Functional flexible substrate in altering substitution phenylene core of fluorinated poly(arylene ether)s

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Abstract: We proposed three degrees n” of phenyl substitution on the middle phenylene core of novel poly(arylene ether)s (PAEs). The PAEs were prepared via nucleophilic displacement of fluorine atoms on the terminal benzene ring with trifluoromethyl-activated bisfluoro monomer. The thermal property of polymers showed ~273 °C glass transition point and ~457 °C decomposition temperature for 5% weight loss. In addition, investigations revealed that spiro-annulated textures resulted from multi-substituted phetaphenylene moiety and trifluoromethyl groups. Furthermore, PAE films were experimentally demonstrated to have wide-range solubility, high transparencies greater than 90% in visible light region, low coefficient of thermal expansion about 30 ppm/°C, low polarities below 2.8 at 1 kHz, and hydrophobicities.

Introduction

Outstanding physical characteristics of poly(aryl ether)s (PAEs) materials has attracted much attention for potential application of polymer substrate in high speed electro-optical system.[1-4] Remarkable thermal stability, high optical transmittance, high glass transition temperature (Tg), low dielectric constant, thermo-oxidative stability, good processability, stable anti-hydrolysis and chemical resistance have become the essential properties of PAEs. [5-10]. In general, a good yield of PAE polymers could be achieved easily via the method of nucleophilic displacement of activated aromatic dihalides with bisphenolates. The leaving group is activated by electro-withdrawing substituent and has a site of un-saturation through a Meisenheimer complex [11, 12]. The synthetic process also provides a convenience to prepare the PAE compounds with demanded substituent and pendent, which strongly affected the physical property of PAEs polymer. Most commercial plastics are prepared by electron affinity and hyper-conjugation, for instance, polyethersulfone (PES), poly(aryl ether sulfone)s (PAES), polyetherimide, poly(aryl ether ketone)s (PAEK) and polyetheretherketone (PEEK). Hedrick and Labadie reported that perfluoroalkyl groups, either in a pendent position or in the main chain, activated fluoro or nitro were displaced by phenoxides.

Moreover, the enhancement of tightly packed circuitry has become an increasingly relevant issue. It was previously demonstrated to decrease the dielectric constant while maintaining thermal and mechanical characteristics of fluorinated films. Trifluoromethyl (-CF₃) groups incorporate into the polymer backbone or flank on
aromatic group, has been known as a special interest characteristic, which were the enhancement of flame resistance, solubility, thermo-oxidative stability along with concomitantly decreased dielectric constant, water absorption and crystallinity. It also serves to increase the gas permeability and electrical insulating property. [13-16]

On the basis of π-π conjugated and stack framework systems, the spiro-annulated PAEs had great influence upon optic-electrics, thermal stability and conformation within molecular interaction, bond length and torsion angle. Spontaneously helical, ladder, lamellar and spherical textures resulted in asymmetric chains [17].

In this study, preparation of the fluorinated PAEs is shown in Scheme 1. Bisfluoro monomers take action on Suzuki coupling, then polymerization use the nucleophilic displacement to generate the spiro-annulated PAEs. Good thermal stability, high optical transmittance, low dielectric constant and low coefficient of thermal expansion of PAEs are demonstrated in the experiment. Additionally, it was found that the crystallitic textures of PAEs were dependent on the number of phenyl substituents of polymers.

**Results and discussion**

Detailed procedure for synthesis of precursors, variationaly phenyl-substituted monomer and Polymers prepared by a modification of the published procedure are outlined in Scheme 1 [18-22].

