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Polymer Design for Thermally Stable Polyimides with Low Dielectric Constant

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Summary: We successfully prepared a series of thermally stable polyimides (PIs) with low dielectric constant (*k*) by introducing bulky diphenyl fluorenylidene moieties in backbone. The lowest *k* was found to be 2.77 among non-fluorinated PIs and 2.35 among fluorinated ones. In order to prove the lowest limit of *k* in PIs, we prepared soluble and thermally stable polyarylenes (PArs) without polar imide linkage with the same aromatic moieties by coupling polymerization. The lowest *k* was 2.7 without fluorine (F) and 2.2 with F atom, which showed also promising for low *k* materials. From these results, PIs we prepared were estimated to the lowest *k* values among PIs. On the basis of statistics on these results, we could express contour lines of *k* as a function of imide concentration and F content with high correlation factor (r= 0.96) in PIs and PArs.

Keywords: dielectric constant, 9,9-diphenyl fluorine, polyarylenes, polyimides, structure-property relations,

Introduction

A challenge for thermally stable polymers in the fields of microelectronics is lowering their dielectric constant (*k*), since at higher wiring density the signal propagation speed depends on the *k* values of the substrate used as interlayer dielectrics.

Aromatic polyimides (PIs) are among the candidate materials with low *k* and thermal stability. Although the most of the thermally stable PIs used in the electronics industry show *k* over 3.0, they have some advantages to apply for this purpose. That is a diversity of monomer synthesis including aromatic diamines and tetracarboxylic dianhydrides on the standpoint of polymer design.

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Our polymer design for PIs with low *k* is based on reducing polar imide concentration (weight fraction of imide linkage by molecular weight (Mw) in repeating unit) which contribute to make *k* higher, as shown examples of the difference of *k* values among Kapton® of Du Pont (*k* = 3.5; imide concentration= 36.6 wt%), Upilex R® of Ube (*k* = 3.2; imide concentration= 27.7 wt%), and Ultem® of GE (*k*= 3.15; imide concentration= 23.6 wt%).

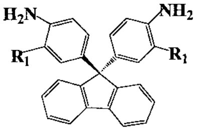
We choose a bulky non-polar aromatic substituent, diphenyl fluorenylidene moieties, which has a possibility to lower *k* with keeping thermal stability, because it combines short aromatic π-conjugation length with a cardo aromatic structure.

In this article we report, 1) synthesis, *k* values and thermal properties of a series of PIs based on substituted diphenyl fluorenylidene moieties in diamines and/or tetracarboxylic dianhydrides, 2) a comparative study of polyarylenes (PArs) without polar imide linkage with the same aromatic moieties in order to prove the lowest limit *k* of PIs, and 3) the relationship between *k* and chemical structure of PIs.

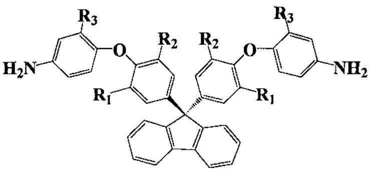
Experimental

Monomer

Among diamines with diphenyl fluorenylidene moieties, a series of diamines, 9,9-bis(4-aminophenyl)fluorene (**1a**), its phenyl substituted derivative (**1b**), 9,9-bis[4-(amino-phenoxy)phenyl]fluorene (**2a**) and its methyl, phenyl and/or trifluoromethyl substituted derivatives (**2b-2g**) except for commercially available **1a**, were prepared.

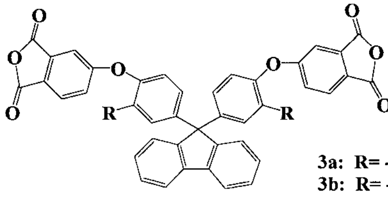


1a: R_1=H
1b: R_1=C_6H_5



2a: R_1=R_2=R_3=H
2b: R_1=C_6H_5, R_2=R_3=H
2c: R_1=H, R_2=R_3=CH_3,
2d: R_1=R_2=R_3=CH_3
2e: R_1=H, R_2=CH_3, R_3=CF_3
2f: R_1= R_2=CH_3, R_3=CF_3
2g: R_1=R_2=C_6H_5, R_3=CF_3

Among tetracarboxylic dianhydrides, four commercially available monomers, pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA), 4,4'-oxydiphthalic anhydride (ODPA), and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), were used. Two dianhydrides, 9,9-bis[(3,4-dicarboxyphenoxy)phenyl] dianhydride (**3a**) and its 3-phenyl substituted derivative (**3b**) were synthesized.



