Synthesis and Properties of Polyguanamines from *N,N'*-Diphenylguanamines and α,ω -Dibromoalkanes

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ABSTRACT: The novel polyguanamines were synthesized by the polycondensation reaction of *N,N'*-diphenylguanamines with α,ω -dibromoalkanes in the presence of sodium hydride. The polyguanamines having inherent viscosities of 0.1–0.3 dL g⁻¹, were obtained quantitatively. They showed *T_g* in the range of 48–94°C and began to lose weight above 400°C in air. The ability as a polymeric phase transfer catalyst of resulting polyguanamines was also investigated. They could use as effective phase transfer catalysts for the reaction of 1-bromooctane with potassium thiocyanates in two-phase system.

KEY WORDS Guanamine / Polyguanamine / 1,3,5-Triazine / Polycondensation / Alkylation / Phase Transfer Catalyst /

Recently,^{1,2} we reported alkylation reaction of 2-amino-4-anilino-6-isopropenyl-1,3,5-triazine (AAIT) with alkyl bromides in the presence of sodium hydride. Alkylation proceeded quantitatively and selectively on the imino position in anilino group through the anilide anion of AAIT.¹ In this connection, the alkylation reaction of 2,4-dianilino-1,3,5-triazine (*N,N'*-diphenyl guanamine) derivatives was investigated for the purpose of preparation of new monomers having long alkyl groups to give comb-like polymers.^{3–7}

Polyguanamines have been known as a class of thermal stable polymers. As a development of above alkylation reaction, we have reported that the synthesis of polyguanamines by condensation polymerization of bisguanamines with α,ω -dibromoalkanes (Scheme 1). The resulting polyguanamines could use as effective phase transfer catalysts for the reaction of 1-bromooctane with potassium thiocyanates.⁸

This paper describes the synthesis of new polyguanamines by polycondensation using alkylation reaction of *N,N'*-diphenyl guanamines (2,4-dianilino-, 2,4-dianilino-6-methyl-, and 2,4-dianilino-6-phenyl-1,3,5-triazine) with α,ω -dibromoalkanes (Scheme 2). The thermal property and ability as a polymeric phase transfer catalyst of the resulting polyguanamines were also investigated.

EXPERIMENTAL

Materials

1,1-Diphenylbiguanide (DPB) was prepared according to a literature procedure.⁹ mp 145°C (lit.⁹ 145–146°C).

Monomer synthesis

2,4-Dianilino-1,3,5-triazine (**1a**) was prepared by reaction of 50.6 g (0.20 mol) of DPB with 35 g (0.58 mol) of methyl formate in 600 ml of methanol at room temperature for 8 h. The white product was filtered off, washed with hot water, and dried to give a yield of 39.9 g (75.7%). **1a** was recrystallized from *N,N*-dimethyl-

formamide. mp 305°C (lit.¹⁰ 307°C). *Anal.* Calcd for C₁₅H₁₃N₅: C, 68.43%; H, 4.98%; N, 26.60%. Found: C, 68.69%; H, 4.85%; N, 26.53%.

2,4-Dianilino-6-methyl-1,3,5-triazine (**1b**) was prepared by reaction of 88.6 g (0.35 mol) of DPB with 35.8 g (0.35 mol) of acetic anhydride in 400 ml of acetone and 14 g (0.35 mol) of sodium hydroxide in 50 ml of water at 0–5°C. The white product was filtered off, washed

Scheme 1.

Scheme 2.

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with hot water, and dried. The filtrate was poured into water to give product. The product was totally yielded 92.1 g (94.9%). **1b** was recrystallized from 2-methoxyethanol. mp 238°C (lit.¹¹ 233.5–235°C). *Anal.* Calcd for C₁₆H₁₅N₅: C, 69.30%; H, 5.45%; N, 25.25%. Found: C, 69.21%; H, 5.47%; N, 25.11%.

