Contents lists available at SciVerse ScienceDirect

### **Reactive & Functional Polymers**

journal homepage: www.elsevier.com/locate/react

# Synthesis of polyguanamines from 2-*N*,*N*-dibutylamino-4,6-dichloro-1,3,5-triazine with aromatic diamines

Kyohei Saito<sup>a</sup>, Naoya Nishimura<sup>b</sup>, Shigeko Sasaki<sup>a</sup>, Yoshiyuki Oishi<sup>a</sup>, Yuji Shibasaki<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry & Bioengineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551, Japan <sup>b</sup> Materials Research Department, Chemical Research Laboratories, Nissan Chemical Industries, Ltd., 2-10-1, Tsuboinishi, Funabasi-shi, Chiba 274-8507, Japan

#### ARTICLE INFO

Article history: Received 22 November 2012 Received in revised form 15 February 2013 Accepted 6 March 2013 Available online 15 March 2013

Keywords: Cyanuric chloride Polyguanamine Condensation polymerization Thermostability Triazine

### ABSTRACT

Solution polycondensation of 2-*N*,*N*-dibutylamino-4,6-dichloro-1,3,5-triazine (BDCT) with various aromatic diamines, including 4,4'-oxydianiline (ODA), *p*-phenylenediamine (*p*PDA), *m*-phenylenediamine (*m*PDA), *o*-tolidine (*o*TD), 4,4'-(9-fluorenylidene)dianiline (BAFL), and 2,4-diamino-6-(*N*,*N*-dibutylamino)-1,3,5-triazine (DABT), was investigated. High molecular weight (>10,000) polyguanamines (PGs) were obtained *via* the polymerization of BDCT with ODA, *p*PDA, *o*TD, and BAFL at 150–180 °C in *N*-methylpyrrolidone (NMP) for 6 h. The polymerizability with BDCT was determined on the basis of the molecular weights of the polymers and the chemical shifts of the NMR data as follows: ODA > *o*TD > BAFL > *p*PDA > *m*PDA  $\gg$  DABT. PGs were obtained from the reaction of BDCT with ODA and *m*PDA in only 55–77% yield, which may be attributed to the formation of cyclic oligomers. All of the polymers generated from reaction of BDCT with ODA, *m*PDA, and BAFL exhibited good solubility in tetrahydrofuran and polar aprotic solvents such as NMP.

© 2013 Elsevier Ltd. All rights reserved.

### 1. Introduction

Cyanuric chloride (CyC) is a commercially available compound that is mainly used for the synthesis of pesticide chemicals, such as atrazine, simazine, anilazine, and cyromazine. One chemically interesting behavior of CyC is the displacement of the chlorine atoms using different amine nucleophiles to generate mono-, di-, and trisubstituted 1,3,5-triazines, the reactivity of which is controlled by temperature [1–3]. ADCT, or 4-amino-2,6-dichloro-1,3,5-triazine, which can be readily obtained through this displacement reaction of CyC using aqueous ammonia, is one of the most elemental structures for use in polymer synthesis; however, the polycondensation of ADCT with difunctional monomers may afford branching structures, resulting in low molecular weight polymers or gelation [4,5]. The synthesis of high molecular weight polyguanamines (PGs) has been reported via the two-phase polycondensation of ADCT with aliphatic diamines, in which the resulting polymers exhibited a high tensile modulus of 3.7 GPa with low toughness, probably due to highly condensed hydrogen bonding [6,7]. Because aromatic diamines have lower nucleophilicity than their aliphatic counterparts, polymerization of ADCT with aromatic diamines was expected to instantly form a gel. Contrary to this expectation, we have found that, in a polar aprotic solvent, the chemoselective polymerization of ADCT with various aromatic diamines occurs, resulting in high molecular weight polymers with excellent thermal properties [8].

Comb polymers are useful materials because of the different solid-state natures of the main- and side-chains, which generally afford long-range phase-segregated structures [9,10]. As part of a series of studies on precisely controlled polycondensation, we reported the synthesis of poly(*N*-alkyl benzamide)s bearing alkyl side chains (PABA<sub>n</sub>, in which n is the number of carbon atoms of the side chain) in order to investigate the packing of the comb-like polymers [11-15]. It was revealed that the packing structure of PABA<sub>n</sub> can be controlled by the parameter n; when n is 0-5 (C0-C5), the packing is governed by the main-chain interactions, and when *n* is over 10 (>C10), it is determined by side-chain packing. PGs having one, two, or three long alkyl side chains  $(-C_{18}H_{37})$  in the repeating unit have been prepared, and the packing behavior was investigated [16-20]. Interestingly, increasing the number of side chains in the repeating unit, the crystallinity by the hexagonal side-chain packing was remarkably increased.

