

Synthesis and Properties of Polyguanamines from Bisguanamines and α,ω -Dibromoalkanes by Alkylation Reaction

Yasuo YUKI,* Hideo KUNISADA, Kazuhiro IIDA,
and Shuji KONDO

*Department of Materials Science and Engineering,
Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466, Japan*

(Received July 24, 1995)

ABSTRACT: The novel polyguanamines were synthesized by condensation reaction of bisguanamines with α,ω -dibromoalkanes in the presence of sodium hydride. The polyguanamines having inherent viscosities of 0.1—0.2 dl g⁻¹, were obtained quantitatively. They began to lose weight around 400—480°C in air. The abilities as polymeric phase transfer catalyst of resulting polyguanamines were also investigated. They could use as effective phase transfer catalysts for the reaction of 1-bromooctane with potassium thiocyanates in toluene-water systems.

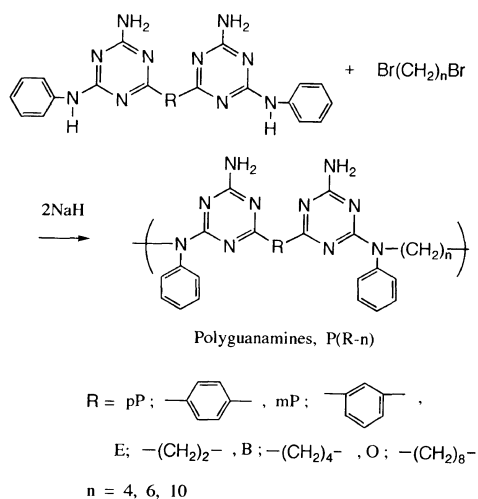
KEY WORDS Guanamine / Bisguanamine / Polyguanamine / α,ω -Dibromoalkane / 1,3,5-Triazine / Polycondensation / Alkylation / Phase Transfer Catalyst /

Polyguanamines, as a thermally stable polymer, have been prepared by the reaction of dibiguanide derivatives with dicarboxylic acid dichlorides or phenyl esters,¹⁻³ or the reaction of diphenoxy-1,3,5-triazines with benzoguanamine as a diamine.⁴ These polyguanamines are soluble in sulfuric acid but insoluble in common organic solvents.

Recently, we reported the alkylation reaction of 2-amino-4-anilino-6-isopropenyl-1,3,5-triazine^{5,6} or 2,4-dianilino-6-isopropenyl-1,3,5-triazine⁷ with alkyl bromides in the presence of sodium hydride with the purpose of monomer synthesis for new comb-like polymers. The alkylation reaction proceeded quantitatively and selectively on the imino position in anilino group through the anilide anion, which could be followed by NMR measurements.⁵

This paper describes the new synthesis of polyguanamines by the alkylation reaction of

bisguanamines with α,ω -dibromoalkanes, as an application of above alkylation reaction (Scheme 1). The thermal properties and the abilities as a polymeric phase transfer catalyst



Scheme 1.

* To whom all correspondence should be addressed.

of the resulting polyguanamines were also investigated.

EXPERIMENTAL

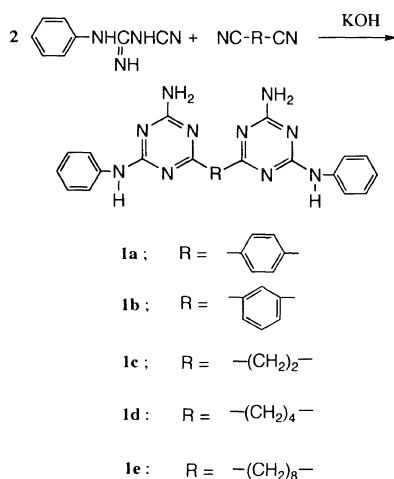
Materials

Phenyldicyanodiamide (PhDD) was prepared according to a literature procedure.⁸ mp 196°C (lit.⁸ 196–197°C).

