SYNTHESIS OF CHARACTERIZATION OF NOVEL POLY(ARYLENE ETHER NITRILE)

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Introduction

Poly(aryl ether nitriles) posses excellent heat resistance and are high-performance engineering thermoplastic, because the high rigid and functional nitrile groups are introduced into the structure of poly(aryl ether)s.[1-3] The polymer exhibits excellent tensile strength compared with the corresponding ketone- or sulfone- containing polymers. The excellent mechanical properties are attributable to dipole--dipole interactions of nitriles. For instance, they may promote adhesion with various materials and present a potential across-linking site. To get better properties, at first, considerable effort was made to modify their thermal structure, in order to improve their thermal properties (e.g. across-linking).

In the last years, more attention was paid to their functionality. This could be achieved either by chemical modification of the polymer or by direct synthesis using functionalized monomer. For many aromatic polymers it was shown that incorporation of 6F groups in the polymer backbone is beneficial. It is now well known that introduction of 6F groups into the polymer backbone enhances the polymer solubility without sacrificing thermal stability. The retention of high thermal stability is attributed to the strong C–F bond. Other effects of the 6F groups are increased glass transition temperature and flame resistance with concomitant decrease of crystallinity and water absorption. The bulky 6F groups also serve to increase the free volume of the polymer, thus improving its electrical insulating characteristics. All these properties, combined with easy processability, make the 6F aromatic polymers very attractive for practical applications.

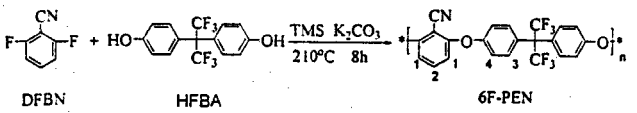
As part of an effort to obtain high-performance, high temperature resistant polymers for microelectronics applications we considered it interesting to synthesize new aromatic poly(aryl ether nitriles) which contain 6F groups . We have investigated the properties of these fluorinated poly(aryl ether nitriles) such as solubility, thermal stability and glass transition.

Experimental

Materials. Hexafluorobisphenol A was purchased from Shanghai yi chao chemical regent plant. 2,6-Difluorobenzonitrile (DFBN) the Aldrich. Anhydrous potassium carbonate(K_2CO_3) was purchased from Tianjin Chemical Reagent Plant. Tetramethylene sulfone(TMS) was obtained from Jinzhou Oil Refinery (purified before used).

Instrumentation. IR spectra were recorded on Nicolet Impact 410 Fouriertransform infrared spectrometer.^{1}H-NMR spectra were recorded using Bruker 500 NMR spectrometer using chloroform-d solvent. Differential scanning calorimetry was performed on a Mettler Toledo DSC821^e. The glass temperature was obtained during the second heating scan at a rate of 20°C/min under flowing nitrogen gas. Thermogravimetric analyses were performed on a Netzch Sta 449c at a heating rate of 20°C /min under a nitrogen atmosphere. The inherent viscosity (η_{iv}) of the polymer was determined using an Ubbelohde viscometer at a concentration of 5mg/ml DMF at 25°C. Gel permeation chromatography (GPC) analyses were carried out on a waters 410 GPC with THF as solvent.

Synthesis of the polymer. A typical synthesis of poly(aryl ether)s was conducted on a 100ml-round bottom flask, equipped with a condenser, mechanical stirrer and nitrogen inlet. A detailed synthetic method designed to prepare PEN from HFBA and DFBN was carried out using the following general procedure. To the flask was added 6.72g (0.02mol) HFBA, 2.78g (0.02mol) DFBN, 3.59g (0.026mol) potassium carbonate, 60ml toluene and 40ml TMS. The mixture was stirred until all the solids dissolved, then it was heated to 140°C and stirred at this temperature under nitrogen for 2h. Then we let the toluene out, the mixture was heated to 210°C and stirred at this temperature under nitrogen for 8h. The structure of the polymer was showed in scheme 1.



DFBN HFBA 6F-PEN

Scheme 1. Synthesis of the Polymer.

Results and Discussion

The structure of fluorinate-PEN was identified by IR and ^{1}H-NMR spectra. All IR spectra exhibited absorption bands at 2238cm^{-1} characteristic for -CN and at 1167cm^{-1} because of -CF_3. Absorption bands which were found at 1254cm^{-1} were attributed to aromatic ether Ar-O-Ar.

The ^{1}H-NMR spectrum of the polymer was also consistent with the proposed structure. The peaks at 6.70ppm were assigned to the 1H(d; 2*H); The peaks at 7.43 ppm were assigned to the 2H(d; 1*H); The peaks at 7.45 ppm were assigned to 3H(d; 4*H); The peak at 7.14 ppm was assigned to the 4H(d; 4*H).

The inherent viscosities of the polymers were in the range of 0.87dl/g. The result of GPC showed that the M_n and the M_w were 60000 and 100000.

At the room temperature, the polymer could be solved in the DMF, DMAc, chloroform, NMP and THF. The improved solubility of the present poly(ether)s compared with the traditional aromatic poly(ether)s was explained by the presence of bulky (3,5-ditrifluoromethyl)phenyl-units.

The thermal stability of the polymer was studied by TGA. The temperature at which a 5% weight loss occured 510°C, and 10% weight loss temperature was as high as 530°C. The glass transition temperature was 195°C. All the thermal properties of the polymer were shown in the **Table 1**.These thermal properties showed us that the polymer has the excellent thermal stability. The reason of the results, we think, was that the nitrile and trifluoromethyl moieties were introduced into the polymer.

Table 1. Thermal properties of the polymer

Polymer	Tg(°C)	DT_5(°C)	DT_{10}(°C)
6F-PEN	195	510	530

Conclusions

A kind of fluorine-containing poly(aryl ether nitrile) was synthesized from an activated difluoro monomer substituted with a nitrile group and a diphenol monomer with a fluorine-containing group. The polymer was found to possess high T_g, good solubility and high decomposition temperature. This polymer exhibits an outstanding capability to be processed from solution into thin and ultrathin films having smooth and defectless surface and good mechanical properties. Potential applications in microelectronics or related advanced fields were foreseen.

References

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