Preparation of Star-Branched Polymers with Cyclotriphosphazene Cores

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ABSTRACT: Hexakis[*p*-(hydroxymethyl)phenoxy]cyclotriphosphazene was prepared by the reaction of hexachlorocyclotriphosphazene with the sodium salt of 4-hydroxybenzaldehyde and subsequent reduction of aldehyde groups to alcohol groups by using sodium borohydride. The bromination reaction was carried out by using hydrobromic acid–sulfuric acid to give hexakis[*p*-(bromomethyl)phenoxy]cyclotriphosphazene. This compound was employed in initiating polymerization of 2-methyl-2-oxazoline to produce six-armed, star-branched polymers. Monofunctional initiator, $N_3P_3(OC_6H_5)_5(OC_6H_4\text{-}p\text{-}CH_2Br)$, was also prepared and used for initiating the polymerization of 2-methyl-2-oxazoline to result in linear polymers. Molecular weights and DP's per an arm of the polymers were determined by gel permeation chromatography and ^1H NMR, respectively. The molecular weight of the linear polymer measured by GPC was much higher than that of the star-branched polymer when their molecular weights determined by ^1H NMR were nearly same. The linear polymer (DP = 31) with a bulky hydrophobic head and a hydrophilic chain exhibited nonionic surfactant behavior, forming micelles above a polymer concentration of about 0.1% by weight. The star-branched polymers had a hydrophobic core and hydrophilic branches. The surface tension of the aqueous solution of the star-branched polymer (DP = 13.4 per branch) decreased very slowly as polymer concentration increased, and any evidence for forming micelles was not observed. *N*-Acetyl groups of star-branched polymers were removed by hydrolysis under acidic conditions to give the polymers with N-protonated poly(ethylenimine) branches.

Introduction

Cyclotriphosphazenes exhibit useful thermal and chemical properties such as self-extinguishibility, flame retardancy, and oil repellance, which are imparted mainly by the presence of nitrogen and phosphorus atoms in the ring.[1,2] Considerable interest exists in the use of cyclotriphosphazenes for improving properties of organic polymers. For the synthesis of cyclotriphosphazenes, hexachlorocyclotriphosphazene is a versatile starting material. Chlorine groups on phosphorus atoms are easily replaced with various nucleophiles to form reactive cyclotriphosphazenes. They have been used as pendants, cross-linking agents, and additives in an effort to improve thermal properties of organic polymers.[3-10] Thermal polymerization of acetylenic group[11] or maleimido group[12,13] substituted cyclotriphosphazene was also reported.

In the present paper, we report on the preparation of star-branched polymers with cyclotriphosphazene cores. Star-branched polymers are important for their enhanced segment density and show unique solution properties compared to linear polymers.[14] From the practical viewpoint, they find uses as cross-linking agents, surface-active agents, and prepolymers for block copolymers.

Cyclotriphosphazenes have the following advantages as branch points. First, the flexible synthetic methodology developed for the preparation of cyclotriphosphazenes with various substituents allows us to obtain multifunctional initiators or terminators with ease. Second, the thermal properties of the cyclotriphosphazene ring mentioned above can be conferred to the resulting polymers, especially, of low molecular weights.

We chose to introduce benzyl halide groups onto the phosphazene ring. Benzyl halide compounds are widely used for initiating ring-opening polymerization of cyclic iminoethers, e.g., 2-alkyl-2-oxazoline.[15,16] They also terminate effectively anionic polymerization of several vinyl monomers.[17,18] All six chloro groups of hexachlorocyclotriphosphazene were replaced by 4-formylphenoxy groups. Formyl groups were converted to bromomethyl groups, resulting in a cyclotriphosphazene containing six reactive sites. Polymerization of 2-methyl-2-oxazoline initiated by the cyclotriphosphazene produced six-armed, star-branched polymers.

