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Synthesis and Characterization of Aromatic Polyimides Containing Perfluorononenyl Groups

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1. Introduction

Fluoropolymers such as poly(tetrafluoroethylene) have proven to be a very interesting and useful class of polymeric materials due to their unique balance of properties: water and oil repellency, low coefficient of friction, low water absorption, low refractive index, low dielectric constant, high thermal stability, and chemical resistance. Therefore, it is of particular interest to incorporate these unique properties into aromatic polyimides. Introduction of perfluoroalkyl or perfluoroalkenyl pendants along the aromatic polyimide backbones is an interesting way of incorporating a high level of fluorine atom into the aromatic polyimides without greatly affecting the backbone stiffness and thus extremely reducing the thermal stability of the polyimides.

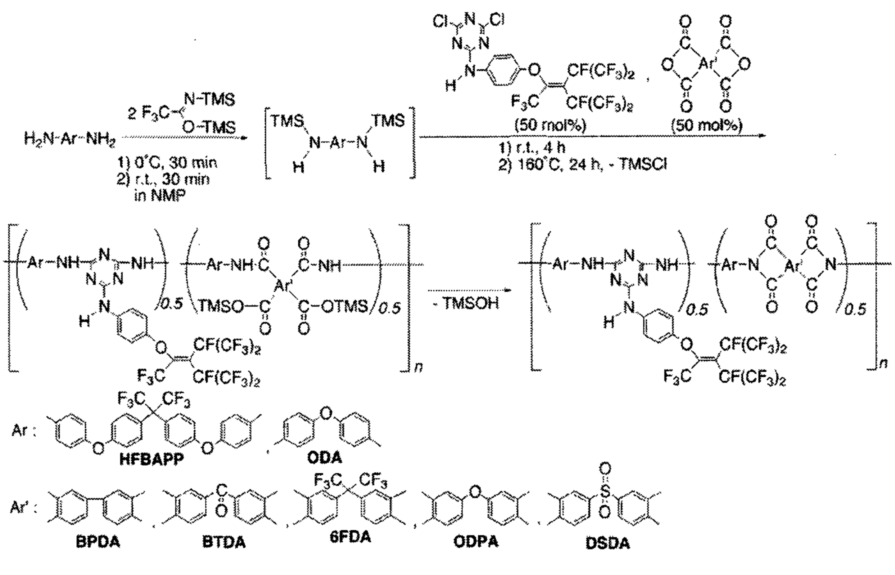
In order to introduce functional pendant groups into the aromatic polyimides, the triazine-containing monomers bearing functional groups have been employed. The triazine-containing aromatic polyimides could be successfully synthesized through one-pot method by the copolymerization of 6-functional group-substituted 2,4-dichloro-1,3,5-triazines, aromatic diamines, and aromatic tetracarboxylic dianhydrides.

In this study, the aromatic polyimides having perfluoroalkenyl groups have synthesized by the copolymerization of perfluorononenyloxyanilino-substituted dichlorotriazine, aromatic diamines, and aromatic tetracarboxylic dianhydrides. The resultant aromatic polyimides were characterized with regard to solubility, thermal properties, surface properties, and mechanical properties.

2. Results and discussion

2.1. Synthesis of polyimides

The fluorine-containing aro-matic polyimides were synthesized through the one-pot procedure by *in situ* silylation method using *N,O*-bis(trimeth-ylsilyl)trifluoro-acetamide (BSTFA) as a silylation agent (Scheme 1).



Scheme 1. Synthesis of polyimides

The copolymeri-zation of *in situ* *N*-silylated aro-matic diamines, fluorinated dichlorotriazine, and aromatic tetracarboxylic dianhydrides was carried out in NMP at room temperature for 4 h and at 160°C for 24 h to give clear and viscous fluorine-containing polyimide solutions with the elimination of neutral and volatile trimethylsilyl chloride and the elimination of trimethylsilanol by high temperature solution imidization.

Table 1 summarizes the results of the synthesis of aromatic polyimides. The polyimides had inherent viscosities of 0.6-1.0 dL/g, number-average molecular weight (M_n) of 69000-106000, and polydispersity (M_w/M_n) of 2.0-2.6.

