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Novel poly(arylene ether)s containing multi-substituted pentaphenylene moiety

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Abstract

Three novel 2-trifluoromethyl-activated bisfluoro monomers have been synthesized successfully using a Suzuki-coupling reaction of 4-fluoro-3-trifluoromethyl phenyl boronic acid with 4,4′-dibromo-*p*-terphenyls with varied phenyl substitution on the middle phenylene ring. Three monomers were converted to a series of phenyl substituted poly(arylene ether)s by nucleophilic displacement of the fluorine atoms on the terminal benzene ring with several bisphenols. The polymers obtained by displacement of the fluorine atoms exhibit weight-average molecular weight up to 2.25×10^5 g/mol in GPC. Thermal analysis studies indicated that these polymers did not show melting endotherms but did show ultrahigh T_g values up to 334 °C in DSC and outstanding thermal stability up to 671 °C for 5% weight loss in TGA under nitrogen atmosphere. The polymers are soluble in a wide range of organic solvents: THF, $CHCl_3$, NMP, DMAc, DMF, toluene, etc., and are insoluble in DMSO and acetone at room temperature. Transparent and flexible films were easily prepared by solution casting from chloroform solution of each of the polymers. The UV absorption spectra of thin films showed no absorption in the visible light region of the spectrum, suggesting a good application to optical transparent materials in the visible light region of the spectrum.

Keywords: Poly(arylene ether); High T_g; Flexible substrate

1. Introduction

Poly(arylene ether)s (PAEs) [1–6] have been attracting a considerable amount of attention due to their excellent physical properties, such as: high level of strength, high glass transition temperature, good processability, good electrical properties, thermo-oxidative stability and chemical resistance.

Most success in preparation of PAEs is achieved by nucleophilic displacement reactions of dihalo or dinitro compounds with alkali–metal bisphenolates. Nucleophilic aromatic substitution occurs when the leaving group is activated by electron-withdrawing substituents. Examples of three commercial engineering plastics prepared this way are polyethersulfone [7,8], polyetherimide [1d] and polyetheretherketone [9,10]. The polyethersulfone involves displacement of halo groups activated by SO_2, usually referred to as a polysulfone even though ether linkages are formed in the polymerization reaction. With the polyetherimide, displacement of the nitro groups is promoted by the electron-withdrawing imide. The polyetheretherketone, involving displacement of halo groups activated by ketone, provides a polymer called PEEK. Based on the common characteristics of the stabilization of negative charges developed on the aryl moiety in the transition state of the nucleophilic halogen displacement reaction through a Meisenheimer complex [11], which lowers activation energy for displacement, Hedrick and Labadie [1] reported that perfluoroalkyl groups either in a

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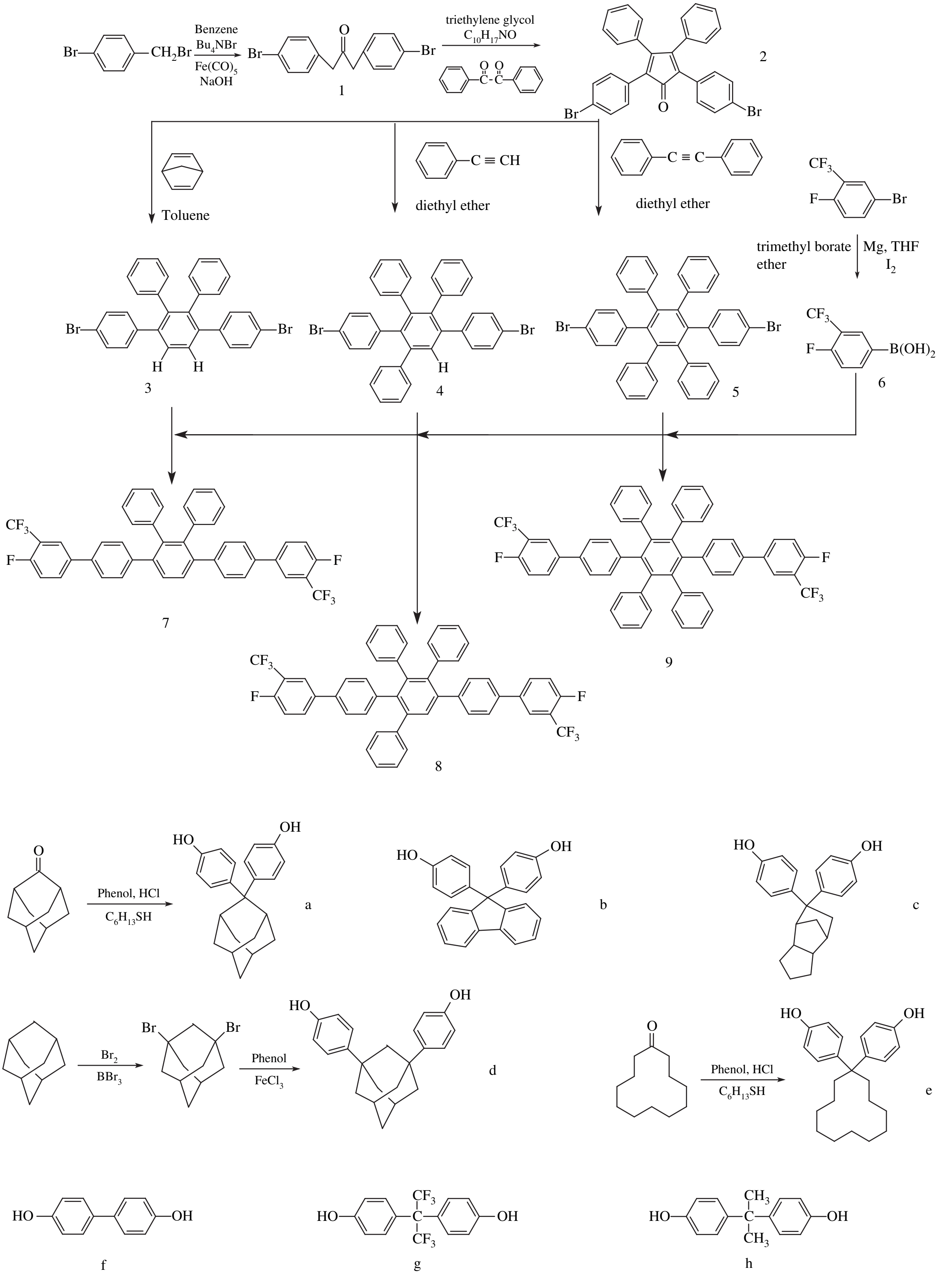
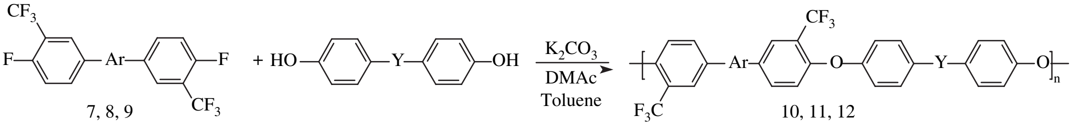
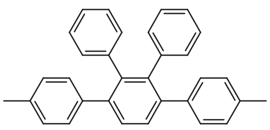
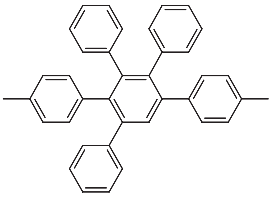
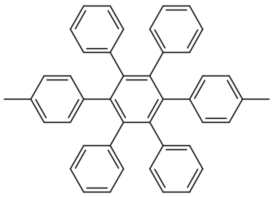
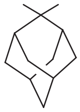
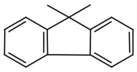
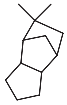
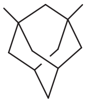
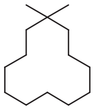
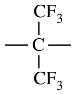
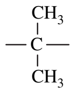


