Novel heteroaromatic polymers derived from 9F-bisphenol*

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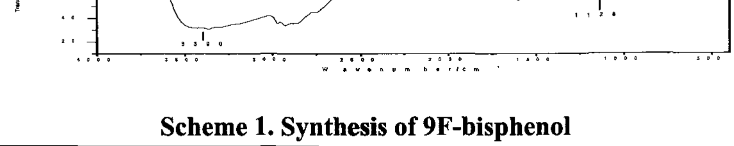
Abstract: A series of heteroaromatic polymers, including polybenzoxazole (PBO) and polypyrrolone (PPy) were synthesized from novel monomers derived from 1,1-bis(4'-hydroxyphenyl)-1-[3',5'-bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane (9F-bisphenol). The trifluoromethyl groups in the polymers endowed them good combined properties, such as enhanced solubility and processability in common solvents, decreased dielectric constants and refractive indices, improved optical transparency in visible light region as well as retained thermal stability. These characteristics make the present polymers good candidates for microelectronic or optoelectronic fabrications.
Keywords: Trifluoromethyl; bisphenols; polybenzoxazole; polypyrrolone; polycondensation

Heteroaromatic polymers (HAPs) are often known for their superior thermal and environmental resistance, high mechanical and dielectric strength; however, also their inferior processability [1]. Thus, functionalization of conventional HAPs aiming at improving their processability while maintaining their inherent merits so as to expanding their application to high-tech areas have been a vigorous topic in the past decades [2]. Among the various modifications, fluorination by incorporation of fluoro-containing substituents in HAPs is playing a more important and effective role [3].

Fluoro-containing groups possess large electronegativities, low molar polarizations, and sometimes bulky molecular volumes; thus, often endow the fluoropolymers with good optical transparency, low humidity absorption, low dielectric constant and refractive indices, and improved processability. Meanwhile, the thermal stability of the polymers can often be maintained due to the outstanding thermal and thermo-oxidative stability of the fluoro groups. In our previous work, a series of HAPs modified with trifluoromethyl (3F) or hexafluoroisopropylidene (6F) have been developed and commercialized due to the availability of the low-cost starting fluoro chemicals [4]. Recently, the rapid progress in organic fluoro chemistry in China makes it possible to produce high-fluoro-content fluoro chemicals, such as 1-bromo-3,5-bis(trifluoromethyl)benzene, 1-amino-3,5-bis(trifluoromethyl)- benzene, and so on. The mass production of the above chemicals provides us good opportunity to develop novel functional HAPs with high fluoro contents for advanced applications.

Thus, in the present presentation, a bisphenol compound, 1,1-bis(4'-hydroxyphenyl)-1-[3',5'-bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane (9F-bisphenol) was first synthesized (Scheme 1). Several HAPs (PBO and PPy) containing three or more $-CF_3$ groups in their structures were introduced. The effects of structure on the properties of the polymers were briefly discussed.



Scheme 1. Synthesis of 9F-bisphenol

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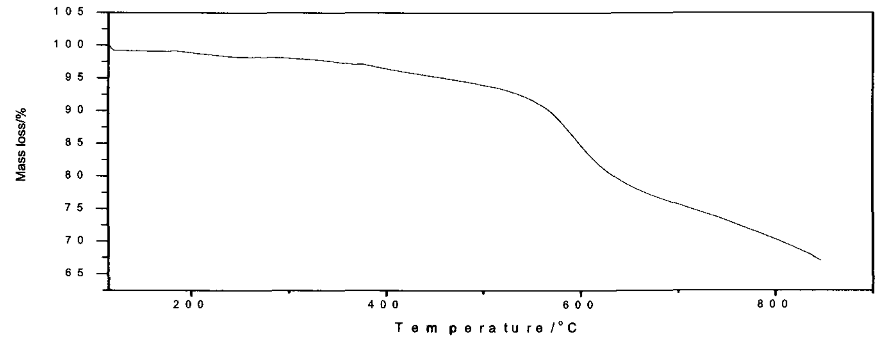
1. Polybenzoxazole (PBO)