![Scheme 1. The synthesis of monomers and polymers.](image-url)

The production of PAEs (P2-C-P4-C) is achieved via the nucleophilic displacement of fluorine atoms on bis(4-fluoro-3-trifluoromethyl)-n''-phenyl-quinquephenyl monomers (7-9). Monomers 7-9 are prepared through Suzuki coupling reactions of 4, 4''-dibromo-phenylsubstituted p-terphenylene (compounds 3-5) with compound 6 in
good yield. Altering the middle phenylene ring of PAEs illustrated three parts as various degree of phenylene ring, flexible ether-bridge (-O-) and pendant group. The series of PAEs illustrated a stereo view in Figure 1. Size exclusion chromatography was used to determine the molar mass distribution and is listed in Table 1. The P3-C possessed lower polydispersity index ($M_w/M_n \sim 1.73$) and high degree of polymerization upon 76.9 (DP) by GPC. This can be attributed to the asymmetry in substituted phenylene ring and catenation angle, which results in different conformation and backbone curvature.

All PAEs exhibit excellent solubility in common solvents such as chloroform, THF, DMAc and NMP. The enhancement of solubility due to the flexible ether group and crystallization of multi-substituted phenylene moiety, furthermore, bulky CF$_3$ were hindered chain packing and interaction to enhance solubility.

### Tab. 1. Yields and molar masses of poly(aryl ether)s.

<table>
<thead>
<tr>
<th></th>
<th>Yield (%)</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2-C</td>
<td>95</td>
<td>38745</td>
<td>2.23</td>
<td>22.1</td>
</tr>
<tr>
<td>P3-C</td>
<td>93</td>
<td>82518</td>
<td>1.73</td>
<td>76.9</td>
</tr>
<tr>
<td>P4-C</td>
<td>92</td>
<td>84145</td>
<td>2.53</td>
<td>43.1</td>
</tr>
</tbody>
</table>

a: Given in g.mol$^{-1}$; determined by gel permeation chromatography in THF by UV-vis detector versus polystyrene standards.
b: polydispersity index
c: degree of polymerization

![Molecular structure and stereo view of PAEs.](image)

**Fig. 1.** Molecular structure and stereo view of PAEs.

Typical spectroscopic data from $^{19}$F and $^1$H, and $^{13}$C NMR assigned the structures of the bisfluoro monomer and the trifluoromethyl groups, respectively. Figure 2 show the spectrum based on $^1$H NMR spectroscopy of monomer 8 (M8) and PAEs P3-C. The $^1$H NMR spectrum (Figure 2 (a)) supports the structure of monomer M8. After polymerization, the appearance of peak a-f in Figure 2 (b) demonstrates the occurrence of nucleophilic displacement on M8. The $^1$H spectrum of the polymer do
not show any signals corresponding to the terminal -OH, which implies success of polymerization.

Fig. 2. $^1$H NMR spectra.

Fig. 3. Absorption and PL spectra of solvent-casting PAE films prepared from (a) dichloromethane and (b) toluene; (c) UV-vis absorption and PL spectra of PAEs were in dichloromethane.
Figure 3 (a) and (b) show UV absorption spectra and photoluminescence (PL) spectra of PAEs (P2-C~P4-C) via solvent-casting with dichloromethane or toluene. Figure 3 (c) were conducted the absorption and PL spectra of PAEs in dichloromethane. The insensitive PL spectra are corresponding to the excitation wavelength in the range 210–320 nm. It is noted that the peak in PL spectra of P2-C~P4-C is 380, 375, and 360 nm, respectively. Stokes shifts of 33, 30, and 29 nm between the emission $\lambda_{\text{max}}$ and the absorption onset is consistent with emission from localized states of $\pi$-$\pi$ stacking band. In addition, a gradual blue shift of the emission $\lambda_{\text{max}}$ of lower energy state is found when the substituent was changed from di-phenyl to tri-phenyl and tetra-phenyl. Herein, the size and number of the substituent, which affected the effective conjugation length, are considered to characterize the emission band. In the sense of effective conjugation length, it becomes longer after polymerization. However, the effect of twist between adjacent planes of the phenylene rings of the main chain is dropped down due to polymerization, and thus results in a smaller geometric effect on the ground-state electronic structure of the PAEs. Moreover, in consequence of asymmetric phenyl rings and unilateral pendant relatively free to rotate along the backbone chain. P3-C and P2-C show great molecular vibration and solvent effect in dichloromethane with inspection of Uv-Vis spectra.