Scheme 1. The synthesis of monomers.

pendent position or in the main chain activate fluoro or nitro displacement by phenoxides.

Panel substrates used for conventional display panels have been made exclusively of inorganic glass, and plastic panels have not yet been put to practical use for a number of reasons. One of the major reasons is that plastic substrates for display [12–14] must satisfy the following requirements at the same time: (1) to be optically transparent to light in the visible



Ar / Y				
a		10a	11a	12a
b		10b	11b	12b
c		10c	11c	12c
d		10d	11d	12d
e		10e	11e	12e
f	–	10f	11f	12f
g	 $-\overset{CF_3}{\underset{CF_3}{C}}-$	10g	11g	12g
h	 $-\overset{CH_3}{\underset{CH_3}{C}}-$	10h	11h	12h

Scheme 2. The synthesis of polymers.

region of the spectrum; (2) to be impervious to moisture, and (3) to be sufficiently stable to withstand the manufacturing thermal processes with high temperatures up to 300 °C.

Because of rapid advancement in the microelectronic industry, the enhanced performance of tightly packed circuitry has become an increasingly relevant issue. Decreasing the dielectric constant while maintaining thermal and mechanical properties of the thin film interlayer dielectric materials [15,16] is highly desirable. Fluorine-containing polymers [9,17,18] are of special interest because of their possible use as gas selective membranes and their enhanced flame resistance, low dielectric constant, and remarkably low water absorption. The trifluoromethyl groups in the polymer backbone enhance polymer solubility without any forfeiture of thermal stability. They also increase the glass transition temperature with a concomitant decrease of crystallinity. This bulky group also serves to increase various properties of polymers, including gas permeabilities [11] and electrical insulating properties. Because of all these interesting properties of the fluorinated polymers, considerable attention has been devoted to the preparation of new classes of fluorine-containing polymers.

In this paper, we report the successful synthesis of the bisfluoro monomers shown in Scheme 1 via Suzuki-coupling [19,20] and subsequent utilization of these monomers in a nucleophilic aromatic substitution polymerization (Scheme 2) with different bisphenols [11,21–23], as well as their characterization.

2. Experimental

2.1. Characterization

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were collected on a Bruker AM-300 WB spectrometer. Chloroform-*d* was used as solvent and tetramethylsilane (TMS) was used as the internal standard. UV spectra were recorded using a DMS-300 spectrophotometer. Thermogravimetric analysis (TGA) was conducted on a PerkinElmer Pyris 1 system with a Hi-Res thermogravimetric analyzer. The heating rate was 20 °C/min, and the nitrogen or air flow rate was 20 cm^3/min. Differential scanning calorimetry (DSC) was run on a PerkinElmer Pyris 1 system. All melting temperatures (T_m) and glass transitions (T_g) were obtained using DSC. The T_g was taken from the reflection point of the step transition, while T_m was taken from the maximum of the endothermic peak in the second heating run. Gel permeation chromatography (GPC) analysis was conducted with a Polymer Laboratories HPLC system equipped with Polymer Laboratories ultra Styragel Mixed-D 3, 2 and 1 (7.8 mm i.d. × 300 mm) columns in series. Polystyrene was used as the standard and tetrahydrofuran as the eluent. Optical quality thin films of polymers were obtained by solvent casting chloroform solutions onto quartz substrates. All the films were dried at 80 °C for 12 h and then at 120 °C for 24 h in a vacuum before measurement. Dynamic mechanical analysis (DMA) was performed on a PerkinElmer Pyris 1 system with a mechanical thermal analysis controller in tension mode on thin film samples under a heating rate of 20 °C/min and a frequency of 1 Hz.

2.2. Materials

All reagents and solvents were purchased from Aldrich Chemical Co., Merck, Lancaster, Fluka or Fisher. Spectroscopic grade dichloromethane was used for all absorption and emission experiments. Diphenyl ether was purchased as dry solvent and used as received. Diethyl ether and tetrahydrofuran (THF) were dried over sodium benzophenone and distilled in an argon atmosphere before use. Toluene was dried over CaH and then distilled in an argon atmosphere and deoxygenated by purging with argon for 30 min before its use in monomer synthesis. Bisphenols 4,4′-dihydroxybiphenyl, 4,4′-(1-methylethylidenelbisphenol (BPA), 4,4′-(hexafluoroisopropylidene)bisphenol (6F BPA) and 9,9′-bis(4-hydroxyphenyl)fluorene were purchased from Aldrich Chemical Co. and used without further purification. All polymerizations were conducted using standard vacuum-line techniques and, in order to remove the water produced by the reaction, a slow stream of argon was passed through the reaction vessel during the course of polymerization.