Experimental Section

Materials and Instrumentation. Hexachlorocyclotriphosphazene (Aldrich) was purified by fractional vacuum sublimation at 60 °C (0.5 mmHg). Reagent-grade solvents were dried and purified as follows: Tetrahydrofuran and 1,4-dioxane were distilled over a sodium–potassium alloy. Carbon tetrachloride was distilled over P_2O_5. Toluene was distilled over CaH_2. All the other reagents were purchased from Aldrich and were used without further purification. Proton-decoupled ^{31}P NMR spectra were obtained with the use of a Bruker AM-300 spectrometer. Chemical shifts were reported in ppm relative to 85% H_3PO_4 at 0 ppm. ^1H NMR spectra were recorded on a Bruker AM-300 or a JEOL PMX60 spectrometer. Gel permeation chromatography was carried out with a Waters HPLC system fitted with a refractive index detector and a Waters Ultrahydrogel 250 column. Water was used as the eluent. Approximate calibration of the column was accomplished by means of narrow molecular weight poly(ethylene glycol) standards obtained from Waters. The surface tension of the polymers in water was measured by a Fisher tensiometer at 22 °C. Elemental analyses were performed by a

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Table 1. Cyclotriphosphazene Characterization Data

compd	^{1}H NMR[a] (ppm)	^{31}P NMR[a] (ppm)	elem anal. (%)
3	6.86, 7.26 (dd, 24H, C_6H_4), 5.23 (t, 6H, OH), 4.49 (d, 12H, CH_2)	3.0	found: C, 57.45; H, 4.81; N, 4.79 calcd: C, 57.74; H, 4.84; N, 4.81
4	6.90, 7.25 (dd, 24H, C_6H_4), 4.50 (s, 12H, CH_2)	3.0	found: C, 40.75; H, 2.94; N, 3.37 calcd: C, 40.32; H, 2.91; N, 3.36
9	6.70–7.30 (m, 29H, C_6H_4 and C_6H_5), 4.49 (s, 2H, CH_2)	3.0	found: C, 55.50; H, 3.87; N, 5.37 calcd: C, 56.50; H, 3.98; N, 5.34

[a] The ^{1}H and ^{31}P NMR spectra were obtained in dimethyl-d_6 sulfoxide.

Carlo Erba 1108 or Perkin-Elmer 240C elemental analyzer at Korea Research Institute of Chemical Technology and Korea Basic Research Center.

Preparation of $N_3P_3(OC_6H_4$-*p*-CHO)$_6$ (2). This compound was prepared according to the literature[19] with minor modification. 4-Hydroxybenzaldehyde (10 g, 82 mmol) was dissolved in toluene (100 mL). The solution was refluxed for 1 h and concentrated to 20 mL by using a Dean–Stark trap. To the concentrate was added tetrahydrofuran (100 mL) and then sodium hydride (1.96 g, 82 mmol). The reaction mixture was stirred for 4 h at room temperature. A solution of hexachlorocyclotriphosphazene (3.16 g, 9.1 mmol) in tetrahydrofuran (20 mL) was added dropwise to the reaction mixture. After stirring for 48 h at refluxing temperature, the product was isolated following the procedure in the literature (yield 83%).

Preparation of $N_3P_3(OC_6H_4$-*p*-$CH_2OH)_6$ (3). To a solution of $N_3P_3(OC_6H_4$-*p*-$CHO)_6$ (2 g, 2.3 mmol) in tetrahydrofuran–methanol (140 mL, 1:1) was added sodium borohydride (0.56 g, 15.0 mmol) at room temperature. The reaction mixture was stirred for 14 h at the same temperature. After evaporation of the solvents, the resulting solids were recrystallized from 90% ethanol to give 1.5 g (yield 75%, mp 213–214 °C). ^{1}H NMR, ^{31}P NMR, and elemental analysis data are summarized in Table 1.

Preparation of $N_3P_3(OC_6H_4$-*p*-$CH_2Br)_6$ (4). $N_3P_3(OC_6H_4$-*p*-$CH_2OH)_6$ (1 g, 1.1 mmol) was dissolved in a mixture of 48% HBr (3.5 mL) and concentrated H_2SO_4 (1 mL), and the solution was refluxed for 5 h. Precipitates were collected by filtration and washed with a copious amount of water. The product was isolated by column chromatography on silica gel (20% ethyl acetate in hexane) to give 1.2 g (yield 85%, mp 146–148 °C). ^{1}H NMR, ^{31}P NMR, and elemental analysis data are summarized in Table 1.

