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Functional Monomers and Polymers CXXII.† Synthesis of Polymethacrylates Containing Nucleic Acid Bases and Their Methylated Derivatives by Copolymerization

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ABSTRACT: Polymethacrylate derivatives containing both nucleic acid bases and methylated nucleic acid bases were prepared by free radical copolymerizations of the corresponding monomers to study the effects of methylation of nucleic acid bases on specific interactions. The methacylate monomer containing 3-methyluracil was prepared by methylation of 1-(2-hydroxyethyl)uracil followed by a reaction with methacrylic anhydride. The free radical copolymerization of this monomer with a monomer containing uracil gave the polymethacrylate containing uracil and 3-methyl uracil units. The polymethacrylate containing adenine and N^6-methyladenine units was also prepared using a similar procedure to that for the uracil derivative.

KEY WORDS Nucleic Acid Bases / 1-Methyluracil / N^6-Methyladenine / Polymethacrylate / Copolymerization /

Much attention has been directed to commonly used alkylating agents such as alkyl sulfonate, alkyl halides, and nitrosoamines, by which a plenty of organic synthesis has been carried out. These compounds are very potent mutagens in bacteria as well as in higher organisms. They alkylate nucleic acids extensively both *in vitro* and *in vivo*, giving rise to several alkylated nucleic acid bases. The chemical basis for their biological effects has not been established, although a number of papers and reviews have been published on the subject.[1-5] However, it is important to study the alkylation of polymers having nucleic acid bases, and the effects of the alkylation of nucleic acid bases on the specific interactions of these bases.

A number of nucleic acid analogs have been prepared and were used for the study of the specific interaction.[6] For the polymethacrylate derivatives of nucleic acid bases, the copolymerization of complementary monomers,[7] formation of the polymer complex,[8] and template polymerization[9] have been reported. In the preceding papers,[10,11] methylations of the polymethacrylate derivatives of uracil and adenine, and the effects of methylation on the polymer complex formation were studied. The methylation reaction of polymers having nucleic acid bases seemed rather complicated. For the uracil containing polymer, methylation by dimethyl sulfate gave a methylated polymer containing 3-methyluracil and 3-methyl-5-sulfonyluracil units.[10] For the adenine containing polymer, methylation by methyl iodide gave the methylated polymer containing 1-methyladenine and 1,N^6-dimethyladenine units.[11] Thus, it was necessary to prepare a polymer containing 3-methyluracil or N^6-methyladenine units by the co-

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polymerization of the corresponding monomers so as to study in detail the effects of alkylated nucleic acid base units on the formation of the polymer complex by the specific interaction of nucleic acid bases.

The present paper concerns the preparation of the methacylate monomer containing 3-methyluracil and its copolymerization with the uracil containing monomer by a free radical initiator. The methacrylate monomer containing N^6-methyladenine was also prepared and copolymerized with the adenine containing monomer. A study of the interactions between these copolymers is presented in the successive paper.[12]

EXPERIMENTAL

Monomer Synthesis

1-(2-Hydroxyethyl)uracil (**3**): Uracil (**1**) was silylated with hexamethyldisilazane to give bis-(trimethylsilyl)uracil (**2**).[13] Compound 2 was reacted with 2-bromoethyl acetate, followed by hydrolysis to give compound 3.[14]

1-(2-Methacryloyloxyethyl)uracil (**4**) (MAOU): The methacrylate monomer of uracil (**4**) was prepared by the reaction of 1-(2-hydroxyethyl)uracil (**3**) with methacrylic anhydride in pyridine solution.[15]

1-(2-Hydroxyethyl)-3-methyluracil (**5**): To a solution of 1-(2-hydroxyethyl)uracil (**3**) (15 g, 0.1 mol) in 200 ml of dimethyl sulfoxide, methyl iodide (10 ml, 0.16 mol) and potassium carbonate (20 g, 0.14 mol) were added, and the mixture was stirred for 45 hr at room temperature in the dark. After the reaction, the solvent was evaporated under vacuum, and the residue was recrystallized from acetone to give colorless crystals (11.3 g, 69%), mp 139—140°C. NMR (D_2O, ppm): 7.65 (d, 1H), 5.91 (d, 1H), 3.92 (s, 4H), and 3.32 (s, 3H).