2.3. Monomer synthesis

For successful preparation of PAEs via nucleophilic displacement reactions of dihalo compounds with alkali–metal bisphenolates, the corresponding monomers **7–9** and bisphenols **a–h** have to be prepared in large quantities to obtain good yields (Scheme 1). While some bisphenols were already known and described in the literature [2,6,21], the synthetic procedures for the other monomers are provided below. Self-coupling [18] of 4-bromobenzyl bromides with catalyst $Fe(CO)_5$ and phase transfer reagent Bu_4NBr in an alkali aqueous solution accomplished **1** in fair yield, which were cyclolized after re-crystallization without further characterization. Cyclolization of **1** with benzil in a solvent mixture of triethylene glycol, benzyltrimethyl ammonium hydroxide, and methanol gave **2** in fair to good yield. Diels–Alder reactions [24] of cyclopentadienone **2** were carried out with 1.1 equiv mol of cyclodiene or acetylenes in dry diphenyl ether, which furnished six-member ring precursors **3–5** in good to excellent yields. Couple reactions of compounds **3–5** were carried out using Suzuki reactions with 2.3 equiv mol of compound **6** in solvent mixture of toluene, sodium carbonate aqueous solution (1 M) and tetrakis(triphenyl phosphine) palladium (0), which furnished monomers **7–9** in good to excellent yields. The detailed procedure for creation of precursors **1–6**, monomers **7–9** and polymers **10–12** could be referred to Supplementary data.

2.3.1. General procedure for the preparation of the monomers (7–9)

Couple reactions of compounds **3–5** were carried out using Suzuki reactions [24] with 2.3 equiv mol of compound **6** in solvent mixtures of toluene, sodium carbonate aqueous solution (1 M) and tetrakis(triphenyl phosphine) palladium (0). These reactions produced monomers **7–9** in good to excellent yields. The detailed procedure for creating each monomer is given separately below.

One equivalent mole of precursors (**3–5**), 0.03 equiv mol of $Pd(PPh_3)_4$, 3.7 equiv mol of Na_2CO_3 were placed in a flame-dried flask. A proper amount of toluene/H_2O (1/1) was added to the reaction vessel. Before the reaction took place, the solution was purged with a slow stream of nitrogen for 10 min and then 2.3 equiv mol of 4-fluoro-3-trifluoromethyl phenyl boronic acid (**6**) was introduced into the solution. The reaction mixture was stirred under reflux for 24 h. The resultant mixture was then passed through a short column packed with silica gel. Evaporation of solvent yielded a crude product, which was purified by column chromatography. The above procedure was used in the synthesis of monomers **7–9**.

2.4. Polymer synthesis

2.4.1. General procedure for the polymerizations

Polymerization reactions were carried out in a 50 ml, three-necked round-bottom flask equipped with a stir bar, a Dean–Stark apparatus fitted with a condenser, and a nitrogen inlet. The flask was charged with monomers **7–9** (0.9 mmol), bisphenol monomers **a–h** (0.9 mmol), potassium carbonate (1.8 mmol), NMP (8 ml) and toluene (15 ml). The solution mixture was then stirred at 130–150 °C for several hours, and, during the course of the reaction, a slow stream of nitrogen was passed through the reaction vessel to remove the water produced by the reaction and then azeotroped with toluene. After all the water had been removed, the reaction solution was stirred under reflux (165 °C) for 8 h. The resultant polymer solution was diluted with 8 ml of THF. The diluted solution was poured into a stirred methanol (250 ml) and the fibrous polymer was precipitated in situ. The precipitated polymers **10–12** were collected by filtration and washed with 10% HCl and H_2O and then vacuum-dried until no solvent was detected in the TGA experiment. For yields and molecular masses, see Table 1.

3. Results and discussion

3.1. NMR spectroscopy

Typical spectroscopic data from ^{19}F and ^{1}H, and ^{13}C NMR spectroscopy are shown in Figs. 1 and 2, and support the structures of the bisfluoro monomer **8** and polymer **11h**, respectively. The ^{19}F NMR spectrum (Fig. 1) of the bisfluoro monomer **8** shows two peaks at the chemical shifts of −62.3 and −118.5 ppm of equal intensity, attributed to the fluorines of the trifluoromethyl groups and of the bisfluoro groups, respectively. After polymerization, the corresponding ^{19}F NMR spectrum of the polymer **11h** is shown in Fig. 2 and presents only a peak at −62.8 ppm attributed to the trifluoromethyl groups, while the signal at −118.5 ppm caused from the bisfluoro groups of the monomer **8** completely disappear due to nucleophilic displacement of the fluorine atoms. The ^{1}H and ^{19}F NMR spectra of the polymers do not show any signals corresponding to the terminal −OH or −F groups, which is indicative of a high degree of conversion. The exact analytical data for all these polymers are listed in the Supplementary data.

Table 1
Yields and molar masses of poly(arylene ether)s

Polymer	Yield (%)	M_n[a]	M_w/M_n	DP[b]
10a	95	76 000	1.68	76
10b	94	60 200	1.80	59
10c	94	76 500	1.67	76
10d	93	59 600	1.83	59
10e	92	74 000	1.84	73
10f	95	15 000	2.14	18
10g	98	28 900	2.30	29
10h	96	8400	1.93	10
11a	90	76 900	1.60	71
11b	96	62 100	2.07	57
11c	93	118 100	1.59	111
11d	94	42 000	1.81	39
11e	93	94 200	1.73	86
11f	93	19 300	2.70	21
11g	89	15 500	2.15	15
11h	91	10 700	2.00	11
12a	90	77 100	1.60	67
12b	95	82 400	1.75	71
12c	96	69 800	2.03	61
12d	95	31 400	1.78	27
12e	95	147 900	1.52	126
12f	97	17 000	2.21	17
12g	92	12 500	2.04	11
12h	96	14 000	2.65	13

[a] Given in g/mol; determined by gel permeation chromatography in THF by UV–vis dector versus polystyrene standards.

[b] Degree of polymerization calculated from M_n according to comonomer composition.

3.2. Molecular weight

Size exclusion chromatography was used to determine the molecular weight of the polymers soluble in THF and the results are listed in Table 1. The molecular weight distributions were essentially unimodal with no evidence of oligomeric or unreacted species, which is also attested by undetectable ^{19}F NMR signals of fluorine end groups of poly(arylene ether)s. The reported values are polystyrene equivalent weights. In any case, these values have to be taken as merely indicative, since calibration with polystyrene may result in questionable results when the polarity and backbone stiffness of the polymers studied deviate strongly from those of polystyrene. Results of the polymerizations are summarized in Table 1. Table 1 shows that the polymers derived from bisphenols with bulky pendents (**a–e**) have a higher degree of polymerization than the ones having smaller pendents (**f–h**). This can be attributed to the difference in catenation angle, which results in different backbone curvature.