Considering the molecular packing between the polymer chains, we expected that the introduction of dibutyl moieties (C4) in the  $NH_2$  group of the ADCT monomer would be sufficient to endow the polymer with good solubility while increasing its mechanical strength through retention of the main-chain interactions in the packing structure.

Herein we report the synthesis of polyguanamines of 2-*N*,*N*-dibutylamino-4,6-dichloro-1,3,5-triazine (BDCT) with aromatic diamines and their thermal properties.





<sup>\*</sup> Corresponding author. Tel./fax: +81 19 621 6322. E-mail address: yshibasa@iwate-u.ac.jp (Y. Shibasaki).

<sup>1381-5148/\$ -</sup> see front matter © 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.reactfunctpolym.2013.03.005

### 2. Experimental

### 2.1. Materials

Dioxane and *N*-methylpyrrolidone (NMP) were dried over calcium hydride (CaH<sub>2</sub>) and distilled under reduced pressure. Tetrahydrofuran (THF) was distilled from sodium-naphthalene under nitrogen. Cesium fluoride (CsF) and lithium chloride (LiCl) were dried at 180 °C for 12 h under reduced pressure before use. The compounds 4,4'-oxydianiline (ODA), *m*-phenylenediamine (*m*PDA), and *p*-phenylenediamine (*p*PDA) were used after sublimation, while *o*-tolidine (*o*TD) and 4,4'-(9-fluorenylidene)dianiline (BAFL) were purified *via* recrystallization from THF/hexane and ethanol, respectively. The intermediate 2,4-diamino-6-chloro-1,3,5-triazine (DACT) was prepared using the modified method reported in the literature [21]. Other reagents and solvents were used as received.

### 2.2. Measurements

Fourier transform infrared (FT-IR) spectra were measured with a Jasco IR-5500 (Jasco Co., Ltd.) using transmittance absorption spectroscopy (KBr tablet method). Nuclear magnetic resonance (NMR) analysis was performed on a Bruker AC-400P spectrometer at 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C measurements. Deuterated dimethylsulfoxide (DMSO- $d_6$ ) was used as the solvent. Number and weight average molecular weights  $(M_n \text{ and } M_w)$  were measured via gel permeation chromatography (GPC) on a Tosoh HLC-8120 GPC equipped with a consecutive polystyrene gel column (TSK-GEL GMHHR-M and GMHHR-N) at 40 °C. NMP containing 0.01 mol/L lithium bromide was used as the eluent at a flow rate of 1.0 mL/min. The column was calibrated using standard polystyrene samples. Thermal analyses were performed on a Seiko thermal analyzer at heating rates of 10 °C/min for thermogravimetric analysis (TGA; TG/DTA 7300) under air or nitrogen, and 20 °C/ min for differential scanning calorimetry (DSC; X-DSC 7000).

## 2.3. Synthesis of 2-(N,N-dibutylamino)-4,6-dichloro-1,3,5-triazine (BDCT)

In a three-necked flask equipped with a dropping funnel and a magnetic stirrer, cyanuric chloride (CyC) (19.50 g, 98.00 mmol) was dissolved in THF (100 mL) and then cooled to -10 °C. To this solution was added dropwise N,N-dibutylamine (12.67 g, 98.00 mmol) and THF (70 mL). After stirring for 2 h, a solution of Na<sub>2</sub>CO<sub>3</sub> (5.61 g, 53.0 mol) in distilled water (60 mL) was added dropwise at this temperature. After stirring for another 2 h, the reaction solution was transferred to a separatory funnel and then washed three times with saturated brine. The organic layer was dried over MgSO4 and filtered. The filtrate was concentrated under reduced pressure to give a viscous, colorless liquid mixed with unreacted CyC as white solids, which was removed by filtration. The separated liquid was purified by vacuum distillation (b.p. = 107–108 °C/0.07 Torr). Yield 16.3 g (65.0%). FT-IR (KBr) v 2953, 2933, 2873 (C-H stretching), 1439 (C=N stretching), 846 (C--Cl) cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>) δ 0.91 (t, 6H, -CH<sub>3</sub>), 1.26-1.32 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.52-1.56 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.52 (t, 4H, -N-CH<sub>2</sub>) ppm. <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>) δ 13.6, 19.3, 28.7, 47.1, 163.7, 168.7. Elemental Anal. Calcd for (C<sub>11</sub>H<sub>18</sub>Cl<sub>2</sub>N<sub>4</sub>): C:47.66 H:6.55 N:20.21%. Found: C:47.78 H:6.39 N:20.29%.

