



Highly soluble and colorless fluorinated poly(ether imide)s based on 4,4'-(2,5-tolylenedioxy)diphthalic anhydride and trifluoro methyl-substituted aromatic bis(ether amine)s

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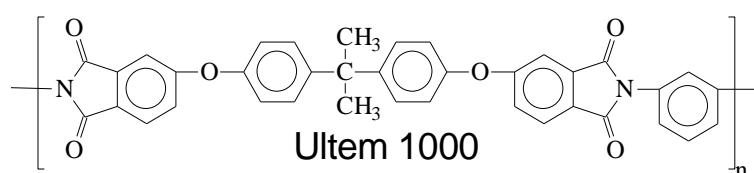
Abstract: A series of novel fluorinated poly(ether imide)s (PEIs) **IVa-h** were synthesized from 4,4'-(2,5-tolylenedioxy)diphthalic anhydride (**I**) and various trifluoromethyl-substituted aromatic bis(ether amine)s (**IIa-h**) via a conventional two-step method with thermal or chemical imidization of the precursor poly(amic acid)s. These PEIs were readily soluble in a variety of organic solvents; they were soluble with a concentration higher than 10% in amide-type polar solvents, ether type solvents, and chlorinated hydrocarbons. The solution-cast films showed a high optical transparency and low color intensity, with an ultraviolet-visible absorption edge of 371- 377 nm and low b^* values (a yellowness index) of 4.9-7.5. These films were strong and tough with tensile strength of 90-103 MPa. They exhibited glass-transition temperatures (T_g) in the range of 207-293 °C, with 10% weight loss temperature in excess of 500 °C in air or nitrogen atmosphere. They also showed low-dielectric constants (2.95-3.37 at 1 MHz) and low moisture absorption (0.20-0.67 wt %).

Introduction

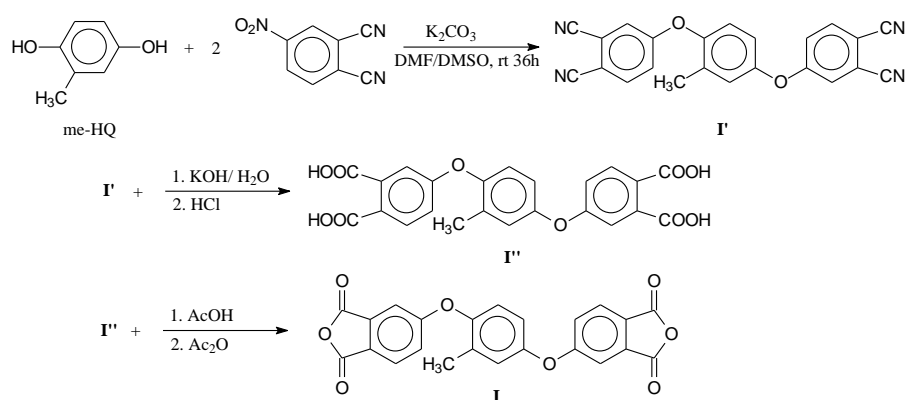
Aromatic polyimides have attracted much interest in microelectronics applications because of their high thermal stability and dielectric performance [1, 2]. However, poor processability in their imidized forms generally limit their application because of high softening temperatures and insolubility. Considerable research efforts have been focused on the synthesis of soluble polyimides that retain the attractive properties of this kind of polymers [3, 4]. Typical approaches include the introduction of flexible linkages [5, 6], bulky lateral groups [7-9], kinked or unsymmetrical units [10-12], and spiro-skeletons [13-16] into the polymer backbone. Another obstacle that may hinder extending the applications of aromatic polyimides in optoelectronic materials is the light or dark-yellow color of their films caused by the intramolecular and intermolecular charge transfer complex (CTC) between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties [17]. By minimizing or eliminating CTC formation, low color or virtually colorless polyimide films with improved transparency can be obtained [18, 19]. Colorless soluble polyimides can be obtained by using aliphatic dianhydride or diamine monomers [20-23]; however, the long term thermal stability is somewhat decreased due to the incorporation of less stable aliphatic segments. Recently, considerable attention has been devoted to the fluorinated aromatic polyimides, especially trifluoromethyl (CF₃)-containing polyimides [24-33]. It was found that the incorporation of bulky CF₃ groups into polyimide backbones resulted in an

enhanced solubility and optical transparency together with a lowered dielectric constant, which attributed to low polarizability of the C-F bond and the increase in free volume. The fluorinated polyimides also provided other merits such as good thermal and thermo-oxidative stability and low moisture absorption.

Poly(ether imide)s (PEIs) have received great attention because they may provide good processability owing to the presence of flexible ether linkages. The development of nucleophilic displacement reactions, and nitrodisplacement reactions in particular, has led to the development of a large class of PEIs from bis(ether anhydride)s and various aromatic diamines [34-36]. An important example is Ultem 1000 resin developed and commercialized by General Electric Co. [37], which exhibits reasonable thermal stability and good mechanical properties together with good moldability.



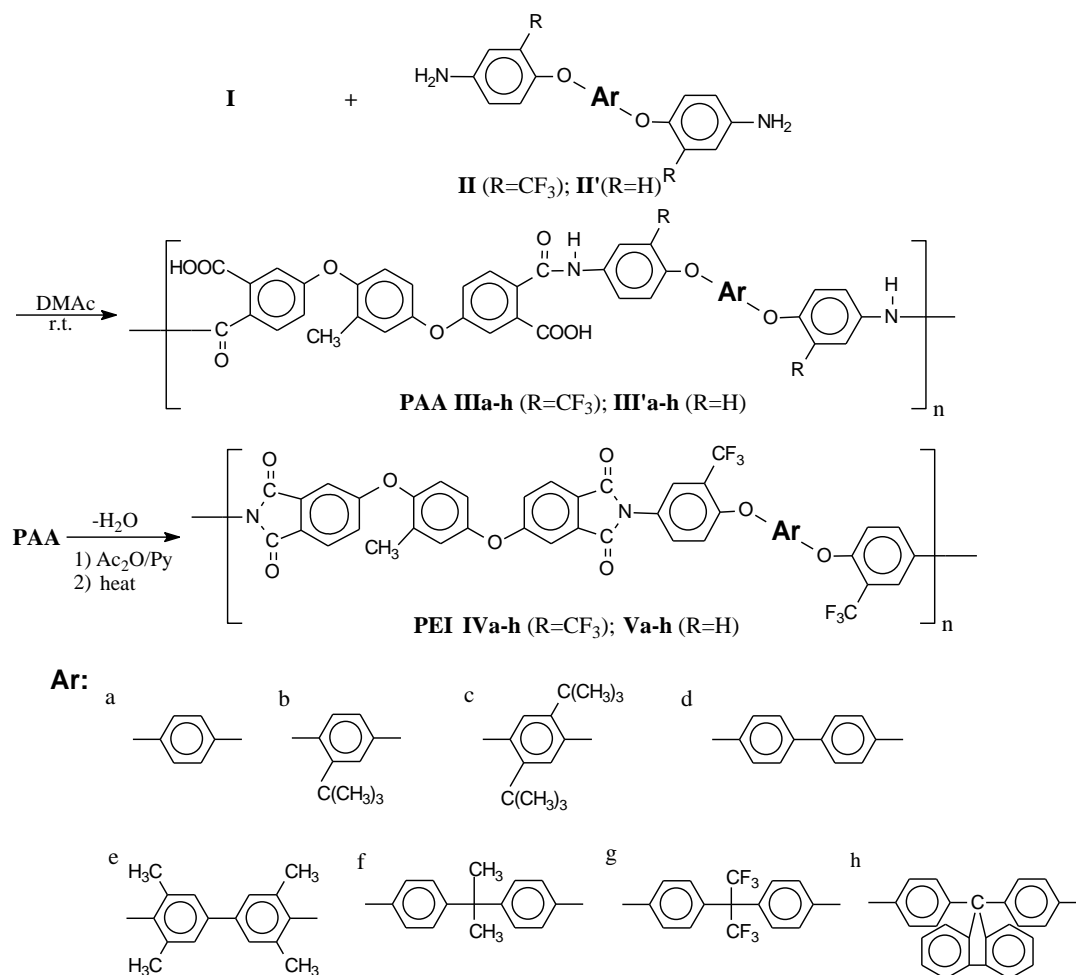
Several papers and patents disclose nitrodisplacement reactions with hydroquinone and subsequent conversion of the intermediate to the bis(ether anhydride) [34-40], which is readily reacted with aromatic diamines to PEIs with 1,4-linked phenylene-ether units. We have previously reported the synthesis and properties of PEIs derived from 4,4'-(2,5-tolylenedioxy)diphthalic anhydride (**I**) [40]. The reported PEIs exhibit reduced T_g as compared to conventional polyimides because of the incorporation of flexible ether linkages in the backbone, but the solubility is still not satisfactory. This work deals with the synthesis and basic characterization of a series of new fluorinated PEIs derived from bis(ether anhydride) **I** with several CF_3 -containing bis(ether amine)s. In addition to the steric effect contributed to the bulky – CF_3 group, the obtained PEIs should exhibit reduced intra- and intermolecular CT interactions because of the decrease in both the electron-donating property of the diamine moiety (caused by the electron-withdrawing CF_3 pendants) and the electron-accepting property of the dianhydride moiety (caused by the electron-donating ether group). These fluorinated PEIs are, thus, more soluble and less colored than conventional polyimides and their counterparts derived from CF_3 -free diamines.