3a: R= -H
3b: R= $-C_6H_5$

Physical Properties

A conventional polymerization method was used to prepare poly(amic acid)s (PAAs) by polyaddition of corresponding diamine and tetracarboxylic dianhydride in aprotic solvent, such as N,N-dimethylformamide (DMF). The PI film was prepared from the PAA solution by thermal imidization with stepwise heating at 80 °C for 20 min., 140 °C for 20 min., 200 °C for 20 min., 250 °C for 20 min., and 300 °C for 20 min.

Relative Mws of PAAs were estimated from inherent viscosities in DMF at a concentration of 0.5 dL/g at 30 °C.

$Td_{5\%}$ (thermal decomposition temperature at 5 % weight loss) was measured by thermogravimetric analysis (TGA) under nitrogen atmosphere with TGA 320 (Seiko Denshi Kogyo Co.) at heating rate of 10 °C/ min. Glass transition temperature (Tg) was measured by DSC 910 (Du Pont Co.) at heating rate 20 °C/ min. under nitrogen flow.

For the measurement of *k* the polymers were spin-coated onto flat conductive substrates (As-doped Si wafer). Aluminum electrode was deposited *in vacuo* through a mask on top of the polymer films. All measurements of *k* were performed at 1 MHz and room temperature in air, using a LCR meter (HP 4284, Hewlett Packard). The film thickness was measured by elipsometry (DVA-36LH, Mizojiri).

Results and Discussion

PIs with Low *k*[1] [2]

Table 1 shows the characteristics of the PIs derived from **1a**, **1b** and commercially available four tetracarboxylic dianhydrides, PMDA, s-BPDA, ODPA and 6FDA. A series of these PIs showed the lower *k* with the lower imide concentration as expected. The PIs without F atom showed relatively low *k*= 3.0-3.3. PIs with F atom showed *k*= 2.6–2.8, with the lowest value, *k*= 2.63, being obtained from **1b** and 6FDA.

Table 1. Characteristics of PIs with 9,9-bis(4-aminophenyl)fluorine (1).

Diamine	Dianhydride	Imide (wt%)	F (calcd) (wt%)	PAA	PI		
				η_{inh} (dL/g)	$Td_{5\%}$ (°C)	Tg (°C)	*k*
1a	PMDA	26.4	0	0.95	548	>450	-
	s-BPDA	23.1	0	0.58	575	420	3.27
	ODPA	22.5	0	0.57	553	345	3.03
	6FDA	18.5	15.1	0.72	533	366	2.81
1b	PMDA	20.5	0	0.60	529	366	-
	ODPA	18.1	0	0.66	543	315	3.00
	6FDA	15.4	12.5	0.41	536	297	2.63

In order to lower *k* by reducing imide concentration, **2a** or **2b** were used instead of **1a** or **1b**. A series of these PIs also showed lower *k* with lower imide concentration, as shown in Table 2. The lowest *k* of the PI without F atom was showed by **2b**/ODPA, to be 2.80. The lowest *k* of the PI with F atom was 2.65, from **2a**, or **2b** and 6FDA. It seems possible to approach the lower limit of *k*, around 2.65, by using the fluorenylidene diamine, **1a**, **1b**, **2a**, **2b**, in combination with commercial aromatic dianhydrides.

PIs with much lower imide concentration were prepared by using some methyl- and/or trifluoromethyl-substituted fluorenylidene diamines, **2c**, **2d**, **2e**, **2f**, and **2g**. In these PIs syntheses PMDA and 6FDA were used as a typical teteracarboxylic dianhydride. Table 3 shows the characteristics of PIs with a series of substituted fluorenylidene diamines.