Anal. Calcd for $C_7H_{10}N_2O_3$: C, 49.41%; H, 5.92%, N, 16.46%. Found: C, 49.36%; H, 5.87%; N, 16.37%.

1-(2-Methacryloyloxyethyl)-3-methyluracil (**6**) (Me-MAOU): To a solution of **5** (5 g, 0.03 mol) in pyridine (40 ml), methacrylic anhydride (5.1 ml, 0.04 mol) was added at 0°C, and the solution was stirred for 65 h at room temperature. After evaporation of the solvent, a saturated aqueous solution of potassium bicarbonate was added to the residue, and the product was extracted with diethyl ether. After evaporation of the diethyl ether, the residual crystals were purified by recrystallization from cyclohexane to give colorless crystals (5.3 g, 75%), mp 56—57°C. IR (KBr, cm^{-1}): 1730, 1700, 1650, 1620, 1460, 1160, and 800. NMR ($CDCl_3$, ppm): 7.22 (d, 1H), 5.88 (d, 2H), 5.73 (d, 1H), 4.27 (m, 4H), 3.35 (s, 3H), and 1.94 (s, 3H). UV (H_2O): λ_{max}, 266 nm (ε 9900); (ethanol): λ_{max}, 264 nm (ε 9000); (dimethyl sulfoxide/ethylene glycol, 3/2, v/v): λ_{max}, 266 nm (ε 9000).

Anal. Calcd for $C_{11}H_{14}N_2O_4$: C, 55.46%; H, 5.92%; N, 11.76%. Found: C, 55.28%; H, 5.90%; N, 11.72%.

9-(2-Hydroxyethyl)adenine (**8**): The hydroxyethyl derivative of adenine (**8**) was prepared by a reaction of adenine (**7**) with ethylene carbonate.[16]

9-(2-Methacryloyloxyethyl)adenine (**9**) (MAOA): The reaction of compound **8** with methacrylic anhydride in dimethylformamide gave the methacrylate monomer **9**.[16]

1-Methyl-9-(2-hydroxyethyl)adenine (**10**): To a solution of 9-(2-hydroxyethyl)adenine (**8**) (10 g, 0.056 mol) in dimethylformamide (400 ml), methyl iodide (10 ml, 0.16 mol) was added, and the solution was stirred for 12 h at room temperature. Methyl iodide (5 ml, 0.08 mol) was further added to the solution which was stirred for an additional 12 h at room temperature. After the solvent had been evaporated under vacuum, the residue was washed with acetone (1200 ml), and recrystallized from ethanol to give colorless crystals of 1-methyl-9-(2-hydroxyethyl)adenine as hydrogen iodide salt (13.5 g, 76%), mp 265—267°C.

Anal. Calcd for $C_8H_{12}N_5OI$: C, 29.92%; H, 3.77%; N, 21.81%; I, 39.52%. Found: C, 29.92%; H, 3.73%; N, 21.78%; I, 39.51%.

N^6-Methyl-9-(2-hydroxyethyl)adenine (**12**): A solution of 1-methyl-9-(2-hydroxyethyl)-adenyl iodide (**10**) (5 g, 0.016 mol) in 0.3 *N* NaOH aqueous solution (120 ml) was stirred for 3 h at 100°C. The solution was then cooled to room temperature, neutralized with 0.2 *N* hydrochloric acid, and concentrated to dryness under vacuum. The residue was recrystallized from ethanol to give colorless crystals (2.5 g, 83%), mp 171—172°C. NMR (D_2O, ppm): 7.95 (s, 1H), 7.90 (s, 1H), 4.14 (m, 4H), and 2.79 (s, 3H).

Anal. Calcd for $C_8H_{11}N_5O$: C, 49.73%; H, 5.74%; N, 36.25%. Found: C, 49.75%; H, 5.67%; N, 36.32%.

