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### Novel Syntheses of Poly(*N*-Alkyltrimethyleneimine)s by a Replacement of Cyanoethyl Groups in Poly(*N*- $\beta$ -Cyanoethyltrimethyleneimine) with Other Alkyl Groups

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## NOVEL SYNTHESSES OF POLY(*N*-ALKYLTRIMETHYLENEIMINE)S BY A REPLACEMENT OF CYANOETHYL GROUPS IN POLY(*N*- $\beta$ -CYANOETHYLTRIMETHYLENEIMINE) WITH OTHER ALKYL GROUPS

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### ABSTRACT

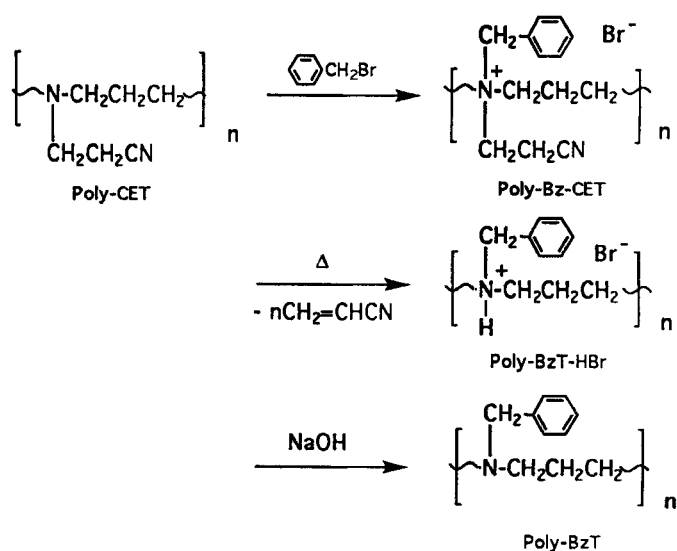
The novel synthesis of poly(*N*-alkyltrimethyleneimine)s by a replacement of cyanoethyl group in poly(*N*- $\beta$ -cyanoethyltrimethyleneimine) (poly-CET) by other alkyl groups is reported herein. The linear poly(*N*-*p*-nitrobenzyltrimethyleneimine) (poly-NBzT) was prepared by alkylation of poly-CET (MW about 6000) with *p*-nitrobenzyl bromide, followed by elimination of cyanoethyl groups by heating. The cyanoethyl groups of poly-CET were completely replaced by *p*-nitrobenzyl groups in this process. Poly(*N*-methyl-trimethyleneimine) (poly-MET) (MW about 3000) was prepared in a similar manner. Further, poly(*N*-alkyltrimethyleneimine)s having two different kinds of *N*-alkyl groups in the polymer chain could be obtained by using various alkylating agents such as benzyl bromide, nitrobenzyl bromide, and methyl iodide.

## INTRODUCTION

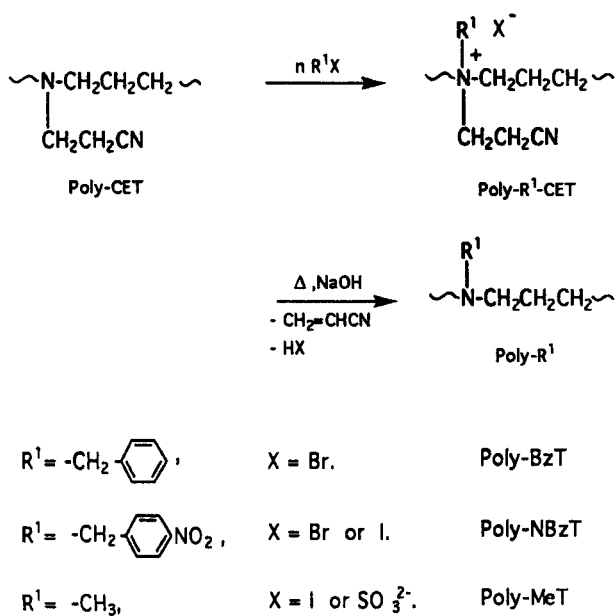
There are few reports on the synthesis of linear polymers having tertiary amino groups as part of the main chain by the ring-opening polymerization of cyclic amines [1] or the polycondensation of alkanediamine and dihaloalkane [2]. The synthesis of linear poly(*N*-alkylalkyleneimine) by those methods is not easy because of the complicated reactions of the amino groups [3], except for linear poly(ethyl-eneimine) which is obtained by such special techniques as the reduction of linear poly(*N*-acetyleneimine) [4] with  $\text{LiAlH}_4$  and the hydrolysis of poly(*N*-2-tetrahydropyranlaziridine) [5].