Table 2. Characteristics of PIs with 9,9-bis(4-aminophenoxyphenyl)fluorene (2).

Diamine	Dianhydride	Imide (wt%)	F (cald) (wt%)	PAA	PI		
				η_{inh} (dL/g)	$Td_{5\%}$ (°C)	Tg (°C)	*k*
2a	PMDA	19.6	0	0.92	546	358	2.91
	s-BPDA	17.7	0	0.61	567	302	2.95
	ODPA	17.4	0	0.78	540	293	2.93
	6FDA	14.9	12.1	1.31	534	293	2.65
2b	PMDA	16.2	0	1.15	544	293	2.82
	s-BPDA	14.9	0	0.54	543	272	2.86
	ODPA	14.6	0	0.61	539	253	2.80
	6FDA	12.8	10.4	0.89	539	268	2.65

PIs with methyl-substituted fluorenylidene diamines showed inferior thermal stability, exhibiting $T_{d5\%}$ of *ca.* 100 °C lower than that of unsubstituted fluorenylidene diamine, owing to aliphatic substituent. On the other hand, PIs with trifluoromethyl-substituted fluorenylidene diamines kept superior thermal stability, which reflects the difference in bond energy between C-F and C-H bond. While the lower imide concentration led to the lower *k*, it was also observed that F content from CF_3 groups in both diamines and tetracarboxylic dianhydrides contributed to reduce *k*.

Table 3. Characteristics of PIs with substituted 9,9-bis(4-aminophenoxyphenyl)fluorene (2).

Diamine	Dianhydride	Imide (wt%)	F (calcd) (wt%)	PAA	PI		
				η_{inh} (dL/g)	$Td_{5\%}$ (°C)	Tg (°C)	*k*
2c	PMDA	18.2	0	0.99	454	312	2.77
	6FDA	14.0	11.4	0.97	446	278	2.62
2d	PMDA	17.5	0	0.62	434	347	2.81
	6FDA	13.7	11.1	0.54	436	307	2.70
2e	PMDA	15.9	13.0	0.77	460	307	2.62
	6FDA	12.7	20.6	0.73	454	281	2.51
2f	PMDA	15.4	12.6	0.69	447	362	2.70
	6FDA	12.4	20.1	0.58	439	309	2.53
2g	PMDA	14.0	11.4	0.60	550	290	2.69
	6FDA	11.4	18.5	0.67	538	269	2.46

In the F-free PIs, methyl-substituted PIs, **2c**/PMDA and **2d**/PMDA, which reached *k*= 2.77-2.81, had higher imide concentration than that of phenyl-substituted **2b**/PMDA. The reason of reversed relation is thought to originate from larger bulkiness of phenyl substituent compared with methyl ones. Introducing plural substituents into **2c** and **2d** resulted in increasing free volume in the PI. In a series of these PIs with F atom, the lowest *k* of the PI, **2g/6FDA**, with thermal stability was 2.46 ($Td_{5\%}$= 538 °C, Tg= 269 °C). *K* values approached *k*= 2.5 more and more closely, which is the lowest *k* value among PIs reported before.[3] [4]

In order to achieve lower *k* by using a bulky fluorenylidene skeleton effectively as diluent to polar imide bond, we tried to introduce bulky substituents not only into diamine but also into tetracarbxylic dianhydride moieties. PI with fluorenylidene moieties both in diamine, **2a** (without F), **2g** (with F), and tetracarbxylic dianhydride, **3a**, and its 3-phenyl substituted, **3b**, were investigated. The results are listed in Table 4.

Table 4. Characteristics of PIs with 9,9-bis[(3,4-carboxyphenoxy)phenyl]fluorene dianhydride (3).