N^6-Methyl-9-(2-methacryloyloxyethyl)-adenine (**13**) (Me-MAOA): To a solution of *N^6*-methyl-9-(2-hydroxyethyl)adenine (**12**) (2.7 g, 0.14 mol) in dimethylformamide (50 ml), methacrylic anhydride (2.7 ml, 0.02 mol) and small amount of triethylamine were added. After the solution was stirred for 5 days at room temperature, the solvent was evaporated under vacuum, and the residue was washed with diethyl ether. The obtained product was recrystallized from ethyl acetate to give colorless crystals (1.7 g, 46%), mp 125—126°C. IR (KBr, cm^{-1}): 3260, 1720, 1610, 1600, 1320, 1310, 1290, 1150, and 1010. NMR ($CDCl_3$, ppm): 8.38 (s, 1H), 7.75 (s, 1H), 5.80 (d, 2H), 4.29 (s, 4H), 3.19 (s, 3H), and 1.90 (s, 3H). UV (H_2O): λ_{max}, 268 nm (ε 15700); (ethanol): λ_{max}, 268 nm (ε 15700); (dimethyl sulfoxide/ethylene glycol, 3/2, v/v): λ_{max}, 270 nm (ε 14600).

Anal. Calcd for $C_{12}H_{15}N_5O_2$: C, 55.16%; H, 5.79%; N, 26.80%. Found: C, 55.16%; H, 5.73%; N, 26.93%.

Copolymerization: The copolymerization was carried out in a sealed tube at 60°C using azobisisobutyronitrile ($(1-2)\times10^{-3}$ mol l^{-1}) as the initiator. The solvents used were dioxane and dimethyl sulfoxide purified in a usual way; the total concentration of the monomers was 4×10^{-2} mol l^{-1}. The copolymer(s) was obtained as precipitates by pouring the content into a large excess of methanol. After filtration, the polymer was dried throughly under vacuum. Contents of the copolymer were measured by NMR spectra.

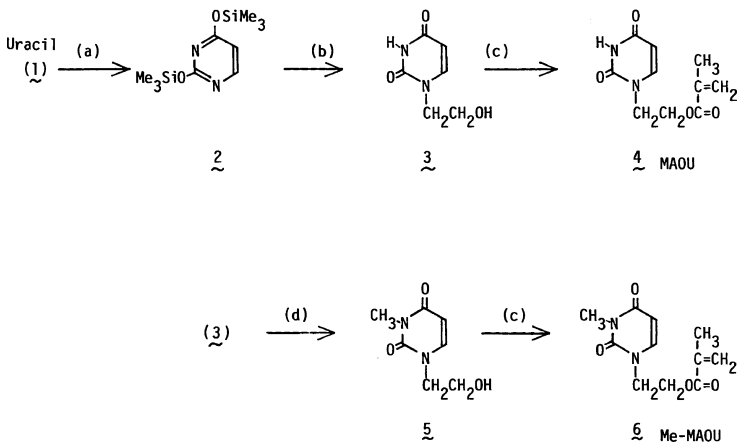
Instrumentation: NMR spectra of the monomeric compounds and copolymers were obtained with a JNM-PS-100 spectrometer. UV spectra were measured by a UNION SM-401 spectrophotometer at 25°C.

RESULTS AND DISCUSSION

Polymethacrylate Containing Uracil and 3-Methyluracil

It is known that the methylation of DNA gives predominantly 7-methylguanosine as the product, and adenine and cytosine bases are also methylated. Uridine is of low reactivity toward most alkylating agents except diazoalkane.[1-4] In our preceding study,[10] the methylation of poly[1-(2-methacryloyloxyethyl)uracil] (polyMAOU) by dimethyl sulfate was found to proceed in dimethylformamide solution at 100°C, but hardly so in dimethyl sulfoxide.[10] In methylation using dimethyl sulfate in dimethylformamide, it was concluded that the N^3 atom of the uracil base was methylated, and the C^5 atom of the base, sulfonated. PolyMAOU was also readily methylated by methyl iodide in dimethyl sulfoxide at room temperature.[10] By reactions using different molar ratios of methyl iodide to uracil units in the polymer, polyMAOU having different degrees of methylations was obtained and is abbreviated as Me-polyMAOU.

Fully methylated polyMAOU can be obtained by polymerization of the corresponding monomer containing 3-methyluracil. The polymers having various content of methylated uracil units can be obtained by copolymerization of the 3-methyluracil containing monomer with the uracil containing monomer. The copolymerization, however, may give polymers with different degrees of polymerization, while the polymer reaction gives polymers with the same degree of polymerization, depending on the starting polymer. The dis-



Scheme 1. (a) $Me_3SiNHSiMe_3$; (b) (i) $CH_3COOCH_2CH_2Br$ (ii) CH_3OH; (c) $[CH_2=C(CH_3)CO]_2$–O; (d) CH_3I, CH_3SOCH_3.

tribution of the methylated uracil units along the polymer chain may also differ between the copolymer and methylated polymer obtained by the polymer reaction. Thus it was of interest to study the effects of uracil unit distribution in the polymer chain on the ability of the polymer to form complexes.