Bisguanamines as Monomers

1,4-Bis(4-amino-6-anilino-1,3,5-triazin-2-yl)benzene (**1a**) was prepared by reaction of 12.9 g (0.10 mol) of terephthalonitrile with 35.6 g (0.23 mol) of PhDD in 120 ml of dimethylformamide (DMF) in the presence of 6.22 g of potassium hydroxide at reflux for 5 h. The solution was cooled to give white product, which was filtered off, washed with methanol and dried. The filtrate was poured into water to give a product. The product was totally yielded 33.7 g (74.7%). **1a** was recrystallized from dimethylformamide. mp 349°C (lit.³ 357°C). *Anal.* Calcd for C₂₄H₂₀N₁₀: C, 64.24%; H, 4.49%; N, 31.23%. Found: C, 64.10%; H, 4.52%; N, 31.38%.

Other monomers (**1b**–**1e**) were prepared by a similar method using the corresponding dinitriles (Scheme 2).



Scheme 2.

1,3-Bis(4-amino-6-anilino-1,3,5-triazin-2-yl)benzene (**1b**). Yield was 74.7%. mp 322°C (lit.³ 327°C). *Anal.* Calcd for C₂₄H₂₀N₁₀: C, 64.24%; H, 4.49%; N, 31.23%. Found: C, 64.43%; H, 4.31%; N, 31.24%.

1,2-Bis(4-amino-6-anilino-1,3,5-triazin-2-yl)ethane (**1c**). Yield was 64.6%. mp 263°C (lit.³ 261°C). *Anal.* Calcd for C₂₀H₂₀N₁₀: C, 59.99%; H, 5.03%; N, 34.98%. Found: C, 60.11%; H, 4.92%; N, 34.97%.

1,4-Bis(4-amino-6-anilino-1,3,5-triazin-2-yl)butane (**1d**). Yield was 41.3%. mp 226°C (lit.³ 243°C). *Anal.* Calcd for C₂₂H₂₄N₁₀: C, 61.67%; H, 5.65%; N, 32.69%. Found: C, 61.67%; H, 8.15%; N, 32.67%.

1,8-Bis(4-amino-6-anilino-1,3,5-triazin-2-yl)octane (**1e**). Yield was 66.6%. mp 220°C (lit.³ 230°C). *Anal.* Calcd for C₂₆H₃₂N₁₀: C, 64.44%; H, 6.66%; N, 28.90%. Found: C, 64.32%; H, 6.68%; N, 28.84%.

Model Compounds

1,4-Bis[4-amino-6-(*N*-hexylanilino)-1,3,5-triazin-2-yl]benzene (**2a**) was prepared by the alkylation reaction of **1a** (2.24 g, 5 mmol) with 1-bromohexane (1.65 g, 10 mmol) in the presence of sodium hydride (60% suspension in paraffin, 0.40 g, 10 mmol) in dimethyl sulfoxide (DMSO) (15 ml) at 60°C for 5 h with stirring. The reaction mixture was poured into water to give 3.10 g (100%) of **2a**, which was recrystallized from tetrahydrofuran (THF). mp 264°C.

Other model compounds, 1,3-bis[4-amino-6-(*N*-hexylanilino)-1,3,5-triazin-2-yl]benzene (**2b**), 1,2-bis[4-amino-6-(*N*-hexylanilino)-1,3,5-triazin-2-yl]ethane (**2c**), and 1,4-bis[4-amino-6-(*N*-hexylanilino)-1,3,5-triazin-2-yl]butane (**2d**) were prepared by a similar method (Table I).

Polycondensation

1a (2.243 g, 5.00 mmol) was added to DMSO (15 ml) in the presence of sodium hydride (0.40 g, 10 mmol) with stirring, and DMSO solution (6 ml) of 1,10-dibromodecane (1.501 g,

5.00 mmol) was added dropwise and stirred at 50°C for 24 h. The reaction mixture was then poured into excess methanol. The isolated polyguanamine P(pP-10) was washed with methanol, reprecipitated from THF into hexane, and dried under vacuum to give a yield of 2.87 g (97.9%).

Other polyguanamines were prepared by analogous procedure (Table III).

