

Synthesis and Properties of Aromatic Poly(guanamine-imide)s Bearing Chelating Pendant Groups

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1. Introduction

Aromatic polyimides have attracted wide interest in the electronics and optoelectronics applications because of their excellent properties such as high thermal stability, good electrical insulation, high mechanical strength, and chemical resistance. In recent years, polyimides having various functional groups such as sulfo groups for a fuel cell membrane, photosensitive groups for a lithographic resist, fluorinated groups for an optical material, and bulky pendant groups for good processability have been required in their fields.

In order to introduce functional pendant groups into the polymer backbones, the triazine-containing monomers bearing functional pendant groups have been employed. Some aromatic polyimides containing triazine rings in the main chain have been synthesized from triazine-containing aromatic diamines.[1-8] In 1977 bulky diphenylamino-substituted polyimides had synthesized by the polymerization of 6-diphenylamino-substituted 2,4-bis(aminoanilino)-1,3,5-triazine and pyromellitic dianhydride.[1] Phosphorus-containing polyimides were synthesized from 6-diethoxyphosphinyl-substituted 2,4-bis(aminophenoxy)-1,3,5-triazine.[4] Crosslinkable polyimides were prepared from 6-unsaturated pendant-substituted 2,4-bis(aminophenoxy)-1,3,5-triazine.[5] Furthermore, second-order nonlinear optical polyimides were synthesized from 6-chromophore-substituted 2,4-bis(aminoanilino)-1,3,5-triazine.[7,8]

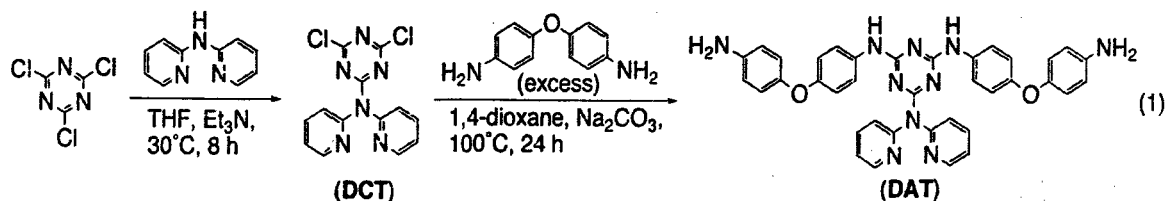
Recently, we reported a simple method for the synthesis of aromatic poly(guanamine-imide)s using dichlorotriazines in place of triazine-containing aromatic diamines. The random poly(guanamine-imide)s could be successfully synthesized through one-pot method by the copolymerization of 6-functional group-substituted 2,4-dichloro-1,3,5-triazines, aromatic diamines, and aromatic tetracarboxylic dianhydrides.[9,10]

In this paper, the aromatic poly(guanamine-imide)s having chelating pendant groups have synthesized by the polymerization of dipyridylamino-substituted triazine-containing aromatic diamine and aromatic tetracarboxylic dianhydrides (diamine method) [eq. (2)], and by the copolymerization of dipyridylamino-substituted dichlorotriazine, aromatic diamine, and aromatic tetracarboxylic dianhydrides (one-pot method) [eq. (3)]. The resultant polymers were characterized with regard to solubility, thermal properties, and adhesion properties.

2. Results and Discussion

2.1. Synthesis of monomer

The novel triazine-containing aromatic diamine with chelating pendant group, 6-(di-2-pyridylamino)-2,4-bis[4-(4-aminophenoxy)anilino]-1,3,5-triazine (DAT), could be easily prepared in two steps [eq. (1)].