The methacrylate monomer having uracil (**4**) (MAOU) was prepared by a reaction of 1-(2-hydroxyethyl)uracil (**3**) with methacrylic anhydride, as shown in Scheme 1. Alternatively, monomer **4** can be prepared by a reaction of the silylated uracil (**2**) with 2-bromoethyl methacrylate.[17] For the preparation of 1-(2-hydroxyethyl)uracil (**3**), a variety of methods have been reported.[14–17] Among them, the following method is convenient and gives the product in a high yield: the silylated uracil (**2**) is reacted with 2-bromoethyl acetate, followed by hydrolysis (Scheme 1).[14] The methacrylate monomer (**4**) was prepared by a reaction of 1-(2-hydroxyethyl)uracil (**3**) with methacrylic anhydride in pyridine solution at room temperature in a high yield (80%).

The methylation of 1-(2-hydroxyethyl)uracil (**3**) was found to proceed almost quantitatively by methyl iodide in dimethyl sulfoxide solution at room temperature. Methylation in dimethylformamide, however, did not proceed under the same conditions to the dimethyl sulfoxide solution, and gave only the starting material. The methylated uracil monomer, 1-(2-methacryloyloxyethyl)-3-methyluracil (**6**) (Me-MAOU) was obtained by a reaction of the hydroxyethyl derivative (**5**) with methacrylic anhydride in pyridine solution (Scheme 1).

Free radical copolymerizations of Me-MAOU with MAOU were carried out at 60°C in dimethyl sulfoxide or in dioxane solution initiated by azobisisobutyronitrile. The results of the copolymerization are tabulated in Tables I and II, where the content of Me-MAOU units in the copolymer was obtained from NMR spectra (Figure 1), and the monomer reactivity ratio was obtained from Fineman–Ross plots. Previously,[7] the free radical copolymerization of the methacrylate monomer containing nucleic acid bases was studied in a variety of solvents at different temperatures. From these studies, the specific interaction between nucleic acid bases was found to influence on the copolymerization behavior, depending on both solvents and temperature. The results in Table II also show solvent dependency, suggesting the presence of an interaction between monomers. In dioxane, the r_1 and r_2 values were found to be similar. In dimethyl sulfoxide, however, these values

Table Ia. Copolymerization of MAOU (M_1) with Me-MAOU (M_2) in dimethyl sulfoxide[a]

M_2 in monomers	Conversion	M_2 in copolymers[b]
mol%	%	unit mol%
0	11.9	0
10	11.8	15.5
20	14.0	23.0
30	19.7	36.0
40	11.5	51.0
60	7.2	67.0
80	18.6	85.0
100	10.9	100

[a] At 60°C for 30 min. [Total monomer] $= 4 \times 10^{-2}$, [Initiator] $= 1 \times 10^{-3}$ mol l^{-1}.
[b] From NMR spectra in dimethyl sulfoxide-d_6 at 90°C.

Table Ib. Copolymerization of MAOU (M_1) with Me-MAOU (M_2) in dioxane[a]

M_2 in monomers	Time	Conversion	M_2 in copolymers[b]
mol%	min	%	unit mol%
10	50	8.9	14.0
20	50	10.9	22.0
30	35	5.2	28.0
40	30	7.6	40.5
60	25	7.8	57.5
80	25	6.8	81.0

[a] At 60°C. [Total monomer] $= 4 \times 10^{-2}$, [Initiator] $= 2 \times 10^{-3}$ mol l^{-1}.
[b] From NMR spectra in dimethyl sulfoxide-d_6 at 90°C.