Catalytic Activities for Substitution Reaction

Catalytic activities of polyguanamines were tested in the two-phase reactions of 1-bromooctane in toluene with potassium thiocyanate in water. In a typical run, a toluene solution (1 ml) of 1-bromooctane (0.319 g, 1.654 mmol), a water solution of potassium thiocyanate (3.88 g, 40 mmol), and polyguanamine P(pP-10) (0.1752 g, 0.299 mmol) were charged in a test tube with a screw-cock. An internal standard (cyclohexylbenzene) was added to the reaction mixture and the tube was heated at 100°C for 30 h with stirring. Then the reaction mixture was poured in petroleum ether to precipitate a solid, and the filtrate was analyzed by gas chromatography. The yield of octyl thiocyanate was 74%.

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 (T_d) 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 chromatography (Ohkura 802T) was used for the yield determination of *n*-octyl thiocyanate.

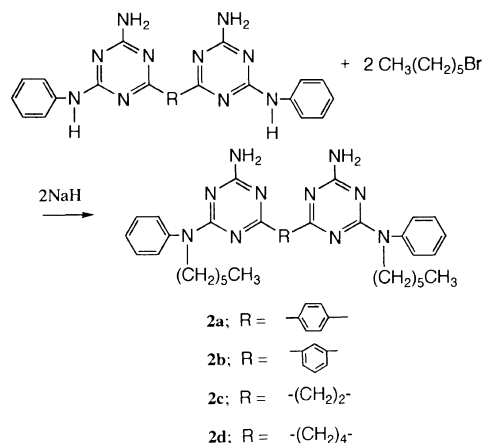
RESULTS AND DISCUSSION

Monomers Synthesis

Five bisguanamines (**1a—1e**) as monomers, were prepared by the reaction of the corresponding dinitriles with double molar quantity of PhDD under alkaline condition (Scheme 2). The elemental analyses of these compounds were in good agreement with the calculated values for the proposed structures.

Model Compounds

The model reactions of bisguanamines with double molar quantity of 1-bromohexane in the presence of sodium hydride were examined (Scheme 3). The results are shown in Table I. The reactions proceeded under mild conditions and gave dialkylated model compounds (**2a—2d**) in an excellent yield. The chemical structures of all model compounds were confirmed by means of elemental analysis, IR, and NMR spectroscopic methods. The NMR spectra of model compounds (Table II) display the signal of *N*-CH $_2$ group at 4.0 ppm. Since the four protons of two amino groups remain at 6.9 ppm for **2a** and **2b**, and 6.7 ppm for **2c**

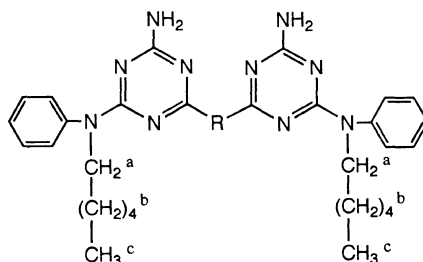


Scheme 3.

Table I. Synthesis of model compounds

Model compound	Temp/Time ^a	Yield %	mp °C	Elementary analysis (calcd)			
	°C/h			C%	H%	N%	
2a	60/ 5	100	264	70.07 (70.10)	7.23 7.19	22.70 22.71;	C ₃₆ H ₄₄ N ₁₀)
2b	r.t./28	99	222	70.14 (70.10)	7.15 7.19	22.71; 22.71;	
2c	r.t./22	99	212	67.71 (67.58)	7.90 7.80	24.31 24.63;	C ₃₂ H ₄₄ N ₁₀)
2d	r.t./22	98	117	68.34 (68.43)	8.15 8.11	23.52 23.47;	

^a Bisguanamine used 5 mmol and 1-bromohexane used 10 mmol in DMSO 13–18 ml.

