# Functional Poly(arylene ether)s Films with High Thermal Stability and Optical Transparency

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<th>Journal:</th>
<th>Soft Materials</th>
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<td>Manuscript ID:</td>
<td>LSFM-2010-0134.R1</td>
</tr>
<tr>
<td>Manuscript Type:</td>
<td>Original Article</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>22-Sep-2010</td>
</tr>
</tbody>
</table>
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| Keywords: | thermal stability, nucleophilic displacement, flexible substrate, film |
Functional Poly(arylene ether)s Films with High Thermal Stability and Optical Transparency

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Abstract:

In the study, the authors proposed four types of the poly(arylene ether)s monomer with remarkable thermal stability and high optical transmittance. The poly(arylene ether)s were synthesized via nucleophilic displacement on a 2-trifluoromethyl-activated bisfluoro monomer, which reacted with bisphenyl pendants. Thermal analysis indicated the poly(arylene ether)s possessed a high glass transition point of ~320°C and the decomposition temperature Td=500°C at a weight loss of 5%. In addition, high transmittance of 92%, low dielectric constant of ~1.9, and good mechanical property of the poly(arylene ether)s film were experimentally verified. The physical property of the poly(arylene ether)s provides high potential as a substrate for various flexible electronics.

1. Introduction

Poly(aryl ether)s materials has been widely explored due to the achievement in desirable physical properties, such as good thermal stability, high mechanical performance, and low dielectric constant [1-6]. In general, the poly(arylene ether)s monomer could be synthesized by the nucleophilic displacement of activated aromatic dihalides, dinitro compounds with alkali-metal bisphenolates [7-10]. The nucleophilic displacement method was also adopted in typical commercial engineering plastic of polyethersulfone [11], poly(aryl ether sulfone)s [11], polyetherimide [7], poly(aryl ether ketone)s [12] and polyetheretherketone [5]. The nucleophilic displacement is an attractive method because high yield of the chemical reaction could be easily achieved via this synthetic approach.
Recently, polymer films are extensively employed as a flexible substrate for highly dense circuit [13-18]. The outstanding mechanical property of the polymer substrate is demanded for fabricating flexible electronics, high thermal stability for device reliability, and low dielectric constant for reducing the parasitics, which significantly affected device performance. It is difficult to develop a material possesses the all advantages mentioned above. However, the poly(aryl ether)s film reveals excellent physical property as a multifunctional polymer substrate.

In this study, the authors prepared four bis-trifluoromethyl-constructed PAEs, attached with different bisphenols pendants, via the nucleophilic displacement. The physical characteristics of PAEs films were strongly dependent on the pattern of the bisphenols pendant and the polymer structure. The PAEs films showed high thermal stability, good mechanics, and a consistent transparency in visible regime. In the following sections, we will in detail describe the synthetic procedure and the physical characteristics of the PAEs material.

2. Experiment

Scheme 1 shows the synthetic procedure of the poly(aryl ether)s (PAEs) in the experiment. A series of PAEs (P-A1, P-A2, P-B1, and P-B2) were carried out through the nucleophilic displacement of the fluorine atoms with activated bisphenols pendants (A1, A2, B1, and B2). The pattern of bisphenols pendant A1 and B1 was a symmetric hexagonal-phenyl-ring, attached with two ethers (-O-) at ortho-position and at papr-position, respectively. A2 and B2 showed an asymmetry hexagonal-phenyl-ring instead of the symmetric hexagonal-phenyl-ring, as illustrated in scheme 1. The bis(4-fluoro-3-trifluoromethyl)-n′′-phenyl-quinquephenyl (FM4) was prepared via Suzuki coupling of 4-fluoro-3-trifluoromethyl phenyl boronic acid on the precursor of 4,4′′-dibromo-phenylsubstituted p-terphenylene (M4). The reaction occurred in a solvent mixture of toluene, Na2CO3(aq), and Pd(PPh3)4. The difference between A-series (P-A1, P-A2) and B-series (P-B1, P-B2) PAEs was due to the linking position of the bisphenols pendant and the position determined the major structure of the PAEs monomers. The polymerization was cleaned with methanol in order to purify the final PAEs. All polymerizations were conducted using standard vacuum-line techniques. A good yield over 80% was
achieved via the synthetic method.