### 2.4. Synthesis of DACT

In a three-necked flask equipped with a dropping funnel and a magnetic stirrer, CyC (35.8 g, 194.0 mmol) was dissolved in

K. Saito et al./Reactive & Functional Polymers 73 (2013) 756-763

acetone (200 mL). Distilled water (200 mL) was then added to the solution, and the mixture was cooled to 0 °C. Into the solution was added dropwise a mixture of 28% aqueous ammonia (473.0 mL, 776.0 mmol). The solution was warmed to 25 °C, and stirring was maintained for an additional 12 h. After confirming that the pH was approximately 8, the reaction solution was poured into water. The white precipitate was collected, washed with THF, and dried at 60 °C under reduced pressure for 12 h. Yield: 9.6 g (34%). Mp 262 °C (DTA). FT-IR (KBr) v 3340, 3176, 3110 (N–H stretching), 1481 (C=N stretching), 797 (C–Cl) cm<sup>-1</sup>. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>)  $\delta$  7.12–7.20 (N*H*<sub>2</sub>) ppm. <sup>13</sup>C-NMR (DMSO- *d*<sub>6</sub>)  $\delta$  167.2, 168.8 ppm.

### 2.5. Synthesis of 2,4-diamino-6-(N,N-dibutylamino)-1,3,5-triazine (DABT)

In a three-necked flask equipped with a reflux condenser and a magnetic stirrer, DACT (5.98 g, 41.0 mmol) was suspended in 400 mL of N,N-dimethylformamide (DMF). Next N,N-dibutylamine (5.32 g, 41.0 mol) and potassium carbonate (5.69 g, 41.0 mol) were added to the mixture in one portion, and the solution was stirred at 130 °C for 24 h under nitrogen. The resulting heterogeneous mixture was poured into water, and the precipitate was collected by filtration, dissolved in THF, and dried over MgSO<sub>4</sub>. Any inorganic materials were then removed by filtration, and the filtrate was concentrated under reduced pressure to give a white solid, which was purified by recrystallization from THF with hexane and dried at 60 °C under reduced pressure for 12 h to give white plate crystals. Yield 5.3 g (54%). FT-IR (KBr) v 3323, 3157, 1680 (-NH<sub>2</sub>), 2959 (C-H stretching), 1433 (C=N of triazine) cm<sup>-1</sup>, <sup>1</sup>H-NMR (DMSOd<sub>6</sub>) δ 0.89 (t, 6H, -CH<sub>2</sub>CH<sub>3</sub>), 1.20-1.29 (m, 4H, -CH<sub>2</sub>CH<sub>3</sub>), 1.43-1.51 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.40 (t, 4H, -NCH<sub>2</sub>-), 6.03 (s, 4H, --NH<sub>2</sub>) ppm. <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>) δ 13.9, 19.7, 29.9, 45.2, 165.4, 167.0 ppm. Elemental Anal. Calcd for (C<sub>11</sub>H<sub>22</sub>N<sub>6</sub>): C:55.43 H:9.30 N:35.26%. Found: C:55.53 H:9.22 N:35.21%.

### 2.6. Synthesis of BDCT-DABT condensation product (BDCT-DABT)

In a two-necked flask equipped with a three-way stopcock and a magnetic stirrer, DABT (0.238 g, 1.00 mmol), NMP (2 mL), and CsF (0.152 g, 1.00 mmol) were placed under nitrogen. BDCT (0.277 g, 1.00 mmol) was slowly added using a syringe at 20 °C, and the resultant solution was stirred at 120 °C for 12 h. The solution was then cooled to room temperature and poured into water containing NH<sub>3</sub> aq. Next, the precipitate was dissolved in THF, dried over MgSO<sub>4</sub>, and filtered. The solution was then evaporated in vacuo to give a white solid. Finally, the product was recrystallized from hexane and dried at 60 °C for 12 h. The yield was 0.12 g (36%). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>) δ 0.84–0.92 (m, 12H, –*CH*<sub>3</sub>), 1.21–1.28 (m, 8H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.49-1.51 (m, 8H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.45-3.56 (t, 8H, -N-CH<sub>2</sub>), 6.49 (s, 2H, NH<sub>2</sub>), 9.66 (1H, NH) ppm. <sup>13</sup>C-NMR (DMSO- $d_6$ )  $\delta$  13.7, 13.7, 13.8, 13.9, 19.4, 19.5, 19.6, 29.1.29.3, 29.5, 29.7, 45.2, 45.5, 45.9, 46.3, 163.5, 163.9, 164.4, 165.3, 167.2, 168.5 ppm.