3.3. Solubility

Solubilities of the polymers are reported in Table 2. It shows that all of the polymers are soluble in common organic solvents such as: chloroform, toluene, and tetrahydrofuran, as well as polar aprotic solvents such as: DMF, DMAc, and NMP. Surprisingly, the polymers only swelled in the presence of DMSO, and the enhanced solubility afforded by 6F groups can be observed in ethyl acetate. Polymers **10g**, **11g** and **12g**, having bisphenol AF, were rapidly dissolved by ethyl acetate while the other polymers were only swelled by this solvent.

3.4. Thermal properties

The thermal properties of the polymers were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA thermograms for **12a–h** are shown in Fig. 3. The polymers were stable up from 436 to 668 °C in nitrogen atmospheres (Table 3). Based on bisphenols' structures, the polymers could be briefly classified into three categories. The first category, polymers **12b** and **12f** having almost fully aromatic main chain, show only one decomposition process, starting at about 600 °C with char residues of 70 and 59% at 800 °C, which was attributed to the degradation of the main chain. In polymers **12g** and **12h**, the second category, possessing small pendent groups of methyl or trifluoromethyl attached to the main chain also show one decomposition process; however, it starts at about 500 °C with char residues of 34 and 31% at 800 °C. The third category, polymers **12a**, **12c–e** having the bulky pendent groups of alkyl cyclics attached to the main chain indicate two decomposition processes for each of the four polymers. The first process, starting at about 435 °C with weight losses of 12, 24, 21 and

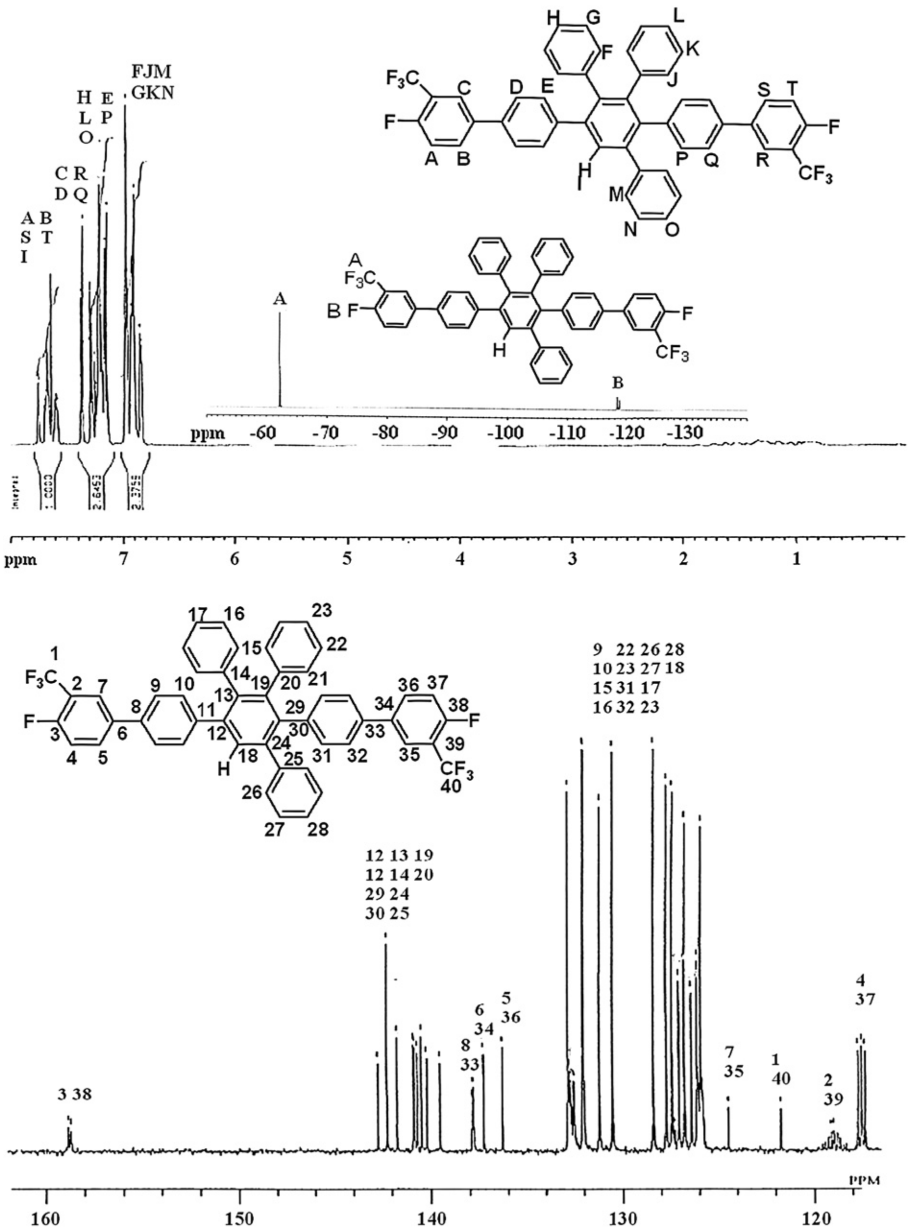


Fig. 1. The spectra of (a) ^{1}H NMR; (b) ^{19}F NMR, and (c) ^{13}C NMR for monomer **8**.

15% for **12a**, **12c**, **12d** and **12e**, respectively, was attributed to the degradation of the alkyl cyclics. The second process, starting at about 550 °C with char residues of 24, 22, 21 and 56% at 800 °C for **12a**, **12c**, **12d** and **12e**, respectively, was attributed to the degradation of the main chain. The high thermal stability of these polymers was confirmed by the high char residues reported in Table 3. The lowest initial thermal degradation temperature of about 435 °C was well above the highest temperature (350 °C) used in DSC experiments; furthermore, the samples were solvent-free within the TGA limits of detection. This guarantees that no artifact will be seen in the DSC studies, which are shown below.