In the study, the physical property of the PAEs was demonstrated by Nuclear magnetic resonance (NMR) spectra, UV-Visible spectra, and the analyses of Thermogravimetric (TGA), Differential scanning calorimeter (DSC), and Gel permeation chromatography (GPC). The molecular structure of the PAEs was identified by NMR spectra (Bruker AM-300WB spectrometer), where chloroform-d and tetramethylsilane were as solvent and as the internal standard respectively. UV-Visible spectra of the PAEs film were recorded by Perkin Elmer Lambda 35 spectroscopy. The thermal feature was demonstrated by TGA and DSC analyses (PerkinElmer Pyris Diamond DSC system). GPC analysis was conducted with a Polymer Laboratories HPLC system, which was equipped with GPC KF-803L columns in series using polystyrene as the standard and THF as the mobile phase. In addition, the dielectric constant (k) and the surface contact angles were estimated by Precision Impedance Analyzer (Agilent 4294A) and KRÜSS DSA 100 (SOPRA GES5). Scanning electronic microscopy showed the morphologies of PAEs film. The above analytical techniques led to a precise description of PAEs material properties.

3. Results and Analysis

In the experiment, the physical property of PAEs polymers was investigated and the result showed that the property was strongly dependent on the pattern of the bisphenols pendant, the monomer structure, and the degree of the polymer crystallization. Figure 1 shows the optical transmittances of the bisphenol pendants (A1, A2, B1, and B2) and the corresponding PAEs monomers. The spectra were acquired from a Fourier transform infrared spectroscopy (FTIR), and that indicated the chemical structure of the molecules. In figure 1 (a), the spectrum of bisphenols pendant A1 was characterized with two feet at around the wavenumber of 3000 and 3500 cm$^{-1}$, attributed to the fluorine atoms and the trifluoromethyl groups respectively. Comparing that to the spectrum of PAEs P-A1, the vanish of the foot at around 3500 cm$^{-1}$ (the evidence of the existence of fluoro-attachment) presented that the nucleophilic displacement of the fluorine atoms occurred on the terminal symmetric-phenyl-ring, integrated with bisphenols. Figure 1 (b), (c), and (d) illustrated the same result. Figure 1 demonstrated
the occurrence of the nucleophilic displacement, as well to the success of the synthesis. Besides, the NMR spectra (not shown in the article, characterized with the FT-Mass, $^1$H and $^{19}$F), was used to further prove the loss of the terminal -OH or -F groups after the chemical reaction.

Figure 2 shows the weight loss curve of the PAEs films and the monomer (FM4). A heating rate of 15°C/min and a nitrogen flow of 20cm$^3$/min were controlled in TGA measurement. The temperature ranged from T=25°C to T=900°C. In Figure 2, P-A1, P-A2, P-B1, and P-B2 film showed high decomposition temperature (5% weight loss) of 510, 470, 550, and 550°C, respectively. About 200°C higher than that of the monomer FM4 (Td~300°C) implied high thermal stability possessed by the PAEs films. The superior thermal stability was referred to the additional bisphenols pendants. In addition, B-series polymer performed better thermal property (higher decomposition temperature) than A-series polymer. Stronger steric hindrance caused by A-series polymer may be the cause of the experiment result. A-series polymer, attached with flexible bisphenyl pendants, revealed an un-neglected steric hindrance to drop the polymers aggregation, as well to decrease the degree of the polymer crystallization.

After heating treatment, a ~10 % char residues of P-A1 and P-B1 (with the symmetric hexagonal-phenyl-ring) higher than that of P-A2 and P-B2 (with the asymmetric hexagonal-phenyl-ring) was considered to be caused by the pattern of the bisphenols pendant. The symmetric structure of the pendant slightly affected the thermal property of the polymers.