Scheme 1. Synthesis of bis(ether anhydride) **I**.

Results and discussion

A novel series of PEIs **IVa-h** were synthesized from bis(ether anhydride) **I** and various fluorinated diamines (**IIa-h**) in DMAc, followed by thermal or chemical imidization of intermediate poly(amic acid)s (PAA **IIIa-h**) (Scheme 2). For comparison, the analogous non-fluorinated PEIs (the **V** series) were also prepared and characterized. The inherent viscosities and average molecular weights of the obtained PEIs **IVa-h** are listed in Tab. 1.



Scheme 2. Synthesis of poly(ether imide)s.

PEIs **IVa-h** had inherent viscosities in the range of 0.7-1.4 dL/g, and the values of \overline{M}_n and \overline{M}_w were recorded in the range of 25,000-50,000 and 41,000-74,000, respectively, relative to standard polystyrene. The polydispersity index (PDI) of the **IV** series is in the range of 1.5-1.7.

The typical FTIR spectra of PAA **IIIa** and PEI **IVa** are shown in Fig. 1. The characteristic absorptions of the PAA appeared at 3500-2500 cm⁻¹ (O-H and N-H stretch) and 1716 and 1668 cm⁻¹ (C=O stretch). The PEI showed the symmetrical and asymmetrical of C=O stretching at 1724, 1778 cm⁻¹, and imide ring deformation of 1052 and 744 cm⁻¹. The disappearance of amide and carboxyl bands indicates a virtually complete conversion of PAA precursor into PEI. Besides, **IVa** was also confirmed by ¹H NMR and ¹³C NMR spectra as shown in the experiment part. The

results of elemental analysis of the PEIs are given in Tab. 2 and the observed values are in good agreement with the calculated values of proposed structures.

Tab. 1. Inherent viscosity and GPC data of poly(ether imide)s.

Polymer ^a	η_{inh}^b (dL/g)	GPC Data of Poly(ether imide)s ^c		
		\overline{M}_n ($\times 10^4$)	\overline{M}_w ($\times 10^4$)	$\overline{M}_w/\overline{M}_n$ (PDI)
IVa	1.3 (1.1)	4.3 (3.9)	6.5 (6.3)	1.5 (1.6)
IVb	1.0 (0.8)	4.3 (3.4)	6.7 (5.4)	1.5 (1.6)
IVc	0.9 (1.4)	3.9 (5.0)	6.3 (7.4)	1.6 (1.5)
IVd	1.5 (0.8)	5.0 (2.7)	7.3 (4.6)	1.5 (1.7)
IVe	1.3 (1.3)	2.5 (4.7)	5.1 (7.0)	2.0 (1.5)
IVf	1.1 (0.7)	4.2 (2.5)	6.6 (4.1)	1.6 (1.7)
IVg	0.8 (0.7)	3.7 (2.6)	6.2 (4.2)	1.7 (1.6)
IVh	0.9 (0.8)	3.9 (3.2)	6.5 (5.1)	1.7 (1.6)

^a) PEIs were obtained by thermal imidization method. ^b) Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C. ^c) Relative to polystyrene standard, using THF as the eluent. ^d) Data in parentheses are those of **IVa-h** obtained by chemical imidization method.

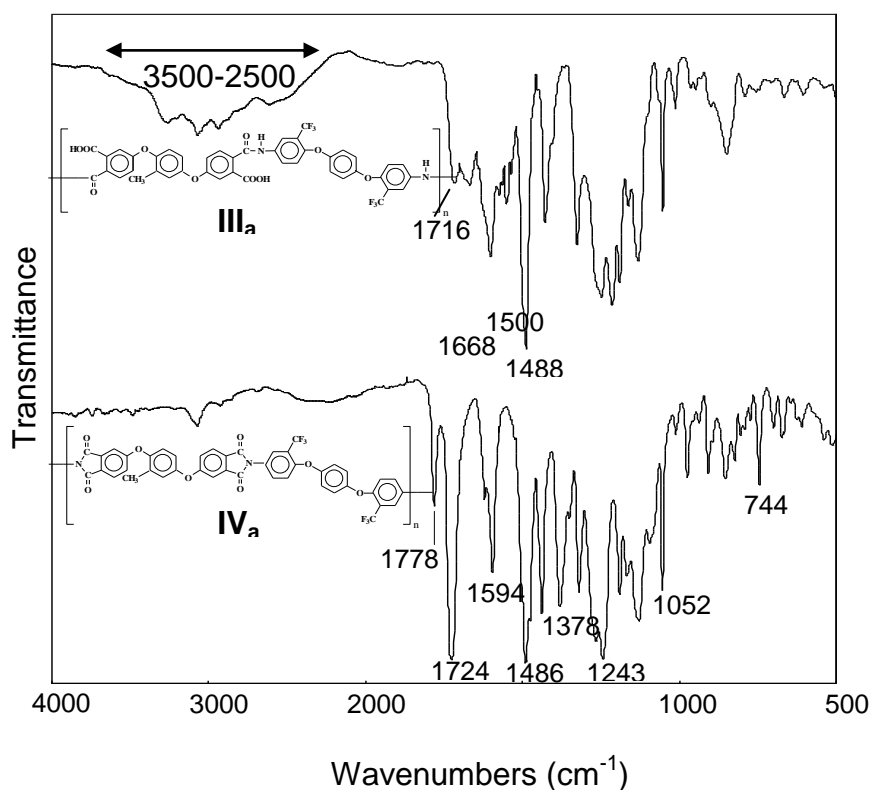


Fig. 1. FTIR spectra of representative PAA **IIIa** and PEI **IVa**.