In a previous paper we reported on synthesis of the high molecular weight linear polymer poly(*N*- $\beta$ -cyanoethyltrimethyleneimine) (poly-CET) by the ring-opening polymerization of *N*- $\beta$ -cyanoethylazetidene [6]. Further, it was reported that syntheses of poly(*N*-benzyltrimethyleneimine) (poly-BzT) by a replacement of the cyanoethyl groups in poly-CET with benzyl groups by alkylation with benzyl bromide, followed by  $\beta$ -elimination of cyanoethyl groups from a quaternary ammonium salt (Scheme 1) [7].

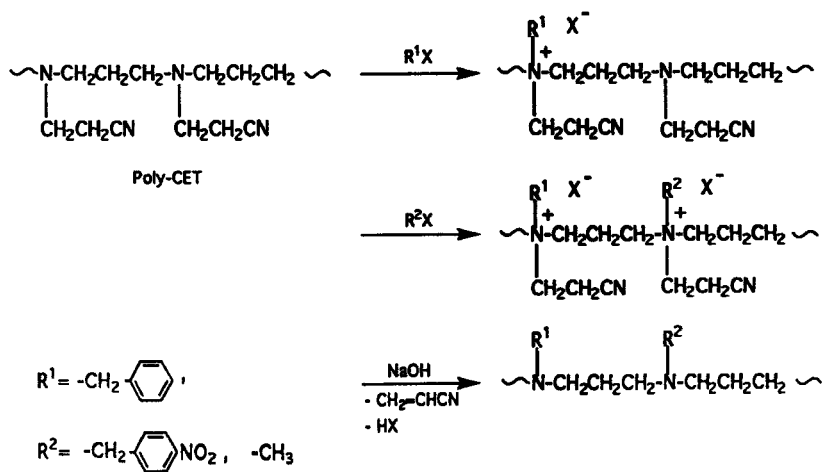
This method is expected to be useful for the novel synthesis of linear poly(*N*-alkyltrimethyleneimine) with any alkyl groups on the nitrogen atom of the polymer. Therefore, in this report we describe the synthesis of poly(*N*-alkyltrimethyleneimine)s by replacement of cyanoethyl groups of poly-CET by other alkyl groups using alkylating agents such as benzyl bromide, methyl iodide, dimethyl sulfate, and *p*-nitrobenzyl bromide (Scheme 2). Further, the synthesis of poly(*N*-alkyltrimethyleneimine)s with two different kinds of *N*-alkyl groups on the nitrogen atom in the polymer chain has been attempted (Scheme 3).



SCHEME 1.



SCHEME 2.



SCHEME 3.

## EXPERIMENTAL

### Materials

Poly-CET as a parent polymer was synthesized by the ring-opening polymerization of *N*-cyanoethylazetidide [6] obtained from azetidide and acrylonitrile [7]. Alkylating agents were obtained from Wako Pure Chemical Industry.

### Procedure

#### Poly(*N*-Benzyltrimethyleneimine) (Poly-BzT)

Benzyl bromide (20 mmol) was added to poly-CET (10 mmol) in acetonitrile (30 mL), then the reaction mixture was heated under reflux for 60 hours. Poly(*N*-benzyltrimethyleneiminium)hydrobromide (Poly-BzT-HBr) precipitated in acetonitrile was neutralized with NaOH (5 mmol) in methanol (10 mL), and the product was dissolved in chloroform (20 mL). The chloroform solution was washed with 1 N NaOH (10 mL) and water successively, and concentrated under reduced pressure. The poly-BzT obtained was washed with dried ether, followed by vacuum drying to constant weight.

#### Poly(*N-p*-Nitorobenzyltrimethyleneimine) (poly-NBzT)

The poly-CET (10 mmol) was reacted with *p*-nitorobenzyl bromide (10 mmol) in acetonitrile under the conditions shown in Table 1. The precipitate was neutralized with NaOH (5 mmol) in methanol (10 mL), and then dissolved in chloroform. The chloroform solution was worked up in a similar manner as above.