Table II. Monomer reactivity ratios of MAOU and Me-MAOU

Monomers		Solvent	r_1	r_2
M_1	M_2			
MAOU	Me-MAOU	Dimethyl sulfoxide	0.79	1.43
		Dioxane	0.85	0.91

differed, while the r_1 and $1/r_2$ values were almost the same and smaller than unity. This suggests that the reactivities of the growing radicals of M_1 (MAOU) and M_2 (Me-MAOU) in dimethyl sulfoxide solution are the same but the reactivity of MAOU is lower than that of Me-MAOU. The low reactivity of MAOU in dimethyl sulfoxide may be caused by the self-association of MAOU.[10]

The NMR spectra of the copolymers are shown in Figure 1. With increasing the content of Me-MAOU units in the copolymers, the N^3–H peak (11.0 ppm) tended to decrease, while the N^3–CH_3 peak (3.16 ppm), to increase. In the case of Me-polyMAOU obtained by methylation of polyMAOU, a higher field shift by 0.1 ppm was observed for the N^3–H peak above 10% methylation of the uracil units.[10] The down-field shift is known for the N^3–H peak of the uracil base by hydrogen bonding,[15] and thus, it was concluded that the self-association of the uracil units in polyMAOU was released by partial methylation of the uracil units, followed by conformational change of the polymer.[10] On the other hand, the higher field shift for the N^3–H in poly(MAOU-*co*-Me-MAOU) obtained by copolymerization was negligible, suggesting the conformational change of the copolymer by the Me-MAOU units to be small and the self-association of the uracil units to be still present in the copolymer. Consequently, it may be assumed that the distribution of Me-MAOU units in poly(MAOU-*co*-Me-MAOU) differs from that in Me-polyMAOU.

The UV spectra of the copolymers are shown in Table III. The λ_{max} values are constant (266 nm), and the ε_{max} values tend to decrease only slightly with an increase in the Me-MAOU units in the copolymers. In the case of Me-polyMAOU, however, the ε_{max} value increased by increasing the methylated uracil units in the polymer.[10] The UV data suggest that the uracil units in poly(MAOU-*co*-Me-MAOU) are self-associated and the uracil units in Me-polyMAOU are hardly undergo any self-association.

The conformational transition of the methacrylate polymer is reported to be observable from viscosity measurements of the polymer.[18,19] In the case of Me-MAOU, the vis-