In Table 1, we summarized the physical property of the PAEs film. The average glass transition temperature (Tg) over 300°C represented the outstanding thermal property as TGA analysis. The thermal stability showed that the PAEs could be treated in a high temperature environment. Highest contact angle of 135.4° suggested a good hydrophobic ability. The less water residual on the polymer surface dropped down the possible pollution. Besides, the PAEs show a low coefficient of thermal expansion (CTE) about 20 ppm/°, which revealed a good mechanical stability. RMS roughness below 6 nm, measured by an atomic force microscopy (AFM), demonstrated good planarization ability. The two mechanical advantages were helpful for the preparation of a stable and smooth substrate. The low
dielectric constant ranged from 1.87 to 2.01, was estimated by a Precision Impedance Analyzer (Agilent 4294A). On the basis of the excellent physical properties, the prepared PAEs revealed high potential as a polymer substrate for high speed electronic devices. On the other hand, the good yield and low polydispersity index (1.89<Mw/Mn<5.30, PDI) indicated the steady synthesis in the experiment.

Figure 3 shows that the A-series PAEs films exhibited ~90% and ~65 % transmittance in visible and in UV band respectively. The uniform transmittance in whole visible band was important to colorful displays without color distortion. The lower transmittance of B-series, as shown in Figure 3, was inferred to the higher degree of polymer crystallization. The interface between the crystallized domains may lead to stronger scattering, which decreased the transmittance. The occurrence of π - π * transition was considered to cause the loss of optical energy in UV band.

In order to investigate the self-arranged behavior of the PAEs monomer, the solution with doping of the PAEs monomer was prepared and that was dropped on a glass substrate. When the solvent (THF) evaporated gradually, the monomers naturally aggregated and self-arranged via the inter-molecular force. Figure 4 shows the scanning electronic microscopy of the PAEs after the solvent completely evaporated. In Figure 4, P-A1 and P-B1 exhibited the folded chain conformation due to the better polymer crystallization. Comparing to P-A1 and P-B1, P-A2 and P-B2 showed a smoother surface naturally formed after the polymer aggregation. The pendant pattern was suggested to be the cause of the difference of polymer self-arranged behavior. In the case of P-B1, clear stick-like structures formed due to the rigid pendant with the symmetric hexagonal-phenyl-ring. However, P-B2 showed more polymer flexibility based on the asymmetric hexagonal-phenyl-ring and the smooth surface was constructed via the isotropic molecular arrangement.

Table 2 shows the solubility of the PAEs. At room temperature, the PAEs with CF3 group were well soluble in most commercial solvent of CHCl3, THF (tetrahydrofuran), DMF (dimethylformamide), DMAc (dimethylacetamide), and NMP (N-methylpyrrolidone), but not in the polar-solvent methonal. The functional trifluoromethyl groups in the polymer backbone led to the distinctive solubility due to
the significant electronegativity. The wide range of organic solvents indicated that the prepared PAEs could be easily processed in various applications.

In a summary, the experiment result demonstrated the excellent physical property of the PAEs film. High yield synthesis and good solubility led to high potential for industry manufacture. In the following, the qualitative discussion on the characteristics of PAEs was described based on the important parameters: monomer structure, pendant pattern, and trifluoromethyl (-CF₃) group.

1. Monomer structure: Comparing to A-series polymer, the thermal stability of B-series polymer was referred the degree of the polymer crystallization. The linear structure of the polymer backbone promoted the aggregate densely. The intense polymer aggregation led to high T_g~320°C and T_d~548°C.

2. Pendant pattern: The pendant with symmetric hexagonal-phenyl-ring or asymmetric hexagonal-phenyl-ring dominated the flexibility of the polymer. The more flexible polymer chain was the basis of the superior planarization ability.

3. Trifluoromethyl (-CF₃) group: Significant electronegativity of fluorine-containing polymers led to remarkable solubility and low dielectric constant.

For detail understanding the effect of monomer structure and pendant pattern on polymer property, a theoretical analysis is required and in progress.