The optical propriety confined to torsional vibrations of multi-phenyl core, flexible ether linkage, bulky CF$_3$ and suspended bisphenol. Steric-hindrance and inductive effect resulted from electron-withdrawing group (-CF$_3$) and bulky pendant to reduce the charge transfer. It might weaken phenyl substitution chain-chain cohesive force.

**Fig. 4.** Thermogravimetric Analysis of monomers and polymer. **a:** compound 9, **b:** compound 8, **c:** compound 7; **A:** P4-C, **B:** P3-C and **C:** P2-C.

Figure 4 conducts the decomposition temperature by TGA measurement that also reveals high thermal tolerance to support the mechanical ability of PAEs and monomers. In addition, Table 2 shows a summary of the characteristics of PAEs. In Table 2, the high decomposition temperature ($T_D^{5\%}$>460°C; 5% weight loss) and the high glass transition temperature ($T_g$>270°C), determined by TGA and DSC, demonstrated that the PAEs possess outstanding thermal property.
angle over 93° implies a well hydrophobic ability. The low coefficient of thermal expansion (CTE) of about 30 ppm/°C and the RMS (root mean square) roughness below 4 nm represent a good mechanical stability and good planarization ability of PAE films by toluene-casting. In addition to the low dielectric constant of ~ 2.7 is an essential property for the reduction of parasitical effect in high-speed electro-optical devices. On the basis of the excellent physical properties, PAEs become a good candidate as a polymer substrate for highly dense electro-optics application.

Tab. 2. Thermal and Performance characteristics of PAEs.

<table>
<thead>
<tr>
<th></th>
<th>a Td (%)</th>
<th>b Tg (°C)</th>
<th>c Contact angle</th>
<th>d CTE ppm/°C</th>
<th>e εcap (1kHz)</th>
<th>f n</th>
<th>g RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2-C</td>
<td>475</td>
<td>275</td>
<td>98.3°</td>
<td>36</td>
<td>2.75</td>
<td>1.61</td>
<td>3.50</td>
</tr>
<tr>
<td>P3-C</td>
<td>460</td>
<td>274</td>
<td>93.1°</td>
<td>27</td>
<td>2.80</td>
<td>1.53</td>
<td>3.21</td>
</tr>
<tr>
<td>P4-C</td>
<td>476</td>
<td>276</td>
<td>96.5°</td>
<td>31</td>
<td>2.61</td>
<td>1.58</td>
<td>3.30</td>
</tr>
</tbody>
</table>

(a): 5% of weight loss at thermal decomposition temperature.
(b): glass-transition temperature by DSC.
(c): Contact angles of polymers by water-sessile drop method.
(d): Thermo-mechanical of expansion coefficient by TMA.
(e): Dielectric constants with capacitance method collect by Precision impedance Analyzer Agilent 4294A.
(f): Average refractive index acquired by an an elipsometer (SOPRA GESS).
(g): Thin film mean of roughness by AFM measurement.

In order to investigate the behavior of self-assembly of the PAEs, a solution of PAEs dissolved in THF was prepared and dropped on a glass substrate. As the solvent gradually evaporated, PAE molecules will aggregate and self-assemble naturally. The morphology of PAEs shot via a scanning electronic microscopy. As a result of asymmetric tri-phenyl substituent rings, the P3-C shows a spiral texture and significantly rough surface. The reason for a great effect on the particular construction of P3-C was due to torsion angle and the relative movement of the phenyl core. The spiro-conformation of P3-C owns the twist of body-centered cell between adjacent planes of the phenylene rings and cyclododecane moiety. In addition, the smooth surface of P2-C and P4-C were referred to the well π-stacking core with symmetrical substituent of phenyl ring.\[23-25\] Furthermore, the X-ray diffraction spectra of PAEs show the diffraction peak at 4.9Å and 10.5Å to indicate the space of stacking phenyl core and the distance between phenyl core and Y-pendant respectively. Interestingly, these quasi amorphous polymers have good transparency and toughness, and further to preserve chemical resistance and thermal tolerance. It may be caused by the spiro-annulated conformation with symmetric phenyl ring and different catenation angle.