The solubility of these polymers is tested in various organic solvents, and the results are summarized in Tab. 3. All the **IV** series PEIs obtained either via thermal (H) or chemical (C) imidization showed excellent solubility above 10wt/v% concentration in amide-type solvents such as NMP, DMAc and DMF, and in chlorinated solvents of chloroform; most of them also showed good solubility above 5wt/v% in ether-type solvents such as dioxane and THF, in phenolic solvent like *m*-cresol and basic

solvent like pyridine. The imidization method can affect the solubility of PEIs. For example, PEIs **IVa-IVf** prepared by chemical imidization showed better solubility in THF than those by thermal imidization. The poor solubility of the thermally cured polyimides might be attributable to side reactions that occurred in the imidization process and that led to partial crosslinking or undesired chemical repeat units within polymer chains. The solubility of the fluorinated **IV** series PEIs was obviously higher than their analogs **Va-h** without the pendent CF_3 groups. This can be attributed to the bulkiness of pendent CF_3 groups which inhibited close packing and reduced the interchain interactions leading to an enhanced solubility. Thus, all the **IV** series PEIs could be easily processed from solutions.

Tab. 2 Elemental analysis of the poly(ether imide)s. ^a

Polymer	Formula	Elemental analysis (%)			
			C	H	N
IVa	$(\text{C}_{43}\text{H}_{22}\text{O}_8\text{N}_2\text{F}_6)_n$ (808.65) _n	Calcd	63.87	2.74	3.46
		Found	63.81	2.93	3.73
IVb	$(\text{C}_{47}\text{H}_{30}\text{O}_8\text{N}_2\text{F}_6)_n$ (864.75) _n	Calcd	65.28	3.50	3.24
		Found	65.22	3.41	3.26
IVc	$(\text{C}_{51}\text{H}_{38}\text{O}_8\text{N}_2\text{F}_6)_n$ (920.86) _n	Calcd	66.52	4.16	3.04
		Found	66.47	3.97	3.14
IVd	$(\text{C}_{49}\text{H}_{26}\text{O}_8\text{N}_2\text{F}_6)_n$ (884.74) _n	Calcd	66.52	2.96	3.17
		Found	66.30	2.77	2.91
IVe	$(\text{C}_{53}\text{H}_{30}\text{O}_8\text{N}_2\text{F}_6)_n$ (936.82) _n	Calcd	67.95	3.23	2.99
		Found	67.44	3.50	3.02
IVf	$(\text{C}_{52}\text{H}_{32}\text{O}_8\text{N}_2\text{F}_6)_n$ (926.83) _n	Calcd	67.39	3.48	3.02
		Found	67.38	3.36	3.08
IVg	$(\text{C}_{52}\text{H}_{26}\text{O}_8\text{N}_2\text{F}_{12})_n$ (1034.77) _n	Calcd	60.36	2.53	2.71
		Found	60.31	2.37	2.72
IVh	$(\text{C}_{62}\text{H}_{34}\text{O}_8\text{N}_2\text{F}_6)_n$ (1048.95) _n	Calcd	70.99	3.27	2.67
		Found	70.77	3.17	2.81

^a) PEIs **IVa-h** were obtained by chemical imidization method with DMAc as solvent.

The transmission UV-visible spectra were measured for the thin films of all PEIs. Typical UV-visible spectra of some representative PEI films are illustrated in Fig. 2. All fluorinated PEI films exhibited cut-off wavelengths shorter than 400 nm and were entirely transparent and colorless. As shown in Table 4, the **IV(C)** PEIs showed a very low yellowness index (b^*) of 5.3-7.5. The slightly higher yellowness index of the thermally imidized PEI films might be a result of thermal oxidation of chain-end amino groups. All the PEIs containing the CF_3 group revealed slightly lower cut-off wavelengths and lower b^* values than their respective CF_3 -free counterparts. The bulky and electron-withdrawing CF_3 group in the diamine moieties was presumably effective in decreasing CT complexes between polymer chains through steric hindrance and the inductive effect (by decreasing the electron-donating property of diamine moieties). The electron-donating ether groups in the dianhydride moiety also contribute somewhat toward decreasing the overall electron affinity of the phthalimide units, and subsequently lower the intermolecular CT interaction. Thus, almost all the **IV** series PEIs could be cast into optically transparent and colorless films. For comparison, the color co-ordinates and cut-off wavelengths of the **V** series PEIs and some common polyimides synthesized from commercially available aromatic

dianhydrides with a non-fluorinated bis(ether amine) **II'a** are also given in Table 4. The films of common polyimides PMDA/**II'a** and BTDA/**II'a** appeared with a deep yellow color and revealed a relatively high b^* value above 80. The ODPA/**4'a** polyimide was pale yellow in color and showed a lowered b^* value of 30.4. In contrast to these conventional polyimides, the film of **Va(H)** showed a very low b^* value of 18.9. Thus, it seems to be that the dianhydride structure is more influential in determining the color intensity of polyimides than the diamine structure.

Tab. 3. Solubility^a of poly(ether imide)s.^b

Polymer	Solvent								
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Py	Dioxane	THF	CHCl ₃
IVa	+++	+++	+++	++	++	+++	++	+(+++)	+++
IVd	+++	+++	+++	s	+++	++ (+++)	++	+(+++)	+++
IVh	+++	+++	+++	s	+++	+++	++	+(+++)	+++
IVd	+++	+++	+++	s (+)	++	+++	+++	+(+++)	+++
IVe	+++	+++	+++	s	++	+++	++(+++)	++(+++)	+++
IVf	+++	+++	+++	s (+)	++(+++)	++(+++)	+++	++(+++)	+++
IVg	+++	+++	+++	+++	+++	++(+++)	+++	+++	+++
IVh	+++	+++	+++	+(++)	+++	+++	+++	+++	+++
Va	--	--	--	--	s	--	--	--	--
Vb	s	s	--	--	++	s	s	--	--
Vc-e	--	--	--	--	--	--	--	--	--
Vf	s	s	s	s	++	++	+	++	+
Vg	+++	++	++	s	+++	+	+	++	+++
Vh	++	+	+++	--	++	+++	+++	+	++

^{a)} +++: 100 mg sample dissolved in 1 mL of solvent (10%); ++: 5%; +: 1%; --: insoluble; s: swelling. ^{b)} PEIs were obtained by thermal imidization method. Data in parentheses are those of **IVa-h** obtained by the chemical imidization method.