Polybenzoxazoles (PBO) represent a class of high performance HAPs that have excellent thermal stability and high mechanical properties. Conventioanl PBOs have widely been used as high strength fibres. Fluorinated PBOs (FPBOs) have attracted much attention in the last decade owing to their desired properties for high-tech fields, especially, their low dielectirc constants and low water absroptions. Noteworthy are the photosensitive PBOs (PSPBO) developed as photoresists for microelectronic fabrication [5]. The common PSPBOs are usually derived from the only commercially available fluorinated bis(*o*-aminophenol) compond, 2,2-bis[(3-amino-4-hydroxy)phenyl]-hexafluoropropane and various aromatic dicarboxylic acids or diacyl chlorides. The poor availability of the corresponding bis(*o*-aminophenol) monomers prohibits the further modification of FPBOs.

In the present work, a series of novel FPBOs containing trifluoromethyls both in the main chain and the side chain have been designed and synthesized (Scheme 2).



Scheme 2. Synthesis of novel bis (o-aminophenol) monomers and polybenzoxazoles

A novel bis(*o*-aminophenol) monomer, 1,1-bis[(3-amino-4-hydroxy)phenyl]-1-[3,5-bis(trifluoro-methylphenyl)]-2,2,2-trifluoroethane (9FAP) was first synthesized with a yield around 70%. Two PBOs were then prepared from the monomer and two analogous diacyl chorides via the poly(*o*-hydroxyamide)s (PHA) intermediates, followed by thermal cyclization procedure. Figure 1 shows the ^{1}H-NMR spectra of 9FAP and PHA-2, in which all the absorptions could be identified.

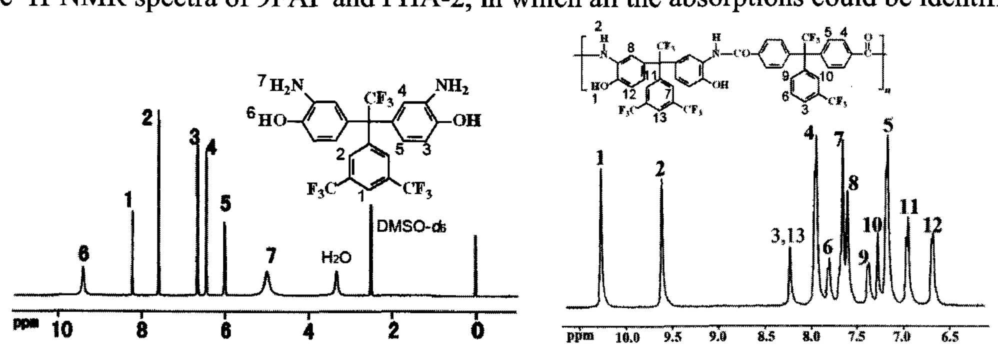


Fig. 1. ^{1}H-NMR spectra of 9FAP (left) and PHA-2 (right)

The thermal and optical properties of the PBO films are summarized in Table 1. The PBOs exhibited good thermal stabilities with glass transition temperatures (T_g) higher than 320 °C, and 5% weight loss temoeratures ($T_{5\%}$) above 510 °C in nitrogen.

The PBO films showed refractive indices lower than 1.55 at 1310 nm and dielectric constants from 2.57-2.62. The n_{av} values decrease with the increasing of the fluoro contents of the polymers, which can be contributed to the low molar refraction of $-CF_3$ groups. Meanwhile, the large molecular volume of the lateral phenyl groups is also beneficial to decrasing the n_{av} values. The dielectric consants of the

PBOs are as low as 2.57. It is also the results of synergic effects of trifuloromethyl and bulky phenyl side chains.

