NOTES

Synthesis and Properties of Polyguanamines from 2,4-Dichloro-6-phenyl-1,3,5-triazine and Diamine

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Recently, we reported the synthesis of polyguanamines (2c) by alkylation reaction of 2,4-dianilino-6-phenyl-1,3,5-triazine with 1,6-dibromohexane in the presence of sodium hydride (Scheme 1).[1] The resulting polyguanamine can be use as an effective phase transfer catalyst for reactions of 1-bromooctane with potassium thiocyanate in toluene-water systems.

It is well known that chlorine atoms attached directly

Scheme 1.

2a : X = H
2b : X = CH₃
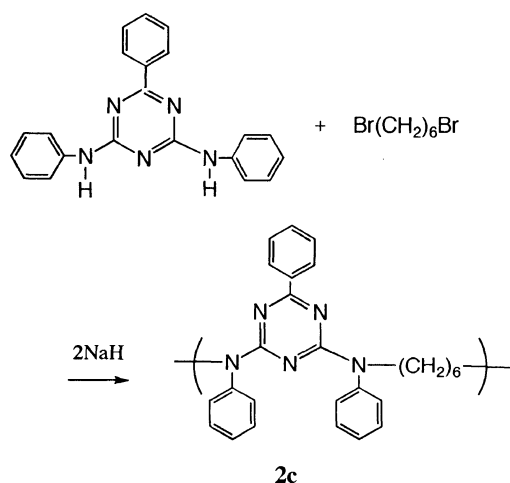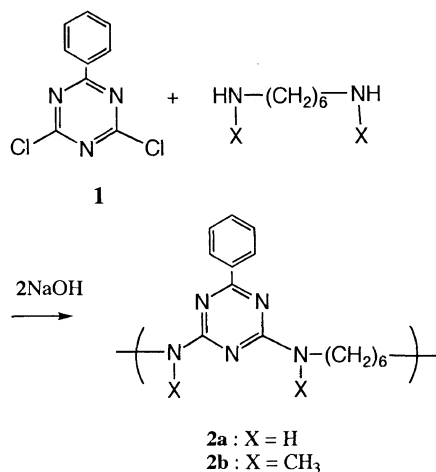
Scheme 2.

to the 1,3,5-triazine ring are very reactive and can be displaced readily by nucleophilic reagents such as amines,[2] alkoxides,[3,4] and mercaptides.[5] It has been reported that reactions of dichlorotriazines with diols,[6-8] diamines,[9-11] or guanamines[12-14] give the corresponding polymers.

This paper describes the polycondensation of 2,4-dichloro-6-phenyl-1,3,5-triazine with hexamethylenediamine and N,N'-dimethylhexamethylenediamine for the synthesis of analogous polyguanamines to 2c (Scheme 2). The effects of N-substituents on thermal properties and ability to act as polymeric phase transfer catalysts of the resulting polyguanamines (2a and 2b) were also investigated.

EXPERIMENTAL

Materials

2,4-Dihydroxy-6-phenyl-1,3,5-triazine was prepared by hydrolysis reaction of 46.5 g (0.25 mol) of benzoguanamine in 150 g of 90 wt% sulfuric acid at 120°C for 15 h. The reaction mixture was poured into water to give a white solid, which was filtered off, washed with water, and dried. Yield 35.9 g (82.0%), mp 288°C (lit.[15] 289—290°C, decomp.).

Monomer Synthesis

2,4-Dichloro-6-phenyl-1,3,5-triazine (1) was prepared by reaction of 36.2 g (0.21 mol) of 2,4-dihydroxy-6-phenyl-1,3,5-triazine with 180 g (1.51 mol) of thionyl chloride and 17.3 g of N,N-dimethylformamide (DMF) at 60°C for 3 h. The excess thionyl chloride was distilled, and the residue was poured into water to give a product. The white product was filtered off, dried, and recrystallized from benzene to give a yield of 22.0 g (47.4%). mp 118°C (lit. 121°C[16] 118—119°C[17]). ^{1}H NMR (δ ppm in CDCl₃); 7.50 (2H, d, m-H), 7.64 (1H, t, p-H), 8.44 (2H, d, o-H). *Anal.* Calcd for C₉H₅N₃Cl₂: C, 48.24%; H, 2.25%; N, 18.75%. Found: C, 48.32%; H, 2.10%; N, 18.53%.

