

Synthesis and Properties of Aromatic Polymers Containing Triazine Units

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ABSTRACT

6-Substituted 1,3,5-triazine-2,4-dichlorides were promising electrophilic monomers for the synthesis of aromatic polymers containing *s*-triazine rings in the main chain. Aromatic polycyanurates and polythiocyanurates were successfully synthesized by the phase-transfer catalyzed or solution polycondensation of triazinedichlorides with bisphenols and aromatic dithiols, respectively. Aromatic polyguanamines were easily prepared through either the solution polycondensation of triazine dichlorides with aromatic diamines or the silylation method using *N,N'*-bistrimethylsilylated aromatic diamines. These polymerization afforded several aromatic polymers such as polysiloxane-containing polymers, thermally crosslinkable polymers, fluorine containing polymers, and polymer-silicahybrids.

1. INTRODUCTION

Polymers containing *s*-triazine rings in the main chain have been attracting attention for a long time, because the majority of aromatic polymers containing heterocyclic rings exhibit high thermal stability. Some triazine-containing polymers such as melamine-formaldehyde polymers and crosslinked polycyanurates derived from dicyanates, have been well accepted as thermosetting resins and found large-scale industrial application. Triazine-containing polymers could be obtained in two ways: one is the polycondensation or polyaddition of monomeric *s*-triazine derivatives, the other is the poly(cyclotrimerization) or the poly(cyclocondensation) of nitrile derivatives.[1]

Recently, we are greatly interested in the synthesis of aromatic polymers using 6-substituted 1,3,5-triazine-2,4-dichlorides as a monomeric *s*-triazine derivative, because a variety of substituents could be attached to the *s*-triazine unit in the polymer backbone. This paper deals with the synthesis and properties of aromatic polymers by the polycondensation of triazinedichlorides with nucleophilic monomers such as bisphenols, aromatic dithiols, and aromatic diamine derivatives.

2. SYNTHESIS OF AROMATIC POLYCYANURATES

The phase-transfer catalyzed polycondensation has been preferably used for the aromatic polycyanurate synthesis from 6-substituted *s*-triazinedichlorides and bisphenols.[2] We adopted this polymerization method to prepare high molecular weight aromatic polycyanurates in organic solvent (dichloromethane, chloroform, or nitrobenzene)-aqueous alkaline solution system using cetyltrimethylammonium bromide (CTMAB) as a phase transfer catalyst at 20-80°C. These polymers were soluble in organic solvents such as *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), chloroform or tetrahydrofuran (THF), giving colorless,

transparent and flexible cast films with tensile strength of 65-100 MPa. The glass transition temperatures and 10% weight loss temperatures of the polymers were in the range of 150-205°C and 390-415°C in air, respectively (Equation 1, Table 1).

A new method for the synthesis of high molecular weight aromatic polycyanurates was developed with the use of alkali carbonates such as potassium carbonate and cesium carbonate as an inorganic base. The solution polycondensation between 6-anilino-1,3,5-triazine-2,4-dichloride and bisphenols with alkali carbonate in NMP at 20°C for 12 h readily afforded aromatic polycyanurates having inherent viscosities of 0.5-1.7 dL/g under mild reaction conditions. Also, we have found that cesium fluoride as a base effectively mediated the solution polycondensation of 6-anilino-1,3,5-triazine-2,4-dichloride with bisphenols, leading to the ready formation of aromatic polycyanurates having high molecular weight.

Polysiloxane polymers exhibit the peculiar and very useful properties such as thermal stability, good electric resistivity, low surface tension, and high gas permeability. However, these polymers suffer disadvantages including very weak mechanical properties. Therefore, we were interested in the incorporation of polysiloxane segments into aromatic polycyanurate backbones, which had high thermal stability and good mechanical properties. The polysiloxane-containing polymers were synthesized by the phase-transfer catalyzed polycondensation of 6-substituted 1,3,5-triazine-2,4-dichlorides with bisphenol A and hydroxyphenyl-terminated polydimethylsiloxane. (Equation 2)