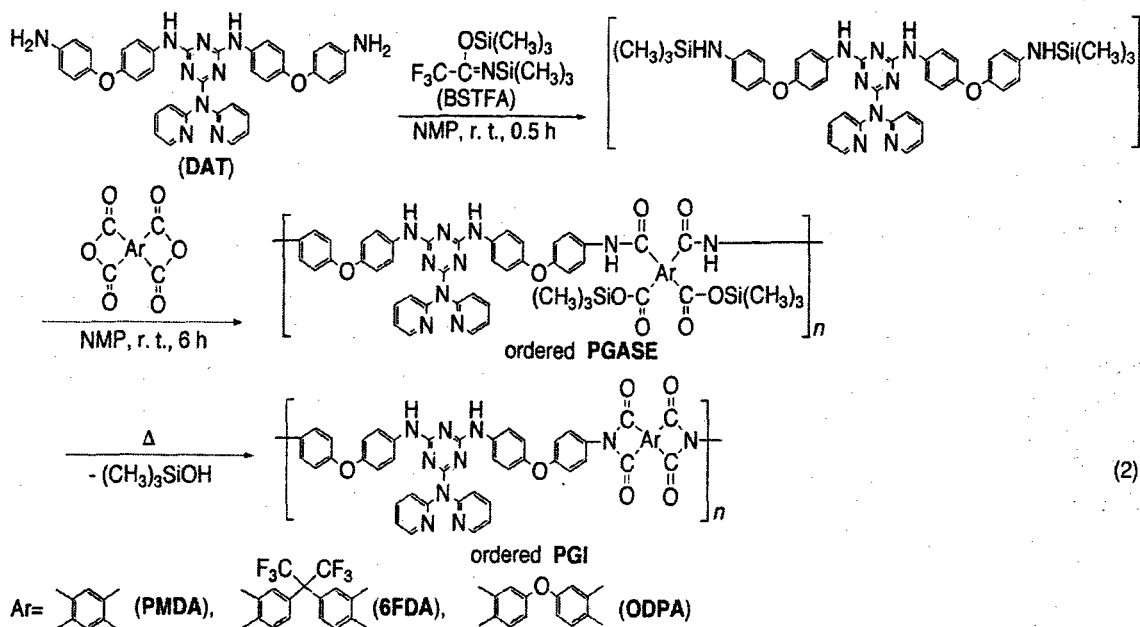


Scheme 1. Synthesis of monomer.

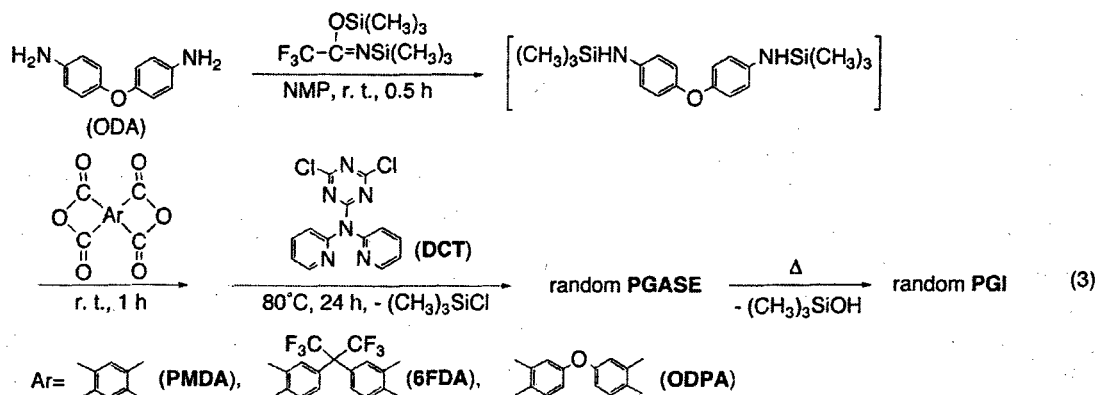
The substitution reaction of di-2-pyridylamine with cyanuric chloride in THF using triethylamine as a base afforded 6-(di-2-pyridylamino)-2,4-dichloro-1,3,5-triazine (**DCT**). The crude product obtained by evaporation of THF was purified by recrystallization from toluene/hexane mixture, and then by sublimation in 46% yield: mp 176-177°C. **DAT** was prepared by the reaction of **DCT** with excess 4,4'-oxydianiline (ODA) in the presence of sodium carbonate in 1,4-dioxane. Unreacted ODA was removed by sublimation at 200 °C/0.1 Torr. The crude product was purified by column chromatography (silica gel, ethyl acetate) in 65% yield: mp 120-121°C.