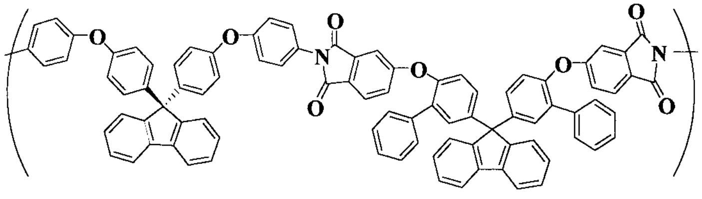
Dianhydride	Diamine	Imide (wt%)	F(calcd) (wt%)	PAA	PI		
				η_{inh} (dL/g)	$Td_{5\%}$ (°C)	Tg (°C)	*k*
3a	**2a**	12.6	0	0.47	542	284	2.80
	2g	10.0	4.1	0.34	558	263	2.61
3b	**2a**	11.1	0	0.51	525	266	2.77
	2g	9.0	3.7	0.35	554	253	2.60

2a/3b with fluorenylidene units in both monomers shows the lowest imide fraction, 11.1 wt%, resulting in the lowest *k* among the F-free PIs which we studied, *k*= 2.77, with keeping thermal stability ($Td_{5\%}$= 554 °C, Tg= 266 °C). Since **3a** and **3b** contain no F atoms, it does not contribute to higher F content in PI by using these tetracarboxylic dianhydrides. It shows the limitation of reducing imide concentration to get lower *k*. These results also suggested that PI with *k*= 2.5 required both reducing imide concentration and the increasing F content.

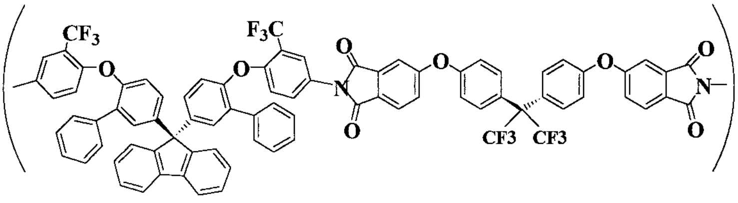
By introducing diphenyl fluorenylidene moieties as bulky cardo structure to reduce polar imide concentration into PI backbone, we successfully prepared non-fluorinated thermal stable **PI (A)**, **2a/3b**, with the lowest *k*, 2.77, and fluorinated PI, **2g/6FDA**, with the lower *k*, 2.46.

To obtain PI with the lowest *k* in fluorinated PI, we prepared **PI (B)** with the lowest *k*, 2.35, by lowering imide concentration from 11.4 to 9.9 wt% by using diamine **2g** and 2,2-bis[(3,4-

dicarboxyphenoxy)]hexafluoropropane dianhydride instead of 6FDA, with keeping 16.1 wt% of F content. By considering imide concentration, in other words, Mw of repeating unit, the lowest imide concentration is limited to around 10 wt%. This PI with the lowest *k* showed high thermal stability $Td_{5\%}$= 549 °C, Tg = 238 °C.



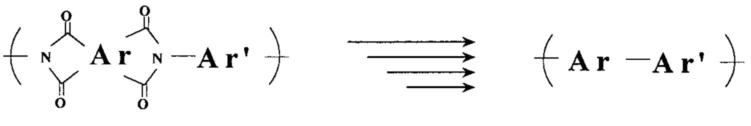
PI (A)



PI (B)

K of PArs as the Lowest Limit of PIs[5]

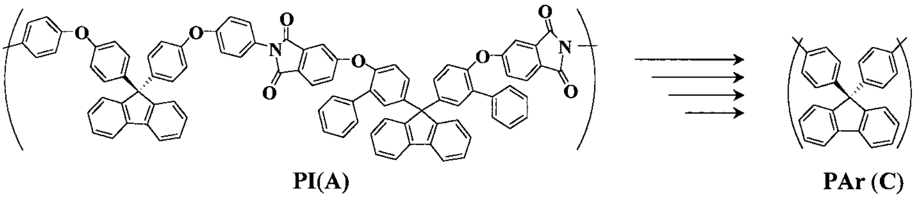
We obtained a series of PIs with lower *k* as mentioned above. However, we have a question whether *k* value of obtained PI is the lowest limit among known PI. In order to solve such a question, we compared *k* values between PI and PAr without polar imide linkage with the same aromatic moieties.