The polymers containing 4-64 wt% of polysiloxane were readily obtained with inherent viscosities of 0.4-1.6 dL/g. The polymers dissolved in DMF, NMP, THF, and dioxane. The polymers gave opaque and flexible cast films from THF solutions. These films had two glass transition temperatures due to the polydimethylsiloxane (-120°C) and aromatic polycyanurate segments (180°C), indicating the phase-separated structure in the polymers. The tensile strength decreased from 80 to 5 MPa and elongation at break increased from 5 to 80%, with increasing amount of polydimethylsiloxane in the polymers. The contact angle values of water on

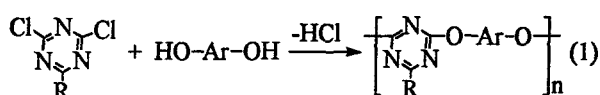
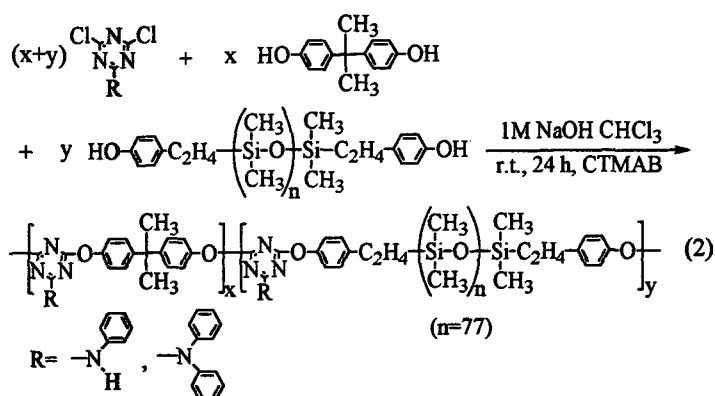


Table 1 Synthesis and Properties of Aromatic Polycyanurates^{a)}

Polymer		$\eta_{\text{inh}}^{\text{b)}$ (dL/g)	T _g ^{d)} (°C)	T ₁₀ ^{e)} (°C)
R	Ar			
		0.75	173	415
		0.62	158	400
		0.63	175	415
		0.66	150	390
		0.77	181	410
		0.98 ^{c)}	202	415
		0.89 ^{c)}	205	390

a) Polymerization was carried out with 2.5 mmol of each monomer and CTMAB (30 mol%) in 5 mL of organic solvent and 5.1 mL of 1M NaOH aqueous solution for 12 h. b) Measured at a concentration of 0.5 dL/g in NMP at 30°C. c) In chloroform. d) Determined by DSC at a heating rate of 20°C/min in nitrogen. e) 10% weight loss temperature, determined by TG at a heating rate of 10°C/min in air.



the cast films were in the range of 90-105°, depending on the polydimethylsiloxane content in the polymers.[3]

To improve the thermal stability and chemical resistance of the aromatic polycyanurates, crosslinkable aromatic copolycyanurates bearing ethynyl moiety pendants were synthesized by the phase-transfer catalyzed polycondensation of 6-anilino-1,3,5-triazine-2,4-dichloride and 6-(4-ethynylanilino)-1,3,5-triazine-2,4-dichloride with bisphenol A (Equation 3, Table 2). The polymers were soluble in polar solvents such as DMF and NMP and gave colorless transparent, and flexible cast films. The result films were thermally crosslinked at 250°C for 1 h to afford cured films, which showed good chemical resistance and high glass transition temperatures ranging from 201 to 263°C and 10% weight loss temperatures of 400-420°C in air, depending on the content of ethynyl moiety in the polymers.[4]