2.2. Properties of polyimides

The polyimides as polymerized were soluble in organic solvents such as *N,N*-dimethylformamide, NMP, THF, 1,4-dioxane, $CHCl_3$. On the other hand, the polyimide films prepared by heating to 300°C did not dissolve in organic solvents and showed good chemical resistance, due to the existence of some aggrega-tion between polyimide mole-cules.

Table 1. Synthesis of Polyimides

Diamine -Ar-	dianhydride -Ar'-	polyimide η_{inh} a) (dL/g)	M_n b) $/10^4$	M_w b) $/10^4$	M_w/M_n b)
HFBAPP	**BPDA**	0.60	7.7	16.2	2.1
	BTDA	1.08	-	-	-
	DSDA	0.68	6.9	15.0	2.1
	6FDA	0.65	8.3	21.9	2.6
	ODPA	0.70	10.6	21.7	2.0
ODA	**6FDA**	0.65	9.4	18.6	2.0
	ODPA	0.63	10.1	21.6	2.1

a) Measured at a concentration of 0.5 g/dL in NMP at 30°C.
b) Determined by GPC on the basis of polystyrene calibration in NMP containing 10 mM LiBr.

All the poly-imides showed a similar decompo-sition behavior characterized by no weight loss below 400°C in air or nitrogen. The temperatures at which 5% weight loss observed for these polymers were in the range of 400-425°C. The glass transition temperatures (T_g) of the polyimides were found to be in the range of 218-255°C, depending on the structure of aromatic diamine and dianhydride components (Table 2). The coefficient of thermal expansion (CTE) of the polyimide films were 67-84 ppm/°C. The higher CTE values of the polyimides may be attributed to the loose packing of the polymer chains caused by low cohesive force of perfluorononenyl pendants.

Table 2. Thermal Properties of Polyimides

diamine -Ar-	Dianhydride -Ar'-	T_g(°C) DSC a)	TMA b)	DMA c)	T_5(°C) air	N_2	CTE (ppm/°C)
HFBAPP	**BPDA**	226	230	214	420	415	67
	BTDA	226	-	-	410	410	-
	DSDA	229	235	220	410	410	80
	6FDA	227	230	215	410	405	82
	ODPA	218	222	205	410	410	71
ODA	**6FDA**	255	258	238·	425	410	84
	ODPA	243	244	227	420	400	80

a) Determined by DSC at a heating rate of 20°C/min in nitrogen. b) Determined by TMA at a heating rate of 10°C/min in nitrogen. c) Determined by DMA at a heating rate of 2°C/min in nitrogen. d) Temperature at which 5% weight loss recorded by TG at a heating rate of 10°C/min.

Table 3 lists the tensile properties and contact angles of water for polyimide films. The films had moderate mechanical properties such as tensile strength of 71-97 MPa, elongation at break of 5-14%, and tensile modulus of 3.0-3.9 GPa. As expected, the polyimide films showed much higher contact angles of water in the range of 101-104°, indicating lower surface energy, compared with the common aromatic polyimides without fluorine atoms.

Table 3. Mechanical and Surface Properties of Polyimide Films

diamine -Ar-	dianhydride -Ar'-	T a) (MPa)	E b) (%)	M c) (GPa)	θ d) (°)
HFBAPP	**BPDA**	72	5	3.3	103
	BTDA	-	-	-	104
	DSDA	80	6	3.0	102
	6FDA	71	14	3.2	102
	ODPA	71	3	3.2	101
ODA	**6FDA**	97	5	3.6	104
	ODPA	93	5	3.9	103

a) Tensile strength. b) Elongation at break.
c) Tensile modulus. d) Contact angle of water.

3. Conclusion

The novel perfluoroalkenylated aromatic polyimides having high molecular weights were successfully prepared through the one-pot method by the copolymerization of *in situ* silylated aromatic diamines, fluorinated dichlorotriazine, and aromatic tetracarboxylic dianhydrides at elevated temperature. The yellow, transparent, and flexible polyimide films with thermal treatment around 300°C exhibited good chemical resistence, water repellency, high glass transition temperature, and moderate mechanical properties. Thus, the present fluorine-containing aromatic polyimides are considered as new class of aromatic polyimides having low surface energy.