

Thermally Stable Polyarylenes with Low Dielectric Constants

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New, thermally stable low dielectric materials are required in semiconductor industry to achieve current goals with respect to signal propagation and wiring density. Organic polymers are suitable, since a broad variety of structures can easily be incorporated to tailor dielectric constant (k) and thermal stability. Especially polyarylenes without polar linkage are promising candidates. A series of polyarylenes was prepared by coupling of aromatic dihalides or bismesylates of bisphenols using Zn and a Ni-phosphine catalyst. Among the non-fluorinated polyarylenes, a copolyarylene derived from bismesylates of 9,9-bis(4-hydroxyphenyl)fluorene and 4,4'-dihydroxyphenyldiphenylmethane showed the lowest $k=2.7$ (@1MHz) with superior thermal stability ($T_{d5\%}$ under $N_2 = 549$ °C). The lowest k among all synthesized polymers was achieved with a fluorinated polyarylene prepared from the bismesylate of 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane with $k=2.2$ (@1MHz), which also showed high thermal stability ($T_{d5\%}$ under $N_2 = 508$ °C).

Key Words: Polyarylene, Low Dielectric Constant, Thermally Stable Polymer, Coupling Polymerization

1. INTRODUCTION

Aromatic polymers, e.g. polyimides, have been widely applied in electronics industry because of their high performance such as superior thermal stability, good mechanical properties as well as chemical resistance. A current target in the electronics field for thermally stable polymer is to lower their dielectric constants (k), since the signal propagation speed and the achievable wiring density in semiconductor devices depend on the k values of the medium between the conducting lines. Considerable efforts have been expended in the last decades to design and synthesize new polymers for this purpose.

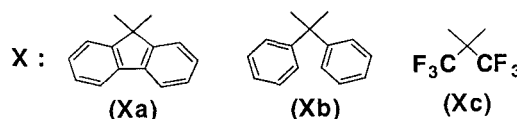
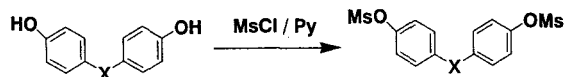
We have already reported a series of low k polyimides having bulky fluorenyliden-moieties in the backbone^{1),2),3)}. These moieties lowered the weight fraction of the polar imide linkage. Among the non-fluorinated polyimides the lowest k values obtained was $k=2.77$ ²⁾, for fluorinated polyimides it showed $k=2.35$ ³⁾. Based on these results we expected that polyarylenes containing fluorenyliden-groups without a polar imide linkage might show even lower k values than the polyimides with such moieties.

In this article, we report the synthesis and characteristics - such as k and thermal properties - of a series of soluble polyarylenes obtained by coupling polymerization.

2. EXPERIMENTAL

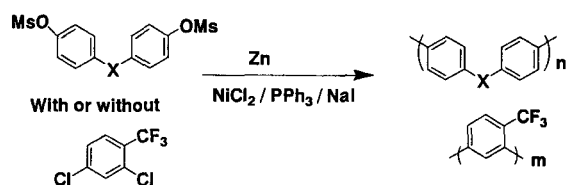
1) Monomer Synthesis

Monomers for the polyarylenes were aromatic dichlorides and/or bismesylates of bisphenols. The dichloride, trifluoromethyl-2,5-dichlorobenzene (TFDCB), and the bisphenols, 9,9-bis(4-hydroxyphenyl)fluorene and 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane, are commercially available and were used as received. The bisphenol, 4,4'-dihydroxyphenyldiphenylmethane, was synthesized from diphenyldichloromethane and phenol by nucleophilic substitution. Mesylates were prepared from the corresponding bisphenols by reaction with methanesulfonyl chloride (MsCl) in the presence of pyridine (Py) as acid acceptor shown below:



2) Polymer Synthesis

Polyarylenes were prepared by $\text{NiCl}_2/\text{PPh}_3/\text{NaI}$ catalyzed reductive coupling of the corresponding aromatic bismesylates and/or dichlorides using Zn in anhydrous dimethylacetamide (DMAc) at 70°C . Reaction time was 20 hrs. The polyarylenes were coagulated in a large excess of methanol. Purification was performed by repeated precipitation of THF solutions in methanol. Recovered polymers were dried overnight *in vacuo* at 80°C .



3) Characterization

Weight-averaged molecular weights (M_w)s of the polyarylenes were measured by GPC using THF as solvent. The GPC was calibrated using a polystyrenes standard.

Thermal decomposition temperature at 5% weight loss ($T_{d5\%}$) was measured with a TGA 320 (Seiko Denshi Kogyo Co.,) at heating rate $10^\circ\text{C}/\text{min}$ under nitrogen.

Glass transition temperature (T_g) was measured by a DSC 910 (Du Pont Co.) at heating rate $20^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

For the measurement of k the polymers were spin-coated onto flat conductive substrates (As doped Si wafer). The film thickness was measured by ellipsometry (DVA-36LH, Mizojiri Co. Ltd). Aluminum electrodes were deposited *in vacuo* through a mask on top of the polymer films. All measurements of k were performed in air, at 1MHz and room temperature using a LCR meter (HP4284 LCR meter, Hewlett Packard Co.,). k was calculated by Eq.1.

$$k = \frac{(C_x - C_r)t}{\epsilon_0 \pi d^2 / 4} \quad (1)$$

Where C_x is the measured capacitance, C_r is the calibrated capacitance, t is thickness of the sample, d is diameter of the electrode and $\epsilon_0 = 8.85 \times 10^{-14}$ C/m. C_r was calculated according to ASTM D150.