4. Conclusion

Four types of poly(arylene ether)s were prepared as functional flexible film. The poly(arylene ether)s films possessed excellent thermal stability (T_d=500°C and T_g=300 °C) and remarkable visible light transparency (90%). The physical properties of the poly(arylene ether)s were significantly affected by the linking position and the type of bisphenol pendants. Due to the excellent physical advantages the prepared PAEs could be a good candidate for flexible electronics.
Reference:


15. US patent no. 4835197, 5658994, 5108840, 5114780, 5145936 and 5155175.


URL: http://mc.manuscriptcentral.com/softmaterials Email: user@test.demo
Table 1 Physical property of PAE

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<th>%d (°C)</th>
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Table 2 Solubility of bisfluoro poly(arylene ether)s at room temperature

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* good, ☑ partial, X bad
Scheme, Figure Captions and Supplemental Material Titles

Scheme 1. The synthesis of monomers and polymers

Figure 1. FTIR spectra of Bisphenols moiety and Polymer

Figure 2. Thermogravimetric Analysis of PAEs

Figure 3. Transmissive spectra of PAEs in UV-VIS light band

Figure 4. SEMs of PAEs monomers
Scheme 1. The synthesis of monomers and polymers
Figure 1. FTIR spectra of Bisphenols moiety and Polymer
Figure 2. Thermogravimetric Analysis of PAEs
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Huang and Lee et al, Figure, 4

Figure 4. SEMs of PAEs monomers
Functional Poly(arylene ether)s Films with High Thermal Stability and Optical Transparency

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Abstract:

In the study, we propose four novel variationally substituent pendant of poly(arylene ether)s with outstanding thermal stability and high optical transmittance. The poly(arylene ether)s are synthesized via nucleophilic displacement on a 2-trifluoromethyl-activated bisfluoro monomer, which reacted with bisphenly pendants. The experimental result shows that the poly(arylene ether)s owned outstanding physical characteristics, such as glass transition point of ~325°C, decomposition temperature Td~540°C at a weight loss of 5%. In addition, high transmittance of 92% in visible region, low dielectric constant of ~1.9 and good mechanical property of the poly(arylene ether)s films were experimentally verified. The well physical property leads to a potential application of poly(arylene ether)s compounds as polymer substrates for electro-optical system.

1. Introduction

Poly(aryl ether)s have been widely explored due to desirably physical characteristics, such as good thermal stability, high mechanical performance, and low dielectric constant, are essential to polymer materials for applications in electro-optical systems [1-6]. In general, the poly(aryl ether)s monomer could be synthesized by the nucleophilic displacement of activated aromatic dihalides, dinitro compounds with alkali-metal bisphenolates [7-10]. The nucleophilic displacement was also adopted in commercially engineering plastics of polyethersulfone [11], poly(aryl ether sulfone)s [11], polyetherimide [7], poly(aryl ether ketone)s [12] and polyetheretherketone [5]. The nucleophilic
displacement is an attractive method because of high yield could be easily achieved via this synthetic approach.

Recently, polymer films are extensively employed as a flexible substrate for highly dense circuit [13-18]. The outstanding mechanical property of the polymer substrate is demanded for fabricating flexible electronics, high thermal stability for device reliability and low dielectric constant for reducing the parasitic. Therefore, to develop new polymer materials with good physical or chemical property becomes more important for improving the performance of optical or electro-optical devices.

In this study, we prepared four bis-trifluoromethyl-constructed PAEs as a multifunctional polymer substrate, which attached with different bisphenols pendants via the nucleophilic displacement. The physical characteristics of PAE films were strongly dependent on the pattern of the bisphenol pendant and the spiro-annulated polymer structure that showed high thermal stability, good mechanics and a consistent transparency in visible regime. In the following, we are in detail to describe the synthetic procedure and the physical characteristics of the PAE materials.