### 2.7. Synthesis of PG of BDCT with various aromatic diamines

*Typical procedure*: All glass vessels were heated in vacuo before use, and filled with and handled in a stream of dry nitrogen. In a two-necked flask equipped with a three-way stopcock, a reflux condenser, and a magnetic stirrer, ODA (0.200 g, 1.00 mmol) was dissolved in dry NMP (2 mL) at room temperature. To this solution, BDCT (0.277 g, 1.00 mmol) and CsF (0.334 g, 2.20 mmol) were added in that order. The mixture was stirred for 10 min, and then the polymerization was performed at 150 °C for 6 h. Next, the polymerization solution was cooled to room temperature, and poured into an excess amount of methanol containing NH<sub>3</sub>aq in order to remove the HCl and inorganic salts generated in the reaction, as well as excess CsF. The fibrous precipitate was dried at 60 °C for 12 h, dissolved in NMP, reprecipitated with methanol, and dried at 200 °C for 12 h under reduced pressure. The yield was 0.23 g (57%). FT-IR (KBr) v 3414 (free guanamine hydrogen N—H), 2956–2871 (C—H stretching), 1587, 1543 (aromatic C=C), 1498 (triazine C=N), 1210 (ether) cm<sup>-1</sup>, <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>)  $\delta$  0.76–0.86 (br, 6H, -CH<sub>2</sub>CH<sub>3</sub>), 1.18–1.26 (br, 4H, -CH<sub>2</sub>CH<sub>3</sub>), 1.26–1.62 (br, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.20–3.62 (br, 4H, -N-CH<sub>2</sub>), 4.91 (terminal NH<sub>2</sub>), 6.80–6.86 (br, 4H, Ar—H), 7.72–8.20 (br, 4H, Ar—H), 8.95 (br, 2H, -NH) ppm. Elemental Anal. Calcd for (C<sub>23</sub>H<sub>28</sub>N<sub>6</sub>O): C:68.29 H:6.98 N:20.78%. Found: C:68.91 H:6.83 N:20.28%.

### 2.8. Synthesis of PG of BDCT with DABT

In a similar manner as that described in Section 2.7., DABT (0.238 g, 1.00 mmol) in NMP (2.0 mL) containing 5 wt% LiCl was mixed with BDCT (0.277 g, 1.00 mmol) and CsF (0.334 g, 2.2 mmol). The mixture was first oligomerized at 100 °C for 3 h to prevent sublimation of the DABT monomer. The oligomeric solution was then heated at 180 °C, and polymerized for 12 h. Next, the mixture was poured into an excess amount of methanol with aq NH<sub>3</sub> to precipitate the polymer. The product was collected by filtration, washed with hot methanol for 3 h, filtered, and then dried at 200 °C for 12 h under reduced pressure. The yield was 0.12 g (51%). FT-IR (KBr) 3414 (free guanamine hydrogen N–H), 3276–3035 (hydrogen-bonded guanamine hydrogen N–H), 2957, 2931, 2871 (C–H stretching), 1616 (triazine C=N), 743 (N–C) cm<sup>-1</sup>.

### 2.9. Monitoring the condensation reaction of BDCT with aromatic diamines by <sup>1</sup>H-NMR

Typical procedure; reaction of DABT with ODA in DMSO- $d_6$ ; In a two-necked flask equipped with a three-way stopcock and a magnetic stirrer bar, ODA (0.200 g, 1.00 mmol), NMP (2 mL), and CsF (0.152 g, 1.00 mmol) were placed under nitrogen. BDCT (0.277 g, 1.00 mmol) was then slowly added using a syringe at -20 °C, and the solution was stirred for 1 h. An aliquot of the reaction solution was diluted with DMSO- $d_6$ , and the sample was measured by <sup>1</sup>H-NMR spectrometer to determine the chemical shift of NH<sub>2</sub> group and the conversion of the diamine molecule.

### 3. Results and discussion

### 3.1. Polymer synthesis

Two types of triazine-containing monomers, DABT and BDCT, were successfully prepared *via* the conventional addition–elimination reaction of CyC, as shown in Scheme 1. The structures of the monomers were characterized by IR, <sup>1</sup>H and <sup>13</sup>C-NMR, and elemental analysis.

For the polyguanamine synthesis, BDCT and the aromatic diamines ODA, *p*PDA, *m*PDA, *o*TD, BAFL, and DABT were selected as the monomers. The polycondensation was performed in NMP at temperatures ranging from 120 to 200 °C for 6 h in the presence of CsF as an acid scavenger, except for the polymerization of BDCT with DABT (Scheme 2). During the polymerization of BDCT with DABT, sublimation and precipitation were observed due to the low reactivity of the two monomers and the low solubility of the



Scheme 1. Synthesis of DABT and BDCT monomers from CyC as a starting material.



Scheme 2. Synthesis of polyguanamines from BDCT with various aromatic diamines.