Table 1 Thermal and optical properties of PBO films

code	T_g (°C)	$T_{5\%}$ (°C)	F.(%)[a]	d (μm)[b]	n_{TE}[c]	n_{TM}[c]	n_{av}[c]	Δn[c]	ε[d]
PBO-1	320	529	27.2	5.58	1.5443	1.5388	1.5425	0.0055	2.62
PBO-2	337	513	31.4	11.55	1.5315	1.5264	1.5298	0.0051	2.57

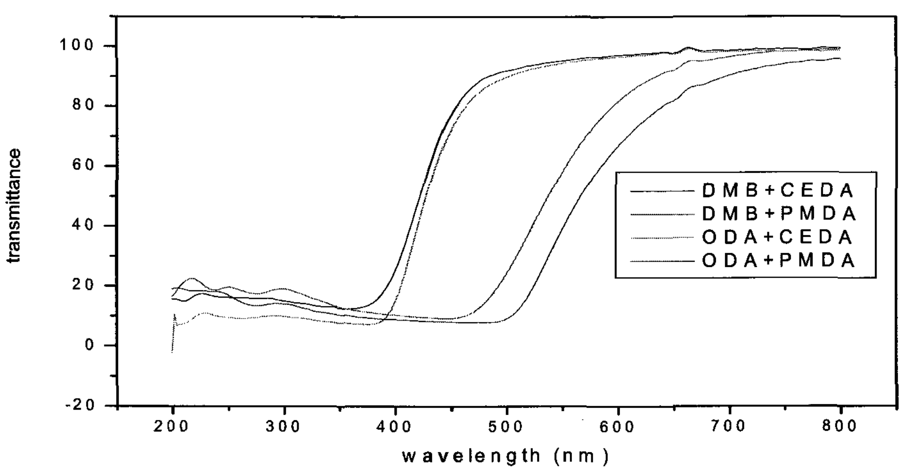
[a] Fluoro content; [b] Film thickness; [c] n_{TE}: in-plane refractive index; n_{TM}: Out-of-plane refractive index; n_{av}: average refractive index; Δn: birefringence; [d] Optical dielectric constants estimated from modified Maxwell's equation as ε=1.1n_{av}^2.

In summary, the present PBOs exhibite good combined properties. The introduction of multiple trifluoromethyl groups effectively lowered the dielectric constants and refractive indices of the polymers. In addition, the PHA precursors showed good optical transparency at 365 nm and high solubility in common solvents. Thus, they might find applications in microlithography.

2. Polypyrrolone (PPy)

Polypyrrolone (PPy), a class of HAPs derived from aromatic tetraamine and dianhydride monomers, was first reported in 1960s. However, since then, PPys have not been widely studied as compared with their analogues such as polyimide (PI) and PBO. The main reason might be ascribed to their high cost of the starting monomers, especially tetraamines. Up to now, membrane for industrial gas separation is the only application for PPy. Nevertheless, some unique characteristics of PPy, including ultra-high radiation resistance and excellent hydrolytic stability, still attract our attention. In our previous work, a series of fluorinated or asymmetrical PPys have been developed [6,7].

In the present work, a series of fluoro-containing PPys have been designed with the aim of expanding their applications to microelectronics. For this reason, a new aromatic tetraamine, 1,1-bis[4-(3',4'-diaminophenoxy)phenyl]-1-[3",5"-bis(trifluoromethyl)phenyl]-2,2,2-trifluoroethane (9FTA) was first synthesized from 9F-bisphenol with a total yield of 60%. Then, a series of PPys were prepared form 9FTA and various dianhydrides (Scheme 3).



Scheme 3. Synthesis of 9FTA and PPys

Figure 2 exhibites the ^{1}H-^{1}H COSY and HSQC spectra of 9FTA, in which all the absorptions of protons and C atoms could be well identified, indicating the good purity of the monomer.

The thermal, mechanical and dielectric properties of the PPy films are tabulated in Table 2. All the films exhibited good thermal stability up to 500 °C and glass transition around 300 °C. The flexible films showed tensile strength higher than 70 MPa. Meanwhile, the PPy films possessed good dielectric properties with high level of surface and volume resistivity. The good dielectric properties could be attributed to their highly conjugated molecular structure and also their low water or moisture uptakes.