Bromination of $N_3P_3(OC_6H_4CH_3)_6$ (5). $N_3P_3(OC_6H_4CH_3)_6$ was prepared according to the literature[20] with minor modification. *p*-Cresol (2.3 g, 93 mmol) was dissolved in toluene (100 mL). The solution was refluxed for 1 h and concentrated to 50 mL by using a Dean–Stark trap. To the concentrate was added tetrahydrofuran (50 mL) and then sodium hydride (2.3 g, 96 mmol). The reaction mixture was stirred for 4 h at room temperature. A solution of hexachlorocyclotriphosphazene (2.5 g, 7.2 mmol) in tetrahydrofuran (20 mL) was added dropwise to the reaction mixture. After stirring for 48 h at refluxing temperature, the product was isolated following the procedure in the literature (yield 85%). To a solution of $N_3P_3(OC_6H_4CH_3)_6$ (2 g, 2.6 mmol) in carbon tetrachloride (100 mL) was added *N*-bromosuccinimide (3 g, 16.9 mmol) and benzoyl peroxide (0.2 g, 0.8 mmol) at room temperature. The solution was stirred for 3 h at the same temperature. Precipitates were removed by filtration. The filtrate was concentrated to 15 mL and added dropwise to a mixture of pentane and acetone (150 mL, 4:1). Precipitates were collected by filtration and column chromatographed on slica gel (20% ethyl acetate in hexane). The products were recrystallized from hexane–methylene chloride to give 2.3 g.

Preparation of $N_3P_3(OC_6H_5)_5(OC_6H_4$-*p*-CHO) (7). The procedure by Allcock and Neenan[21] was followed with modification. To a solution of phenol (7.52 g, 80 mmol) in THF (120 mL) was added sodium hydride (1.92 g, 80 mmol). After stirring for 4 h at room temperature, a solution of hexachlorocyclotriphosphazene (5.0 g, 14.4 mmol) in THF (80 mL) was added dropwise to the solution. The reaction mixture was stirred for 24 h at room temperature. A solution of the sodium salt of 4-hydroxybenzaldehyde in THF (30 mL) prepared from 4-hydroxybenzaldehyde (2.44 g, 20 mmol) and sodium hydride (0.48 g, 20 mmol) was added dropwise to the reaction mixture. After stirring for 20 h at refluxing temperature, the mixture was filtered through a silica gel column (5 × 15 cm). The filtrate was concentrated by evaporation under reduced pressure. The product was isolated by column chromatography on silica gel (20% ethyl acetate in hexane) as a clear oil, which was solidified in several days at room temperature (yield 52%).

Preparation of $N_3P_3(OC_6H_5)_5(OC_6H_4$-*p*-$CH_2OH)$ (8). The procedure by Allcock and Neenan[21] was followed. The product was isolated by column chromatography on silica gel (ethyl acetate–hexane) as a clear oil, which was solidified in several days at room temperature. From compound 7 (3.8 g, 5.3 mmol) and sodium borohydride (0.20 g, 5.3 mmol) was obtained 3.4 g of the product (89% yield).

Preparation of $N_3P_3(OC_6H_5)_5(OC_6H_4$-*p*-$CH_2Br)$ (9). To a solution of compound 8 (1.5 g, 2.0 mmol) in 1,4-dioxane (20 mL) was added dropwise a solution of phosphorus tribromide (0.65 g, 2.4 mmol) in 1,4-dioxane (10 mL), and the reaction mixture was stirred for 10 h at room temperature. The solvent was removed by evaporation under reduced pressure. The residue was dissolved in chloroform (50 mL). The solution was washed with water (2 × 20 mL) and dried over anhydrous magnesium sulfate. After filtration and evaporation, the product was isolated by column chromatography on silica gel (20% ethyl acetate in hexane) as an oil (1.4 g, 85% yield). ^{1}H NMR, ^{31}P NMR, and elemental analysis data are summarized in Table 1.