2. Experiment

Scheme 1 shows the synthetic procedure of poly(aryl ether)s (PAEs) in the experiment. A series of PAEs (P-A1, P-A2, P-B1 and P-B2) were carried out through the nucleophilic displacement of the fluorine atoms with activated bisphenols (A1, A2, B1 and B2). The pattern of bisphenol pendant A1 and B1 was a symmetric hexagonal-phenyl-ring that attached with two ethers (-O-) at ortho-position and at para-position, respectively. A2 and B2 showed an asymmetric hexagonal-phenyl-ring to illustrate in scheme 1. The bis(4-fluoro-3-trifluoromethyl)-n’’-phenyl-quinquephenyl (FM4) was prepared via Suzuki coupling of 4-fluoro-3-trifluoromethyl phenyl boronic acid on the precursor of 4,4’’-dibromo-phenylsubstituted p-terphenylene (M4). The reaction occurred in a solvent mixture of toluene, Na2CO3 and Pd(PPh3)4. The difference between A-series (P-A1, P-A2) and B-series (P-B1, P-B2) PAEs was due to the linking position of the bisphenols that determined the major conformation of the PAE polymers. The polymerized compound was subsequently cleaned with methanol and the fibrous polymer was precipitated in situ. All polymerizations were conducted under standard
vacuum-line techniques. A good yield over 80% was achieved through the nucleophilic displacement as polymerization.

In the study, the identification of the PAEs was demonstrated by FT-Mass, Fourier transform infrared spectroscopy (FTIR) and Nuclear magnetic resonance (NMR; Bruker AM-300WB spectrometer) spectra where chloroform-d and tetramethylsilane were as solvent and internal standard respectively. The Polydispersity index of PAEs was measured via Gel permeation chromatography (GPC) analysis which was accomplished with a Polymer Laboratories HPLC system equipped by GPC KF-803L columns in series using polystyrene as the standard and THF as the mobile phase. The thermal feature was demonstrated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) (Perkin Elmer PYRIS 1 and PerkinElmer Pyris Damond DSC system). Additionally, The physical and optical investigation of the PAEs was demonstrated by the following measurements led to a precise description of PAE properties. A spectrometer (Perkin Elmer Lambda 35) was used to record the UV-Visible spectra of PAE films. The dielectric constant (k) and the surface contact angles were estimated by Precision Impedance Analyzer (Agilent 4294A) and KRÜSS DSA 100 (SOPRA GES5). Scanning electronic microscopy showed the morphologies of PAE films.

3. Results and Analysis

In the experiment, the result of functional PAEs showed that the physical property was strongly dependent on the pattern of the bisphenols, such as the conformation and the degree of the polymer crystallization. Figure 1 shows the FTIR spectra of the bisphenol pendants (A1, A2, B1, and B2) and the corresponding PAE polymer that indicated the vibrational characteristics of the monomers. In figure 1 (a), the spectrum of bisphenols pendant A1 was characterized with two feet at the wavenumber of 3000 and 3500 cm⁻¹ to attribute for the fluorine atoms and the trifluoromethyl groups respectively. Comparing that to the spectrum of PAEs P-A1, the vanish of the foot at around 3500 cm⁻¹ (the evidence of the existence of fluoro-attachment) presented that the nucleophilic displacement of the fluorine atoms occurred on the terminal symmetric-phenyl-ring to integrate with bisphenols. Figure 1 (b), (c), and (d) illustrated the same result. Figure 1 demonstrated the occurrence of the nucleophilic
displacement, which were as well to the success of the synthesis. Besides, the NMR spectra (Supporting information shown the characterized with the $^1$H NMR, FT-Mass, $^1$H and $^{19}$F), was used to further prove the loss of the terminal -OH or -F groups after the chemical reaction.