#### Poly(*N*-Methyltrimethyleneimine) (Poly-MET)

Poly-CET (10 mmol) was reacted with methyl iodide (10 mmol) for 24 hours at room temperature in acetonitrile, followed by refluxing for 48 hours. The viscous polymer which precipitated was washed with NaOH (1 g) in water (15 mL), and then was dialyzed with water by using cellulose tubing (Size 20/32, Viscose Sales Corp.) for 24 hours. The polymer which precipitated was collected and washed with dry ether, followed by vacuum drying to constant weight.

#### Poly(*N*-Benzyl-*N-p*-nitrobenzyltrimethyleneimine) (Poly-Bz-NBzT)

Benzyl bromide (5 mmol) was added to poly-CET (10 mmol) in acetonitrile (30 mL) and then the reaction mixture was refluxed for 18 hours. After the disappearance of benzyl bromide was confirmed by GLC, *p*-nitrobenzyl bromide (15 mmol) was added to the reaction mixture, and then the reaction mixture was refluxed for 24 hours. The precipitate was treated in a similar manner as poly-BzT.

#### Poly(*N*-Benzyl-*N*-methyltrimethyleneimine) (Poly-Bz-MeT)

Benzyl bromide (5 mmol) was added to poly-CET (10 mmol) in acetonitrile (30 mL) and the reaction mixture was refluxed for 48 hours. After the disappearance of benzyl bromide was confirmed by GLC, methyl iodide was added to this reaction mixture. The reaction mixture was stirred for 80 hours at room temperature, fol-

TABLE 1. Synthesis of Poly(*N*-Alkylethyleneimine)<sup>a</sup>

Run	RX, mmol	Time, h	Polymer					
			R	Yield, %	$\eta_{sp}/C^b$	mp, °C	R <sup>1</sup> , % <sup>c</sup>	MW
1	20 <sup>d</sup>	60	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> —	89	1.31	°	100	6000 <sup>f</sup>
2	15 <sup>g</sup>	60	<i>p</i> NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> —	41	0.53	91–93	95	
3	10 <sup>g</sup>	72	<i>p</i> NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> —	91	1.07	94–96	100	
4	15 <sup>h</sup>	40	<i>p</i> NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> —	57	0.10	75–80	< 80	
5	20 <sup>i</sup>	36	CH <sub>3</sub> —	37	3.44	°	98	3000 <sup>f</sup>
6	10 <sup>i</sup>	48	CH <sub>3</sub> —	45	4.11	°	69	
7	15 <sup>i</sup>	24	CH <sub>3</sub> —	59	5.52	°	61	
8	10 <sup>j</sup>	60	CH <sub>3</sub> —	80	1.48	°	87	

<sup>a</sup>Poly-CET, 10 mmol, in refluxing CH<sub>3</sub>CN, 30 mL.

<sup>b</sup>C = 0.5 g/100 mL HCOOH at 30°C.

<sup>c</sup>Content of alkyl groups (R) in polymer obtained.

<sup>d</sup>Benzyl bromide.

<sup>e</sup>Greasy polymer.

<sup>f</sup>MW: GPC (standard polystyrene).

<sup>g</sup>*p*-Nitrobenzyl bromide.

<sup>h</sup>*p*-Nitrobenzyl iodide.

<sup>i</sup>Methyl iodide: Carried out at room temperature for 24 hours at first.

<sup>j</sup>Dimethyl sulfate.

lowed by heating under reflux for 48 hours. The reaction mixture was worked up in a similar manner as above.

#### Poly(*N*-Methyl-*N*-nitrobenzyltrimethyleneimine) (Poly-Me-NBzT)

Methyl iodide (6.7 mmol) was added to poly-CET (10 mmol) in acetonitrile (10 mL) and stirred for 48 hours at room temperature. Then *p*-nitrobenzylbromide (6.7 mmol) was added to the reaction mixture and the reaction mixture was refluxed for 36 hours. The viscous precipitate in acetonitrile was dialyzed overnight with water by using cellulose tubing, washed with dry ether, followed by vacuum drying to constant weight.

## RESULTS AND DISCUSSION

The synthesis of poly-BzT from poly-CET by the method shown in Scheme 1 was described in a previous paper [8]. The result is listed in Table 1 (Run 1). From the <sup>1</sup>H-NMR spectrum data of poly-BzT shown in Fig. 1(A), it was found that the cyanoethyl groups of poly-CET were replaced completely by benzyl groups. In a previous paper [8] we described that the elimination of acrylonitrile from poly-CET, which had been quaternized with benzyl bromide, occurs readily by heating without the need for any base. This method is to be expected for the novel synthesis of linear poly(*N*-alkyl-trimethyleneimine) in general.