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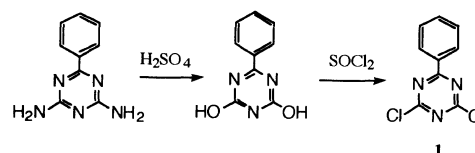
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Reaction of 1 with Hexamethylenediamine

1 (2.24 g, 10.0 mmol) and hexamethylenediamine di-hydrochloride (1.89 g, 10.0 mmol) were added to tetra-hydrofuran (THF) (60 ml) and 8 N sodium hydroxide aq (7 ml) with stirring. The reaction mixture was stirred for 8 h at room temperature. A small amount of insoluble compound in THF (**3a**) was filtered off to yield 0.10 g (3.8%). The filtrate was poured into methanol to give polyguanamine **2a**. The isolated **2a** was washed with methanol, reprecipitated from THF into diethyl ether, and dried *in vacuo* to give a yield of 2.23 g (82.9%). **2a**: T_g 95°C. IR (KBr) 3420, 3260, 2920, 2850, 1590, 1540, 1410, 1370, 1220, 820, 780, 700 cm^{-1}. *Anal.* Calcd for $C_{15}H_{19}N_5$: C, 66.89%; H, 7.11%; N, 26.00%. Found: C, 66.07%; H, 7.17%; N, 25.76%. **3a**: mp 268°C. MS m/z 187.0, 269.1 (M$^+$, Calcd 269.4). *Anal.* Calcd for $C_{15}H_{19}N_5$: C, 66.89%; H, 7.11%; N, 26.00%. Found: C, 66.84%; H, 7.25%; N, 25.80%.

Reaction of 1 with N,N'-Dimethylhexamethylenediamine

1 (2.24 g, 10.0 mmol) and N,N'-dimethylhexamethyl-enediamine (1.47 g, 10.0 mmol) were added to THF (25 ml) and 4 N sodium hydroxide aq (6 ml) with stirring, and the reaction mixture was stirred for 24 h at room temperature. A small amount of insoluble compound in THF (**3b**) was filtered off in the amount of 0.23 g (7.7%). The filtrate was poured into methanol to give polyguanamine **2b**. The isolated **2b** was washed with methanol, reprecipitated from THF into hexane, and dried *in vacuo* in a yield of 2.48 g (83.5%).

2b: T_g 57°C. IR (KBr) 2920, 2850, 1590, 1540, 1500, 1390, 1310, 1200, 1050, 975, 810, 780, 700, 650 cm^{-1}. *Anal.* Calcd for $C_{17}H_{23}N_5$: C, 68.66%; H, 7.79%; N, 23.55%. Found: C, 68.34%; H, 7.77%; N, 23.55%.
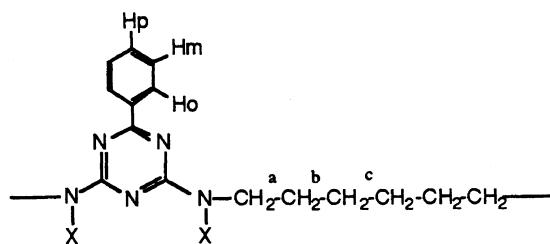
3b: mp 240°C. MS m/z 215.0, 229.2, 243.1, 256.1, 270.2, 284.0, 298.1 (M$^+$, Calcd 297.4). *Anal.* Calcd for $C_{17}H_{23}N_5$: C, 68.66%; H, 7.79%; N, 23.55%. Found: C, 68.70%; H, 7.92%; N, 23.30%.