Figure 2 shows the weight loss curve of the PAE films and the monomer (FM4). A heating rate of $15^\circ$C/min and a nitrogen flow of $20\text{cm}^3/\text{min}$ were acquired from TGA measurement that ranged from $T=50^\circ$C to $T=900^\circ$C. In Figure 2, the P-A1, P-A2, P-B1 and P-B2 film showed high decomposition temperature ($5\%$ weight loss) of $510$, $470$, $550$ and $550^\circ$C, respectively that implied high thermal stability for PAE films. The superior thermal stability was referred to the additional bisphenol pendants. In addition, B-series polymer performed better thermal property (higher decomposition temperature) than A-series polymer. A sterically encumbered hindrance caused by A-series polymer could be suggested to experiment result. A-series polymer that attached with flexible bisphenyl pendants to reveal an un-neglected sterical hindrance to enhance the polymers aggregation, as well to decrease the degree of the polymer crystallization.

In TgA curve, a $\sim 10\%$ char residues of P-A1 and P-B1 (with the symmetric hexagonal-phenyl-ring) was higher than that of P-A2 and P-B2 (with the asymmetric hexagonal-phenyl-ring), which considered to be caused by the pattern of the bisphenols pendant. The unilateral pendant along backbone was strongly affected the thermal property of the polymers.

Table 1 summarized the physical property of the PAE films. The average glass transition temperature (Tg) over $300^\circ$C represented the outstanding thermal property as TGA analysis. The thermal stability showed the PAEs to be treated in a high temperature environment. Highest contact angles of $135.4^\circ$ suggested a good hydrophobic ability that implied less water residual and negative waterlogged polymer surface with Sessile drop method. Besides, the PAEs revealed a good mechanical stability to show a low coefficient of thermal expansion (CTE) about $20\text{ppm}/^\circ$C. The RMS roughness was below 6 nm, which measured by an atomic force microscopy (AFM) to demonstrate good planarization ability. Both of mechanical ability was helpful for the preparation of a stably flexible substrate. The low dielectric constant ranged from $1.87$ to $2.01$, was estimated by a Precision
Impedance Analyzer (Agilent 4294A). On the basis of the excellent physical properties, the prepared PAEs revealed high potential as a polymer substrate for high speed electronic devices. On the other hand, the good yield and low polydispersity index (1.89<Mw/Mn<5.30, PDI) indicated the steady synthesis in the experiment.

Figure 3 shows the A-series PAEs films exhibited ~90% transmittance in visible light region. The uniform transmittance in whole visible band was important to colorful displays without color distortion. The lower transmittance of B-series as shown in Figure 3, which was inferred to the higher degree of polymer crystallization. The interface between the crystallized domains may lead to stronger scattering that decreased the transmittance. Additionally, the occurrence of π-π* transition was considered to cause the loss of optical energy in ultraviolet area.

In order to investigate the self-arranged behavior of the PAE polymers, the solution with doping of PAEs was prepared and then dropped on a glass substrate. When the solvent (THF) evaporated gradually, the polymers naturally aggregated and self-arranged behavior via the inter-molecular force. Figure 4 shows the scanning electronic microscopy of the PAEs after the solvent completely evaporated. In Figure 4, P-A1 and P-B1 exhibited the folded chain conformation due to the fully symmetric and spiro-annulated pendant. Contrary to P-A1 and P-B1, the P-A2 and P-B2 showed a smoother surface naturally formed after the polymer aggregation. The pendant pattern was suggested to be the cause of polymer self-arranged behavior and crystallization. In the case of P-B1, clear stick-like structures formed due to the rigid pendant with the symmetric hexagonal-phenyl-ring. However, P-B2 showed more polymer flexibility based on the asymmetric hexagonal-phenyl-ring and the smooth surface was constructed via the segmental motion of anisotropic phenyl pendant.

Table 2 shows the solubility of the PAEs at room temperature. The PAEs with CF3 group were well soluble in most commercial solvent of CHCl3, THF (tetrahydrofuran), DMF (dimethylformamide), DMAc (dimethylacetamide), and NMP (N-methylpyrrolidone), but not in the polar-solvent methonal. Cause of functional trifluoromethyl groups in the polymer backbone led to the distinctive solubility due to the significant electronegativity. The utilization of widely organic solvents indicated that the
prepared PAEs could be easily processed in various applications.