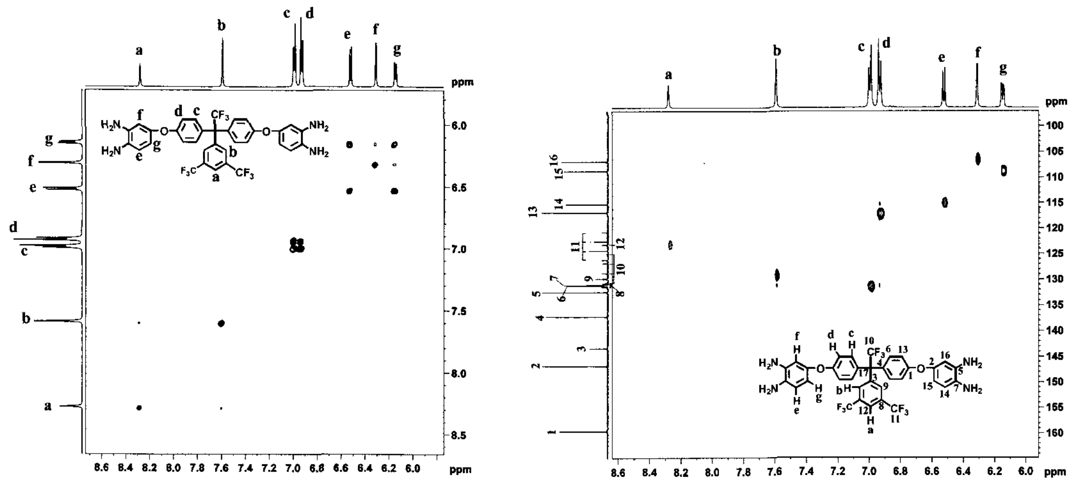


Fig. 2. ^{1}H-^{1}H COSY (left) and HSQC (right) spectra of 9FTA (600MHz, DMSO-d_6)

Table 2 Thermal, mechanical and dielectric properties of PPy films

code	T_g (°C)	$T_{5\%}$ (°C)	T_s [a] (MPa)	T_m [a] (GPa)	E_b [a] (%)	R_v [b] ($\times 10^{15}$ Ω·cm)	R_s [b] ($\times 10^{14}$ Ω)	W_u [c] (%)	T_{500nm} [d] (%)
PPy-1	302	531	72	2.3	4.8	6.4	4.7	1.3	70
PPy-2	315	529	76	2.3	4.2	5.2	2.7	1.1	52
PPy-3	316	529	79	2.3	5.2	5.9	7.3	1.3	72
PPy-4	-	505	82	2.2	4.8	5.5	6.0	1.4	45

[a] T_s: tensile strength; T_m: tensile modulus; E_b: elongation at break; [b] R_v: volume resistivity; R_s: surface resistivity; [c] Water uptakes at 25 °C; [d] Transmittance at 500 nm with a film thickness around 10 μm.

The hydrolytic stability of the PPy films were also investigated. The freestanding PPy films (8.0 × 1.0 × 0.005 cm^3) were immersed in a boiling NaOH solution (10%) in a 250-mL, round-bottom flask fitted with a condenser. It was found that all the PPy films exhibited excellent alkaline hydrolysis resistance which retained their original shapes and toughness after boiling 7 days in the NaOH solution. Also after boiling 8 hours in the solution, the tensile strength could retain as high as 56% of the original values.

In summary, the multi-trifluoromethyl-substituted PPys exhibited good combined properties, including good mechanical and dielectric properties, high thermal stability as well as excellent hydrolytic stability. They might find applications in gas separation, integrated circuit fabrication and other high-tech industry.

References

[1] Y. Imai, *React Funct Polym*, **1996**, 30, 3~15

[2] P. M. Hergenrother, *High Perform Polym*, **2003**, 15, 3~45

[3] G. Maier, *Prog. Polym. Sci.*, **2001**,26, 3~65

[4] H. S. Li, J. G. Liu, K. Wang, L. Fan, S. Y. Yang, *Polymer*, **2006**, 47, 1443~1450

[5] K. Fukukawa, M. Ueda, *Polym J*, **2006**, 38, 405~418

[6] J. G. Liu, L. F. Wang, H. X. Yang, H. S. Li, Y. F. Li, L. Fan, S. Y. Yang, *J Polym Sci, Part A: Polym Chem*, **2004**, 42, 1845~1856

[7] J. G. Liu, X. J. Zhao, H. X. Yang, H. S. Li, L. Fan, S. Y. Yang, *Macromol Chem Phys*, **2006**, 207, 1272~1277