Table 1		
Polymerization of BDC	T with various diamine	s.ª

Run	Diamine	Additive	Temp. (°C)	Time (h)	Yield (%)	$M_n^{\rm b}$	$M_w/M_n^{\rm b}$	Remarks
1	ODA	-	120	6	55	13,000	3.9	-
2	ODA	-	150	6	57	22,000	2.9	_
3	ODA	-	180	6	56	16,000	2.4	_
4	pPDA	-	150	6	87 <sup>c</sup>	3000	3.2	Partially insoluble
5	pPDA	-	180	6	93°	11,600	2.5	Partially insoluble
6	mPDA	-	150	6	56 <sup>c</sup>	6800	3.2	_
7	mPDA	-	180	6	77 <sup>c</sup>	5900	2.2	_
8	oTD	-	150	6	92°	12,100	5.5	Partially insoluble
9	oTD	-	180	6	97°	16,800	9.9	Partially insoluble
10	BAFL	-	150	6	71 <sup>d</sup>	12,600	5.2	-
11	BAFL	-	180	6	75 <sup>d</sup>	17,000	5.9	-
12	BAFL	-	200	6	74 <sup>d</sup>	17,000	5.9	-
13	DABT	LiCl	100/180	3/12	51 <sup>c</sup>	1500	3.5	Partially soluble

<sup>a</sup> Conditions; Monomers = 1.0 mmol, CsF = 2.2 mmol, LiCl = 5 wt%, NMP = 2 mL.

<sup>b</sup> Determined by GPC (NMP with LiBr, PSt).

<sup>c</sup> Purified only by washing with hot MeOH.

<sup>d</sup> Purified by reprecipitation with MeOH.



Scheme 3. Synthesis of model compounds.

#### Table 2

Chemical shift of *ipsoC* on <sup>13</sup>C NMR spectrum in DMSO-*d*<sub>6</sub>.

Compound			CI N CI N N Bu <sup>N</sup> Bu	$\begin{array}{c} CI \searrow N \swarrow N \searrow N \swarrow NH_2 \\ N \swarrow N \searrow N \searrow N \\ Bu \overset{N}{} Bu Bu \overset{N}{} Bu \end{array}$
Abbreviation	CyC	ADCT	BDCT	BDCT-DABT
Chemical shift (ppm)	172.6 <sup>a</sup>	169.3	168.8	168.5

<sup>a</sup> Measured in CDC1.

condensation products. To prevent these unfavorable conditions, the polymerization was performed in two steps (100 °C for 3 h and 180 °C for 12 h) in the presence of 5 wt% LiCl in order to cleave the hydrogen bonds between the products.

Table 1 summarizes the results of the polycondensation reactions. When the polymerization was conducted using BDCT and ODA, the  $M_n$  values of the polymers increased with the polymerization temperature and reached a maximum of 22,000 at 150 °C (run 1–3). On the other hand, the maximum  $M_n$  of the polymers prepared from BDCT with BAFL, oTD, pPDA, mPDA, and DABT were 17,000, 16,800, 11,600, 6800, and 1500, respectively. When using these diamines as the comonomer for the polymerization of BDCT, the  $M_n$  of the polymers typically increases at higher polymerization temperatures. These results indicate that the polymerizability of the diamines with BDCT is in the following order: ODA > oTD  $\approx$  BAFL > pPDA > mPDA  $\gg$  DABT.

### 3.2. Evaluation of the monomer reactivity based on NMR study

In order to further evaluate the polymerizability of the monomers, aromatic diamines were reacted with BDCT (Scheme 3) and an NMR study was carried out, as shown in Tables 2 and 3. Basically, the rate of the addition–elimination reaction of chlorotriazine with an aromatic amine is strongly affected by the electron density of the *ipso* carbon and that of the nitrogen atom. Based on the chemical shift data measured in the <sup>13</sup>C-NMR spectra, the electron density of the *ipso* carbon atom decreased in the following order; BDCT–DABT (168.5 ppm) > BDCT (168.8 ppm) > ADCT (169.3 ppm) > CyC (172.6 ppm). For instance, CyC undergoes quantitative reaction with an equimolar amount of aniline in NMP at 0 °C, whereas BDCT–DABT shows no reactivity for aniline under the same reaction conditions. On the other hand, the reactivity of

### Table 3

Reaction of diamine with BDC	, and the chemical shift of NH2 <sup>a</sup>
------------------------------	--

Run	Diamine	Conversion (%)	Yield (%)		$\delta$ (ppm) of NH <sub>2</sub>			
	$H_2NArNH_2$	H <sub>2</sub> NArNH <sub>2</sub>	BDCT-NHArNH <sub>2</sub>	BDCT-NHArNH-BDCT	$H_2NArNH_2 \delta_1$	BDCT–NHArNH <sub>2</sub> $\delta_2$	$\delta_2 - \delta_1$	
1	ODA	55	27	28	4.79	4.95	0.16	
2	pPDA	52	40	12	4.19	_	-	
3	mPDA	47	45	2	4.66	5.05	0.39	
4	oTD	5	5	<1	4.79	5.02	0.23	
5	BAFL	2	2	<1	4.93	5.07	0.14	
6	DABT	<1	<1	<1	6.03	6.49	0.46	

<sup>a</sup> Measured by <sup>I</sup>H NMR in DMSO-d<sub>6</sub>. Conversion of diamine compounds, and the yields of the products were all estimated by <sup>I</sup>H NMR measurements.