2.2. Synthesis of poly(guanamine-imide)s (PGIs)

The poly(guanamine-imide)s (**PGIs**) were synthesized through diamine procedure [eq. (2)] and one-pot procedure [eq. (3)] by *in situ* silylation method using *N,O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) as a silylation agent. Table 1 summarizes the results of the synthesis of poly(guanamine-amic acid silyl ester)s (**PGASEs**) and **PGIs**.



Scheme 2. Synthesis of poly(guanamine-imide)s by diamine method.



Scheme 3. Synthesis of random poly(guanamine-imide)s by one-pot method.

Polyaddition of *N*-silylated **DAT** prepared by *in situ* silylation with BSTFA, and aromatic tetracarboxylic dianhydrides was carried out in *N*-methyl-2-pyrrolidone (NMP) at room temperature for 6 h to give **PGASEs**. The inherent viscosities of **PGASEs** were in the range of 0.4-0.5 dL/g. **PGASEs** were subjected to thermal imidization at 250°C for 1 h to be converted to

yellow and transparent PGIs with ordered structures in the elimination of trimethylsilanol. The PGIs had inherent viscosity of around 0.5 dL/g, number average molecular weight (M_n) of 14000-20000 and polydispersity (M_w/M_n) of 1.6-1.7. The PGASEs derived from 6FDA and ODPAs were also converted by the solution imidization in NMP at 200 °C for 3 h to the corresponding PGIs having inherent viscosities of 0.6-0.7 dL/g, M_n of 23000-25000, and M_w/M_n of 2.2-2.6. However, PGI derived from PMDA was not obtained due to the polymer precipitation during the solution imidization in NMP.

The one-pot method is convenient procedure for the synthesis of PGIs with random sequence. The copolymerization of *N*-silylated ODA prepared by *in situ* silylation, aromatic tetracarboxylic dianhydrides, and dichlorotriazine (DCT) at 80 °C in NMP afforded viscous random PGASE solutions with the

elimination of neutral and volatile trimethylsilyl chloride. The PGASEs were converted to yellow and transparent random PGI films in the elimination of trimethylsilanol by thermal imidization at 250 °C for 1 h or solution imidization at 200 °C for 3 h. The inherent viscosities of PGASEs and PGIs were 0.3-0.6 dL/g. These viscosity values of the polymers obtained by one-pot method were almost the same as those of the polymers prepared by diamine method.

2.3. Properties of poly(guanamine-imide)s (PGIs)

The solubility and thermal properties of the PGI films are shown in Table 2. PGI-I derived from PMDA were not soluble in organic solvents. However, PGI-II and PGI-III derived from 6FDA and ODPAs, respectively, were soluble in polar solvents such as *N,N'*-dimethylacetamide (DMAc), NMP, and *m*-cresol. PGI films obtained by diamine method had better solubility than those by one-pot method due to the different monomer sequence. PGIs obtained by one-pot method had a random copolymer structure. Some homopolyimide segments with comparatively poor solubility exist in the copolymer structures.

The thermal properties of PGI films are also listed in Table 2. The 10% weight loss temperatures (T_{10}) of PGIs in air and nitrogen atmosphere were observed in the range of 410–425 °C and 415–435 °C, respectively. The glass transition temperatures (T_g) of PGI films were in the range of 230–276 °C by DSC depending on the rigidity of tetracarboxylic dianhydride component. The T_g values of PGIs obtained by one-pot method were somewhat higher than those obtained by diamine method because of existence of some homopolyimide segments in the copolymer structures.