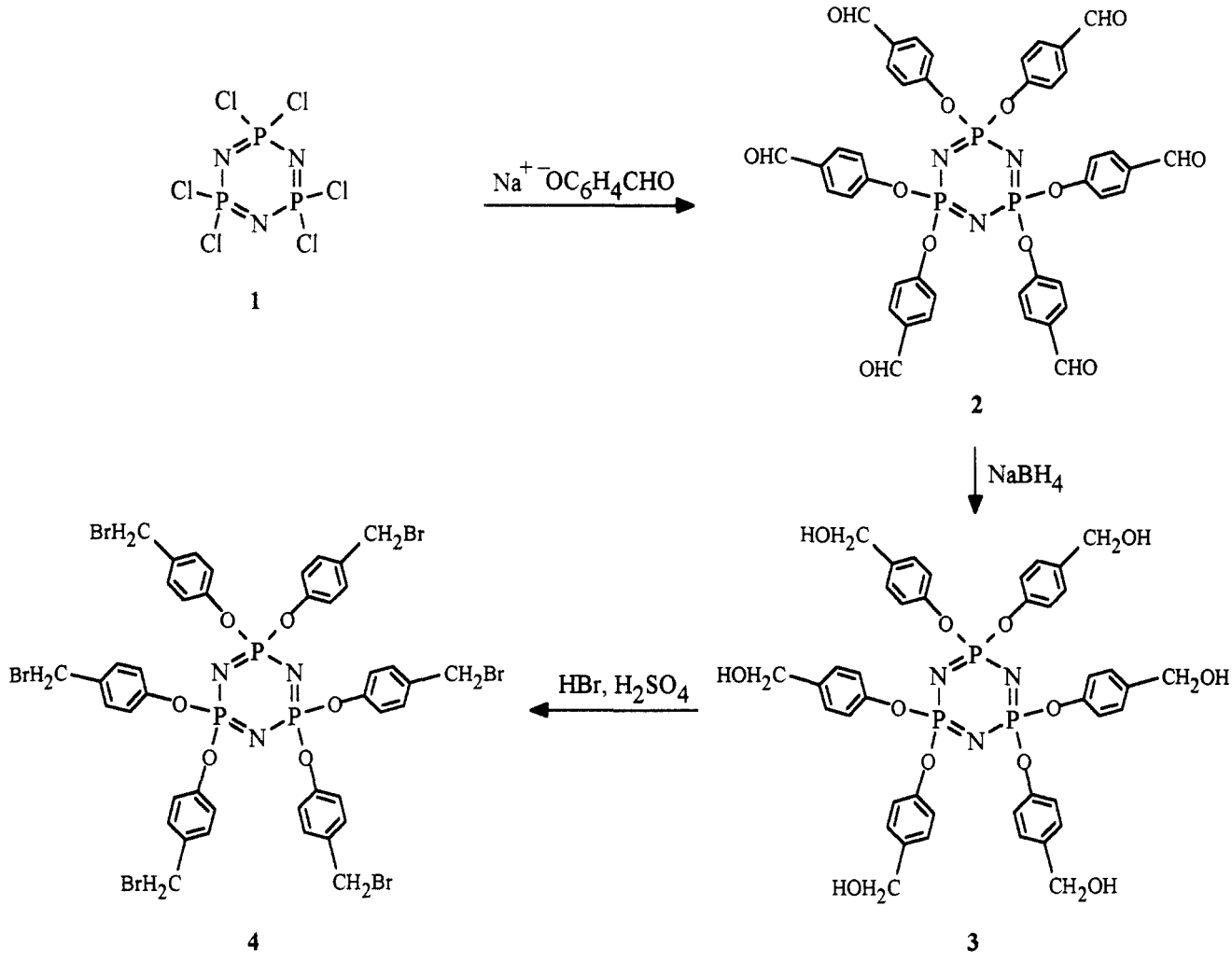
Polymerization of 2-Methyl-2-oxazoline. Compound 4 (0.6 g, 0.48 mmol) or 9 (1.0 g, 1.3 mmol) and the appropriate amount of 2-methyl-2-oxazoline were weighed into a 15-mL polymerization tube. The tube was then cooled in a dry ice–acetone bath and evacuated. The tube was removed from the bath and allowed to thaw. The tube was sealed after repeating the freeze–thaw cycle twice more and placed in the oil bath at 80 °C. After 12 h, the resulting amber glassy polymer was dissolved in methylene chloride (20 mL). The solution was added dropwise to diethyl ether (300 mL) and the precipitated polymer was collected by filtration. The polymer was further purified by precipitation twice more from methylene chloride into diethyl ether and then dried at 80 °C (1–2 mmHg). The remaining oxazolinium end groups were hydrolyzed as follows. A polymer (1 g) was dissolved in an aqueous 0.1 N NaOH solution (20 mL). After stirring for 5 h at room temperature, the resulting solution was dialyzed