2,4-Dianilino-6-phenyl-1,3,5-triazine (**1c**) was prepared by reaction of 88.6 g (0.35 mol) of DPB with 50 g (0.35 mol) of benzoyl chloride and 14 g (0.35 mol) of sodium hydroxide in 400 ml of acetone and 50 ml of water at 0–5°C. The white product was filtered off, washed with hot water, and dried to give a yield of 80.6 g (67.9%). **1c** was recrystallized from 2-methoxyethanol. mp 210°C (lit.¹² 212–213.5°C). *Anal.* Calcd for C₂₁H₁₇N₅: C, 74.32%; H, 5.05%; N, 20.63%. Found: C, 74.20%; H, 5.13%; N, 20.53%.

Polycondensation

A typical example of polymerization follows.

1c (1.697 g, 5.00 mmol) was added to dimethyl sulfoxide (DMSO) (10 ml) in the presence of sodium hydride (0.40 g, 10 mmol) with stirring, and then dimethyl acetamide (DMA) solution (16 ml) of 1,10-dibromodecane (1.501 g, 5.00 mmol) was added dropwise at 60°C. The reaction mixture was stirred at room temperature for 22 h, and was poured into excess methanol. The precipitate was collected by filtration and washed with methanol. Then, the product was dissolved in tetrahydrofuran (THF) for reprecipitation, and a small amount of insoluble compound in THF (**2c**) was filtered off (0.13 g, 5.3%). The filtrate was poured into methanol to give polyguanamine. The isolated polyguanamine **3i** was dried *in vacuo* to give a yield of 2.14 g (89.6%). Total yield was 2.27 g (94.9%). ¹H NMR (CDCl₃) δ 1.25 (br s, (CH₂)₈, 16H), 3.98 (t, 2NCH₂, 4H), 7.34 (br s, 2C₆H₅ + 2H_m + H_p, 13H), 8.25 (br s, 2H_o, 2H).

Other polyguanamines **3a–3h** were prepared in a similar manner (Table I), and a small amount of insoluble compounds in THF (**2a** and **2b**) was obtained for the synthesis of **3e** and **3c**, respectively (Table II).

Catalytic Activity for Substitution Reaction

Catalytic activity of polyguanamines was tested in the two-phase reactions of 1-bromooctane with potassium thiocyanate. In a typical run, a toluene solution (1 ml) of 1-bromooctane (0.319 g, 1.654 mmol), 5 ml of 8 mol l⁻¹ solution of potassium thiocyanate in water (3.88 g, 40 mmol), and **3i** (0.1428 g, 0.299 mmol) were charged in a test tube with a screw cap. Cyclohexylbenzene as an internal standard was added to the reaction mixture and the tube was stirred at 100°C for 30 h. Then the reaction mixture was poured in petroleum ether to precipitate a solid. The filtrate was analyzed by gas chromatography.

The yield of octyl thiocyanate was obtained.

Catalytic Activity for Reduction of Ketone

In a typical run, a solution of acetophenone (1.5 mmol) in 4 ml of benzene, sodium borohydride (1.2 mmol), 1% aqueous sodium hydroxide (0.1 ml) and triazine compound (0.15 mmol) were added in a glass tube with screw cap. The mixture was stirred at room temperature for 24 h. Then the solution was acidified by 10% HCl to pH 5–6, and poured into petroleum ether to precipitate the polymer. The organic layer was analyzed by gas chromatography.

Measurement

Elementary analyses were performed on a Yanaco CHN corder MT-3 analyzer. ¹H NMR spectra were recorded on a Hitachi R-600 (60 MHz) or a Varian XL-200 (200 MHz) spectrometer. Molecular weight of polymers was determined by gel permeation chromatography (GPC) on a TOSOH HLC-803D with G2000H, G3000H, and GMH TSK gel-columns and a differential refractometric detector in THF. The columns were calibrated with a set of monodisperse polystyrene standards. The glass transition temperature (*T*_g) of polymers was determined by differential scanning calorimetry (DSC) on a Rigaku-Denki DSC-8230 at a heating rate of 20°C min⁻¹. Decomposition temperature of polymers was measured by the thermogravimetry on a Rigaku TG-DTA 8112 BH thermal analyzer system at a heating rate of 10°C min⁻¹. Gas chromatograph (Ohkura 802T) was used for the yield determination by the internal standard method.