Fig. 1. Optimized geometry of the condensation products of BDCT with (a) ODA, (b) pPDA, (c) mPDA, and (d) oTD, estimated using MM2 calculations.

aromatic amines can be roughly estimated based on the chemical shift of the <sup>1</sup>H-NMR spectra as follows:

pPDA (4.19 ppm) > mPDA (4.66 ppm) > ODA, oTD (4.79 ppm) > BAFL (4.93 ppm) > BDCT-ODA (4.95 ppm) > BDCT-oTD (5.02 ppm) ~ BDCT-mPDA (5.05 ppm) ~ BDCT-BAFL (5.07 ppm) > DABT (6.03 ppm) > DABT-BDCT (6.49 ppm).

The conversion of the diamine compounds in the reaction with BDCT is approximately related to the nucleophilicity estimated by <sup>1</sup>H NMR measurements described above. Namely, ODA has moderate reactivity for BDCT, thus giving the condensation product BDCT-NHArNH<sub>2</sub>, which further could react with BDCT to give BDCT-NHArNH-BDCT as shown in Table 3. In the case of the conjugated diamines such as *p*PDA, they originally exhibit very high reactivity for BDCT, but the main products were the equimolar condensation compounds. The generating HCl may form salts with the amine compounds in the reaction solution, prohibiting the further condensation reaction of the condensation product as well as the reaction of the original diamine with BDCT. The difference in the chemical shifts  $(\delta_2 - \delta_1)$  of ODA and BDCT-ODA is 0.16, and that of DABT and BDCT-DABT is 0.46, which is approximately threefold higher than in the ODA case. DABT is a weak nucleophile for BDCT, and the nucleophilicity of the nitrogen atom in BDCT-DABT is sig-

able 4				
olubilitv	of	polv	mers <sup>a</sup>	

Polymer	DMF	DMAc	NMP	DMSO	THF	Acetone	CHC1 <sub>3</sub>
Poly(BDCT-ODA)	++	++	++	±	++	-	-
Poly(BDCT-pPDA)	±	±	±	±	±	-	-
Poly(BDCT-mPDA)	++	++	++	±	++	-	-
Poly(BDCT-oTD)	±	±	±	±	±	-	-
Poly(BDCT-BAFL)	++	++	++	±	++	-	-
Poly(BDCT-DABT)	Ŧ	Ŧ	Ŧ	-	-	-	-

<sup>a</sup> Polymer 10 mg/solvent 5 mL (++ soluble at room temperature; + soluble after heating;  $\pm$  partially insoluble;  $\mp$  partially soluble; – insoluble).

nificantly weakened due to the electron-withdrawing effect of the BDCT unit. These results clearly support the obtained  $M_n$  data for the polymers that are presented in Table 1.

### 3.3. Conformations of the repeating units of the polymers

The yield of the polymers obtained from the reaction of BDCT with ODA and *m*PDA was approximately 60%, which is extraordinarily low for polycondensation polymers. Fig. 1 shows the



Fig. 2. DSC profiles of (a) poly(BDCT-ODA), (b) poly(BDCT-pPDA), (c) poly(BDCT-mPDA), (d) poly(BDCT-oTD), and (e) poly(BDCT-BAFL).

**Table 5**Thermal properties of polymers.

Polymer	$M_n$	$T_g^{a}$ (°C)	N <sub>2</sub>		Air	
			$T_{d5}^{\mathbf{b}}$ (°C)	$T_{d10}^{\rm b}$ (°C)	$T_{d5}^{\rm b}$ (°C)	$T_{d10}^{\rm b}$ (°C)
Poly(BDCT-ODA)	22,000	145	459	472	318	350
Poly(BDCT-pPDA)	11,600	163	444	464	332	371
Poly(BDCT-mPDA)	6800	130	457	471	426	462
Poly(BDCT-oTD)	16,800	135	459	475	341	391
Poly(BDCT-BAFL)	17,000	237	464	479	342	383

<sup>a</sup> Determined by DSC in nitrogen at a heating rate of 20 °C/min.