against water for 2 days by using a cellulose membrane (M_w cutoff 1000) and then concentrated to dryness with a freeze dryer. Anal. Calcd for $C_{169.2}H_{284.6}N_{34.8}O_{43.8}P_3$ (polymer **10a**): C, 56.76; H, 7.45; N, 13.62; C/N, 4.17. Found: C, 55.01; H, 7.48; N, 13.22; C/N, 4.16. Anal. Calcd for $C_{363.6}H_{604.8}N_{83.4}O_{92.4}P_3$ (polymer **10b**): C, 56.59; H, 7.90; N, 15.14; C/N, 3.74. Found: C, 54.87; H, 7.98; N, 14.59; C/N, 3.76. Anal. Calcd for $C_{594}H_{1008}N_{141}O_{150}P_3$ (polymer **10c**): C, 56.54; H, 8.05; N, 15.65; C/N, 3.61. Found: C, 54.62; H, 8.03; N, 15.19; C/N, 3.60. Anal. Calcd for $C_{161}H_{249}N_{34}O_{38}P_3$ (polymer 11): C, 57.52; H, 7.47; N, 14.17; C/N, 4.06. Found: C, 56.85; H, 7.44; N, 14.02; C/N, 4.05. ^{1}H NMR (polymer **10b** in DMSO-d_6): δ 1.9–2.3 (br, $COCH_3$), 3.2–3.7 (br, NCH_2), 4.4–4.6 (br, $PhCH_2$), 6.8–7.2 (br, C_6H_4). ^{1}H NMR (polymer 11 in $CDCl_3$): δ 1.9–2.3 (br, $COCH_3$), 3.2–3.7 (br, NCH_2), 4.4–4.6 (br, $PhCH_2$), 6.7–7.3 (br, C_6H_4 and C_6H_5).