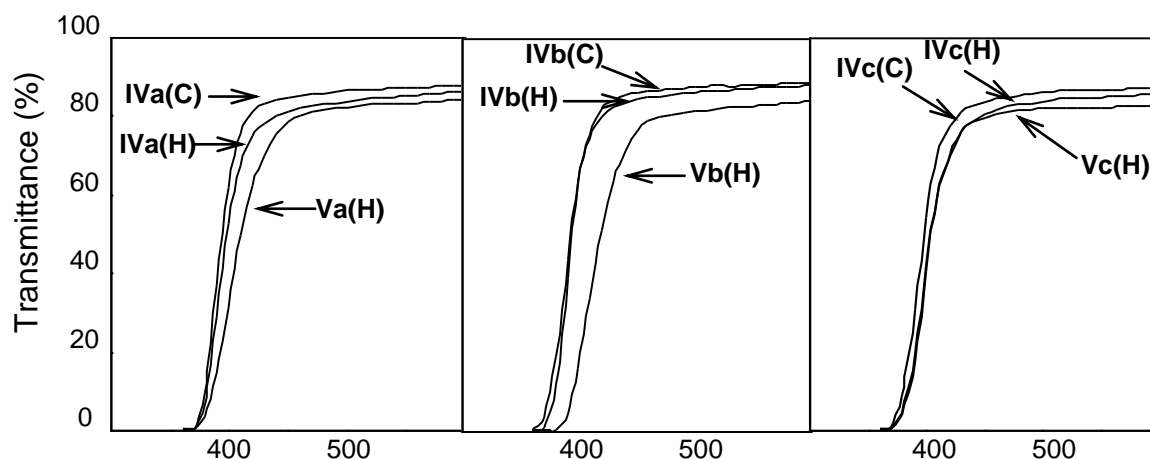


Fig. 2. UV-visible spectra of PEI films.

The tensile properties of the polyimide films are reported in Table 5. These polymer films showed similar type of behavior with respect to the elastic deformation range at small strains. The **IV** series PEIs showed tensile strengths at break of 90-103 MPa, elongations at break of 12-16%, and initial moduli of 1.7-2.3 GPa. The tensile

properties of the **IV** series PEIs are comparable with those of the **V** series analogs. These results indicate that the incorporation of the CF₃ group into the structure of PEIs not only improves solubility but also retains the good mechanical properties. All these polymer films possess good tensile properties indicating that they are strong materials.

Tab. 4. Color coordinates and the λ_0 values from UV-vis spectra of polyimide films.

Polymer	Film Thickness (μm)	Color Coordinates ^a			Cut-off Wavelength (λ_0 , nm)
		b*	a*	L*	
blank		1.1	-0.5	94.7	
IVa	49 (44) ^b	11.0 (5.3) ^b	-3.0 (-1.5) ^b	89.1 (89.7) ^b	379 (373) ^b
IVb	51 (47)	12.4 (6.0)	-3.3 (-1.5)	91.2 (90.4)	379 (374)
IVc	53 (54)	11.6 (7.2)	-3.0 (-2.0)	89.5 (90.0)	378 (376)
IVd	45 (43)	10.9 (5.6)	-2.6 (-1.7)	90.9 (93.2)	378 (375)
IVe	41 (55)	10.6 (7.1)	-2.8 (-2.2)	92.9 (92.3)	378 (376)
IVf	51 (55)	13.2 (5.6)	-2.4 (-1.6)	92.0 (92.5)	380 (375)
IVg	46 (53)	10.3 (4.9)	-1.5 (-1.1)	91.4 (90.7)	378 (371)
IVh	47 (61)	12.6 (7.5)	-2.5 (-1.2)	88.1 (92.6)	379 (377)
Va	51	18.9	-5.5	88.0	382
Vb	47	15.5	-2.8	89.1	375
Vc	45	16.3	-4.6	91.3	378
Vd	55	18.8	-5.6	91.1	380
Ve	49	19.6	-4.6	90.0	380
Vf	41	16.2	-2.2	91.5	378
Vg	48	14.4	-3.7	93.6	374
Vh	43	15.9	-2.7	91.3	375
PMDA-II'a	39	80.5	3.7	84.8	440
BTDA-II'a	37	87.8	2.3	86.5	446
BPDA-II'a	38	65.9	-11.7	90.6	424
DSDA-II'a	54	60.1	-11.8	91.2	417
ODPA-II'a	50	30.4	-7.4	81.8	387

^a) The color parameters were calculated according to a CIE LAB equation. L* indicates lightness; 100 means white, while 0 implies black. A positive a* means red color, while a negative a* indicates green color. A positive b* means yellow color, while a negative b* implies blue color. ^b) PEIs were obtained by thermal imidization method. Data in parentheses are those of **IVa-h** obtained by chemical imidization method.

The thermal behavior data of the PEIs, collected from DSC and TGA curves, are also summarized in Table 5. The T_g values of the **IV(H)** series PEIs, determined by DSC, are in the range of 207-293 °C. The decreasing order of T_g values generally correlated with the flexibility of the diamine moieties. PEI **IVf(H)** showed the lowest T_g values (207 °C) because of the presence of flexible isopropylidene linkage, whereas PEI **IVe(H)** exhibited the highest T_g value of 293 °C due to the presence of rigid tetramethylbiphenyl unit in the diamine moiety. As expected, the methyl- or *t*-butyl-substituted PEIs exhibited higher T_g values than the corresponding unsubstituted PEIs due to the hindrance effect of the chain rotation in the substituted polymers. In most cases, slightly decreased T_g values for the **IV** series compared to the **V** series might be a result of reduced electronic interactions and less dense packing caused

by the bulky pendent CF_3 groups. The thermal stability of the thermally cured PEIs was evaluated by dynamic TGA conducted at a heating rate of $20\text{ }^\circ\text{C}/\text{min}$. The temperatures of 10% weight loss (T_{10}) in nitrogen and air atmospheres were determined from original TGA thermograms. The T_{10} values of the **IV(H)** series were recorded in the range of $493\text{-}557\text{ }^\circ\text{C}$ in nitrogen and $492\text{-}554\text{ }^\circ\text{C}$ in air, comparable to or slightly higher than those of the **V** analogs.

Tab. 5. Tensile properties and thermal properties data of poly(ether imide)s.^a

Polymer	Strength at Break (MPa)	Elongation to Break (%)	Initial Modulus (GPa)	T_g ($^\circ\text{C}$) ^b	T_{10} ($^\circ\text{C}$) ^c		Char Yield (%) ^d
					In N_2	In Air	
IVa	103	13	2.1	213	539	537	54
IVb	99	15	1.8	227	508	505	49
IVc	101	14	2.0	245	493	492	41
IVd	91	16	2.1	225	548	529	59
IVe	98	14	1.8	293	503	500	48
IVf	96	12	2.2	207	523	525	56
IVg	90	14	1.7	217	538	541	53
IVh	103	15	2.3	257	553	553	63
Va	113	10	2.3	227	514	547	52
Vb	107	8	1.8	232	500	508	45
Vc	97	9	2.0	247	489	492	42
Vd	103	9	2.1	236	525	553	59
Ve	89	11	1.9	297	515	515	55
Vf	85	11	2.0	220	506	520	50
Vg	99	9	2.2	231	534	545	49
Vh	116	7	2.5	275	537	553	62

^{a)} PEIs were obtained by thermal imidization method. ^{b)} The midpoint temperature of baseline shift on the second heating DSC trace (heating rate $20\text{ }^\circ\text{C}/\text{min}$). ^{c)} Decomposition temperature at a 10% weight loss by TGA at a heating rate of $20\text{ }^\circ\text{C}/\text{min}$. ^{d)} Residual weight percentages at $800\text{ }^\circ\text{C}$ under nitrogen flow.