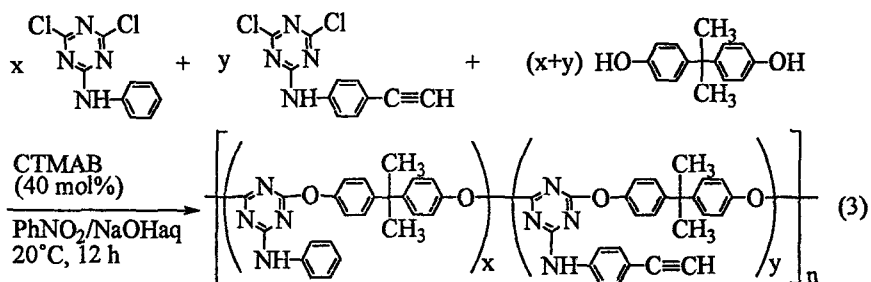


Table 2 Synthesis and Properties of Cured Polycyanurate Films

x/y	$\eta_{\text{inh}}^{\text{a)}$ (dL/g)	T _g ^{b)} (°C)	T ^{c)} (MPa)	E ^{c)} (%)
100/0	0.96	201	80	3
90/10	0.58	203	77	3
80/20	0.97	221	85	3
70/30	1.82	231	19	2
60/40	1.62	241	23	2
50/50	1.19	263	-	-

a) Measured for uncured polycyanurates at a concentration of 0.5 g/dL in NMP at 30°C.

b) Determined by TMA at a heating rate of 10°C/min.

c) Tensile strength d) Elongation at break

Table 3 Synthesis and Properties of Fluorine-Containing Polycyanurates^{a)}

Polymer		$\eta_{\text{inh}}^{\text{b)}$ (dL/g)	T _g ^{c)} (°C)	$\theta^{\text{d)}$ (deg.)
R	Ar			
-NH-C ₆ H ₅	-C ₆ H ₄ -O-C ₆ H ₄ -	0.77(NMP)	183	74
-NH-C ₆ H ₄ -CF ₃		0.82(NMP)	194	82
-NH-C ₆ H ₄ -(CF ₂) ₃ CF ₃		0.68(NMP)	172	96
-NH-C ₆ H ₄ -CH ₂ -C(CF ₃) ₂ -CF ₃		0.29(NMP)	156	-
-NH-C ₆ H ₄ -O-CF(CF ₃) ₂ -CF ₃		0.44(THF)	204	108
-N(CH ₃)-C ₆ H ₄ -O-CF(CF ₃) ₂ -CF ₃		0.85(CHCl ₃)	175	109
-NH-C ₆ H ₄ -5F		1.34(HMPA)	177	-
-O-C ₆ H ₄ -5F		0.80(HMPA)	154	-

a) Polymerization was carried out with 2.5 mmol of each monomer and CTMAB (30 mol%) in 5 mL of organic solvent and 5.1 mL of 1M NaOH solution at 20 - 60°C for 12 - 24 h.

b) Measured at a concentration of 0.5 g/dL at 30°C.

c) Determined by DSC at a heating rate of 20°C/min in nitrogen.

d) Contact angle of water

Fluoropolymers have peculiar properties such as high water repellency, low lubricity, low frictional coefficient, low refractive index, low dielectric stability, due to low polarizability of C-F bond and high C-F bond energy. Therefore, it is of particular interest to incorporate these unique properties into the aromatic polymers. Novel fluorine-containing aromatic polycyanurates were easily synthesized using triazine-dichlorides having

fluoroalkyl or fluoralkenyl pendant groups (Equation 4, Table 3). These polymers dissolved in organic solvents such as THF or NMP, and afforded the colorless, transparent and flexible cast films having low surface free energy. The glass transition temperatures of the polymers were in the range of 156-204°C and 10% weight loss temperatures were above 400°C in air.[5]

The phase transfer-catalyzed polycondensation starting from 6-substituted 1,3,5-triazine-2,4-dichlorides and aromatic dithiols afforded aromatic polysulfides containing s-triazine rings (Equation 5). Table 4 summarized the synthesis and properties of aromatic polysulfides.