Table II. ¹H NMR data of model compounds in DMSO-*d*₆ (δ ppm)

Model compound	NH ₂ (4H, br s)	Ph (10H, s)	CH ₂ ^a (4H, t)	(CH ₂) ₄ ^b (16H, br s)	CH ₃ ^c (6H, t)	R
2a	6.93	7.40	4.06	1.29	0.87	8.37 (4H, s)
2b	6.90	7.42	4.06	1.28	0.84	9.21 (1H, s), 8.38 (2H, d), 7.55 (1H, t)
2c	6.66	7.24	3.91	1.26	0.82	2.74 (4H, s)
2d	6.68	7.25	3.93	1.21	0.81	2.39 (4H, t), 1.65 (4H, t)

and **2e**, respectively, any side reaction does not occurred on the pendant amino groups. The signal of phenyl protons became singlet absorption by alkylation on imino group in anilino group as previously reported.¹

Preparation of Polyguanamines

On the basis of the results on the model reaction, polyguanamines were prepared by the polycondensation of bisguanamines with 1,4-dibromobutane, 1,6-dibromohexane, and 1,10-dibromodecane. Scheme 1 shows the structures of the polyguanamines, and the results of synthesis of polyguanamines are listed in Table

III. Polyguanamines P(R-*n*) were successfully obtained in almost quantitative yields with inherent viscosities of 0.1–0.2 dl g⁻¹. The precipitation of the polymers occurred during the course of most of the polycondensation because of relatively low solubilities of polymers. This may be the reason of the polymers with relatively low viscosity values.

The structures of these polymers were 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 CH₂ stretching band at 2950 and 2850 cm⁻¹,

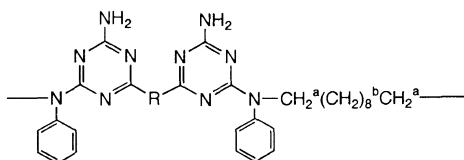
Polyguanamine from Bisguanamine and α,ω -Dibromoalkane

Table III. Syntheses of polyguanamines from bisguanamines and α,ω -dibromoalkanes

Polymer	Solvent ^a	Yield %	η_{sp}/c^b dl g ⁻¹	GPC ^c		Elementary analysis (calcd)		
	ml			$M_n/10^3$	M_w/M_n	C%	H%	N%
P(pP-4)	DMSO(15) & DMA(8)	100	0.19	—	—	67.45 (66.92)	5.33 5.21	27.22 27.87; C ₂₈ H ₂₆ H ₁₀)
P(pP-6)	DMSO(40)	103	0.19	—	—	68.27 (67.91)	5.84 5.70	25.89 26.40; C ₃₀ H ₃₀ N ₁₀)
P(pP-10)	DMSO(21)	98	0.17	—	—	69.35 (69.60)	6.68 6.53	23.61 23.87; C ₃₄ H ₃₈ N ₁₀)
P(mP-4)	DMSO(14)	101	0.17	—	—	67.31 (66.92)	4.96 5.21	27.57 27.87; C ₂₈ H ₂₆ N ₁₀)
P(mP-6)	DMSO(12)	101	0.20	—	—	67.51 (67.91)	5.79 5.70	25.72 26.40; C ₃₀ H ₃₀ N ₁₀)
P(mP-10)	DMSO(21)	101	0.14	—	—	69.79 (69.60)	6.71 6.53	23.50 23.87; C ₃₄ H ₃₈ N ₁₀)
P(E-4)	DMSO(10) & DMF (8)	97	0.06	—	—	63.28 (63.42)	5.97 5.77	30.74 30.82; C ₂₄ H ₂₆ N ₁₀)
P(E-6)	DMSO(8) & DMA(8)	82	0.13	2.4	1.4	64.71 (64.71)	6.32 6.27	28.96 29.02; C ₂₆ H ₃₀ N ₁₀)
P(E-10)	DMSO(18)	102	0.17	3.4	1.6	66.42 (66.89)	7.65 7.11	26.51 26.00; C ₃₀ H ₃₈ N ₁₀)
P(B-4)	DMSO(8) & DMF(20)	99	0.12	1.6	1.2	64.55 (64.71)	6.00 6.27	29.04 29.02; C ₂₆ H ₃₀ N ₁₀)
P(B-6)	DMSO(8) & DMA(8)	85	0.13	2.3	1.4	65.83 (65.86)	6.81 6.71	27.84 27.43; C ₂₈ H ₃₄ N ₁₀)
P(B-10)	DMSO(16)	102	0.16	3.3	1.6	67.81 (67.82)	7.57 7.47	24.27 24.71; C ₃₂ H ₄₂ N ₁₀)
P(O-4)	DMSO(16)	105	0.14	3.6	1.3	66.80 (66.89)	7.12 7.11	26.08 26.00; C ₃₀ H ₃₈ N ₁₀)
P(O-6)	DMSO(16)	102	0.15	4.9	1.5	68.08 (67.82)	7.32 7.47	24.60 24.71; C ₃₂ H ₄₂ N ₁₀)
P(O-10)	DMSO(21)	103	0.25	13.7	1.7	69.79 (69.42)	8.33 8.09	21.76 22.49; C ₃₆ H ₅₀ N ₁₀)

^a Bisguanamine 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 NMP at 30°C. ^c Determined by GPC in THF using polystyrene as a standard.