They left more than 41% char yield at $800\text{ }^\circ\text{C}$ in nitrogen. It is quite reasonable that the methyl- or *t*-butyl-substituted PEIs began to decompose at lower temperatures compared with the unsubstituted ones. The TGA data indicate that these fluorinated PEIs had high thermal stability regardless of the introduction of CF_3 groups.

The dielectric constants of the thermally imidized PEI films are listed in Table 6. The **IV(H)** series had lower dielectric constants (2.95-3.37 at 1 MHz) than the corresponding nonfluorinated homologues **V** series (3.19-3.73 at 1 MHz). The decreased dielectric constants could be attributable to the presence of bulky CF_3 groups in the polymer chains. The strong electronegativity of the fluorine atom resulted in very low polarizability of the C-F bonds, combined with the high free volumes of the CF_3 group, and endowed the PEIs with lowered dielectric constants. Besides, **IVg** and **Vg** exhibited the lowest dielectric constants in each series because of the additional bulky hexafluoroisopropylidene group in diamine moieties.

Tab. 6. Moisture Absorption and Dielectric Constants of Poly(ether imide)s.

Polymer ^a	Film Thickness (μm)	Moisture Absorption (%)	Dielectric Constant (Dry) ^b			
			1 kHz	10 kHz	1 MHz	40 MHz
IVa	77	0.43	3.32	3.31	3.24	3.31
IVb	112	0.29	3.38	3.18	3.14	3.19
IVc	62	0.23	3.46	3.42	3.37	3.45
IVd	53	0.67	3.26	3.25	3.19	3.26
IVe	49	0.51	3.40	3.39	3.35	3.43
IVf	98	0.34	3.36	3.27	3.10	3.19
IVg	89	0.20	3.03	2.99	2.95	3.01
IVh	78	0.44	3.28	3.27	3.23	3.29
Va	43	0.57	3.79	3.79	3.73	3.80
Vb	39	0.41	3.63	3.60	3.54	3.62
Vc	47	0.39	3.71	3.66	3.62	3.71
Vd	53	0.67	3.69	3.64	3.55	3.61
Ve	53	0.73	3.65	3.61	3.56	3.62
Vf	41	0.63	3.92	3.90	3.85	3.94
Vg	49	0.33	3.27	3.23	3.19	3.22
Vh	42	0.69	3.55	3.53	3.49	3.51

^a) PEI samples were obtained by the thermal imidization method. ^b) Measured by DEA at room temperature (dry dielectric constant).

Conclusions

A series of novel fluorine-containing PEIs (**IVa-IVh**) were synthesized from 4,4'-(2,5-tolylenedioxy)diphthalic anhydride (**I**) with various CF_3 -substituted aromatic bis(ether amine)s by two-step thermal or chemical imidization method. These poly(ether imide) films showed excellent solubility in various organic solvents, including low boiling point solvents, and could be cast into virtually colorless and strong films. They also exhibited moderately high T_g s and good thermal stability, together with low dielectric constants. Thus, this series of PEIs demonstrated a good combination of properties and may be of interest for optical and optoelectronic applications.

Experimental part

Materials

According to a well-developed synthetic method [41-48], the trifluoromethylated aromatic bis(ether amine)s were prepared from the chloro-displacement of 2-chloro-5-nitrobenzotrifluoride with corresponding aromatic diols in the presence of potassium carbonate in dimethyl sulfoxide (DMSO), followed by Pd/C-catalyzed hydrazine reduction; they included 1,4-bis(4-amino-2-trifluoromethylphenoxy)-benzene (**Ila**; mp = 132-133 °C) [41], 1,4-bis(4-amino-2-trifluoromethylphenoxy)-2-*tert*-butylbenzene (**Ilb**; mp = 164-165 °C) [42], 1,4-bis(4-amino-2-trifluoromethylphenoxy)-2,5-di-*tert*-butyl benzene (**Ilc**; mp = 215-216 °C) [43], 4,4'-bis(4-amino-2-trifluoromethylphenoxy) biphenyl (**Ild**; mp = 155-156 °C) [44], 4,4'-bis(4-amino-2-trifluoromethylphenoxy)-3,3', 5,5'-tetramethylbiphenyl (**Ile**; mp = 256-257 °C) [45], 2,2-bis[4-(4-amino-2-trifluoro methylphenoxy)phenyl]propane (**Ilf**; mp = 131-132 °C)

[46], 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]hexafluoropropane (**IIg**; mp = 65-66 °C) [47], and 9,9-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]fluorene (mp: 239-240 °C, **IIh**) [48]. *N,N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

Synthesis of 4,4'-(2,5-tolylenedioxy)diphthalic anhydride (**I**)

The bis(ether anhydride) monomer, 4,4'-(2,5-tolylenedioxy)diphthalic anhydride (**I**), was synthesized according to a well-developed method by a three-step reaction [40]. Bis(ether anhydride)s **I** (10.7 g, 77%; mp: 221 °C) was synthesized starting from the nitro-displacement reaction of 4-nitrophthalodinitrile (13.80 g, 100 mmol) with methylhydroquinone (6.21 g, 50 mmol) in DMF or DMSO (100 mL) and toluene (70 mL) mixture in the presence of potassium carbonate as the base, followed by the alkaline hydrolysis of the intermediate bis(ether dinitrile), 4,4'-(2,5-tolylene dioxy)diphthalonitrile (**I'**), (13.7 g, 81% yield; mp: 215 °C) and the cyclodehydration by chemical method with acetic anhydride of the resulting bis(ether diacid), 4,4'-(2,5-tolylenedioxy)diphthalic acid (**I''**), (15.12 g, 85% yield). The synthetic route is outlined in Scheme 1. FTIR spectra (Fig. 3), ¹H NMR spectra (Fig. 4), ¹³C NMR (Fig. 5) spectra, and elemental analysis were used to confirm the structure, and the spectroscopic data are listed as follows.

IR (KBr) of **I'**: 2229 (CN), 1191 cm⁻¹ (C-O). ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm) of **I'**: 8.12 (d, 1H, H_{b'}, *J* = 8.1 Hz), 8.10 (d, 1H, H_b, *J* = 8.1 Hz), 7.84 (d, 1H, H_{a'}, *J* = 2.5 Hz), 7.76 (d, 1H, H_a, *J* = 2.5 Hz), 7.53 (dd, 1H, H_{c'}, *J* = 8.7, 2.5 Hz), 7.43 (dd, 1H, H_c, *J* = 8.7, 2.5 Hz), 7.26 (d, 1H, H_f, *J* = 2.6 Hz), 7.24 (d, 1H, H_d, *J* = 8.7 Hz), 7.14 (dd, 1H, H_e, *J* = 8.7, 2.7 Hz), 2.12 (s, 3H, H_g). ¹³C NMR (125 MHz, DMSO-*d*₆, δ, ppm) of **I'**: 161.18 (C^{8'}), 161.07 (C⁸), 151.12 (C^{10'}), 148.78 (C^{13'}), 136.27 (C^{6'}), 136.21 (C⁶), 132.70 (C^{11'}), 123.76 (C^{12'}), 123.08 (C^{9'}), 122.26 (C^{7'}), 122.11 (C⁷), 121.32 (C^{3'}), 121.13 (C³), 119.95 (C^{14'}), 116.78 (C^{4'}), 116.69 (C⁴), 115.87 (C^{1,1'}), 115.39 (C^{2,2'}), 108.20 (C^{5'}), 107.95 (C⁵), 15.68 (C^{15'}). ELEM. ANAL. Calcd. for C₂₃H₁₂O₈ (376.37) of **I'**: C, 73.40%; H, 3.21%; N, 14.89%. Found: C, 73.11%; H, 3.35%; N, 14.82%