In a summary, the experiment result demonstrated the excellent physical property of the PAE films. A good yield synthesis and well solubility led to high potential for industry manufacture. In the following, the qualitative discussion on the characteristics of PAEs was described based on the important parameters: monomer structure, pendant pattern, and trifluoromethyl (-CF₃) group.

1. Monomer structure: Comparing to A-series polymer, the thermal stability of B-series polymer was referred the degree of the polymer crystallization. The linear backbone of PAEs promoted the aggregate densely. The intense of B-series led to high $T_g \approx 325\, ^\circ C$ and $T_d \approx 540\, ^\circ C$.

2. Pendant pattern: The pendant with symmetric hexagonal-phenyl-ring or asymmetric hexagonal-phenyl-ring dominated the flexibility of the polymer. The more flexible polymer chain was the basis of the superior planarization ability.

3. Trifluoromethyl (-CF₃) group: Significant electronegativity of fluorine-containing polymers led to remarkable solubility and low dielectric constant.

For detail understanding the effect of monomer structure and pendant pattern on polymer property, a theoretical analysis is required and in progress.

4. Conclusion

Four novel poly(arylene ether)s were prepared as functional flexible films. The PAE films possessed excellent thermal stability (approach of $T_d \approx 540\, ^\circ C$ and $T_g \approx 325\, ^\circ C$) and remarkable visible light transparency (90%). The physical properties of the poly(arylene ether)s were significantly affected by the linking position and the type of bisphenol pendants. Due to the excellent physical advantages the prepared PAEs could be a good candidate for flexible electronics.
Reference:


15. US patent no. 4835197, 5658994, 5108840, 5114780, 5145936 and 5155175.


<table>
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<tr>
<th>Polymer</th>
<th>Tm (°C)</th>
<th>Tg (°C)</th>
<th>Contact angle</th>
<th>CTE (ppm/°C)</th>
<th>$n_{av}$ (UM)</th>
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<td>510</td>
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<td>1.99</td>
<td>4.10</td>
<td>5.30</td>
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<td>P-B2</td>
<td>540</td>
<td>318</td>
<td>114.3°</td>
<td>16.9</td>
<td>2.01</td>
<td>3.27</td>
<td>4.20</td>
<td>89.3</td>
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Table 2 Solubility of bisfluoro poly(arylene ether)s at room temperature

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<th>Polymer</th>
<th>Methanol</th>
<th>Toluene</th>
<th>CHCl₃</th>
<th>THF</th>
<th>DME</th>
<th>DMEa</th>
<th>PBMA</th>
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<td>PA-1</td>
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</tbody>
</table>

* #: good, □: general or partial, ×: bad
Scheme, Figure Captions and Supplemental Material Titles

Scheme 1. The synthesis of monomers and polymers

Figure 1. FTIR spectra of bisphenol moiety and Polymer (Transmission mode)

Figure 2. Thermogravimetric Analysis of PAEs

Figure 3. Transmissive spectra of PAEs in UV-VIS light band

Figure 4. SEMs of PAE monomers
Huang and Lee et al, Scheme, 1

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Huang and Lee et al, Figure, 1

Figure 1. FTIR spectra of bisphenols moiety and Polymer (Transmission mode)
Figure 2. Thermogravimetric Analysis of PAEs
Huang and Lee et al, Figure, 3

Figure 3. Transmissive spectra of PAEs in UV-VIS light band
Huang and Lee et al, Figure, 4

Figure 4. SEMs of PAE monomers
The synthesis and influence of arylen ether positions and phenyl substituents on the physical properties of functional fluorinated polymers
Huang and Lee et al, Figure 1

The 1H and 13C NMR spectra of P-B1
The phase transition temperature acquired by differential scanning calorimeter (DSC) (PerkinElmer Pyris Damond DSC system)
UV-Vis and PL spectra of PAEs presented the occurrence of π-π* transition that was considered to cause the loss of optical characteristics.
A real sample of P-B2 film prepared by spin-cast which thickness was 0.3mm
Investigation of PAE films collected from XRD to demonstrate semi-crystal phase in broad FWHM.