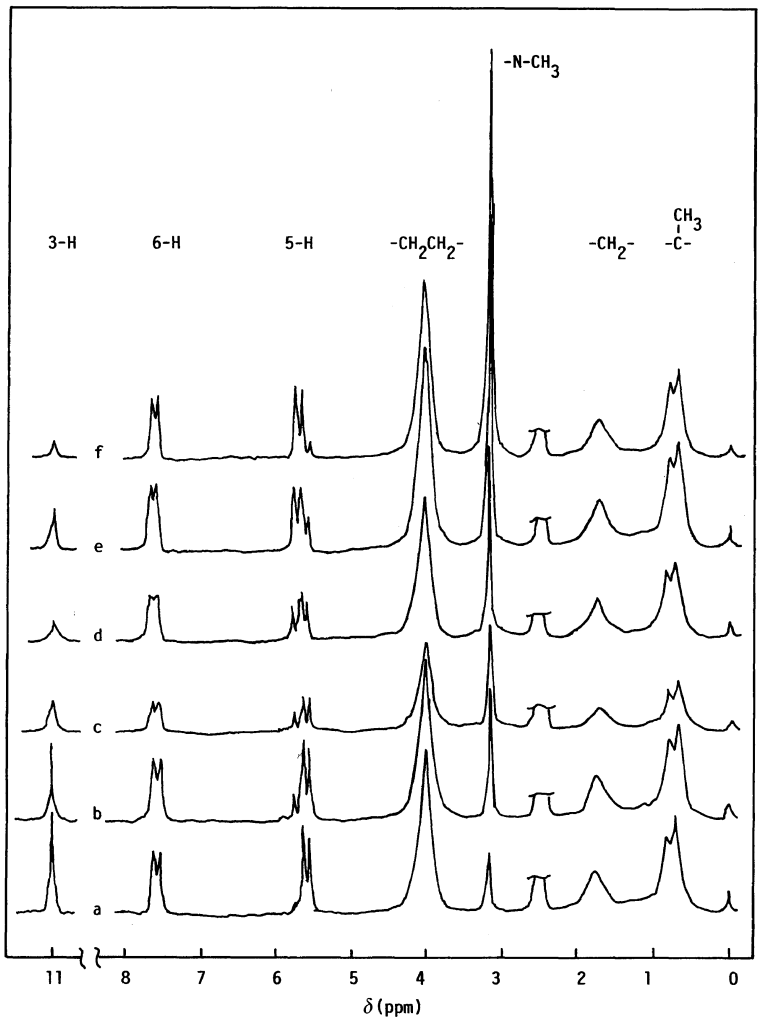


Figure 1. NMR Spectra of poly(MAOU-*co*-Me-MAOU) in dimethyl sulfoxide-d_6 at 90°C. Me-MAOU units in the copolymers (%): a) 85; b) 67; c) 51; d) 36; e) 23; f) 16.

Table III. Copolymers of MAOU with Me-MAOU

Me-MAOU in copolymers	Viscosity,[a] $[\eta]$	UV spectra[a]	
unit mol%	dl g^{-1}	λ_{max}	ε_{max}
16	0.31	266	7500
23	0.38	266	7000
36	0.82	266	6800
51	0.22	266	6900
67	0.34	266	6400
85	0.74	266	6700
100	0.30	266	6700

[a] In dimethyl sulfoxide at 25°C.

cosity was found to increase with increasing the content of methylated uracil units in the polymer, and showed a maximum value around 20% methylation.[10] This was attributed to the decrease in self-association of uracil units in the polymer by increasing the methylated uracil units, accompanied by conformational transition of the polymer. Viscosity data on the copolymers are tabulated in Table III. High viscosity values were observed for copolymers having 36 and 85% Me-MAOU units. However, the relationship between vis-

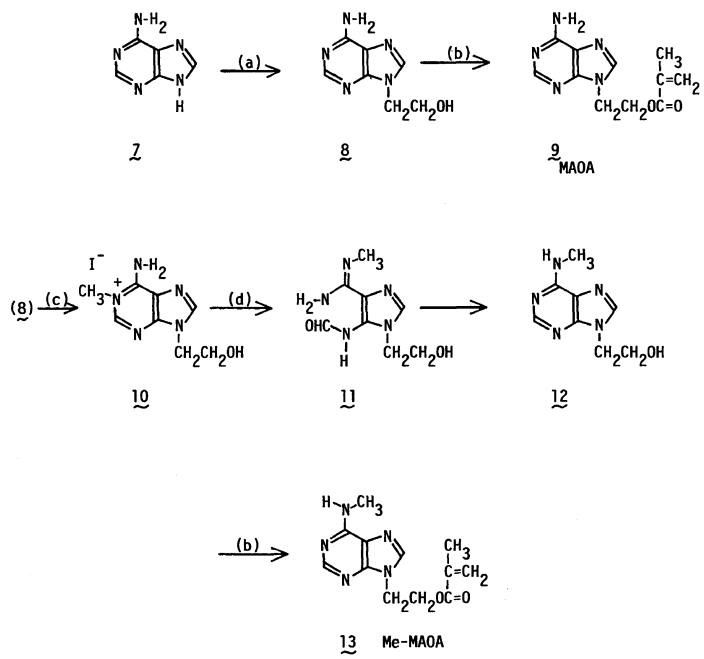
cosity and conformational transition of the copolymers is difficult to show since the degree of copolymerization may be different.

Polymethacrylate Containing Adenine and N^6-Methyladenine

The reactive sites of 9-substituted adenine bases, such as adenosine, are the ring nitrogen atom (N^1, N^3, and N^7) and exocyclic amino group (C^6–NH_2). Direct alkylation of adenosine, however, gives only 1-alkyladenosine.[20-23] Thus 1-methyladenosine was obtained in a quantitative yield using either methyl iodide or methyl *p*-toluenesulfonate in dimethylacetamide.[20] Treatment of 1-methyladenosine with mild alkali causes the Dimroth reaarangement to afford the N^6-methyl derivative.[20,23-25] When methylation is performed at approximately pH 8, the products include, besides 1-methyladenosine, N^6-methyladenosine and 1,N^6-dimethyladenosine.[22] In these reactions, 7-methyladenosine and 3-methyladenosine are minor products.