<sup>b</sup>  $T_{d5}$  and  $T_{d10}$  are the temperatures for 5% and 10% decomposition of the polymers, respectively (in nitrogen or air, heating rate 10 °C/min).

optimized geometry of the condensation products of BDCT with aromatic diamines as estimated using MM2 calculations. From these model structures, it can be seen that polymers from BDCT with *o*TD and *p*PDA seem to have a kink arrangement, whereas those from BDCT with ODA or *m*PDA have a fold-back conformation, which would be more favorable for the formation of cyclic oligomers, and thus may cause the low yields in the polymerization of BDCT with ODA or *m*PDA.

#### 3.4. Properties of the polymers

Table 4 shows the solubility of the prepared polymers. Polymers obtained from the reaction of BDCT with ODA, mPDA, and BAFL exhibited good solubility, even in THF and aprotic solvents, but some portions of poly(BDCT-pPDA) and poly(BDCT-oTD) were insoluble in these solvents. The bulky pendent BAFL moiety, the flexible ether linkage of ODA, and the large free-volume-demand kinked mPDA structure effectively minimized the polymer-polymer interactions, providing sufficient solubility for the corresponding polymers. However, poly(BDCT-DABT) is practically insoluble due to all of the melamine units in the polymer backbone, and thus a high molecular weight was not obtainable for this system using conventional solution polymerization (Table 1, run 13). The thermal properties of the polymers measured using a DSC and TG/ DTA system are presented in Fig. 2 and Table 5. The glass transition temperatures  $(T_g)$  of poly(BDCT-mPDA), poly(BDCT-oTD), and poly(BDCT-ODA) are within from 130 to 145 °C. The fold-back structure of BDCT-mPDA as illustrated in Fig. 1, interruption of the polymer-polymer packing by the methyl substituents, or the flexible ether linkage of ODA probably lower the  $T_g$  values. On the other hand, the  $T_g$  values of poly(BDCT-pPDA) and poly(BDCT-BAFL) are 163 and 237 °C, respectively. These high



**Fig. 3.** Expanded FT-IR spectra of (a) poly(BDCT-ODA), (b) poly(BDCT-*p*PDA), (c) poly(BDCT-*m*PDA), (d) poly(BDCT-oTD), (e) poly(BDCT-BAFL), and (f) poly(BDCT-DABT).

values may be due to a rigid-rod structure or prevention of rotation of the polymers resulting from introduction of bulky pendent groups. The 5% weight-loss temperatures ( $T_{d5}$ ) of the polymers under nitrogen are around 450 °C, indicating that the prepared PGs have high thermostability. In our previous work, PGs, synthesized



Scheme 4. Plausible mechanism in polymerization system.

by the chemoselective polycondensation of ADCT with aromatic diamines, showed poor solubility, because of the highly strong interaction between NH<sub>2</sub> moiety and guanamine units [8]. For instance, polymerization of ADCT with ODA only provided the low molecular weight PG with  $M_n$  of 1500, and PG from ADCT with BAFL showed solubility only in an aprotic solvent like NMP. Of course, the resulting all aromatic PGs having NH<sub>2</sub> functional group showed high thermostability, the glass transition temperatures ( $T_g$ ) of 266 °C, and  $T_{d5}$  of 477 °C thanks to the strong polymer mainchain packing. In our present study, poly(BDCT-BAFL) shows high  $T_g$  (237 °C), and  $T_{d5}$  (464 °C), comparable to those of poly(ADCT-BAFL). These results clearly indicate that the introduced dibutyl group effectively enhanced the solubility, but did not disturb the main-chain packing, resulting in the high thermostability.

### 3.5. IR study of the polymers

In the IR analysis of the polymers, in addition to the characteristic absorption corresponding to melamine (C=N) at 1498 cm<sup>-1</sup>, aromatic secondary amine and aromatic ether (Ar–NH–Ar and A–O–Ar, respectively) groups can be observed at 1210 cm<sup>-1</sup>, and the guanamine hydrogen (NH) can be observed at 3000– 3700 cm<sup>-1</sup>. Fig. 3 represents the expanded IR spectra of the polymers. The PG prepared from the reaction of BDCT with ODA shows a strong absorption at 3414 cm<sup>-1</sup>, which can be assigned to a free NH stretching absorption. In contrast, in the IR spectra of poly(BDCT-*p*PDA) and poly(BDCT-oTD), a broad absorption with the maximum at 3189 cm<sup>-1</sup>, corresponding to hydrogen bonding of guanamine group, can also been observed. Thus, there should be strong packing within the polymer structures. These results also support the conclusions regarding the polymer solubilities.