RESULTS AND DISCUSSION

Model Reaction

N-Alkylation reaction was followed by the measurement of NMR spectroscopy as a model reaction (Figure 1). When **1b** was treated with double molar quantity of sodium hydride in DMSO-*d*₆, the solution became red (*λ*_{max}; 548 nm, *ε*; 6.24) immediately, and the spectra of **1b** was changed significantly. The signal of imino proton on anilino groups of **1b** at 9.76 ppm was disappeared, and the chemical shifts of phenyl protons were displaced to higher field (*o*-protons; 7.82 to 7.52 ppm, *m*-protons; 7.37 to 7.10 ppm, and *p*-proton; 7.05 to 6.65 ppm). The chemical shift of methyl protons was also displaced from 2.31 to 1.99 ppm. The NMR spectrum after addition of excess ethyl iodide into above solution, showed the signals of ethyl protons attached to imino group at 1.05 and 3.86 ppm. Further, the signal of phenyl protons became singlet at 7.30 ppm, because of introducing alkyl group to *N*-position of anilino group. The signals of 1.77 and 3.24 ppm based on excess ethyl iodide. These results indicate that *N*-alkylation to anilino groups of **1b** occurred quantitatively through anilide anion (Scheme 3).

Synthesis of Polyguanamines

On the basis of the results on model reaction, polyguanamines were prepared by polycondensation of guanamines (**1a**, **1b**, and **1c**) with 1,4-dibromobutane, 1,6-dibromohexane and 1,10-dibromodecane in the presence of sodium hydride. Scheme 2 shows the structures of the

Figure 1. ^1H NMR spectra of (A) **1b** in $\text{DMSO}-d_6$, (B) **1b** in $\text{NaH}-\text{DMSO}-d_6$ solution, and (C) after addition of excess ethyl iodide to (B).

Scheme 3.

polyguanamines **3a–3i**. The results of polycondensation are summarized in Table I. Polyguanamines were successfully obtained in almost quantitative yields. Some polymers contained a small amount of insoluble compound in THF as a impurity. These impurities (**2a**, **2b**, and **2c**) will be discussed in the later section. The yield for **3c**, **3e**, and **3i** in Table I included that of these impurities. The structure of the resulting polymers was identified by elementary analysis, IR, and NMR spectroscopy. The results of the analysis agreed well with the calculated values. IR spectra of polyguanamines showed characteristic CH_2 stretching band at 2950 and 2850 cm^{-1} , in addition to usual absorption bands of 1,3,5-triazine which appeared at 1420 and 820 cm^{-1} . The characteristic N-H stretching band at 3300 cm^{-1} observed for monomers was disappeared for polymers.

Table I. Syntheses of polyguanamines

Polymer	Solvent ^a	Yield	η_{sp}/c^b	GPC ^c		Elementary analysis (Calcd)			
	ml	%	dl g ⁻¹	$M_n/10^3$	M_w/M_n	C%	H%	N%	
3a	DMSO (15) & DMA (8)	100	0.07	2.9	1.3	71.63 (71.90)	5.90 6.03	22.17 22.06;	C ₁₉ H ₁₉ N ₅)
3b	DMSO (40)	103	0.15	9.7	1.8	72.64 (73.02)	6.87 6.71	20.10 20.27;	
3c	DMSO (21)	98 ^d	0.29	14.1	1.7	74.83 (74.78)	7.73 7.78	17.20 17.44;	C ₂₁ H ₂₃ N ₅)
3d	DMSO (14)	101	0.09	3.4	1.4	72.35 (72.48)	6.20 6.39	21.17 21.12;	C ₂₀ H ₂₁ N ₅)
3e	DMSO (12)	101 ^d	0.09	3.2	1.3	73.75 (73.51)	7.18 7.01	19.15 19.48;	C ₂₂ H ₂₅ N ₅)
3f	DMSO (21)	101	0.21	13.0	2.5	75.17 (75.14)	8.13 8.00	16.43 16.85;	C ₂₆ H ₃₃ N ₅)
3g	DMSO (10) & DMF (8)	97	0.07	2.0	1.3	76.54 (76.31)	5.58 5.89	17.52 17.80;	C ₂₅ H ₂₃ N ₅)
3h	DMSO (8) & DMA (8)	82	0.11	8.0	1.4	76.53 (76.93)	6.50 6.46	16.38 16.61;	C ₂₇ H ₂₇ N ₅)
3i	DMSO (10) & DMA (16)	95 ^d	0.21	12.1	1.9	78.04 (77.95)	7.60 7.39	14.34 14.66;	C ₃₁ H ₃₅ N ₅)