Table IV. ¹H NMR data of polymers P(R-10) in DMSO-*d*₆ (δ ppm)



Polymer	NH ₂ (4H, br s)	Ph (10H, s)	CH ₂ ^a (4H, br s)	(-CH ₂) ₈ ^b (16H, br s)	R
P(pP-10)	6.98	7.28	4.00	1.15	8.29 (4H, s)
P(mP-10)	6.91	7.30	4.02	1.14	9.19 (1H, s), 8.34 (2H, br s), 7.55 (1H, t)
P(E-10)	6.73	7.26	3.88	1.14	2.81 (4H, br s)
P(B-10)	6.70	7.27	3.91	1.18	2.38 (4H, br s), 1.67 (4H, br s)
P(O-10)	6.73	7.27	3.87	1.18	2.36 (4H, br s), 1.18 (12H, br s)

in addition to usual absorption bands of amino-1,3,5-triazine which appeared at 1500–1600, 1420, and 820 cm^{-1} . The NMR spectra of a series of P(R-10) (Table IV) are very similar to those of the corresponding model compounds.

Solubilities of polymers were examined. All polyguanamines are soluble in dipolar aprotic solvents such as *N*-methyl pyrrolidone (NMP), *N,N*-dimethyl acetamide (DMA), and DMSO, and acidic solvent such as formic acid and sulfuric acid, but insoluble in common organic solvents. Polyguanamines without phenylene moiety in the main chain are soluble in dioxane and THF. The molecular weights of the polymers measured by GPC in THF using polystyrene as a standard were 1–5 $\times 10^3$, except P(O-10) with higher molecular weight because the polycondensation proceeded in homogeneous solution.

Thermal Properties

Glass transition temperatures (T_g) of polyguanamines were evaluated by means of DSC measurements (Table V). T_g s of polyguanamines containing phenylene moiety such as P(pP-*n*) and P(mP-*n*) were observed in the range of 154–224°C higher than those of P(E-*n*), P(B-*n*), and P(O-*n*) without phenylene moiety. T_g s of P(R-*n*) decreased with increasing number of methylene group in the main chain for “R” series as well as for “n” series.

Decomposition temperatures (T_d) of polymers were determined by TGA measurement.

The results are summarized in Table VI. T_d s of polyguanamines containing phenylene group were above 450°C, and those of containing only alkylene group were 400–450°C.

Catalytic Activity for Substitution Reaction

Poly(4-vinylpyridine) is well known as a polymeric ligand. One of authors previously reported that the polymers containing 2-pyridylthio group in the main chain¹⁰ as well

Table V. Glass transition temperatures (T_g) of polyguanamines, P(R-*n*)

<i>n</i>	$T_g/^\circ\text{C}^a$					
	R;	pP	mP	E	B	O
4		197	224	142	116	96
6		164	207	128	109	86
10		177	154	107	89	76

^a Glass transition temperature was measured by DSC at a heating rate of 20°C min⁻¹.

Table VI. Decomposition temperatures (T_d) of polyguanamines, P(R-*n*)

<i>n</i>	$T_d/^\circ\text{C}^a$					
	R;	pP	mP	E	B	O
4		476	478	401	418	427
6		468	478	446	440	436
10		458	458	441	434	443

^a Decomposition temperature was determined by TGA at a heating rate of 10°C min⁻¹.