In the DSC scans of **12a–h** (Fig. 4), T_g values were in the range 262–334 °C depending on the bisphenol used in the synthesis. The T_g is known to depend on several factors such as the rigidity of the main polymer chain, chain symmetry and intermolecular forces, but in our PAEs it most likely depends on the barriers to rotation along the main polymer chain. As expected, polymer **12a–e**, containing bulky pendent groups between bisphenols, show T_g values higher than the ones shown from the other polymers **12f–h** because the introduction of bulky pendent groups results in a lower degree of freedom with rotation along the polymer main chain. Furthermore, as stated in a previous study [25], the bicyclic bisphenol connector in the polycarbonate based on 4,4-di(4-hydroxyphenyl)norbonane greatly increased the T_g relative to the polycarbonate based on bisphenol A. The presence of a rigid, multicyclic bisphenol connector group appears to produce the same effect in poly(arylene ether)s. The T_g values listed in Table 3 decrease gradually from polymer **12a–e** due to

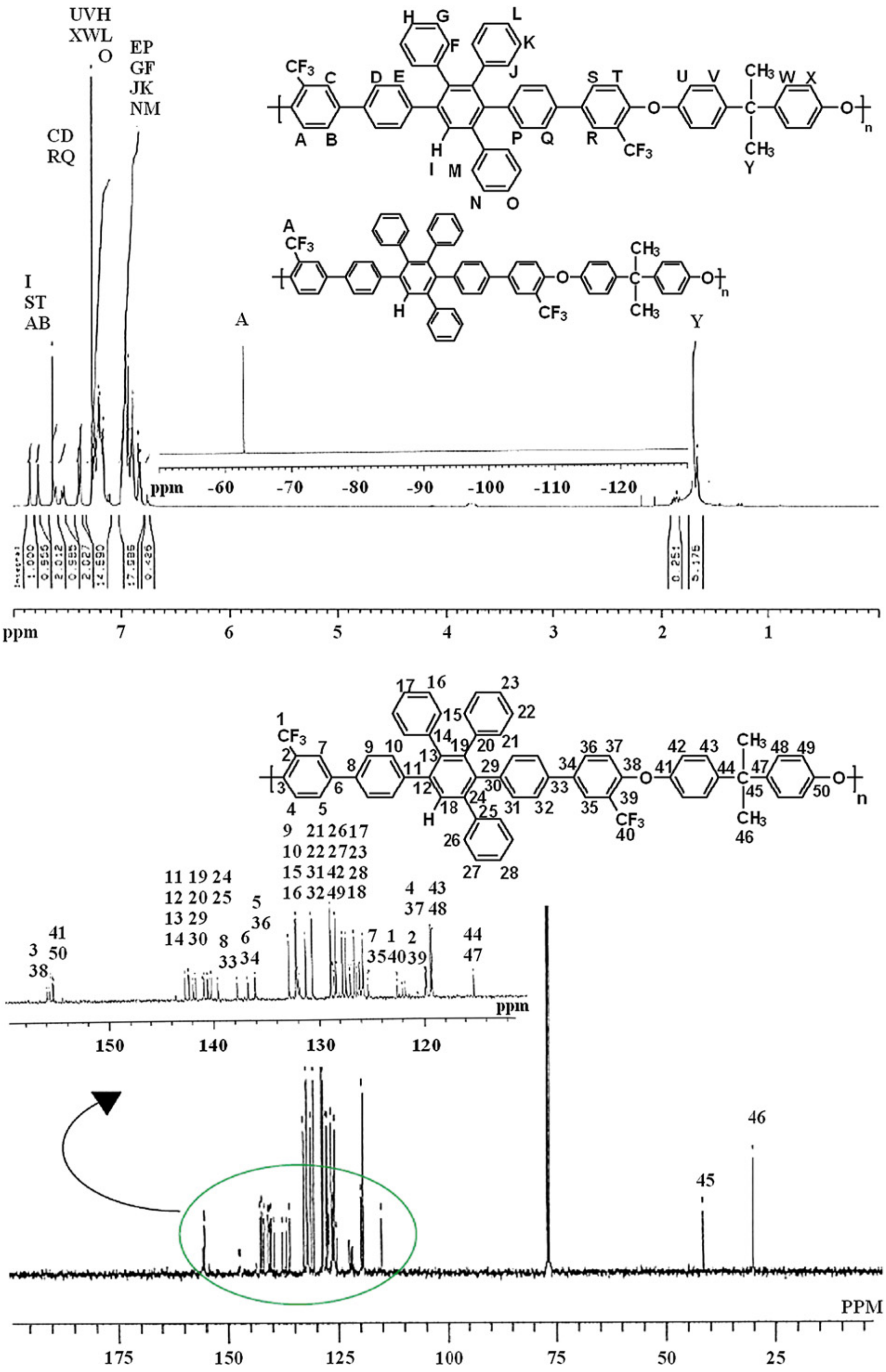


Fig. 2. The spectra of (a) ^{1}H NMR, (b)^{19}F NMR, and (c) ^{13}C NMR for polymer **11h**.

a gradual decrease in rigidity of pendent groups. The T_g of **12a** is 72 °C higher than that of the poly(arylene ether) based on bisphenol A (**12h**) and 2 °C higher than that of the poly(arylene ether) based on 4,4-(9-hydroxyphenyl)fluorene (**12b**). This last comparison is of particular interest as the fluorenylidene connector group is quite rigid and has a higher molecular mass than the 2,2-adamantylidene group. On the other hand, owing to rigidity polymer **12f** shows higher T_g than polymers **12g** and **12h**, and polymer **12g** exhibits a higher T_g with respect to polymer **12h** because of the stronger interchain interactions due to the polar $-CF_3$ groups which partially balance their flexibilizing effect. Similar trends are also observed and shown in Fig. 5 for polymers **10a**–**h** and **11a**–**h**.

On the other hand, when comparing T_g values (shown in Fig. 5) in different bisfluoro monomer structures, it was predicted and confirmed that all the tetraphenyl-substituted polymers **12a**–**h** would have the highest T_g values followed by

Table 2
Solubilities of poly(arylene ether)s[a]

Polymer	NMP	DMF	DMSO	THF	Chloroform	Ethyl acetate	Toluene	DMAc
10a	+	+	−	+	+	−	+	+
10b	+	+	−	+	+	−	+	+
10c	+	+	−	+	+	−	+	+
10d	+	+	−	+	+	−	+	+
10e	+	+	−	+	+	−	+	+
10f	+	+	−	+	+	−	+	+
10g	+	+	o	+	+	+	+	+
10h	+	+	−	+	+	−	+	+
11a	+	+	−	+	+	−	+	+
11b	+	+	−	+	+	−	+	+
11c	+	+	−	+	+	−	+	+
11d	+	+	−	+	+	−	+	+
11e	+	+	−	+	+	−	+	+
11f	+	+	−	+	+	−	+	+
11g	+	+	o	+	+	+	+	+
11h	+	+	−	+	+	−	+	+
12a	+	+	−	+	+	−	+	+
12b	+	+	−	+	+	−	+	+
12c	+	+	−	+	+	−	+	+
12d	+	+	−	+	+	−	+	+
12e	+	+	−	+	+	−	+	+
12f	+	+	−	+	+	−	+	+
12g	+	+	o	+	+	+	+	+
12h	+	+	−	+	+	−	+	+

[a] Key: +: soluble at room temperature; o: soluble at refluxing; −: insoluble at refluxing.