IR (KBr) of **I''**: 2500–3500 (O–H), 1703 (C=O), 1280 cm⁻¹ (C–O–C). ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm) of **I''**: 7.77 (d, 1H, H_{b'}, *J* = 8.4 Hz), 7.75 (d, 1H, H_b, *J* = 8.4 Hz), 7.16 (dd, 1H, H_{c'}, *J* = 8.7, 2.7 Hz), 7.14 (d, 1H, H_{a'}, *J* = 2.7 Hz), 7.14 (d, 1H, H_a, *J* = 2.7 Hz), 7.14 (dd, 1H, H_c, *J* = 8.7, 2.7 Hz), 7.04 (d, 1H, H_f, *J* = 2.4 Hz), 7.03 (d, 1H, H_d, *J* = 8.5 Hz), 7.02 (dd, 1H, H_e, *J* = 8.5, 2.4 Hz), 2.13 (s, 3H, H_g). ¹³C NMR (125 MHz, DMSO-*d*₆, δ, ppm) of **I''**: 168.73 (C^{1'}), 168.62 (C¹), 167.58 (C^{2'}), 167.51 (C²), 159.71 (C^{8'}), 159.46 (C⁸), 152.04 (C^{10'}), 149.14 (C^{13'}), 136.86 (C^{4'}), 136.68 (C⁴), 132.26 (C^{11'}), 131.61 (C^{6'}), 131.50 (C⁶), 125.89 (C^{5'}), 125.18 (C⁵), 123.02 (C^{7'}), 122.60 (C⁷), 119.16 (C^{3'}), 118.79 (C³), 117.25 (C^{12'}), 116.73 (C^{9'}), 115.29 (C^{14'}), 15.86 (C^{15'}).

IR (KBr) of **I**: 1851, 1781 (C=O stretch), 1280 cm⁻¹ (C - O - C). ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm) of **I**: 7.77 (d, 1H, H_{b'}, *J* = 8.2 Hz), 7.76 (d, 1H, H_b, *J* = 8.2 Hz), 7.17 (dd, 1H, H_{c'}, *J* = 8.4, 2.65 Hz), 7.15 (d, 1H, H_{a'}, *J* = 2.7 Hz), 7.14 (d, 1H, H_a, *J* = 2.7 Hz), 7.14 (dd, 1H, H_c, *J* = 8.4, 2.7 Hz), 7.05 (d, 1H, H_f, *J* = 2.4 Hz), 7.04 (d, 1H, H_d, *J* = 8.6 Hz), 7.02 (dd, 1H, H_e, *J* = 8.6, 2.4 Hz), 2.13 (s, 3H, H_g). ¹³C NMR (125 MHz, DMSO-*d*₆, δ, ppm) of **I**: 168.75 (C^{1'}), 168.64 (C¹), 167.60 (C^{2'}), 167.53 (C²), 159.73 (C^{8'}), 159.48 (C⁸), 152.06 (C^{10'}), 149.16 (C^{13'}), 136.88 (C^{4'}), 136.70 (C⁴), 132.38 (C^{11'}), 131.62 (C^{6'}), 131.50 (C⁶), 125.90 (C^{5'}), 125.19 (C⁵), 123.04 (C^{7'}), 122.61 (C⁷), 119.17

(C³), 118.80 (C³), 117.25 (C¹²), 116.75 (C⁹), 115.32 (C¹⁴), 15.88 (C¹⁵). ELEM. ANAL. Calcd. for C₂₃H₁₂O₈ (416.34) of **I**: C, 66.35%; H, 2.91%. Found: C, 65.86%; H, 3.02%.

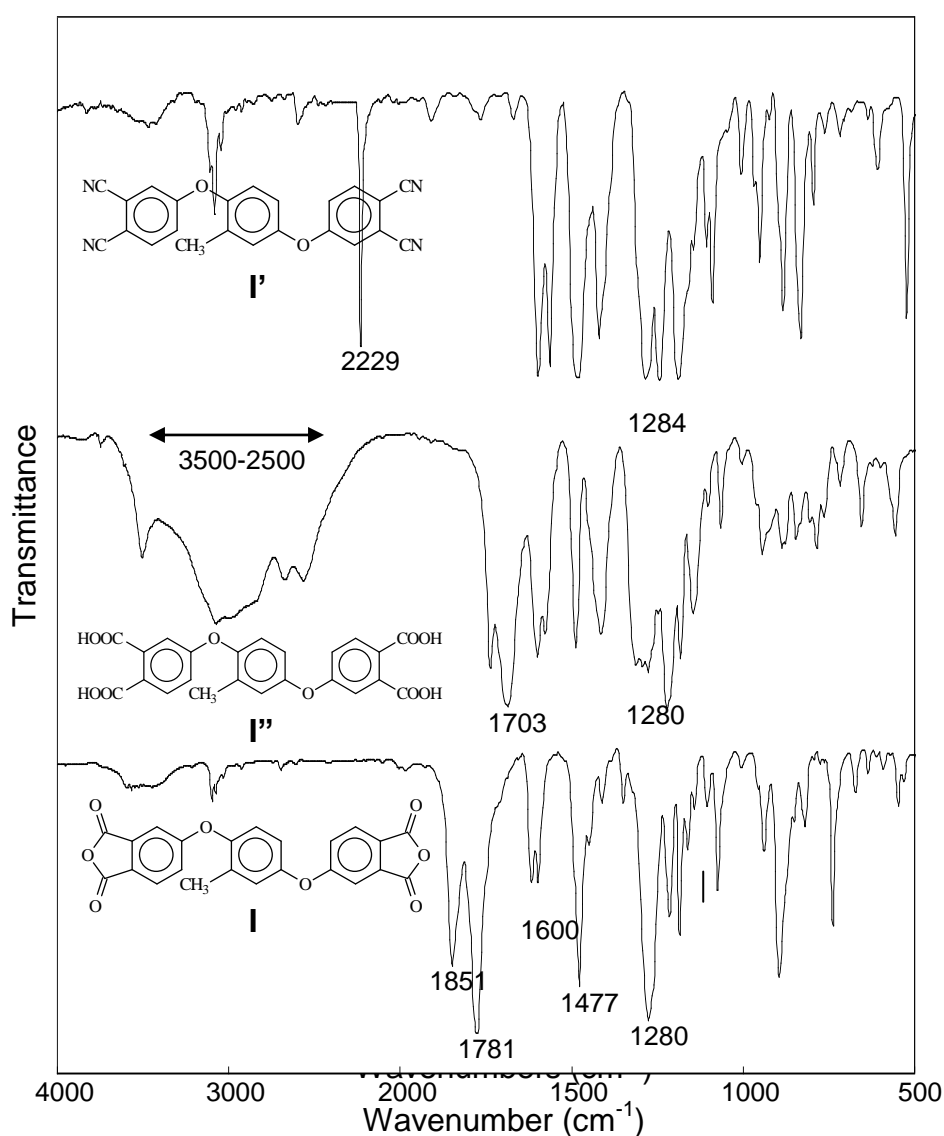


Fig. 3. FTIR spectra of bis(ether dinitrile) **I'**, bis(ether diacid) **I''** and bis(ether anhydride) **I**.