3. Results and Discussion

Generally polyarylenes have a tendency to poor solubility owing to the rigid and conjugated polymer structure. One possibility to improve or increase solubility for polymers is to introduce bulky substituents into the backbone and/or to create irregular structures, e.g. by copolymerization.

Bulky fluorenyliden-substituents have been shown to be capable of increasing solubility while keeping high thermal stability⁴⁾ and lowering k , which was also reported by us for a series of polyimides^{1),2),3)}. Polyarylenes derived from the fluorenyliden-monomer (Xa) were therefore expected to combine good solubility

with good thermal properties and low k . High molecular weight poly(Xa), that is soluble in amidic solvents such as N-methylpyrrolidone (NMP) or DMAc, was easily obtained by coupling polymerization of the corresponding bismesylate (Table 1, Entry 1). It showed the expected thermal characteristics, $T_{d5\%}$ higher than 550°C and T_g higher than 300°C , but we could not measure k value since it was not possible to obtain smooth films from amidic solvents.

A polyarylene derived from (Xb) prepared (Table 1, Entry 2), which was expected to have similar solubility, k and thermal stability. However, only an insoluble crystalline polymer formed. The molecular weight was probably low because of the precipitation of polymer during polymerization.

Copolymerization of Xa and Xb was the next approach to improve solubility. A copolymer of (Xa)/(Xb)=60/40 has been found to be amorphous (Table 1, Entry 3). It exhibited $k = 2.7$ (@1MHz), measured with appropriate coated film prepared from cyclohexanone (CHN) solutions. Like poly(Xa) the thermal stability was high, $T_{d5\%}$: 549°C , $T_g > 300^\circ\text{C}$. As expected, k is slightly lower than the lowest k of our previously reported polyimides ($k=2.77$ @1MHz)⁴⁾.

In order to get polyarylenes with even lower k , we tried to introduce fluorine atoms as shown in Table 2.

Copolymerization of bismesylate of the fluorenyliden-monomer (Xa) and TFDCB, which is one of the simplest fluorine-containing commercially available monomer, was investigated (Table 2, Entry 4-6). The higher content of TFDCB, the lower was M_w of the obtained copolymer. TFDCB probably does not have sufficient high reactivity for polymerization. Solubility changed also with the composition of the copolymers. Copolymers with the composition, (Xa/TFDCB):80-50/20-50 (molar ratio) showed k value in the range of 2.5-2.6, lower than those of the polyarylenes without fluorine atoms.

A promising candidate for polyarylenes with very low k is considered to be derived from bismesylate of 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (Xc). A homopolymer with high molecular weight could be obtained (Table 2, Entry 8). It showed with $k=2.2$ the lowest dielectric constant among our polyarylenes. This result was in a agreement with previous results of fluorinated fluorenyliden-substituted polyimides containing similar structures that had $k=2.35$ (@1MHz)⁴⁾, slightly higher due to the polar imide-ring.

In summary, in our investigation of thermally stable polymers with low k , polyarylenes have been proven to be reasonable chemical structures. Polyarylenes showed lower k values -2.7 without fluorine atom and 2.2 with fluorine atom - than thermally stable aromatic polyimides containing similar structures.

References

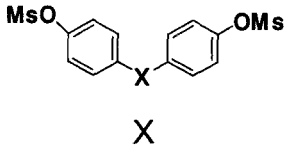
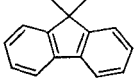
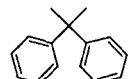
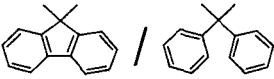
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(Received December 7, 2000; Accepted January 31, 2001)

(Table 1) Characteristics, k values, M_w , thermal properties and solubility of non-fluorinated Polyaryrenes

Entry		M_w	T_g (°C)	T_d (°C)	k (@1MHz)	Solubility		
						NMP	CHN	EL ^{*3)}
1		13000	>300	562	*1)	++	-	-
2		*2)	- Tm: 336	512	*2)	-	-	-
3	 (60/40)	12400	>300	549	2.7	++	++	-

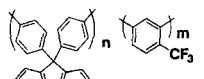

*1) Smooth-surface- film, suitable for k - measurement, cannot be obtained.

*2) Insoluble any organic solvents owing to crystalline polymer

*3) EL: Ethyl lactate

Solubility (at room temperature); ++: Soluble, -: Insoluble.

(Table 2) Characteristics, k values, M_w , thermal properties and solubility of fluorinated Polyaryrenes.

Entry			M_w	T_g	T_d	k	F (wt%) (calcd)	Solubility			
	n	m						NMP	CHN	EL	n-HEX
1	100	0	13000	>300	562	*1)	0	++	-	-	-
5	80	20	11700	>300	567	2.6	4.04	++	++	-	-
6	50	50	9600	>300	553	2.5	12.38	++	++	-	-
7	20	80	5600	>300	511	*1)	25.54	+	++	-	-
8	0	100	4500	>300	<500	*2)	39.55	-	-	-	++
9			27000	249	508	2.2	37.72	++	++	++	-

*1) Smooth-surface- film, suitable for k - measurement, cannot be obtained.*2) To low M_w to prepare coating film

Solubility (at room temperature); ++: Soluble, +: partially soluble, -: Insoluble.