### 3.6. Polymerization mechanism

Scheme 4 illustrates the plausible polymerization pathway for BDCT with aromatic diamines. As an aromatic diamine, ODA is a highly reactive non-conjugated monomer, and thus the nucleophilicity of the nitrogen atom would be preserved, even after the condensation reaction, resulting in high molecular mass polymers. *pPDA, mPDA, and oTD* are highly reactive conjugated monomers

towards BDCT, but the nucleophilicity of the nitrogen after the condensation should decrease due to the resonance effect. BDCT is a poorer nucleophile compared to the above-mentioned diamine monomers, and the reactivity of the intermediate should be dramatically decreased. For this reason, it was difficult to realize the polycondensation of DABT with BDCT.

### 4. Conclusion

We reported the synthesis and polymerizability of several polyguanamines using the conventional solution polycondensation method. The polymerizability against BDCT was determined based on the molecular weights of the polymers and the chemical shifts of the NMR spectra to be as follows: ODA > oTD > BAFL > pPDA > mPDA  $\gg$  DABT. All of the polymers exhibited high thermostability (5% weight-loss temperature in N<sub>2</sub> above 444 °C), and the polymers prepared from the reaction of BDCT with ODA, mPDA, and BAFL exhibited good solubility in THF and polar aprotic solvents such as NMP, which indicated that the dibutyl group should be the good choice to enhance the solubility of the polymers, preserving sufficient polymer main-chain interactions as a highly thermally stable polymeric material. These results should be useful for the synthesis of various types of PGs with control of the packing between the polymer chains.

### Acknowledgement

This study is supported by Eno Research Foundation in 2012.

### References

- [1] M. Goi, Yuki Gosei Kagaku Kyokaishi 18 (1960) 327–331.
- [2] P. de Hoog, P. Gamez, W.L. Driessen, J. Reedijk, Tetrahedron Lett. 43 (2002) 6783-6786.
- [3] A. Chouai, E. Simanek, J. Org. Chem. 73 (2008) 2357-2366.
- [4] H.K. Reimschuessel, A.M. Lovelace, E.M. Hagermann, J. Polym. Sci. 40 (1959) 270-272.
- [5] G.F. Ehlers, J.D. Ray, J. Polym. Sci., Part A-1 4 (1966) 1645-1646.
- [6] D.W. Wang, M.M. Fisher, J. Polym, Polym. Chem. Ed. 21 (1983) 671–677.
- [7] N. Irles, J. Puiggalí, J.A. Subirana, Macromol. Chem. Phys. 202 (2001) 3316– 3322.
- [8] Y. Shibasaki, T. Koizumi, N. Nishimura, Y. Oishi, Chem. Lett. 40 (2011) 1132– 1134.

763

- [9] G. Riess, G. Hurtrez, P. Bahadur, in: H.F. Mark, J.I. Kroscwitz (Eds.), Encyclopedia of Polymer Science and Engineering, vol. 2, Wiley, New York, 1985. p. 324.
- [10] I.W. Hamley, The Physics of Block Copolymers, Oxford University Press, New York, 1998.
- [11] Y. Shibasaki, Y. Abe, N. Sato, A. Fujimori, Y. Oishi, Polym. J. 42 (2010) 72–80.
- [12] A. Fujimori, S. Chiba, N. Sato, Y. Abe, Y. Shibasaki, J. Phys. Chem. B 114 (2010) 1822–1835.
- [13] S. Chiba, N. Sato, Y. Abe, Y. Shibasaki, A. Fujimori, Trans. Mater. Res. Soc. Jpn. 35 (2010) 307–310.
- [14] N. Sato, S. Chiba, Y. Abe, Y. Shibasaki, A. Fujimori, Trans. Mater. Res. Soc. Jpn. 35 (2010) 315–318.
- [15] S. Chiba, N. Abe, Y. Shibasaki, A. Fujimori, Trans. Mater. Res. Soc. Jpn. 36 (2011) 145-148.
- J.-K. Lin, H. Kunisada, S. Kondo, Y. Yuki, Kobunshi Ronbun. 45 (1988) 831–837.
  J.-K. Lin, Y. Yuki, H. Kunisada, S. Kondo, J. Appl. Polym. Sci. 40 (1990) 2123–
- [17] J.-K. Lin, Y. Yuki, H. Kunisada, S. Kondo, J. Appl. Polym. Sci. 40 (1990) 2123– 2133.
- [18] J.-K. Lin, Y. Yuki, H. Kunisada, C. Miyagawa, S. Kondo, Polym. J. 21 (1989) 709-717.
- [19] J.-K. Lin, Y. Yuki, H. Kunisada, M. Kondo, S. Kondo, Polym. J. 22 (1990) 47–55.
  [20] J.-K. Lin, Y. Yuki, H. Kunisada, S. Kondo, Polym. J. 22 (1990) 92–102.
- [21] J.T. Thurston, J.R. Dudley, D.W. Kaiser, I. Hechenbleikner, F.C. Schaefer, D.
- Holm-Hansen, J. Am. Chem. Soc. 73 (1951) 2981–2983.