Catalytic Activity for Substitution Reactions

Catalytic activity of polyguanamines was assessed in two-phase reactions of 1-bromooctane with potassium thiocyanate, as described previously.[1]

RESULTS AND DISCUSSION

Synthesis of Polyguanamines

Polyguanamines **2a** and **2b** were prepared by the polycondensation of 1 with hexamethylenediamine and N,N'-dimethylhexamethylenediamine in the presence of sodium hydroxide, respectively. A small amount of insoluble compound in THF (**3a** and **3b**) was obtained as impurity. The results of analysis of polymers agreed well with calculated values. IR spectra showed charac-teristic CH$_2$ stretching band at 2920 and 2850 cm^{-1}, in addition to usual absorption bands of 1,3,5-triazine which appeared at 1540, 1410—1390, and 820—810 cm^{-1}. The characteristic N–H stretching band at 3260 cm^{-1} was observed for **2a**. Chemical shifts of **2a**, **2b**, **3a**, and **3b** are summarized in Table I. The NMR spectrum of **2b** measured in chloroform-d at room temperature shows the signal of N-CH$_3$ as two peaks at 3.10 and 3.20 ppm, and N-CH$_2$ at 3.60 and 3.72 ppm at about 1 : 1 strength, respectively. But at 50°C the signal of N-CH$_3$ became one peak at 3.15 ppm, and that of N-CH$_2$ at 3.66 ppm. The reason for this may be that the C–N bond between triazine and amino group has the property of double bond and free rotation is restricted.
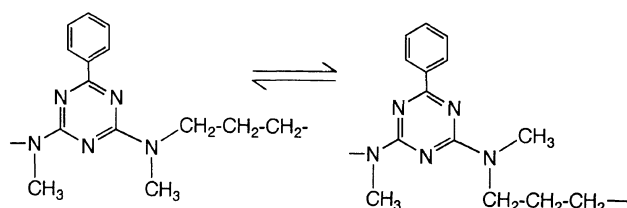
Table I. ^{1}H NMR of **2a**, **2b**, **3a**, and **3b** δ ppm

| Compd.	Solvent	Temp/°C	H_o	H_m	H_p	X	H_a	H_b	H_c
2a	(CD$_3$)$_2$SO	60	8.32	7.47		7.02	3.34	1.56	1.35
			(2H, br s)	(3H, br s)		(2H, s)	(4H, br s)	(4H, br s)	(4H, br s)
	CF$_3$COOD	r.t.	7.98	7.72	7.89	—	3.78	1.86	1.60
			(2H, d)	(2H, t)	(1H, t)		(4H, t)	(4H, br s)	(4H, br s)
2b	CDCl$_3$	r.t.	8.45	7.43		3.10, 3.20	3.60, 3.72	1.65	1.40
			(2H, br s)	(3H, br s)		(3H + 3H, br s)	(2H + 2H, br s)	(4H, br s)	(4H, br s)
	CDCl$_3$	50	8.45	7.43		3.15	3.66	1.65	1.40
			(2H, br s)	(3H, br s)		(6H, s)	(4H, br s)	(4H, br s)	(4H, br s)
	CF$_3$COOD	r.t.	8.06	7.69	7.80	3.47	3.81	1.88	1.57
			(2H, d)	(2H, t)	(1H, t)	(6H, s)	(4H, br s)	(4H, br s)	(4H, br s)
3a	CF$_3$COOD	r.t.	7.98	7.72	7.91	—	3.74	1.88	1.59
			(2H, d)	(2H, t)	(1H, t)		(4H, t)	(4H, br s)	(4H, br s)
3b	CF$_3$COOD	r.t.	8.06	7.64	7.80	3.47	3.81	1.88	1.57
			(2H, d)	(2H, t)	(1H, t)	(6H, s)	(4H, br s)	(4H, br s)	(4H, br s)

The spectra of polyguanamines shifted to lower field in trifluoroacetic acid-d than in DMSO or chloroform-d, because the protonation to triazine ring occurs in trifluoroacetic acid.

