Poly(arylene ether nitrile)s with Trifluoromethyl Groups

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Introduction

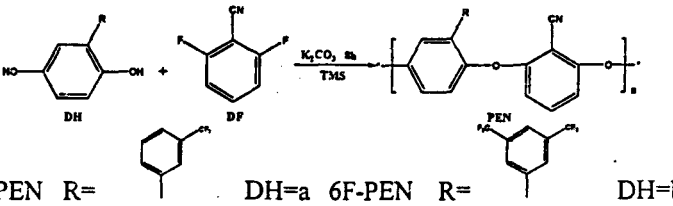
Poly (arylene ether)s are well recognized high performance engineering thermoplastics. These materials have outstanding physical properties including high modulus, toughness, high thermal stability, and chemical resistance. Poly(arylene ether nitrile)s exhibit some excellent performance compared with the corresponding polymers contained ketone, sulfone, or other groups, because the high rigid and functional nitrile groups are introduced into the structure of poly (arylene ether)s. [1-6] Pendent nitrile groups are expected to confer some advantages, for instance, they may promate adhesion with various materials and also present a potential cross-linking site. In the last years, more attention is paid to their functionality. This could be achieved either by chemical modification of the polymer or by direct synthesis using functionalized monomer.

Among the possible applications of poly (arylene ether)s are the use as optical devices, insulating materials in microelectronics (ILD and IMD), membrance materials (e.g. for gas separation membrane) and so on. Fluorine-containing polymers are of special interest, because of their low dielectric constants and remarkably low water absorption, while the incorporation of fluorine atoms into the polymer chains also leading to decrease color and crystallinity of the polymers. This added solubility is sometimes referred to the "fluorine effect". The retention of high thermal stability is attributed to the strong C-F bond. They also increase the glass transition temperature with concomitant decrease of crystallinity. The bulky - CF_3 group also serves to increase the free volume of the polymer, thereby improving various properties of polymers, including gas permeabilities and electrical insulating properties.

Because of all these interesting properties of the fluorinated polymers and the polymers contained nitrile group, considerable attention has been devoted to preparation of new classes of fluorine- containing poly(arylene ether nitrile)s. Recently, we had reported the synthesis of a series of novel trifluoromethylated aromatic poly(aryl ether ketone)s. The primary aim of this work is to illustrate the effect of trifluoromethyl group on the properties of poly (arylene ether), such as inherent viscosity, solubility, thermal properties, dielectric constant and moisture absorption.

Experimental

Materials. The polymers (6F-PEN, 3F-PEN) were synthesized by our lab[6].The structure of polymers were confirmed by FTIR, MS and ^{1}H-NMR.



Scheme 1. Structures of the monomers and polymers

Instrumentation. Gel permeation chromatography (GPC) analyses were carried out on a waters 410 GPC with THF as solvent. Dielectric constants were obtained on Hewlett Packard 16541B/4194A at 1MHz.

Results and Discussion

Gel permeation chromatography (GPC)

All the polymers have high molecular weights as indicated by GPC and inherent viscosity measurement. The synthesized polymers have very narrow molecular weight distributions, indicating that these bisphenols are very reactive. Table 1 shows these properties of PENs.

Table 1. Polymerization of PENs

Polymer	η_{iv} (dl/g)	$M_n(10^4)$	$M_w(10^5)$	M_w/M_n
3F-PEN	0.98	4.0	21.4	5.34
6F-PEN	0.89	3.4	13.3	3.95

Dielectric properties

The dielectric constants of fluorined-PENs were determined from a Hewlett Packard 16541B/ 4194A at 1MHz and are given in table 2. The dielectric constant of 6F-PEN was lower than that of 3F-PEN, indicating that 6F- groups improve the insulating ability of the polymer. There are three main ways that fluorine incorporation can affect the dielectric constant changing the hydrophobicity with eliminates water changing the free volume, and changing the total polarizability. The first will only be discussed their moisture absorption. But the second and the third will be only briefly mentioned here.

Table 2. Dielectric Properties of PENs.

Polymer	Dielectric constant	Water Absorption (%)	Fluorine content (%)
3F-PEN	3.05	0.51	17.38
6F-PEN	2.95	0.46	28.79

Conclusions

Two kinds of novel, amorphous poly (arylene ether nitrile) have been synthesized by the nucleophilic displacement polymerization of bisphenols with activated bifluoro compounds. All the polymers have high molecular weight. The polymers are amorphous and soluble in solvents such as NMP, DMF and DMAc. The presence of pendent trifluoromethyl groups in polymers increases fractional free volume and lowers dielectric constants, while increasing solubility without forfeiture of thermal stability. The dielectric constants also depended on the fluorine content: the values decreased as the amount of fluorine increased. The relationship between the extent of fluorination and dielectric constant was studied and it was found that fluorination reduced the dielectric constant as expected .In conclusion, 6F-PEN had lower dielectric with more fluorine content and free volume compared with 3F-PEN.

References and Notes.

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