In the following, we summarized the important factors which affected the characteristics of PAE polymers.

a. Molecular structure: The P4-C with symmetrical phenyl ring, showed better thermal stability (\(T_g\)~276 °C and \(T_d\)~476 °C). The symmetric structure was considered to promote the crystallization of polymer molecules. In addition,
the asymmetrical phenyl substituent of P3-C resulted in a low degree crystallization, but good for planarizability.

b. Trifluoromethyl (-CF$_3$) group: Strong electronegativity of fluorine-containing polymers led to the low dielectric constant. This will benefit high speed electronics.

Conclusions

In the study, we prepared a series of poly(arylene ether)s possessed excellent thermal stability ($T_d^{5\%}$~476 °C and $T_g$~276 °C) and remarkable transparency (>90%) in visible band. The physical property was dependent on the number of phenyl of the substituent. On the basis of the outstanding property, the PAEs were good candidates as polymer substrate for electro-optical applications.

Experimental

Materials

Commercial reagents and solvents were distilled and deoxygenated under nitrogen atmosphere before use. The bisphenols “Y” (1,1-dihydroxydiphenyl cyclododecane) are shown in Scheme 1. Polymerizations were under standard vacuum-line techniques and, dehydrated with a slow stream of nitrogen in the reaction vessel.

Synthesis of variationaly phenyl-substituted monomers and Polymers

The synthetic process of PAEs (P2-C, P3-C and P4-C) is illustrated in Scheme 1. The productions of PAEs were achieved via the nucleophilic displacement of fluorine atoms on 2-perfluoroalkyl-activated bisfluoro monomers (M7-M9). Monomers M7-M9 are prepared through Suzuki coupling reactions of compounds 3-5 with compound 6 in solvent mixtures of toluene, sodium carbonate aqueous solution and tetrakis(triphenyl phosphine) palladium. The reaction solution was stirred under reflux for few hours. Subsequently, the resultant polymer solution takes through a short column to purify by column chromatography. The six-member ring precursors 3-5 are prepared via Diels-Alder reactions of cyclopentadienone with cyclodiene or acetylenes in dry diphenyl ether. The entire synthesis of PAEs is carried out with a standard vacuum-line technique and a slow stream of nitrogen is passed the reaction vessel for dehydration.

Instrumentation and Characterization

$^1$H NMR spectra were measured by Varian UNITY INOVA-500 spectrometer, tetramethylsilane in chloroform-d solvent was used as the internal standard. UV-Visible spectra were recorded by Perkin Elmer Lambda 35 spectroscope. Thermogravimetric analysis (TGA) was carried out in Hi-Res PerkinElmer Pyris 1 system for measuring the decomposition temperature ($T_d^{5\%}$, 5% of weight loss). The rate of heating and of nitrogen flow was controlled at 15 °C/min and 20 cm$^3$/min, respectively. The melting temperatures ($T_m$) and the glass transition ($T_g$) were obtained via the utilization of differential scanning calorimeter (PerkinElmer Pyris Damond DSC system). Gel permeation chromatography (GPC) analysis was conducted with a Polymer Laboratories HPLC system equipped with GPC KF-803L. The synthesized PAEs were characterized, in detail, by these measurements. In addition, the dielectric constant (k) and the surface contact angle were estimated by
Precision Impedance Analyzer (Agilent 4294A) and KRÜSS DSA 100 (SOPRA GES5), respectively.

References