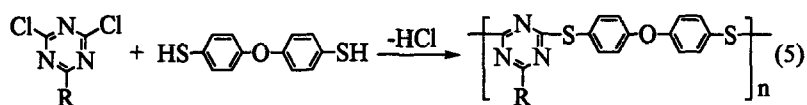
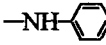
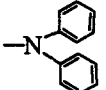
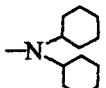


Table 4 Synthesis and Properties of Aromatic Polysulfides^{a)}

R	$\eta_{\text{inh}}^{\text{b)}$ (dL/g)	T _g ^{c)} (°C)	T _m ^{c)} (°C)	T ₅ ^{d)} (°C)
	0.50(NMP)	169	-	365
	insoluble	-	310	410
	0.43(OCP)	200	-	370

- a) Polymerization was carried out with 2.5 mmol of each monomer in 5 mL of nitrobenzene and 5.1 mL of 1M NaOH solution for 24 h in the presence of CTMAB (30 mol%).
b) Measured at a concentration of 0.5 g/dL at 30°C.
c) OCP, o-chlorophenol.
d) Determined by DSC at a heating rate of 20°C/min in nitrogen.
e) 5% weight loss temp., determined by TG at a heating rate of 10°C/min in air.

2. SYNTHESIS OF AROMATIC POLYGUANAMINES

Aromatic polyguanamines having high molecular weights were found to be synthesized by the solution polycondensation of 6-substituted 1,3,5-triazine-2,4-dichlorides and aromatic diamines in amide-type polar solvents such as NMP at 80-100°C. Addition of CaCl₂ or LiCl (5 wt%) to the polymerizationsolvent improve the solubility of the polymers prepared. Therefore, the polymerization smoothly proceeded to produce higher molecular weight polymers.

A novel method for the synthesis of high molecular weight aromatic polyguanamines has been

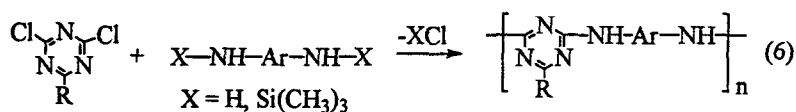
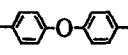


Table 5 Synthesis and Properties of Aromatic Polyguanamines^{a)}

Polymer		$\eta_{\text{inh}}^{\text{b)}$ (dL/g)		T _g ^{c)} (°C)	T ₁₀ ^{d)} (°C)	T/E/M ^{e)} (MPa) (%) (GPa)
R	Ar	Conventional method	Silylation method			
		0.49	0.97	205	380	104 / 4 / 3.1
		0.55	0.86	202	375	105 / 5 / 3.1
		0.50	1.08	241	395	114 / 7 / 2.7
		-	0.71	210	440	-
		-	1.14	216	350	102 / 6 / 3.5
		-	1.27	206	340	104 / 5 / 2.9

- a) Polymerization was carried out with 1.5 mmol of each monomer in 4 mL of NMP at 60-140°C for 24 h.
b) Measured at a concentration of 0.5 dL/g in NMP at 30°C.
c) Determined by DSC at a heating rate of 20°C/min in nitrogen.
d) 10% weight loss temperature, determined by TG at a heating rate of 10°C/min.
e) T/E/M, Tensile strength/elongation at break/tensile modulus

developed by the use of *N,N'*-bis(trimethylsilyl)-substituted aromatic diamines.[6] The solution polycondensation of 6-substituted 1,3,5-triazine-2,4-dichlorides with *N*-silylated aromatic diamines in NMP at 100-140°C gave readily polymers having higher inherent viscosities of 0.6-1.2 dL/g with the elimination of trimethylsilyl chloride under neutral reaction conditions, compared with conventional method using non-silylated diamines (Equation 6, Table 5). The aromatic polyguanamines were easily soluble in organic solvents such as DMSO, DMF, and NMP. Pale yellow, transparent, and tough cast films were obtained from NMP solution. The mechanical properties of the films were tensile strength of 102-114 MPa, elongation at break of 5-7%, and tensile modulus of 2-3 GPa. The glass transition temperatures of the polymers were in the range of 202-241°C, depending on the substituent on triazinedichlorides and the diamine component. The polymers showed the 10% weight loss temperatures of 340 - 440°C in air.