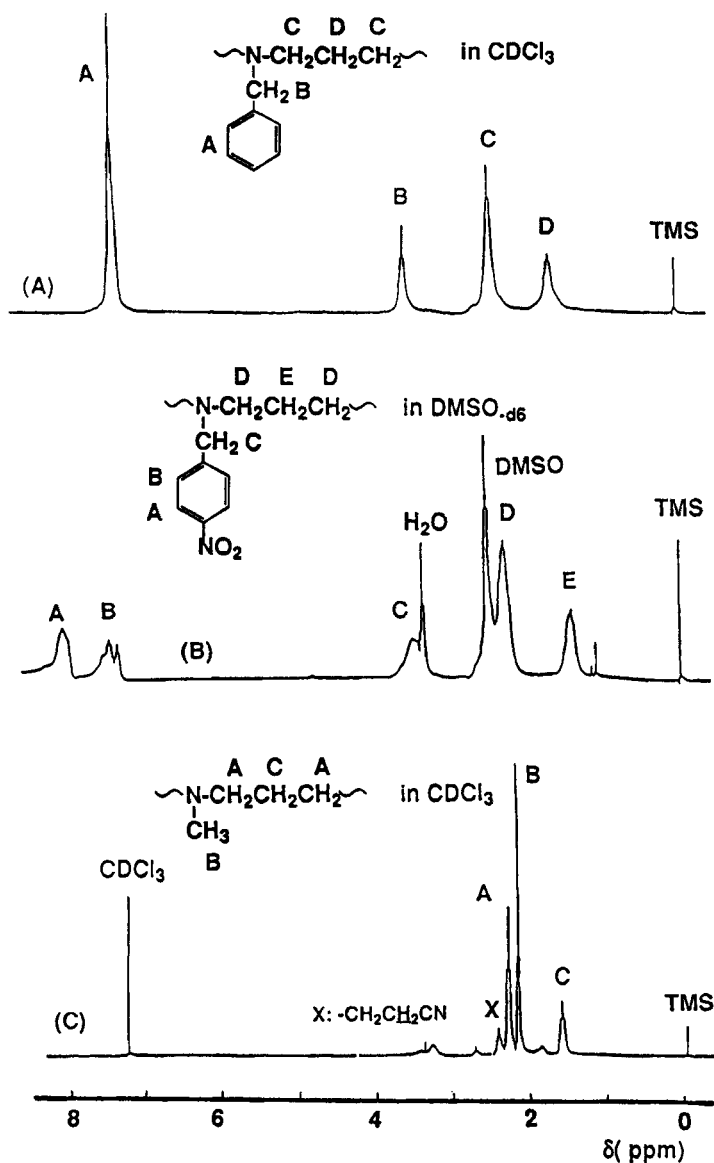
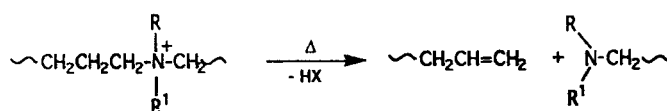


FIG. 1. <sup>1</sup>H-NMR spectra of poly-BzT (A), poly-NBzT (B), and poly-MET (C) obtained from poly-CET.

Therefore, attempts have been made to synthesize poly(*N*-alkyltrimethyleimine)s with other alkylating agents, such as benzyl bromide, methyl iodide, dimethyl sulfate, and *p*-nitrobenzyl bromide as shown in Scheme 2. At first we attempted to synthesize poly(*N*-*p*-nitrobenzyltrimethyleneimine) (poly-NBzT) with *p*-nitrobenzyl bromide or *p*-nitrobenzyl iodide. The results are listed in Table 1 (Runs 2, 3, and 4). The use of equimolar amount of *p*-nitrobenzyl bromide to the amino groups in poly-CET gave a white powder (poly-NBzT, mp 94–96°C), and the



SCHEME 4.