Table 3
Thermal properties of poly(arylene ether)s

Polymer	T_g[a] (°C)	T_d[b] (°C)	T_d^{5c} (°C)
10a	294	528	602
10b	294	648	658
10c	285	461	497
10d	276	499	525
10e	267	441	479
10f	243	667	671
10g	240	619	626
10h	210	610	617
11a	310	491	527
11b	305	650	657
11c	294	474	512
11d	284	499	514
11e	277	436	495
11f	274	636	643
11g	249	635	640
11h	237	628	632
12a	334	507	540
12b	332	668	671
12c	318	471	528
12d	314	498	537
12e	298	437	471
12f	299	635	635
12g	271	640	644
12h	262	621	625

[a] Glass transition temperature was measured by DSC and the reflection point was taken as T_g.

[b] Initial decomposition temperature was recorded on TGA at a heating rate of 20 °C/min under N_2 and the onset temperature was taken as T_d.

[c] Temperature at which 5% weight loss recorded on TGA at a heating rate of 20 °C/min under N_2.

triphenyl-substituted polymers **11a–h**, and then diphenyl-substituted polymers **10a–h** due to a gradual decrease in number of substituents on middle phenylene, which causes less restriction for rotating the substituents along the polymer backbone.

In addition, Table 3 tells that the T_gs of 2,2-adamatane PAEs **10–12a** are much higher than those of 1,3-adamatane PAEs **10–12d**. Since the phenyl rings are connected to the same carbon atom the 2,2-adamatane PAEs form a 60° gauche conformation easier, and therefore results in an increased energy barrier for rotating the 2,2-adamantane pendent group along the main chain. That is to say that the adamantane rings of the 1,3-isomers are relatively free to rotate along the main polymer chain, while those 2,2-isomers are constrained in their relative position and rotational freedom by steric interactions. This imparts an increase in T_g by restricting segmental mobility, while providing good solubility due to decreased packing and increased free volume. Additionally, the main polymer chain based on the 2,2-isomer is more 'kinked' than for the 1,3-isomer because the phenyl rings are connected to the same carbon atom. Both effects influence the T_g of these polymers. The greater degree of conformational constraints in

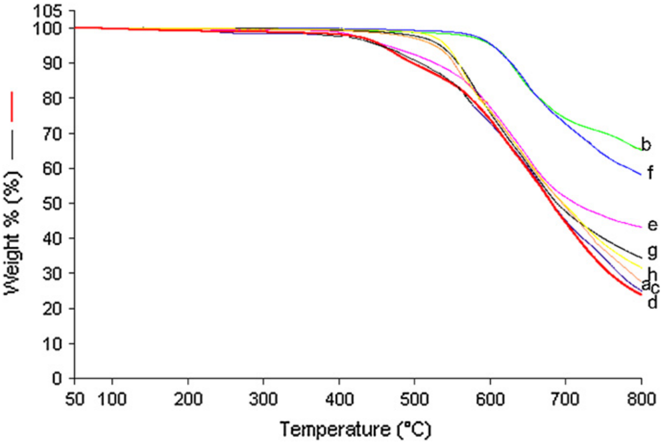


Fig. 3. TGA thermograms of polymer **12** series: (a) **12a**; (b) **12b**; (c) **12c**; (d) **12d**; (e) **12e**; (f) **12f**; (g) **12g** and (h) **12h**.

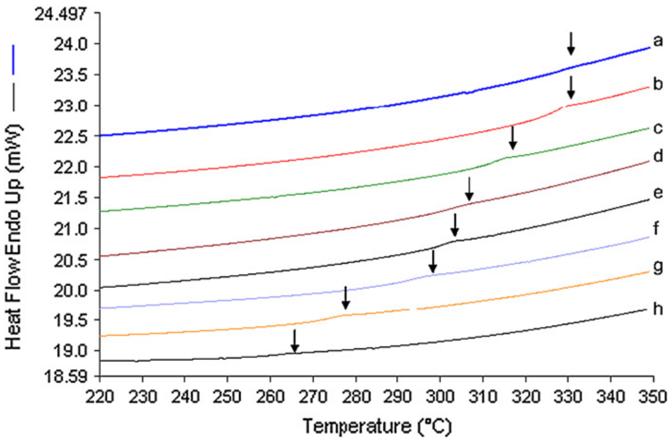


Fig. 4. DSC thermograms of polymer **12** series: (a) **12a**; (b) **12b**; (c) **12c**; (d) **12d**; (e) **12e**; (f) **12f**; (g) **12g** and (h) **12h**.

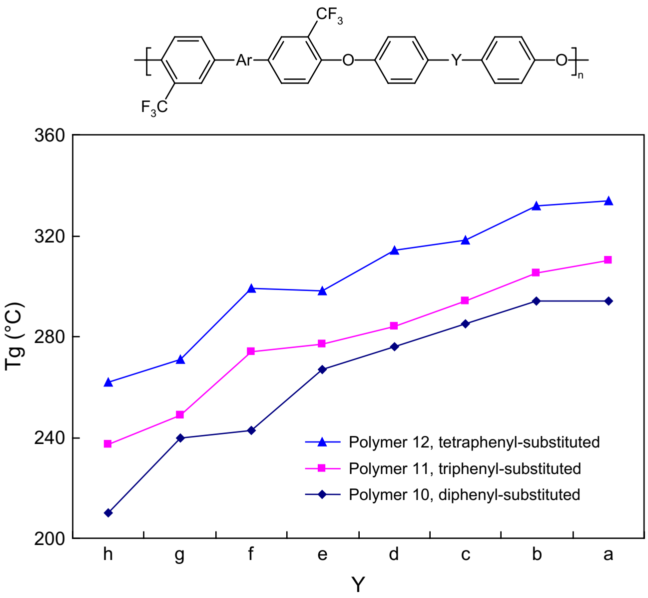


Fig. 5. Glass transition temperatures (T_g/°C) of the poly(arylene ether)s by DSC versus bisphenols' geometries (*Y*).

2,2-adamantane PAEs is most likely responsible for the differences in physical properties of these PAEs based on isomers of adamantane bisphenol. Therefore, the difference in T_g values between polymers **10–12a** and polymers **10–12d** can be ascribed to the hindrance effect of the chain rotation in the adamantane-substituted polymers.