Aromatic polyguanamines have high surface free energy due to the polar aminotriazine structures. The fact had led to the suggestion that the introduction of perfluoroalkyl or perfluoroalkenyl pendant groups into the polymers as a side chain would result in new class of polymeric materials having low surface free energy. Novel fluorine-containing aromatic polyguanamines were successfully synthesized by the solution polycondensation of fluorinated

1,3,5-triazine-2,4-dic

chlorides with aromatic diamines in polar aprotic solvents such as NMP, 1,3-dimethyl-2-imidazolidone (DMI), and hexamethylphosphoramide (HMPA) (Equation 7, Table 6).[5] Some polymerization was mediated by cesium fluoride as a base, giving the polymers having higher molecular weight. As the content of fluorine atom in the polymers increased, some properties such as solubility, tensile strength, thermal stability, and surface free energy decreased. The polymers, which have bulky perfluoroalkenyl groups, maintained their high glass transition

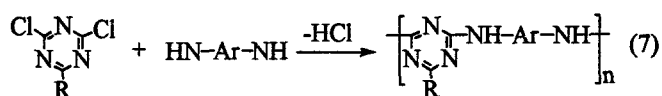
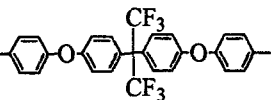
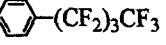
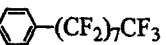
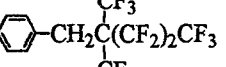
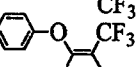
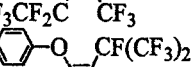
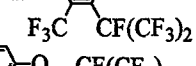


Table 6 Synthesis and Properties of Fluorine-Containing Polyguanamines^{a)}

Polymer		$\eta_{\text{inh}}^{\text{b)}$ (dL/g)	T _g ^{c)} (°C)	$\theta^{\text{d)}$ (deg.)	T / E / M ^{e)} (MPa) (%) (GPa)
R	Ar				
-NH- 		0.74(NMP)	197	80	95 / 7 / 1.5
-NH- 		0.77(HMPA)	185	88	76 / 4 / 1.8
-NH- 		0.58(HMPA)	176	92	60 / 5 / 1.4
-NH- 		0.45(HMPA)	165	97	38 / 5 / 1.3
-NH- 		0.60(NMP)	177	90	64 / 8 / 1.1
-NH- 		1.07(THF)	188	90	65 / 3 / 1.5
-NH- 		0.48(NMP)	200	106	57 / 8 / 1.5
-N(CH ₃)- 		0.57(NMP)	201	105	35 / 4 / 1.2

a) Polymerization was carried out with 1.5 mmol of each monomer in 4 mL of polar aprotic solvent at 80-200°C for 3-24 h.

b) Measured at a concentration of 0.5 g/dL at 30°C.

c) Determined by DSC at a heating rate of 20°C/min in nitrogen.

d) Contact angle of water.

e) T/E/M, Tensile strength/elongation at break/tensile modulus

temperatures of 188-200°C. These fluorine-containing aromatic polyguanamines had higher thermal stability and better mechanical properties, compared with the fluorine-containing aromatic polycyanurates.

In order to improve the thermal and mechanical properties of aromatic polyguanamines, the incorporation of inorganic silica into polyguanamines was performed by the preparation of polyguanamine-silica hybrid materials via a sol-gel process. We designed and synthesized new triazinedichlorides having alkoxyethyl grafting sites for the silica during a sol-gel process. This reactive sites improve interfacial adhesion through the covalent bonding between the matrix polyguanamine and the individual silica particles. The silylation method was utilized for the preparation of aromatic polyguanamines containing alkoxyethyl groups. The polycondensation of the triazinedichloride having alkoxyethyl moieties with *N*-silylated aromatic diamine produced the polymers having alkoxyethyl pendants by the elimination of neutral trimethylsilyl chloride. The sol-gel reaction of tetraethoxysilane was carried out in the presence of the aromatic polyguanamines containing alkoxyethyl groups, affording polyguanamine combined with silica particles, as shown in equation 8. [7] Table 7 summarizes the preparation and properties