yield was about 90%. The  $^1\text{H-NMR}$  spectrum of poly-NBzT (Table 1, Run 3) in  $\text{DMSO-}d_6$  is shown in Fig. 1(B). The  $^1\text{H-NMR}$  spectrum consists of five absorptions, two due to phenyl protons (A:  $\delta 8.08$ , 2H and B:  $\delta 7.40$ , 2H), one from the methylene proton attached to the phenyl group (C:  $\delta 3.49$ , 2H), one from the methylene proton adjacent to the tertiary amino groups (D:  $-\text{N}-\text{CH}_2-$   $\delta 2.26$ , 4H), and the last one from the methylene proton in the center of the trimethylene group (E:  $-\text{CH}_2-$   $\delta 1.41$ , 2H). Those peaks agree closely with that of *N,N'*-diethyl-*p*-nitrobenzylamine. The IR spectrum of poly-NBzT indicated the peaks of  $\nu_{\text{C-N}}$  at  $850\text{ cm}^{-1}$ ,  $\nu_{\text{s NO}_2}$  at  $1335\text{ cm}^{-1}$ , and  $\nu_{\text{as NO}_2}$  at  $1505\text{ cm}^{-1}$ . It is shown by the  $^1\text{H-NMR}$  and IR spectra that all of cyanoethyl groups in poly-CET were completely replaced by *p*-nitrobenzyl groups. However, in this reaction the use of a large excess of *p*-nitrobenzyl bromide or *p*-nitrobenzyl iodide to the amino group resulted in a lower reduced viscosity and a lower overall yield. This is assumed to be due to main chain scission of the poly(quaternary ammonium salt) as shown in Scheme 4. Consequently, it was found that the use of an equimolar amount of *p*-nitrobenzyl bro-

TABLE 2. Synthesis of Poly(Trimethyleneimine) with Different Alkyl Groups on N Atoms in the Main Chain<sup>a</sup>

Run	Alkyl group	Yield, %	$\eta_{\text{sp}}/C^{\text{b}}$	mp, °C	R <sup>1</sup> , % <sup>c</sup>	R <sup>2</sup> , % <sup>c</sup>	MW
9	$\text{C}_6\text{H}_5\text{CH}_2$ <sup>-d</sup>	89	1.12	°	50	47	9700 <sup>f</sup>
	<i>p</i> $\text{NO}_2\text{C}_6\text{H}_5\text{CH}_2$ <sup>-e</sup>						
10	<i>p</i> $\text{NO}_2\text{C}_6\text{H}_5\text{CH}_2$ <sup>-g</sup>	99	0.49		50	45	
	$\text{C}_6\text{H}_5\text{CH}_2$ <sup>-h</sup>						
11	$\text{C}_6\text{H}_5\text{CH}_2$ <sup>-h</sup>	82	1.0		50	46	
	$\text{CH}_3$ <sup>-i</sup>						
12	$\text{CH}_3$ <sup>-i</sup>	24	0.25		50	46	
	<i>p</i> $\text{NO}_2\text{C}_6\text{H}_5\text{CH}_2$ <sup>-j</sup>						

<sup>a</sup>Poly-CET, 10 mmol, refluxed in  $\text{CH}_3\text{CN}$ , 30 mL.

<sup>b</sup> $C = 0.5\text{ g}/100\text{ mL HCOOH}$  at  $30^\circ\text{C}$ .

<sup>c</sup>Content of R<sup>1</sup> and R<sup>2</sup> groups in polymer.

<sup>d</sup>Poly-Bz-NBzT: Reacted with benzyl bormide at first.

<sup>e</sup>Greasy polymer.

<sup>f</sup>MW: GPC (standard polystyrene).

<sup>g</sup>Poly-NBz-NBzT: Reacted with *p*-nitrobenzyl bormide at first.

<sup>h</sup>Poly-Me-BzT: Reacted with benzyl bormide at first.

<sup>i</sup>Poly-Me-NBzT: Reacted with methyl iodide at first.