The amino group at 6-position of adenine base is important for bringing about a specific interaction with uracil or thymine bases, and the alkylation of N^6-position inhibits this interaction. As shown in the preceding paper, poly[9-(2-methacryloyloxyethyl)adenine]-(polyMAOA) can be methylated by methyl iodide in dimethyl sulfoxide solution to give the methylated polyMAOA (Me-polyMAOA).[11] The methylated polymer, however, was found to contain adenine, 1-methyladenine, and 1,N^6-dimethyladenine units. It was thus necessary to prepare the polymer by copolymerization of the corresponding monomers instead of the polymer reaction to obtain the polymer having a N^6-methyladenine unit.

The methacrylate monomers containing adenine (**9**; MAOA) and N^6-methyladenine (**13**; Me-MAOA) were prepared according to Scheme 2. The reaction of adenine (**7**) with ethylene carbonate catalyzed by sodium hydroxide gave 9-hydroxyethylated adenine (**8**) in a high yield.[16] From compound **8** with methacrylic anhydride, MAOA (**9**) was prepared.[16] Alternatively, monomer **9** can be



Scheme 2. (a) ethylene carbonate; (b) methacrylic anhydride; (c) methyl iodide; (d) NaOH aq.

prepared by a reaction of 2-bromoethyl methacrylate with sodium salt of adenine.[17]

The methylation of 9-(2-hydroxyethyl)-adenine (**8**) was carried out using methyl iodide in dimethylformamide at room temperature to give 1-methyl-9-(2-hydroxyethyl)-adenine as iodide salt (**10**). The selection of the solvent was important for this reaction. For example, the starting hydroxyethyl derivative (**8**) was recovered for the reaction in ethanol, and a small amount of methylated product (**10**) was obtained for the reaction in dimethyl sulfoxide. When dimethylformamide was used as the solvent, product **10** could be obtained in a high yield (76%). The 1-methyladenine derivative (**10**) was then treated with 0.3 *N* NaOH aqueous solution for 3 h at 100°C to give the N^6-methyladenine derivative (**12**). This reaction is known as the Dimroth rearrangement which forms intermediate **11**.[26] The reaction of the N^6-methyl derivative (**12**) with methacrylic anhydride proceeded at room temperature in dimethylformamide with a small amount of triethylamine to give Me-MAOA monomer (**13**).

The free radical copolymerization of MAOA (**9**) with Me-MAOA (**13**) was carried out under the same conditions as those for the uracil derivatives and the results are tabulated in Tables IV and V. The monomer reactivity ratios in Table V are quite different from those of the uracil derivatives in Table II. In the case of the adenine derivative, the r_1 and r_2 values in dimethyl sulfoxide were almost the same but were smaller than unity in dioxane solution, suggesting low homopolymerizability and high alternating tendency. This may arise from difference in solvation between adenine and uracil bases, as was the case for the methylation reaction.

The NMR spectra of the copolymers of the adenine derivatives are shown in Figure 2. The spectra were measured in D_2O–DCl where the adenine base is present in a protonated form. With increasing the content of Me-MAOA units in the copolymer, the N^6-methyl peak (3.9 ppm) tended to increase, and the 2-H and 8-H peaks of the adenine base (9.2 ppm) and N^6-methyl peak shifted to a higher field. However, it was difficult to compare the data for the copolymers with those for Me-poly-

Table IVa. Copolymerization of MAOA (M_1) with Me-MAOA (M_2) in dimethyl sulfoxide[a]

M_2 in monomers	Conversion	M_2 in copolymers[b]
mol%	%	unit mol%
0	14.1	0
10	12.9	10
20	8.6	20
30	11.1	29
50	11.1	50
60	10.5	62
80	9.4	83
100	9.4	100

[a] At 60°C for 30 min. [Total monomer] $= 4 \times 10^{-2}$, [Initiator] $= 1 \times 10^{-3}$ mol l^{-1}.
[b] From NMR spectra in D_2O–DCl at 90°C.

Table IVb. Copolymerization of MAOA (M_1) with Me-MAOA (M_2) in dioxane[a]

M_2 in monomers	Time	Conversion	M_2 in copolymers[b]
mol%	min	%	unit mol%
10	75	13.7	10.2
20	120	8.5	22.0
30	150	11.8	30.5
40	180	14.3	39.1
60	180	13.7	55.0
80	240	17.3	77.7

[a] At 60°C. [Total monomer] $= 4 \times 10^{-2}$, [Initiator] $= 2 \times 10^{-3}$ mol l^{-1}.
[b] From NMR spectra in D_2O–DCl at 90°C.