Hydrolysis of Star-Branched Polymers. A polymer (1 g) was dissolved in 5 N HCl, and the solution was refluxed for 5 h. The solution was dialyzed against water for 2 days by using a cellulose membrane (M_w cutoff 1000) and then concentrated to dryness with a freeze dryer.

Results and Discussion

Scheme 1 outlines the synthesis of hexakis[*p*-(bromomethyl)phenoxy]cyclotriphosphazene. Reaction of hexachlorocyclotriphosphazene with the sodium salt of

Scheme 1



Scheme 2

$P_3N_3(OC_6H_4CH_3)_6$ —(N-bromosuccinimde, benzoyl peroxide, CCl_4)→ $P_3N_3(OC_6H_4CH_2Br)_x(OC_6H_4CHBr_2)_y(OC_6H_4CH_3)_z$

5 6

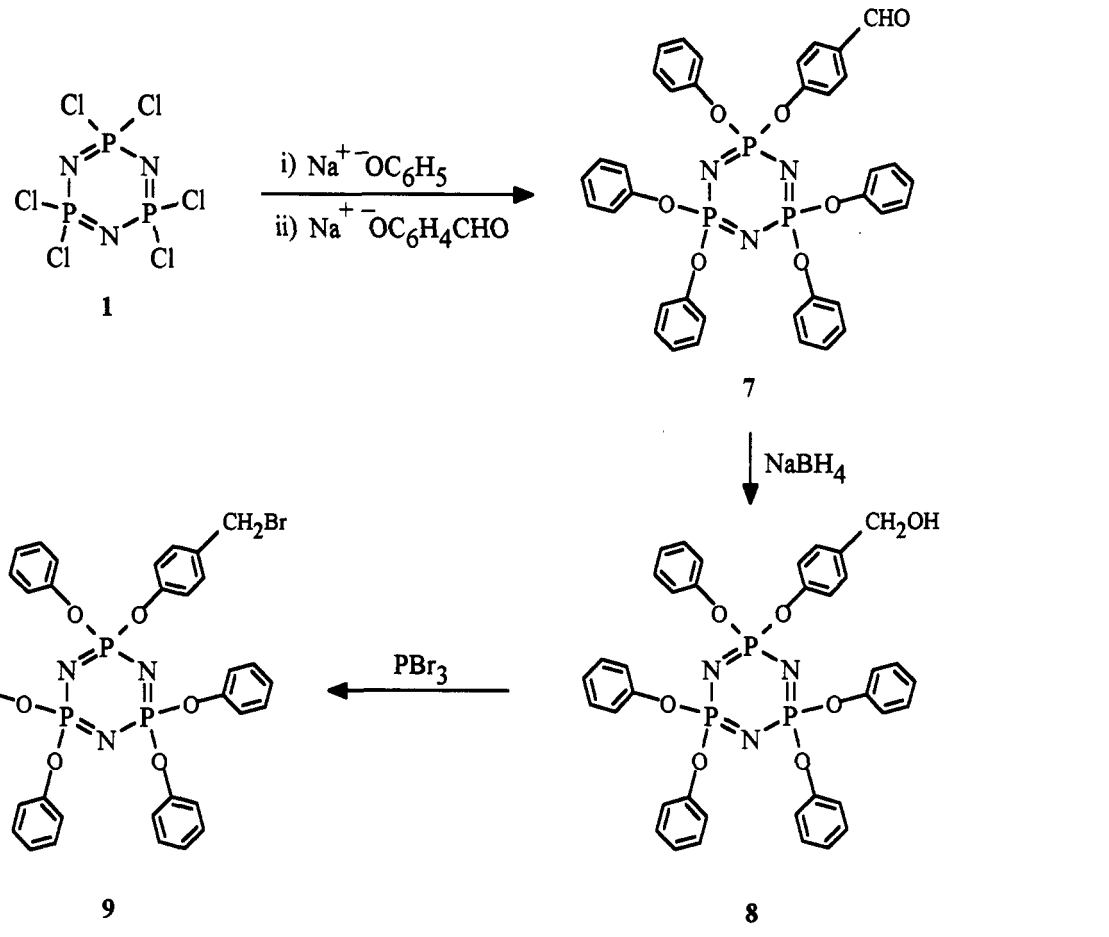
4-hydroxybenzaldehyde yielded $N_3P_3(OC_6H_4\text{-}p\text{-}CHO)_6$ (**2**). Aldehyde groups of compound **2** were easily reduced to alcohol groups by using sodium borohydride. Several reagents are available for converting alcohols to alkyl bromides. Bromination reagents based on phosphorus compounds were found unemployable, however, because they formed insoluble intermediates through reaction with the hydroxyl groups of compound **3**. The bromination reaction was achieved by using hydrobromic acid–sulfuric acid. Compound **4** was characterized by elemental analysis and ^{31}P and ^1H NMR spectroscopy (Table 1). ^1H NMR spectroscopy showed that all six hydroxyl groups were replaced by bromo groups. In the spectrum, two doublet peaks for aromatic ring protons appeared at 6.90 and 7.25 ppm and a singlet peak for bromomethyl group protons was observed at 4.50 ppm.

As an alternative route for the preparation of compound **4**, a bromination reaction of compound **5** with *N*-bromosuccinimide and benzoyl peroxide was attempted according to the literature[20] (Scheme 2). The product was isolated by column chromatography and further purified by recrystallization. ^1H NMR spectroscopy showed two peaks at 6.8 and 2.6 ppm in addition to the peaks for aromatic ring protons and bromomethyl protons. They were assigned to dibromomethyl protons and unreacted methyl protons. When calculated based on peak area, 70% and 22% of methyl groups on a phosphazene ring were converted into methyl bromides and methyl dibromides, respectively, and the other 8% of methyl groups were unreacted. Since the ^1H NMR spectrum measured after further recrystallization was little changed, it was concluded that bromomethyl groups and one or more dibromomethyl groups existed on the same ring.