^a Guanamine and α,ω -dibromoalkane were used 5 mmol, respectively, and polymerized at room temperature for 22–24 h. ^b $c = 0.2$ g dl⁻¹ in THF at 30°C. ^c Determined by GPC in THF using polystyrene as a standard. ^d The yield includes a small amount of insoluble compound in THF.

Table II. Characterization of insoluble impurities.

Compd.	Yield	mp	Elementary analysis (Calcd)			Mass ^a
	%	°C	C%	H%	N%	m/z (rel. intensity)
2a	6.9	268	74.02 (73.51)	6.82 7.01	19.16 19.48;	207 (98), 213 (100), 287 (45), 361 (5, M ⁺)
2b	1.4	221	74.47 (74.78)	7.88 7.78	17.06 17.44;	133 (100), 207 (99), 213 (98), 287 (22), 361 (6), 401 (8, M ⁺)
2c	5.3	241	78.20 (77.95)	7.46 7.39	14.33 14.66;	133 (100), 207 (98), 213 (97), 291 (43), 287 (60), 339 (45), 361 (20), 477 (15, M ⁺)

^a Molecular weight: **2a**, 359.5; **2b**, 401.6; **2c**, 477.7.

The NMR spectra of **3d**–**3f** are similar to that of the model reaction described above. The inherent viscosities of polymers were in the range of 0.1–0.3 dl g⁻¹ and the molecular weights were estimated to be $M_n = 2000$ –14000 by GPC measurement. The values of viscosities and M_n increased with the length of alkylene group in monomers.

Solubilities of Polymers

All polyguanamines are soluble in dioxane, THF, chloroform, benzene, *N*-methylpyrrolidone (NMP), DMA, and acidic solvent such as formic acid and sulfuric acid, but insoluble in acetone, alcohol and hexane. **3c**, **3f**, and **3i** were insoluble in DMSO.

Insoluble Impurities

A small amount of insoluble impurities in THF (**2a**, **2b**, and **2c**) was obtained for the synthesis of **3e**, **3c**, and **3i**, respectively. The characterization of these compounds is shown in Table II. They showed high melting point and insolubility in common organic solvents. Their structures were identified by elementary analysis, IR, ¹H-NMR, and mass spectroscopy. The results of the analysis agreed well with that of calculated values of corresponding polymers. Their IR spectra and NMR spectra measured in trifluoroacetic acid-*d*₁ are similar

to those of corresponding polymers. But comparing with NMR data obtained in deuterio chloroform, the chemical shifts of polyguanamines were displaced to lower field in trifluoroacetic acid-*d*₁, such as methylene protons in the main chain of **3i** from 3.98 ppm to 4.25 ppm (*N*-CH₂), 1.25 ppm to 2.00 ppm (*N*-CH₂CH₂), and 1.25 ppm to 1.54 ppm (6CH₂), because protonation to triazine ring would occur in trifluoroacetic acid. The parent peak of mass spectra of **2a**, **2b**, and **2c** coincide in position with the molecular weight of 1:1 condensation product. These results show that these impurities would be the cyclization compounds.

2a ; R = Me, n = 6

2b ; R = H, n = 10

2c ; R = Ph, n = 10

Table III. Thermal properties of polyguanamines

Polymer	T_g^a	T10 ^b
	°C	°C
3a	91	421
3b	72	447
3c	55	437
3d	85	444
3e	67	413
3f	48	422
3g	94	448
3h	74	428
3i	62	408

^a Glass transition temperature was measured by DSC at a heating rate of 20°C min⁻¹. ^b Temperature of 10% weight loss was determined by TGA at a heating rate of 10°C min⁻¹.