Synthesis of Polyimides

(a) Thermal imidization (H)

The synthesis of PEI **IVa** was used as example to illustrate the general synthetic route. Diamine **IIa** (0.2996 g, 0.7 mmol) was dissolved in 4.6 mL dried DMAc. After **IIa** was completely dissolved, dianhydride **I** (0.2912 g, 0.7 mmol) was added to the solution in one portion. The mixture was stirred at room temperature for 10 h to form a viscous PAA solution. The PAA solution then was poured into a glass culture dish (diameter 7 cm), which was placed in a 100 °C oven for 1 h to remove the solvent. The semidried PAA film was further dried and imidized by sequential a heating rating of 2 °C/min to 250 °C, then held at 250 °C for 30 min. By being soaked in water, a flexible film of

IVa(H) was self-stripped off from the glass surface. The inherent viscosity was 1.3 dL/g at a concentration of 0.5 g/dL at 30 °C in DMAc.

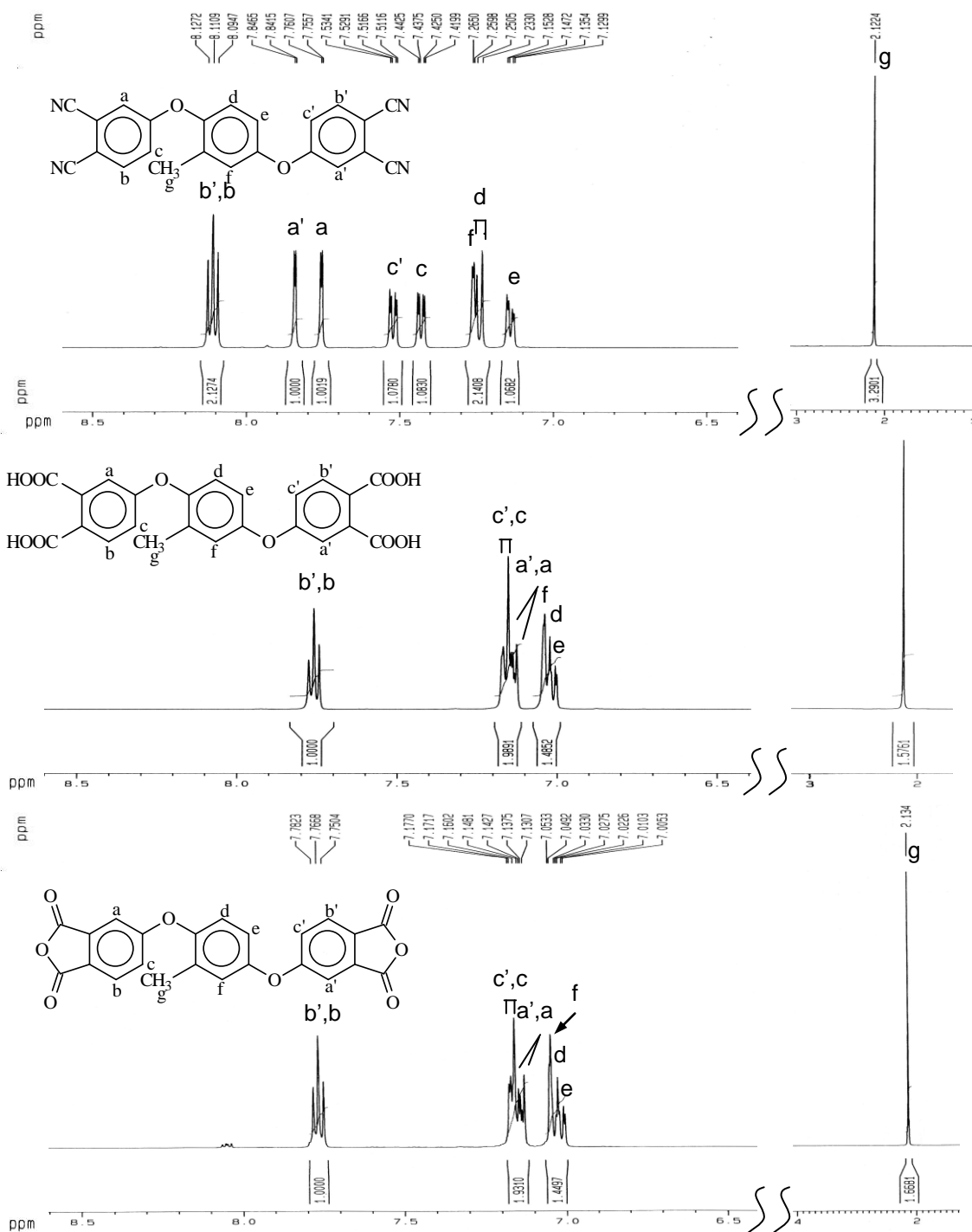


Fig. 4. ^1H NMR spectra of **I'**, **I''** and **I** in $\text{DMSO-}d_6$.

(b) Chemical imidization (C)

A pot of 10 wt% PAA solution in DMAc was prepared from each 0.7 mmol of bis(ether amine) **IIa** and bis(ether anhydride) **I** by the same procedure as described above. Then, 2 mL of acetic anhydride/pyridine (volume ratio 2/1) was added to PAA

solution. The mixture was stirred at 80-90 °C for 1 h, and then the resulting solution was poured into a glass culture dish, which was placed in an oven at 110 °C for 30 min to evaporate the solvent and form a thin solid film. The semidried PEI film was further heated to 200 °C and held at that temperature for 2 h to remove the residual solvent. Inherent viscosity of **Ia(C)** was 1.1 dL/g, as measured at a concentration 0.5 g/dL in DMAc at 30 °C.