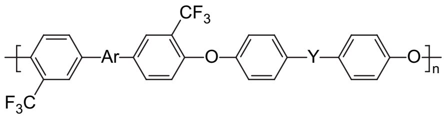
By comparison with previous studies [2], the published T_g values are collected and listed in Table 4. It shows that the T_g values increase gradually from *p*-terphenylene, *p*-quaterphenylene to tetraphenyl-substituted *p*-pentaphenylene PAEs, based on different bisfluoro monomer structures due to a gradual increase in the rigidity of main chain structures. On the other hand, when comparing T_g values in different bisphenol monomer structures, it indicates that the T_g values increase gradually from BPA, 6F BPA, biphenyl to fluorenylidene PAEs due to a gradual increase in rigidity and/or steric hindrance of substituent structures.

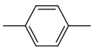
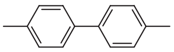
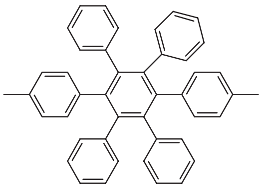
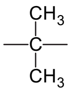
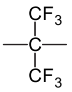
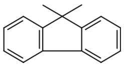
3.5. Photophysical properties

3.5.1. UV absorption spectra

The UV absorption spectra of monomers **7–9** in dichloromethane are shown in Fig. 6 and for comparison the absorption and emission λ_{max} of monomers **7–9** and the PAEs **10–12a–e** are summarized in Table 5. The UV absorption spectra (Fig. 6) in dichloromethane revealed that three monomers have π–π* transitions with λ_{max} between 292–228 nm. The spectrum of monomer **7** shows a λ_{max} at 292 nm and two small shoulders at ca. 260 and 228 nm. When the spectrum of monomer **7** (two substituents) is compared with that of monomer **8** (three substituents), it is seen that the extra-substituent on the middle phenylene ring has effected a blue shift to 290 nm and a decreased intensity of the peak. At the same time the shoulder at ca. 260 nm has been increased in intensity. On comparing the tetra-substituted monomer **9**, the effects are enhanced; the peak at 292 nm has now been blue shifted to 287 nm and further decreased in intensity, while the intensity of the peak at ca. 228 has been increased. The observations deduced above show that the π–π* transitions showed gradual blue shifts from **7** to **9**, suggesting decreasing electron delocalization along the chain as the side-groups changed from diphenyl-substituted monomer **7** to triphenyl-substituted monomer **8**, and tetraphenyl-substituted monomer **9**.

Table 4
Glass transition temperatures (T_g/°C) of the poly(arylene ether)s by DSC and their comparison with similar polymers



Y \ Ar			
 $-\overset{CH_3}{\underset{CH_3}{C}}-$	174	–	262
 $-\overset{CF_3}{\underset{CF_3}{C}}-$	179	210	271
–	209	257	299
	234	300	332

It should be noted that the wavelengths are shifted only by a small amount in conjunction with the number of substituents on the central phenylene ring, but the intensities are changed

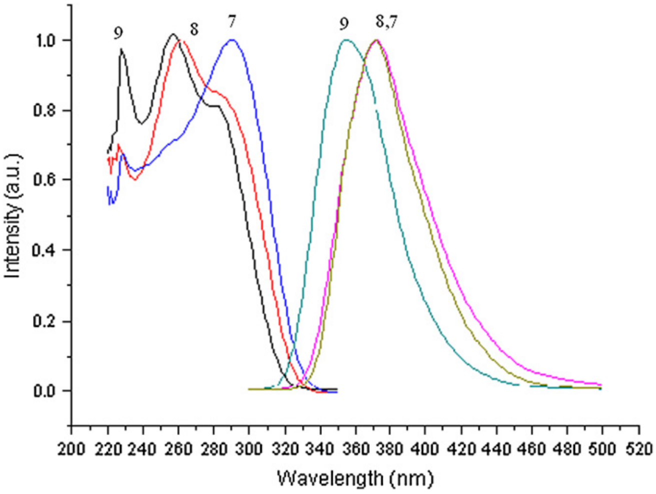


Fig. 6. UV absorption and photoluminescence spectra of the bisfluoro monomers **7–9** in dichloromethane.

Table 5
Absorption and photoluminescence characteristics of monomers and polymers

Compound	Absorption λ_{max}[a] (nm)	Emission λ_{max}[a,b] (nm)	Stokes shift[c] (nm)
7	228/260/292[d]	371	45
8	228/261[d]/291	370	49
9	228[d]/259/287	355	39
10a	228/261/300[d]	373	34
10b	228/260/298[d]	372	35
10c	228/260/299[d]	373	35
10d	228/261/299[d]	373	35
10e	228/260/298[d]	372	35
11a	228/261[d]/298	370	39
11b	228/260[d]/297	371	41
11c	228/261[d]/297	370	40
11d	228/262[d]/297	370	40
11e	228/260[d]/297	371	40
12a	228[d]/261/290	352	23
12b	228[d]/259/288	352	24
12c	228[d]/260/289	352	25
12d	228[d]/260/289	353	26
12e	228[d]/259/288	352	25

[a] At 10^{-3} g/dL in THF.
[b] Excited at absorption λ_{max}.
[c] Stokes shift = emission λ_{max} − the absorption onset.
[d] Major band in the spectrum.

significantly as the numbers of substituents are altered. Upon comparing the absorption bands of monomers **8** and **9** with those of monomer **7**, in both instances (monomers **8** and **9**) the intensities are greatly shifted. Therefore, it may be that intensities are, in general, more sensitive to slight changes in the angle between the rings than they are to wavelengths. This also indicates that although there are three major absorption bands for each monomer, the number of excitons responsible for each absorption band varies substantially as the numbers of substituents are altered.

A similar trend of blue shift is observed in corresponding polymer solutions as seen by comparing the absorption spectra of PAEs **10a–e** (diphenyl-substituted) and PAEs **11a–e** (triphenyl-substituted) to those of PAEs **12a–e** (tetraphenyl-substituted) nearly independent of bisphenol monomers. However, the degrees of blue shift caused by substituted side-groups for polymers decrease, which indicates lesser reductions in the electron delocalization of the polymer main chain, than that of monomers. From Table 5, it is clear that the UV absorption λ_{max} of polymers becomes longer than that of corresponding monomers. In the sense of effective conjugation length, this indicates that it becomes longer after polymerization. On the other hand, however, the effect of twist between adjacent planes of the phenylene rings of the main chain, which varies with the number of side-chain substitutes of bisfluoromonomers, is reduced due to polymerization, and thus results in a smaller geometric effect on the ground-state electronic structure of the PAEs. This indicates that the stress caused by the twist between adjacent planes of the phenylene rings of the main chain can be somehow released by introducing a soft ether linkage via polymerization.