Thermal Properties

The thermal properties of polymers are showed in Table III. These polyguanamines showed T_g in the range of 41–94°C, and T_g decreased with increasing number of methylene groups of main chain. Furthermore, T_g decreases in the following order; Ph > H > Me with regard to the effect of substituent of 6-position.

As a decomposition temperature of polymers, the temperature of 10% weight loss (T10) was determined by TGA measurement. T10 of polyguanamines were above 400°C.

Catalytic Activity for Substitution Reaction

Polymers are soluble in benzene and toluene, therefore phase transfer of alkali metal ion from water into these organic solvents should be possible if polymers are effective phase transfer reagents.

The catalytic activity of these polymers was tested with the reaction of 1-bromooctane with potassium thiocyanate. These reactions were carried out in toluene/water solutions in the presence of polymers and their monomeric analog (benzoguanamine and *N,N,N',N'*-tetramethylbenzoguanamine).

The results are summarized in Table IV. As can be seen from the table, monomeric compounds and benzyltriethylammonium chloride acted as phase transfer catalysts and gave octyl thiocyanate in 46–47% yields. The polymers gave octyl thiocyanate in above 90% yields at [triazinyl group]/[substrate] = 0.182. It should be noted that the catalytic activity of these polymers is superior to that of their monomeric analog. This observation can be understood by assumption that a potassium cation interacts with several active sites⁸ to form a complex, and the resulting anion attacks the substrate. This cooperative coordination of active sites would function effectively in polymers.

The effect of substituent of 6-position of polymers on catalytic activity was tested at [triazinyl group]/[substrate] = 0.091. The series of polymers **3a–3f** gave octyl thiocyanate in 87–97% yields, but **3g–3i** gave in 43–53% yields. This may be that the cooperative coordination would be somewhat prevented by steric effect of phenyl group.

Table IV. Yield of octylthiocyanate of the reaction of 1-bromooctane with potassium thiocyanate under two-phase condition using polyguanamines as a phase-transfer catalyst

Catalyst	Yield ^a (%) at [triazine]/[substrate] =	
	0.182	0.091
None	17	—
BTEAC ^b	47	—
BG ^c	47	—
TMBG ^d	46	19
3a	94	87
3b	98	91
3c	98	97
3d	97	87
3e	95	91
3f	99	95
3g	91	43
3h	96	50
3i	88	53
3i ^e	98	—

^a Conditions: 1-bromooctane = 1.65 mmol in 1 ml toluene; potassium thiocyanate = 8.0 mol l⁻¹ (in water), 5 ml; catalyst = 0.3 mmol at 100°C for 30 h under stirring. ^b Benzyltriethylammonium chloride. ^c Benzoguanamine. ^d *N,N,N',N'*-Tetramethylbenzoguanamine. ^e Recovered polymer used as a catalyst.

Table V. Reduction of acetophenone by sodium borohydride under two-phase conditions using polyguanamines as a phase-transfer catalyst

Catalyst	Yield ^a /%
None	7
3a	33
3b	17
3c	31
3d	20
3e	16
3f	27
3g	18
3h	23
3i	24

^a Conditions: acetophenone = 1.50 mmol in 4 ml of benzene; sodium borohydride = 1.2 mmol in 1 ml of 1 wt% NaOH (aq); catalyst = 0.15 mmol at room temperature for 24 h under stirring.

The recovered polymer also worked as phase transfer catalyst and the yield became higher. The mechanistic idea that quaternized triazinyl compound produced through the reaction of a triazine ring with alkyl bromide might serve as the phase transfer catalyst can not be ruled out since alkylated polyvinylpyridine is known to accelerate the nucleophilic substitution in two-phase system.¹³ But one of authors previously reported that the quaternization reaction would not occurred to the polymer containing 2-pyridylthio group under these condition.¹⁴ Further, IR and NMR spectra of recovered polymer agreed with those of original one.

The catalytic effect for the reduction of acetophenone by sodium borohydride was investigated to obtain clear evidence about the participation of triazinyl group. The results are listed in Table V.

The reduction of acetophenone proceeded in the pre-

sence of polymers. Although alkylation of triazine is not possible in this system, polymers served as a catalyst.

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