for 4 h was more roughness, and appeared some small embossments. It was because of the high temperature treatment caused the crosslinking reaction of the cyanide. The digital images were showed in Fig. 2(b) and (d), after the high
temperature treatment the color of PES-t-Ph. film became brilliant orange. These results indicated the PES-t-Ph. film could down the crosslinking reaction.

Scheme 1. Synthesis and cure reaction schematic diagram of the copolymerization PES-t-Ph.

Figure 1. The 1H NMR spectra of PES-t-Ph. under DMSO-6d

Fig. 3a was the DSC curves of untreated PES-t-Ph. film and PES-t-Ph. films treated at 340 co. with different times, and the glass transition temperature (Tag) of this curves were listed in Table 1. As clearly observed that the Tag increased with the increasing of treatment time. The Tag of untreated PES-t-Ph. is 212.3 co., and reaches 221.7 co. after 6 h high temperature treatment.

The thermal stability of these films was studied by using TGA measurement and show in Fig. 4. The initial decomposition temperature (T5%) of each curves were listed in Table 1, are 508.8 co., 518 co., 540.7 co. and 546.6 co. for untreated PES-t-Ph., PES-t-Ph. 340 oC-2h, PES-t-Ph. 340 oC-4h and PES-t-Ph. 340 oC-6h, respectively. With the increasing of treatment time, the thermal stability was getting better gradually.
Figure 2. SEM images (a, c) and digital images (b, d) of untreated PES-t-Ph. film and the film heated at 340 °C for 4 h.

The gel content was tested by soxlet extraction. It took 12 h extraction in NMP solution. And the result was listed in Table 1, it was obvious that gel content increased with the increasing of treatment time.

Figure 3. DSC (a) and TGA (b) curves of untreated PES-t-Ph. film and PES-t-Ph. films treated at 340 °C with different times.

Table 1. The glass transition temperature (Tag), initial decomposition temperature (T5%) and gel content of untreated PES-t-Ph. film and PES-t-Ph. films treated at 340 °C with different times

| Nimble | Untreated | 340 °C-2h | 340 °C-4h | 340 °C-6h |
|--------|-----------|-----------|-----------|-----------|
| Tag(°C) | 212.3 | 217.4 | 219.6 | 221.7 |
| T5%(°C) | 508.8 | 518.0 | 540.7 | 546.6 |
| Gel content(%) | 0 | 3.4 | 6.7 | 10.1 |

4. Conclusion
In this study, a novel of cross-linkable copolymerization PES-t-Ph. had been firstly synthesized by nucleophile substitution reaction. The effects of crosslink reaction on thermal property of PES films were studied. The 1H NMR spectroscopy spectra have confirmed that the phthalonitrile group was connected to PES chain terminal. The DSC, TGA and gel content testing indicated the thermal stability getting better after high temperature treatment. The Tag and T5% reaches 221.7 °C and 546.6 °C after the PES films treatment at 340 °C for 6 h. The exhibited excellent thermal stability of the
copolymerization PES-t-Ph. makes it to be a good candidate in the application of heat resistant materials.

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References
[1] F. Wang, M. Hickner, Y.S. Kim, T.A. Zawodzinski, J.E. McGrath, Direct polymerization of sulfonated poly(arylene ether sulfone) random (statistical) copolymers: candidates for new proton exchange membranes, Journal of Membrane Science, 197 (2002) 231-242.
[2] W. Wu, B. Wei, J. Feng, B. Chi, S. Liao, X. Li, Y. Yu, Synthesis and Properties of Symmetric Side-Chain Quaternized Poly(Arylene Ether Sulfone)s for Anion Exchange Membrane Fuel Cells, Macromolecular Chemistry and Physics, 219 (2018) 1700416.
[3] D.H. Cho, K.H. Lee, Y.M. Kim, S.H. Park, W.H. Lee, S.M. Lee, Y.M. Lee, Effect of cationic groups in poly(arylene ether sulfone) membranes on reverse electrodialysis performance, Chem Commun (Camb), 53 (2017) 2323-2326.
[4] X. Li, Y. Yu, Y. Meng, Novel quaternized poly(arylene ether sulfone)/Nano-ZrO(2) composite anion exchange membranes for alkaline fuel cells, ACS Appl Mater Interfaces, 5 (2013) 1414-1422.
[5] H. Guo, Z. Chen, J. Zhang, X. Yang, R. Zhao, X. Liu, Self-promoted curing phthalonitrile with high glass transition temperature for advanced composites, Journal of Polymer Research, 19 (2012).
[6] R. Yang, R. Wei, K. Li, L. Tong, K. Jia, X. Liu, Crosslinked polyarylene ether nitrile film as flexible dielectric materials with ultrahigh thermal stability, Sci Rep, 6 (2016) 36434.
[7] P.X. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, K.P. Wang, S. Kaliaguine, Synthesis and characterization of sulfonated poly(ether ether ketone) for proton exchange membranes, Journal of Membrane Science, 229 (2004) 95-106.
[8] F. Meng, Y. Zhan, Y. Lei, R. Zhao, J. Zhong, X. Liu, Electrospun magnetic fibrillar polyarylene ether nitriles nanocomposites reinforced with Fe-phthalocyanine/Fe3O4 hybrid microspheres, Journal of Applied Polymer Science, 123 (2012) 1732-1739.
[9] Y. Zou, J. Yang, Y. Zhan, X. Yang, J. Zhong, R. Zhao, X. Liu, Effect of curing behaviors on the properties of poly(arylene ether nitrile) end-capped with phthalonitrile, Journal of Applied Polymer Science, 125 (2012) 3829-3835.