For comparison with the initiator containing six reactive sites, monofunctional initiator **9** was also prepared according to Scheme 3. Compound **7** was obtained by following the procedure in the literature[21] except that pentaphenoxychlorocyclotriphosphazene was not isolated before reaction with the sodium salt of *p*-hydroxybenzaldehyde. The aldehyde group of compound **7** was reduced to an alcohol group by using sodium borohydride. The bromination reaction of compound **8** with 48% HBr–concentrated H_2SO_4 was unsuccessful because the compound was insoluble in the aqueous acids. The reaction was accomplished by using phosphorus tribromide in 1,4-dioxane. No precipitation occurred during the reaction, unlike that of compound **3**. Compound **9** was characterized by elemental analysis and ^{31}P and ^1H NMR spectroscopy (Table 1).

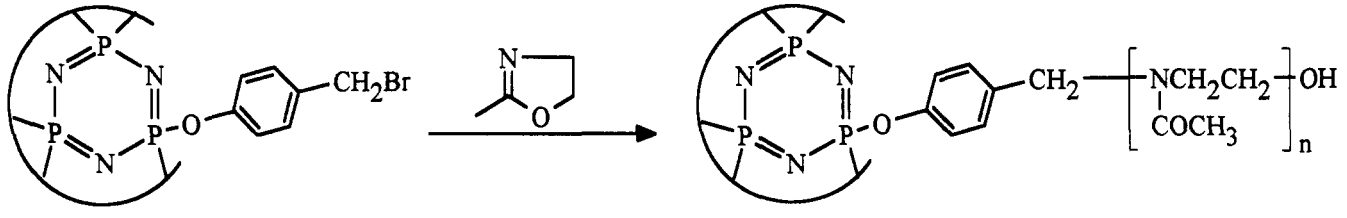
Polymerization of 2-methyl-2-oxazoline initiated by compound **4** or **9** was carried out in the bulk state at 80 °C (Scheme 4). The polymers were purified by precipitation from methylene chloride in diethyl ether. To convert the remaining oxazolinium end groups into

Scheme 3



1 7 9 8

Scheme 4



4 (or 9) 10 (or 11)

Table 2. Polymerization Results of 2-Methyl-2-oxazoline

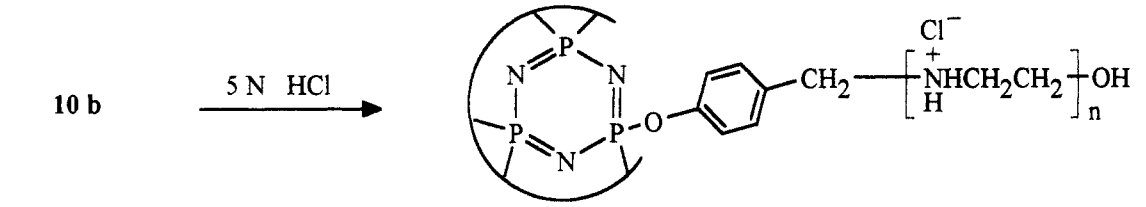
				GPC results[a]				
polymer	initiator	yield, %	[M]/[I]	M_n	M_w	PDI	DP[b]	calcd M_n[c]
10a	4	92	30	4100	4900	1.2	5.3	3600
10b	4	95	80	10100	13000	1.3	13.4	7700
10c	4	96	130	23300	24300	1.1	23.0	12600
11	9	90	30	8200	8300	1.1	31.0	3400

[a] Measured by using poly(ethylene glycol) standards and water as the eluent. [b] Degree of polymerization per a branch determined by ^{1}H NMR spectroscopy. [c] Calculated from the number-average degree of polymerization on the basis of six-armed, star-branched structures of the polymers.

hydroxyl groups, the polymers were treated with an aqueous NaOH solution and then purified by dialysis against water. Polymerization results are summarized in Table 2.