The adhesion of PGI films to copper plate was evaluated by a crosscut adhesion test at room temperature. PGIs had better adhesion properties compared with conventional aromatic

Table 1. Synthesis of PGASEs and PGIs

Method	Dianhydride	PGASE		PGI
		η_{inh}^c (dL/g)	η_{inh}^c (dL/g)	Imidization ^d
Diamine ^a	PMDA	0.56	- ^e	T
	6FDA	0.47	0.50	T
	ODPA	0.55	0.51	T
	PMDA	-	- ^f	S
	6FDA	-	0.61	S
	ODPA	-	0.70	S
One-pot ^b	PMDA	0.56	- ^e	T
	6FDA	0.61	0.54	T
	ODPA	0.33	0.55	T
	PMDA	-	- ^f	S
	6FDA	-	0.48	S
	ODPA	-	0.65	S

a) Polyaddition was carried out with DAT (2.5 mmol), aromatic tetracarboxylic dianhydride (2.5 mmol), and BSTFA (5.0 mmol) in NMP (10 mL) at r. t. for 6 h. b) Polyaddition was carried out with ODA (5.0 mmol), aromatic tetracarboxylic dianhydride (2.5 mmol), DCT (2.5 mmol), and BSTFA (10 mmol) in NMP (10 mL) at 80 °C for 24 h. c) Measured at a concentration of 0.5 g/dL in NMP at 30 °C. d) T, thermal imidization; S, high temperature solution imidization. e) Insoluble in organic solvents. f) Not obtained.

polyimides. Introduction of dipyridylaminotriazine units into the polyimide structure enhanced the adhesion to a copper plate due to chelating with copper surface.

Table 2. Solubility and thermal properties of PGIs

Method	Polymer (Imidization ^{a)})	T _g (°C)			T ₁₀ ^{e)} (°C)		Solvent ^{f)}		
		DSC ^{b)}	DMA ^{c)}	TMA ^{d)}	Air	N ₂	DMAc	NMP	<i>m</i> -cresol
Diamine	PIG-I (T)	270	285	281	425	435	-	-	-
	PIG-II (T)	252	259	260	415	435	++	++	+
	PIG-III (T)	234	244	243	415	430	+	+	+
	PIG-II (S)	243	253	251	425	435	++	++	++
	PIG-III (S)	230	238	221	410	415	+	++	+
One-pot	PIG-I (T)	276	304	284	415	425	-	-	-
	PIG-II (T)	258	263	263	415	435	+	+	+
	PIG-III (T)	245	241	248	410	425	-	+	-
	PIG-II (S)	235	256	252	410	425	++	++	+
	PIG-III (S)	234	243	244	415	425	-	+	-

a) T, thermal imidization; S, high temperature solution imidization. b) Obtained by DSC under nitrogen atmosphere at a heating rate of 20°C/min. c) Obtained by DMA under nitrogen atmosphere at a heating rate of 2°C/min. d) Obtained by TMA under nitrogen atmosphere at a heating rate of 10°C/min.

e) 10% weight loss temperature by TG at a heating rate of 10°C/min. f) Solubility: ++, soluble at room temperature; +, soluble at room temperature after heating; -, insoluble.

3. Conclusion

The aromatic poly(guanamine-imide)s having chelating pendant groups could be successfully synthesized either by conventional two-step procedure starting from aromatic diamine containing dipyridylaminotriazine and aromatic tetracarboxylic dianhydrides, or by simple one-pot method starting from dipyridylamino-substituted dichlorotriazine, aromatic diamine, and aromatic tetracarboxylic dianhydrides. Some poly(guanamine-imide)s were soluble in organic solvents such as *N*-methyl-2-pyrrolidone and afforded the yellow and transparent cast films. The films had high glass transition temperatures of 230–276°C, 10% weight loss temperatures around 410–425°C in air, and good adhesion to copper plate.

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