The solubility of polymers was examined. All polyguanamines (**2a**—**2c**) are soluble in THF, N-methyl-2-pyrrolidone, N,N-dimethylacetamide, and acidic solvents such as formic acid and sulfuric acid, but insoluble in acetone, alcohol, and hexane. **2b** and **2c** are soluble in dioxane, benzene, and chloroform, but **2a** is insoluble. **2a** is soluble in dimethyl sulfoxide (DMSO), but **2b** and **2c** are insoluble. The inherent viscosities (η_{sp}/c) of **2a** and **2b** measured at $c = 0.2 \, \text{g dl}^{-1}$ in THF at 30°C were 0.18 and $0.19 \, \text{dl g}^{-1}$, respectively. Molecular weights were estimated as $\bar{M}_n = 9.600$ ($\bar{M}_w/\bar{M}_n = 1.9$) for **2a** and 10.500 ($\bar{M}_w/\bar{M}_n = 2.3$) for **2b** by GPC measurement in THF using polystyrene as the standard.

Glass transition temperatures (T_g) of **2a**, **2b**, and **2c** evaluated by DSC measurements at a heating rate of $20°\text{C min}^{-1}$ were 95°C, 57°C, and 74°C, respectively. T_g decreases in the following order; **2a** > **2c** > **2b** since **2a** forms hydrogen bonds. The temperature for 10% weight loss (T_{10}) was determined by TGA measurement at a heating rate of $10°\text{C min}^{-1}$. T_{10}s of **2a**, **2b**, and **2c** were 422°C, 377°C, and 428°C, respectively.

Formation of 3a and 3b

3a and **3b** showed high melting points and insolubility in common organic solvents. Their structures were identified by elementary analysis, IR, ^1H NMR, and mass spectroscopy. The results of analysis agreed well with calculated values of the corresponding polymers. Their NMR spectra in trifluoroacetic acid-d and IR spectra are similar to those of the corresponding polymers (Table I). The parent peaks of mass spectra of **3a** and **3b** agreed with the 1:1 condensation products. These results show that **3a** and **3b** may be analogous cyclization compounds obtained from 2,4-dianilino-6-substituted-1,3,5-triazine with α,ω-dibromoalkane previously.[1]

3a ; X = H
3b ; X = CH₃
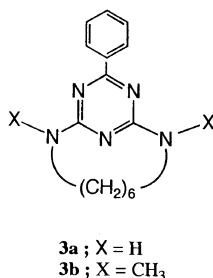
Catalytic Activity for Substitution Reactions

The catalytic activity of polyguanamines was assessed for reactions of 1-bromooctane in toluene with potassium thiocyanate in water under two-phase (**2b** and **2c**) or three-phase (**2a**) conditions. The results are summarized in Table II.

$$n\text{-}C_8H_{17}Br + KSCN \xrightarrow{\text{Catalyst}} n\text{-}C_8H_{17}SCN + KBr$$
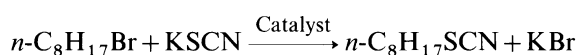
The reaction was achieved in the presence of mono-

Table II. Yields of octylthiocyanate of the reaction of 1-bromooctane with potassium thiocyanate under toluene/water condition using polyguanamines as a phase-transfer catalyst

Catalyst	Yield[a] %
BG[b]	47
TMBG[c]	46
2a	97
2b	97
2c	96

[a] Conditions: 1-bromooctane = 1.65 mmol in 1 ml toluene; potassium thiocyanate = $8.0 \, \text{mol l}^{-1}$ (in water), 5 ml; and catalyst = 0.3 mmol at 100°C for 30 h under stirring. [b] Benzoguanamine. [c] N,N,N',N'-Tetramethylbenzoguanamine.

meric analogs (benzoguanamine and N,N,N',N'-tetramethylbenzoguanamine) and polyguanamines. Monomeric analogs gave octyl thiocyanate in 46—47% yield and polymers gave the product in above 90% yield. The catalytic activity of polymers is superior to that of monomeric analogs. These observations may be explained by assuming that potassium cations interact with several active sites to form a complex, and thiocyanate anions attack the substrate. This cooperative coordination of active sites may occur readily in polymers.[1,18]

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