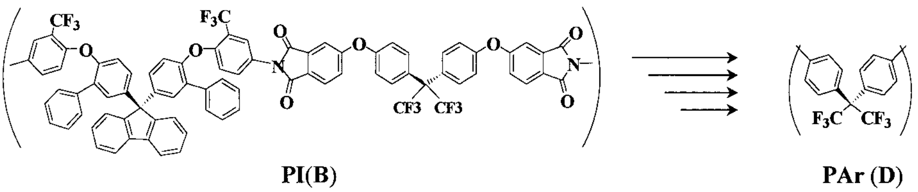
polyimide with polar linkage

polyarylene without polar linkage

In case of F-free PI with the lowest *k*, 2.77, a major chemical structure which contributes to lower *k* in PI is fluorenylidene moiety. Poly(diphenylfluorenylidene-diyl) is corresponding **PAr (C)** to this PI in more simple structure. It may show *k* lower than 2.77.



Moreover, in case of fluorinated PI with the lowest *k*, 2.35, a major chemical structure which contributes to lower *k* in PI, a main structure of 6FDA unit. Poly(2,2-diphenyl-hexafluoro-propane-diyl), **PAr (D)**, is corresponding PAr. It may show k lower than 2.35.

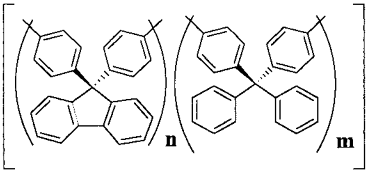


Anyway the comparison of *k* value between PIs and PArs is significant to prove the lowest limit of *k* values among PIs.

There are some methods to prepare PArs by coupling polymerization. A typical synthesis of PArs is using Zn and nickel-phosphine catalyst. Aryl dichlorides and/or bis-methansulfonates (so-called bis-mesylates) of bisphenols were used as functional groups for coupling reaction according to the method by Percec *et al.*[6] [7] We used bisphenols as a starting monomer unit, because of availability of a variety of commercialized bisphenols.

Poly(diphenylfluorenilydene-diyl), **PAr (C)**, was successfully prepared with superior thermal properties, Tg higher than 300 °C and $Td_{5\%}$= 562 °C with high Mw (>13000 by GPC). However, *k* of this PAr was impossible to measure in accuracy owing to insufficient solubility for spin-coating processing.

To improve solubility of this PAr, we tried copolymerization with bis-mesylates of 1,1-bis(4-hydroxyphenyl)diphenylmethan, a similar structure to bis(4-hydroxyphenyl)fluorene. Copolymers (**PAr (E)**) showed improved solubility, to be soluble in NMP, cyclohexanone and even THF with keeping high thermal stability.



PAr (E)

K of copolymer with composition of molar ratio 60 to 40 mol% could be measured as 2.7. This copolymer can be also considered as a candidate of low *k* polymers with thermal stability ($Td_{5\%}$=549 °C, Tg>300 °C). Since the difference in *k* values between the PI and the PAr is less than 0.1, *k* of our non-fluorinated PI showed the lowest limit of *k* among PIs.

In case of fluorinated PAr, PAr from bismesylate of Bisphenol AF could be prepared with high Mw (27000 by GPC). It showed a good solubility, to be soluble in NMP, cyclohexanone, THF, chloroform and even in ethyl lactate recognized as a safe solvent in IC industry. However, thermal properties ($Td_{5\%}$= 508 °C, Tg= 249 °C) were not better than those of PI. *K* showed 2.2, the lowest value among our PIs and PArs. It has a little difference between that of the PI (*k*= 2.35). It is owing to the difference of F content between the PAr and the PI. The PAr has higher F content with 37.7 wt%. On the other hand, PI with *k*= 2.35 has 16.1wt% of F. Considering the different F content in polymers, *k* of our fluorinated PI estimated to be the lowest limit of *k* among PIs.