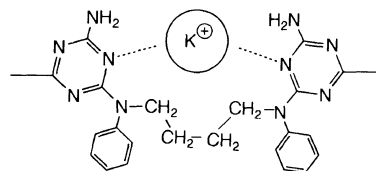
Table VII. Yield of octylthiocyanate of the reaction of 1-bromooctane with potassium thiocyanate under two-phase condition using polyguanamines, P(R-*n*), as a phase-transfer catalyst

Catalyst	Yield ^a /%	Catalyst	Yield/%	Catalyst	Yield/%
None	24	BTEAC ^b	47	2a	56
P(pP-4)	99	P(pP-6)	89	P(pP-10)	74
P(mP-4)	95	P(mP-6)	65	P(mP-10)	77
P(E-4)	99	P(E-6)	96	P(E-10)	93
P(B-4)	99	P(B-6)	76	P(B-10)	99
P(O-4)	99	P(O-6)	70	P(O-10)	99

^a Conditions: 1-bromooctane = 1.65 mmol; potassium thiocyanate = 8.0 mol l⁻¹ (in water), 5 ml; and catalyst = 0.3 mmol at 100°C for 30 h under stirring. ^b Benzyltriethylammonium chloride.

as in the side chain¹¹ worked as polymeric phase-transfer catalyst. The catalytic activity of polyguanamines was tested for the reaction of 1-bromooctane in toluene with potassium thiocyanate in water. Polymers were insoluble in toluene, therefore the reaction proceeded under a triphase system. The results are summarized in Table VII. As can be seen from Table VII, the reaction was achieved in the presence of model compound **2a** and polyguanamines. The activity of **2a** was higher than that of benzyltriethylammonium chloride (BTEAC), a typical phase-transfer catalyst. Further, it should be noted that the catalytic activity of polymers is superior to that of model-compound. These observations can be understood by assumption that a potassium cation interacts with several active sites to form a complex, and the resulting anion attacks the substrate. This cooperative coordination of active sites would function effectively in polymers. Since the pendant amino group of guanamine works as an electron-donating one, the basicity of nitrogen atoms in triazine ring is higher than that of pendant amino group. Morimoto¹² reported that the protonation of 2,4-diamino-1,3,5-triazine and 2,4-diamino-6-methyl-1,3,5-triazine occurred to nitrogen atom of 3-position in triazine ring because the both neighboring carbons bear amino group. Therefore the active site of guanamine will be nitrogen atom in triazine ring. Furthermore, the activity of a series of polymer containing butylene group P(R-4) is a little superior to

that of P(R-6) and P(R-10). This may be that two guanamine groups work cooperatively through shorter butylene group. However, the quantitative evaluation of the reactivity of these polyguanamines requires further studies.



REFERENCES

1. Y. Yuki, T. Kakurai, and T. Noguchi, *Kobunshi Kagaku*, **29**, 127 (1972).
2. Y. Yuki, K. Sumiyosi, T. Kakurai, and T. Noguchi, *Kobunshi Kagaku*, **29**, 942 (1972).
3. T. Seo, H. Ishiwata, and T. Kakurai, *Nippon Kagaku Kaishi*, 2419 (1974).
4. H. K. Reimschuessel, A. M. Lovelace, and E. D. Hgaerman, *J. Polym. Sci.*, **40**, 136 (1959).
5. H. Kunisada, Y. Yuki, S. Kondo, J. Miyatake, and C. Maeda, *Polym. J.*, **22**, 559 (1990).
6. H. Kunisada, Y. Yuki, S. Kondo, K. Adachi, and N. Takahashi, *Polymer*, **33**, 3512 (1992).
7. H. Kunisada, Y. Yuki, S. Kondo, and H. Igarashi, *Polymer*, **32**, 2283 (1991).
8. F. H. S. Curd and F. L. Rose, *J. Chem. Soc.*, 729 (1946).
9. D. Sheehan, A. P. Bentz, and J. C. Petropoulos, *J. Appl. Polym. Sci.*, **6**, 47 (1962).
10. S. Kondo, M. Nakanishi, and K. Tsuda, *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 581 (1985).
11. S. Kondo, M. Nakanishi, K. Yamane, A. Horibe, and K. Tsuda, *J. Appl. Polym. Sci.*, **32**, 4255 (1986).
12. G. Morimoto, *Nihon Kagaku Zasshi*, **87**, 785, 790 (1966).