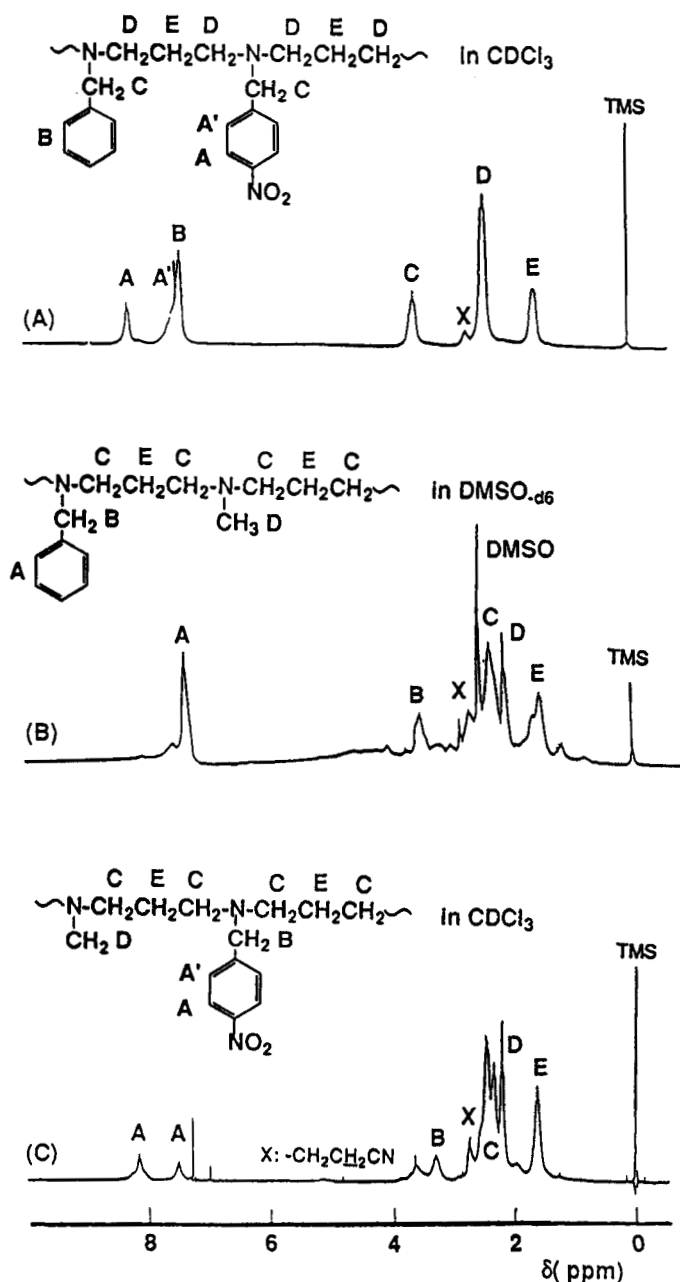


FIG. 2. <sup>1</sup>H-NMR spectra of poly-Bz-NBzT (A), poly-Bz-MET (B) and poly-ME-NBzT (C) obtained from poly-CET.

vide to the amino groups in the polymer gave the most satisfactory result (Table 1, Run 3).

To test the generality of this method (Scheme 2), the synthesis of poly(*N*-methyltrimethyleneimine) (poly-MET) was attempted using methyl iodide or dimethyl sulfate. The results are listed in Table 1 (Runs 5-8). The poly-MET was

obtained as a white, greasy polymer with a molecular weight of about 3000 (GPC, polystyrene standard in THF) (Run 5). The highest degree of conversion (98%) of cyanoethyl groups on poly-CET into methyl groups was achieved by the use of an excess of methyl iodide. From the  $^1\text{H-NMR}$  spectrum of the poly-MET shown in Fig. 1(C) with peak assignments, a slight residual cyanoethyl group in poly-MET was observed. Poly-MET showed a higher reduced viscosity compared with poly-BzT and poly-NBzT in formic acid. It can be presumed that this phenomenon is due to the higher basicity of poly-MET.

From these results it appears feasible to synthesize linear poly(*N*-alkyltrimethyleneimine)s having a variety of alkyl groups on the nitrogen atom in the main chain.

Further, the syntheses of poly(*N*-alkyltrimethyleneimine) having two kinds of alkyl groups on the nitrogen atoms in the polymer chain (Scheme 3) has been demonstrated. The results are shown in Table 2 (Run 9).

The polymer poly-Bz-NBzT was a white, greasy substance with a molecular weight of about 9700 (GPC, polystyrene standard in THF). The structure was proven from its  $^1\text{H-NMR}$  (Fig. 2, A) and IR (Fig. 3, A). The assignment of the NMR and IR signals are given in their figures. The IR spectrum shows absorptions assigned to  $\nu_{\text{C-N}}$  ( $850\text{ cm}^{-1}$ ),  $\nu_{\text{s NO}_2}$  ( $1335\text{ cm}^{-1}$ ), and  $\nu_{\text{as NO}_2}$  ( $1505\text{ cm}^{-1}$ ). Consequently, it has been confirmed that the main chain of poly-Bz-NBzT is made up of *N*-benzyltrimethyleneimine units (50%) and *N-p*-nitrobenzyltrimethyleneimine units (47%).