Table V. Monomer reactivity ratios of MAOA and Me-MAOA

Monomers		Solvent	r_1	r_2
M_1	M_2			
MAOA	Me-MAOA	Dimethyl sulfoxide	1.01	1.06
		Dioxane	0.76	0.56

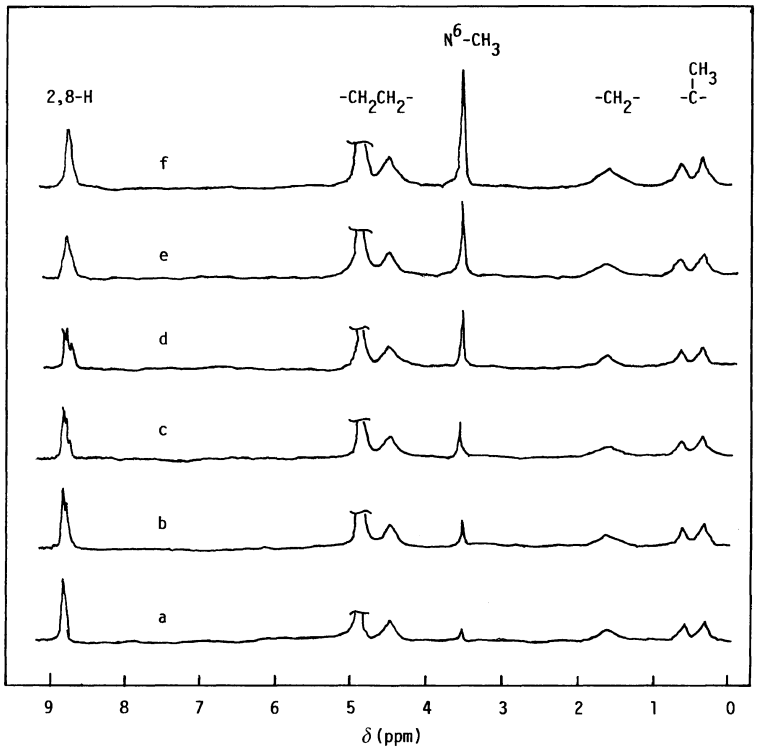


Figure 2. NMR Spectra of poly(MAOA-*co*-Me-MAOA) in D_2O–DCl at 90°C. Me-MAOA units in the copolymers (%): a) 83; b) 62; c) 50; d) 29; e) 20; f) 10.

Table VI. Copolymers of MAOA with Me-MAOA

Me-MAOA in copolymers	Viscosity,[a] $[\eta]$	UV spectra[a]	
unit mol%	dl g^{-1}	λ_{max}	ε_{max}
10	0.28	268	9700
20	0.20	269	9300
29	0.23	269	9800
50	0.26	270	9800
62	0.22	270	9900
83	0.26	271	9900
100	0.26	271	10200

[a] In dimethyl sulfoxide–ethylene glycol (3:2, v/v) at 25°C.

MAOA prepared by the polymer reaction, since the latter polymer contained both 1-methyl and 1,N^6-dimethyladenine units. UV and viscosity data for the copolymers are tabulated in Table VI. With an increase in the Me-MAOA units in the copolymers, the λ_{max} values shifted to longer wavelengths and ε values increased, since the N^6-methyladenine derivatives had substantially longer λ_{max} and higher ε values than those of the adenine derivatives. As for the viscosity values, no considerable difference was observed for all the copolymers measured. Thus, no remarkable change in conformation seems to occur by increasing the Me-MAOA units in poly(MAOA-*co*-Me-MAOA).

In conclusion, two kinds of copolymers, poly(MAOU-*co*-Me-MAOU) and poly(MAOA-*co*-Me-MAOA) were prepared by copolymerization of the corresponding monomers. In these copolymers, the nucleic acid bases of the nucleic acid analogs, polyMAOU and polyMAOA, are partially methylated. These copolymers may serve as models for methylated polynucleotides, in studying the effects of methylation of nucleic acid

bases on the ability of complementary polymers to form complexes. The results of an interaction study are reported in the successive paper.[12]

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