In solid state, typical UV absorption spectra for PAEs **10b**, **11b** and **12b** are shown in Fig. 8. Comparing the spectra in solutions (Fig. 7), the bands at ca. 228 nm disappeared and instead of showing red-shifted absorption shoulders at 326, 320 and 317 nm for PAEs **10b**, **11b** and **12b**, respectively. This could be attributed to aggregate formation, which causes elimination of vibronic resolution at 228 nm and also results in an extra absorption at longer wavelength.

3.5.2. Photoluminescence spectra

The photoluminescence spectra of the monomers and polymers were investigated in solution and in the solid state. The emission spectra in dilute dichloromethane solutions (0.0001 g/dL) are shown in Figs. 6 and 7, and the data are summarized in Table 5. The PL spectra are insensitive to the excitation wavelength in the range 230–300 nm. All the data presented here were obtained by excitation at the wavelength of the respective absorption maximum. All the PL spectra in dilute solution show a very similar pattern with only one featureless peak. In addition, the PL spectra show relatively small Stokes shifts of 25 ~ 49 nm between the emission λ_{max} and the absorption onset, which is consistent with emission from localized states of 0–0 band. Interestingly, we also found that the emission λ_{max} of lower energy state was gradually blue shifted as the substituent was changed from diphenyl to triphenyl and tetraphenyl. This indicates that the emission band was strongly associated with the size and number of the substituents, which affected the torsion angle and the relative movement of the phenyl rings. Therefore, we tentatively conclude that the emission spectrum is characterized by effective conjugation length which could be manipulated by the size and number of the substituents.

The photoluminescence (PL) spectra of PAEs **10–12e** thin films are shown in Fig. 8. For all three PAEs, the PL spectra consist of three major emission bands. The emission bands with the shortest wavelength in each spectrum possess small Stokes shifts of 35–48 nm, which is characteristic of isolated chain emission as seen in dilute solutions. In addition to isolated chain emission, all other bands have large Stokes shifts

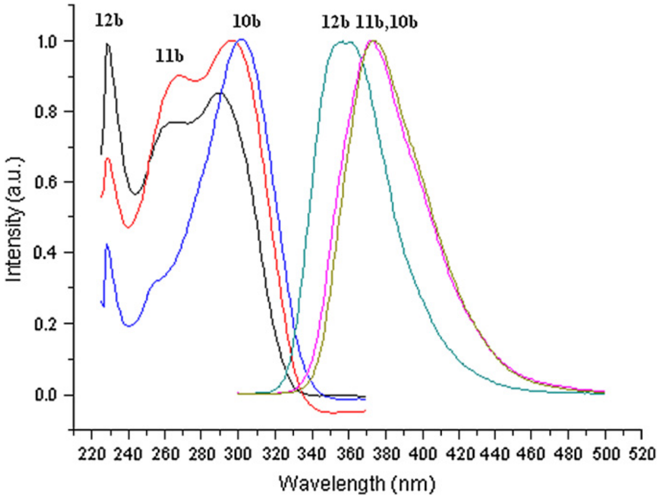


Fig. 7. UV absorption and photoluminescence spectra of the PAEs **10b**, **11b** and **12b** in dichloromethane.

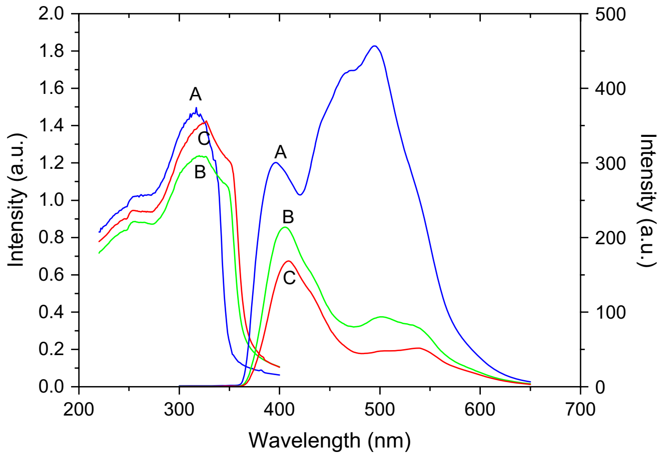


Fig. 8. UV absorption and photoluminescence spectra of films of the PAEs: (a) **12b**; (b) **11b**, and (c) **10b**.

of 122–176 nm between the emission λ_{max} and the absorption onset, which is characteristic of aggregate or excimer emission of solid films of many conjugated polymers [26]. Interestingly, the emission bands at longer wavelength of polymers **11e** and **10e** show not only broad and featureless but also relatively low in intensity, which is characteristic of excimers. In contrast, compared to PAEs **10e** and **11e** the PAE **12e** with four substituents has relatively high emission intensity for longer wavelength bands due to a more twisted structure and relatively large intermolecular distances. We therefore conclude that the solid-state emission of the PAEs **10**–**11e** originates from excimers; however, the emission band of PAEs **12e** is tentatively assigned to emission from intermolecular aggregates in view of their relatively high emission intensity.

4. Conclusion

A new class of high-temperature, high-T_g polymers, the poly(arylene ether)s, have been synthesized via a nucleophilic aromatic substitution reaction of bisfluoro-pentaphenyl monomers with bisphenolates generating the arylene ether linkages. The electron-withdrawing pendent groups of trifluoromethyl activate a nucleophilic fluoro displacement polymerization. The nucleophilic displacement polymerization reactions were conducted in NMP in the presence of potassium carbonate to give high molecular weight polymers. Glass transition temperatures of the poly(arylene ether)s increase with increasing pendant phenyls in the bisfluoro pentaphenyl monomers. The materials experienced 5% weight losses above 500 °C by thermogravimetric analysis, indicative of their high thermal stability. All of the polymers could be readily processed from solution to derive flexible transparent films. The effects of the number of substituents on the UV absorption and PL spectra of bisfluoro pentaphenyl monomers and respective polymers are also studied. The band position and intensity shifts observed are correlated with the number of substituents. It is suggested that the substituents may modify the energies and population of both the ground and the excited states of the molecules.

Acknowledgment

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi: 10.1016/j.polymer.2007.09.042.

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