Relationship between *k vs.* Chemical Structure in PIs and PArs[5]

Next issue is to prove the relationship *k vs.* chemical structure of PIs and PArs. Contour lines of *k* could be obtained as a function of imide concentration (wt%) and F content (wt%) by our

31 experimental points of PIs and PArs on the basis of statistics with high correlation factor (r= 0.96) (Figure 1).

This figure tells that; 1) *K* is estimated by chemical structure of repeating unit. 2) At higher imide concentration, *k* is mainly affected by imide concentration. 3) The lowest *k* of PI with F-free PI is estimated to be *ca.* 2.7 judging from imide concentration, in other words Mw of repeating unit.

To achieve PI with *k* lower than 2.5, imide concentration has to be lower than 12 wt% (*ca.* 1170 or higher Mw of repeating unit) and F content higher than 12 wt%.

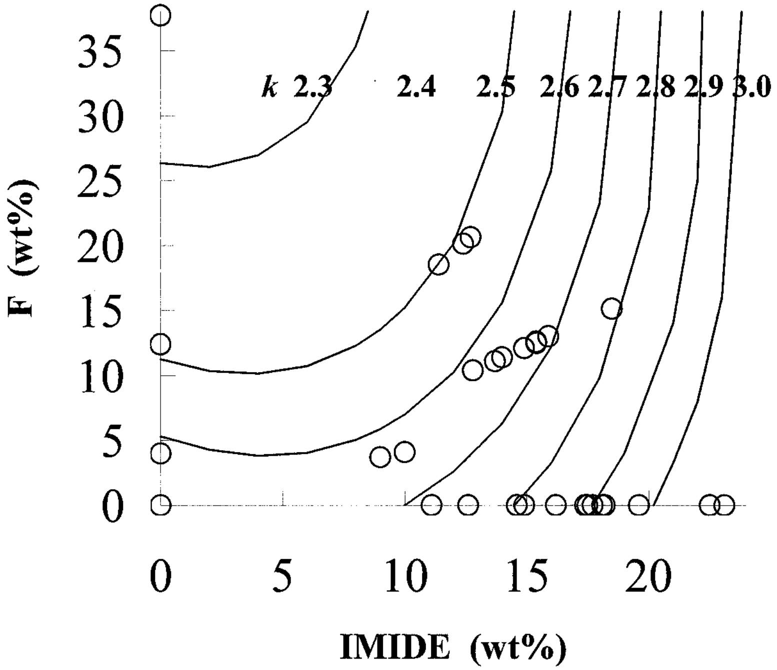


Fig. 1. Plots of *k* *vs*. imide (wt%) and F (wt%); (o; experimental data).

Conclusions

1) By introducing a bulky cardo structure, fluorenylidene moieties, into PI backbone, we successfully prepared F-free PI with the lowest *k*= 2.77, (Td$_{5\%}$= 525 ^{o}C, Tg= 266 ^{o}C), and fluorinated PI with the lowest *k*= 2.35 (Td$_{5\%}$= 549 ^{o}C, Tg= 238 ^{o}C).
2) A series of the thermally stable and low *k* PArs were obtained, which contained the similar main moieties of above PIs. F-free with fluorenylidene moiety showed *k*=2.7, (Td$_{5\%}$= 549 ^{o}C, Tg>300 ^{o}C) fluorinated showed *k*= 2.2 (Td$_{5\%}$= 508 ^{o}C, Tg= 249 ^{o}C). Such soluble PArs also proved to be promising as low *k* materials with thermal stability.
3) Based on the results of the low *k* PAr with corresponding structure of the PIs, we could estimate that PI with fluorenylidene moieties showed the lowest limit of *k* among PIs.
4) Using 31experimental data set of *k* values of our PIs and PArs, contour lines of *k* as a function of imide (wt%) and F (wt%) could be obtained on the basis of statistics with high correlation factor. We can estimate *k* values from the chemical structure of repeating unit of PI and PArs.

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