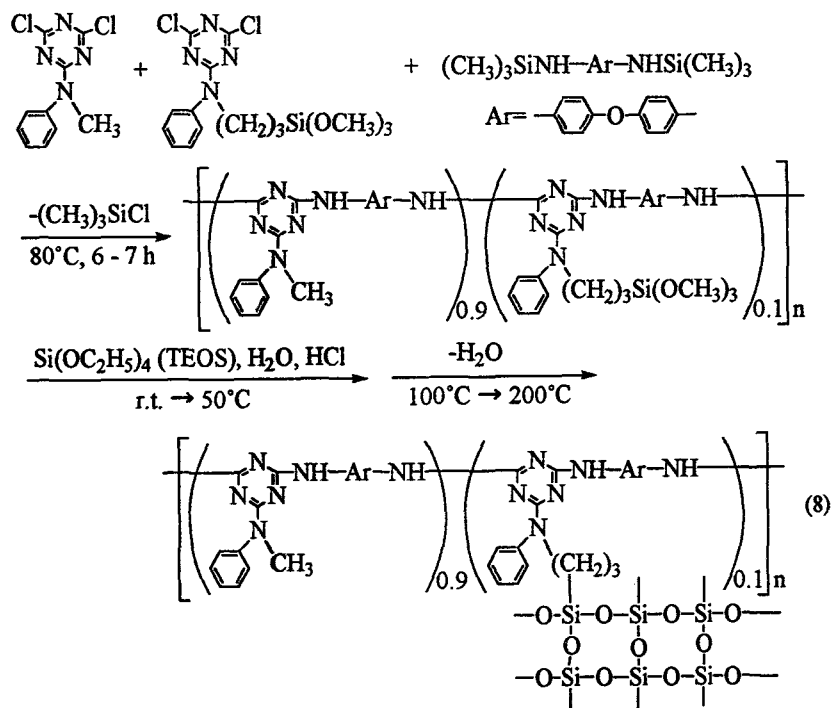


Table 7 Preparation and Properties of Polyguanamine-Silica Hybrid Films

Silica ^{a)} (wt%)	Tg ^{b)} (°C)	T ₁₀ ^{c)} (°C)	Ash ^{d)} (%)	T / E / M ^{e)} (MPa) (%) (GPa)	Remarks ^{f)}
0	170	375	0	105 / 4 / 2.5	tra
2	189	420	1	113 / 7 / 2.5	tra
8	201	435	9	137 / 9 / 2.8	tra
11	207	450	11	148 / 8 / 3.1	tra
14	210	445	12	120 / 6 / 3.1	opa
19	207	450	19	108 / 6 / 2.5	opa
24	203	450	22	64 / 4 / 2.7	opa
34	204	430	32	32 / 4 / 1.5	opa

a) Calculated SiO_2 content.

b) Determined by DMA at a heating rate of 2°C/min in nitrogen.

c) 10% weight loss temperature, determined by TG at a heating rate of 10°C/min in air.

d) Determined by TG at 800°C in air

e) T/E/M, Tensile strength/elongation at break/tensile modulus.

f) tra, transparent film; opa, opaque film.

of polyguanamine-silica hybrid films. The films containing the silica content less than 11 wt% were yellow and transparent, whereas the films with higher silica content were yellow and opaque. Phase-separation of the opaque films occurred in drying process of precursor films. The silica particles were dispersed homogeneously in the polymer matrix. The particle size increased with increasing the silica contents. The results of dynamic thermomechanical analysis indicated that the polyguanamine-silica hybrid materials showed higher glass transition temperature and higher storage modulus than the polyguanamine film.

modulus over glass transition temperature. The thermal stability and mechanical properties of the hybrid films were higher than those of the parent polymer film without silica. The hybrids having silica content of 11 wt% had better properties; that is, glass transition temperature of 207°C, 10% weight loss temperature of 450°C, a tensile strength of 148 MPa, an elongation at break of 8%, and a tensile modulus of 3.1 GPa.

3. CONCLUSION

A variety of aromatic polymers containing *s*-triazine units in the main chain could be easily synthesized using 6-substituted *s*-triazinedichlorides. Since a tremendous variety of substituents can be attached to the triazine ring of the polymer backbone, these polymers exhibit a various chemical and physical properties, which make them suitable for many applications. Therefore, these triazinedichlorides can be regarded as new class of functional condensation monomers for the synthesis of a variety functional condensation aromatic polymers.

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