In the ^{1}H NMR spectra of star-branched polymer **10b** and compound **4**, the peaks for aromatic ring protons and methylene protons of the polymer core appeared at the same positions as those of the initiator. The peaks for methyl protons and *N*-methylene protons of the polymer chain showed up at 1.9–2.3 and 3.2–3.7 ppm, respectively. The number-average degree of polymerization (DP) per arm was calculated from the peak area ratio of phenyl protons to methyl protons in the ^{1}H NMR spectrum. The polymerization of 2-methyl-2-oxazoline is known to follow a living polymerization pathway.[15] The number-average degree of polymerization of the polymers was found to be close to the feed ratio of monomer to initiator. For polymers **10a–c** molecular weights measured by gel permeation chromatography were higher than those calculated from the number-average degree of polymerization on the basis of six-armed, star-branched structures of the polymers probably because poly(ethylene glycol) standards were used for calibration. The number-average molecular weight of polymer **10a** with a DP per arm of 5 was 4100, while the number-average molecular weights of polymer **10b** with a DP per arm of 13 and of polymer **10c**

Scheme 5



12

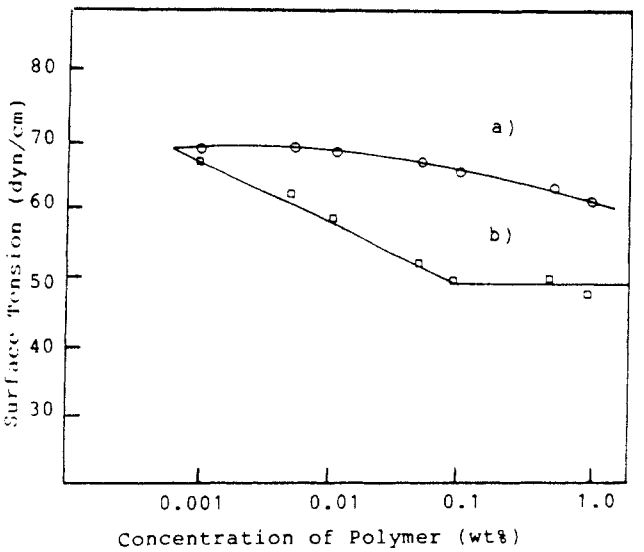


Figure 1. Concentration–surface tension relationships for (a) polymer **10b** and (b) polymer **11**.

with a DP per arm of 23 were 10100 and 23300, respectively. Polymerization of 2-methyl-2-oxazoline initiated by compound **9** resulted in linear polymer **11**. The degree of polymerization was 31, which was determined from the peak area ratio of phenyl protons to methyl protons in the ^{1}H NMR spectrum. The number-average molecular weight measured by gel permeation chromatography was 8200. This value was much higher than that of star-branched polymer **10a** of which the calculated molecular weight from the ^{1}H NMR spectrum was nearly equal to that of linear polymer **11**. This result was attributable to the fact that a linear polymer had a larger radius of gyration in a solution than a star-branched polymer when their molecular weights were same.

Polymers **10a–c** and **11** were soluble in water and other polar solvents such as acetone, chloroform, methanol, and *N,N*-dimethylformamide. Figure 1 shows concentration and surface tension relationships of star-branched polymer **10b** and linear polymer **11**. The surface tension was measured in water to examine the surfactant nature of the polymers. Polyoxazolines containing hydrophobic initiating groups or terminating groups have been investigated as potential polymeric surfactants.[22-26] Linear polymer **11** with a bulky hydrophobic head and a hydrophilic chain exhibited nonionic surfactant behavior. The critical micelle concentration was found to be about 0.1% by weight. The polymer solution showed a surface tension of 49 dyn/cm above the critical micelle concentration. Star-branched polymer **10b** had a hydrophobic core and hydrophilic branches. The surface tension of the aqueous solution of polymer **10b** decreased very slowly as the polymer concentration increased, and any evidence for forming micelles was not observed.

N-Acetyl groups of star-branched polymer **10b** were removed by hydrolysis under acidic conditions to give the polymer with N-protonated poly(ethylenimine) branches (Scheme 5). It was soluble in water but precipitated by adjusting the solution to pH 8 with 1 N NaOH. In the ^{1}H NMR spectrum of the polymer with N-protonated poly(ethylenimine) branches measured in D_2O, the peak for *N*-methylene protons was observed at 2.9–3.3 ppm and the peak from acetyl groups at 1.9–2.3 ppm almost disappeared. The degree of polymerization per arm of the hydrolyzed polymer determined from the peak area ratio of phenyl protons to methylene protons was little changed compared with that of the polymer before hydrolysis.

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