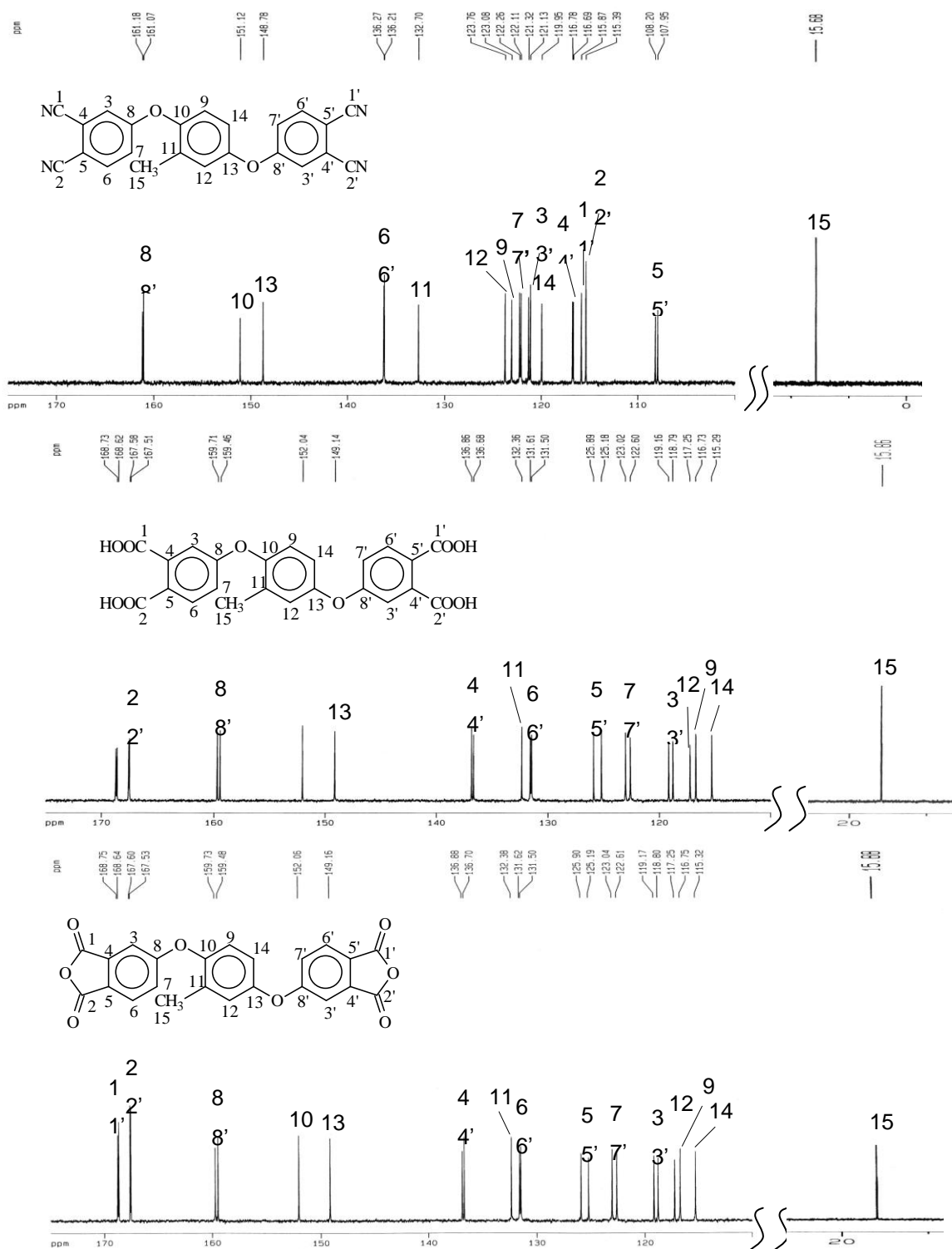
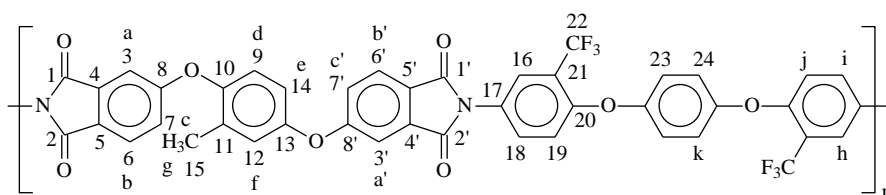


Fig. 5 ^{13}C NMR spectra of **I'**, **I''**, and **I** in DMSO-d_6 .

IR (film) of **IVa**: 1778, 1724 (asymmetric and symmetric imide C=O stretch), 1594-1486 (aromatic C=C stretch), 1378 (C-N stretch), 1243 (C-O stretch), 1052, 744 cm^{-1} (imide ring deformation). ^1H NMR (500 MHz, $\text{DMSO-}d_6$, δ , ppm) of **IVa**: 7.99 (d, 1H, H_b , $J = 8.5$ Hz), 7.98 (d, 1H, H_b , $J = 8.5$ Hz), 7.92 (d, 2H, H_h , $J = 2.5$ Hz), 7.71 (dd, 2H, H_i , $J = 7.2, 2.5$ Hz), 7.51 (d, 1H, H_c , $J = 8.5$ Hz), 7.47 (s, 1H, H_a), 7.40 (d, 1H, H_c , $J = 8.3$ Hz), 7.34 (s, 1H, H_a), 7.26 (s, 4H, H_k), 7.25 (d, 2H, H_j , $J = 7.2$ Hz), 7.25 (s, 1H, H_f), 7.23 (d, 1H, H_d , $J = 8.6$ Hz), 7.15 (d, 1H, H_e , $J = 8.6$ Hz), 2.17 (s, 3H, H_g). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$, δ , ppm) of **IVa**: 166.14 (C^1), 166.06 (C^1), 162.89 (C^2), 162.74 (C^2), 154.39 ($\text{C}^{8,8'}$), 152.01 (C^{10}), 151.94 (C^{13}), 149.17 (C^{24}), 134.38 (C^4), 134.26 (C^4), 133.29 (C^{20}), 132.56 (C^{17}), 126.72 (C^9), 126.14 (C^6), 125.96 (C^6), 125.50 (C^{11}), 124.06 ($\text{C}^{5,5'}$), 123.97 (C^{22} , quartet, $^1J_{\text{C-F}} = 273$ Hz), 123.33 (C^{18}), 123.08 (C^7), 122.87 (C^7), 121.87 (C^{19}), 121.61 (C^{23}), 119.46 (C^{12}), 119.34 (C^{21} , quartet, $^2J_{\text{C-F}} = 31$ Hz), 119.09 ($\text{C}^{3,3'}$), 111.91 (C^{16}), 110.45 (C^{14}), 15.75 (C^{15}).



Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. ^1H and ^{13}C NMR spectra were measured on a Bruker AV-500 FT-NMR spectrometer. Elemental analyses were run in a PerkinElmer model 2400 CHN analyzer. Inherent viscosities were determined at a 0.5 g/dL concentration with an Ubbelohde viscometer at 30 °C. Weight-average molecular weights (\overline{M}_w) and number-average molecular weights (\overline{M}_n) were obtained via gel permeation chromatography (GPC) on the basis of polystyrene calibration using Waters 2410 as an apparatus and THF as the eluent. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050. Measurements were carried out on 7–10 mg film samples heated in flowing nitrogen or air (90 cm^3/min) at a heating rate of 20 °C/min. DSC analyses were performed on a TA Instruments DSC 2010 in flowing nitrogen (40 cm^3/min) at a heating rate of 20 °C/min. Mechanical properties of the films were measured with an Instron model 1130 tensile tester with a 5 kg load cell at a crosshead speed of 5 mm/min on strips approximately 50-60 μm thick and 0.5 cm wide with a 2 cm gauge length. An average of at least five individual determinations was used. The color intensity of the polymers was evaluated by a GretagMacbeth Color-Eye 3100 colorimeter. Measurements were performed for the films at an observational angle of 10° and with a Commission International de l'Eclairage (CIE)-D illuminant. A CIE LAB color difference equation was used. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Shimadzu UV-1601 UV–vis spectrophotometer. The dielectric property of the polymer films was tested by the parallel-plate capacitor method with a Hewlett Packard 4194A dielectric analyzer. Gold electrodes were vacuum-deposited on both surfaces of dried films. Experiments were performed at 25 °C in a dry chamber. The equilibrium water uptake was determined by the weighing of the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 3 days.

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