From the synthesis of poly-Bz-NBzT described above, the reaction of poly-CET with *p*-nitrobenzyl bromide followed by benzyl bromide has been demonstrated. The result was listed in Table 2 (Run 10). The  $^1\text{H-NMR}$  and IR spectra of the polymer agree very closely with that of poly-Bz-NBzT obtained by means of the method described above.

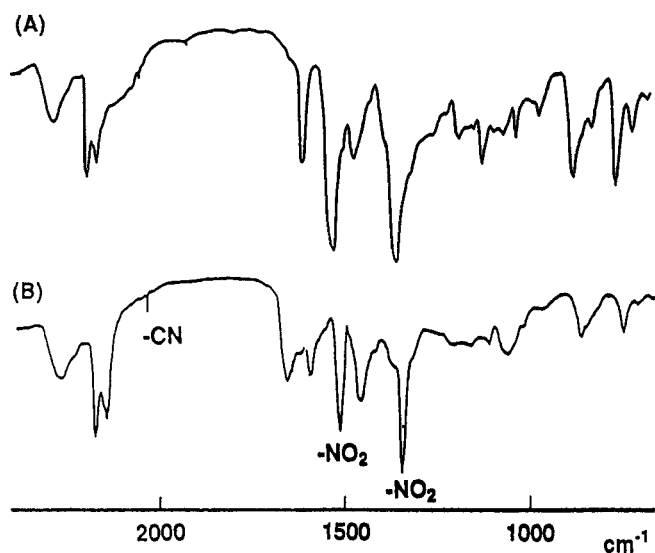


FIG. 3. IR spectra of poly-Bz-NBzT (A) and poly-ME-NBzT (B) obtained from poly-CET (KBr disk).

TABLE 3. Solubility of Poly(*N*-Alkyltrimethyleneimine)s<sup>a</sup>

Alkyl group	(CH <sub>3</sub> ) <sub>2</sub> CO	CHCl <sub>3</sub>	CH <sub>3</sub> CN	THF	DMSO	CH <sub>3</sub> OH
CNCH <sub>2</sub> CH <sub>2</sub> —	+	+	+	—	—	—
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> —	+	+	—	+	+	—
<i>p</i> NO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> —	+	—	—	+	+	—
CH <sub>3</sub> —	—	+	—	—	+	+
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> —	—	+	—	+	+	—
<i>p</i> NO <sub>2</sub> C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> —	—	+	+	—	+	+
CH <sub>3</sub> —	—	—	—	—	+	+
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> —	—	—	—	—	+	+

<sup>a</sup>+ = soluble, — = insoluble.

The syntheses of poly-Bz-MeT and poly-ME-NBzT containing two different kinds of *N*-substituted alkyl groups such as benzyl-*p*-nitrobenzyl-, or methyl groups was worked up in the same manner as described above. The results are listed in Table 2 (Runs 11 and 12). <sup>1</sup>H-NMR and IR spectra obtained from these polymers are shown in Fig. 2(B, C) and Fig. 3(B, C). It was confirmed that the polymers are composed of the two different kinds of alkyl groups as pendant groups.

The synthesis of linear poly(*N*-alkyltrimethyleneimine) containing two different kinds of alkyl groups on the nitrogen atom in the main chain by a one-pot method has been shown. However, the <sup>1</sup>H-NMR spectrum of these polymers indicated a peak of  $\delta$ 2.26, attributed to a slight residual of cyanoethyl groups in the polymer, and the IR spectrum of it indicated a peak at 2240 cm<sup>-1</sup> ( $\nu_{C\equiv N}$ ) as evidence for trace quantities, too. The solubilities of the polymers thus prepared are listed in Table 3.

## CONCLUSION

It has been found that novel poly(*N*-alkyltrimethyleneimine)s having varying alkyl groups on the nitrogen atom in the main chain can be synthesized by means of an alkylation of poly-CET, followed by elimination of cyanoethyl groups from the quaternary polymer intermediate. Further, the synthesis of linear poly(*N*-alkyltrimethyleneimine) containing two different kinds of alkyl groups has been demonstrated.

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