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SHORT COMMUNICATION

Syntheses of Novel Polycations Containing Nucleic-Acid Bases*

Tsuneo OKUBO and Norio ISE

Department of Polymer Chemistry, Kyoto University, Kyoto, Japan.

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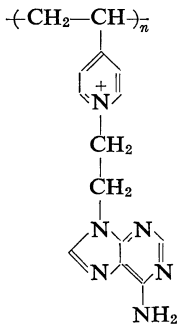
It is most useful for biological investigations to synthesize polymers containing nucleic-acid bases. The preparation of various kinds of such polymers has been tried by many researchers.[1] These polymers, however, were either neutral or anionic; no cationic polymers were synthesized. We wish to report here on the syntheses of novel polycations containing nucleic-acid bases.

The polymers were obtained by quaternization of poly(4-vinylpyridine) with *N*-chloroethyl-adenine, -thymine and -theophylline in dimethylformamide. Ethanol, nitromethane, or nitroethane as solvent was ineffective for the quaternization. The chloroethylated bases were prepared by chlorination of the corresponding hydroxyethylated compounds with thionylchloride.[2] The hydroxyethylated bases were synthesized from nucleic-acid bases and ethylene carbonate in dimethylformamide.[2-4]

The quaternization reaction of poly(4-vinylpyridine) (6 g, 60 mmol) with 9-(2′-chloroethyl)-adenine (12.5 g, 60 mmol) was performed in 40 m*l* of dimethylformamide at 85°C for 3 days under a nitrogen atmosphere. The precipitated product was thoroughly washed with dimethylformamide and dioxane, and then refluxed with ethanol. By drying the precipitate *in vacuo* poly[4-vinyl-*N*-2′-(9-ethyladeninyl)pyridinium chloride] (APVP) was obtained as a hygroscopic, slightly yellow powder. The degree of quaternization (97%) was obtained both from the chloride ion analysis with $AgNO_3$ and from the elemental analysis. The yield was 85%. *Anal.* calcd for $C_{14}H_{15}N_6Cl$: C, 55.5%; H, 5.0%; N, 27.8%; Cl, 11.7%. Found: C, 54.8%; H, 5.5%; N, 26.8%; Cl, 11.1%. The UV absorption peak of APVP was at 255 nm in 0.2-*M* KCl aqueous media.



(APVP)

Poly[4-vinyl-*N*-2′-(1-ethylthyminyl)pyridinium chloride] (TPVP) was prepared by heating 1-(2′-chloroethyl)thymine (11.5 g, 60 mmol) and poly-(4-vinylpyridine) (6 g, 60 mmol) in dimethylformamide (13 m*l*) at 85° for 24 hr. After cooling, the reaction solution was poured into dioxane. The precipitate was dried *in vacuo*. The product was a highly hygroscopic, slightly yellow powder. The yield was 70%. The degree of quaternization was 82%. The maximum absorption of TPVP was at 265 nm in aqueous 0.2-*M* KCl solutions.

Poly[4-vinyl-*N*-β-(7-ethyltheophyllinyl)pyridinium chloride] (THPVP) was synthesized by heating 7-β-chloroethyltheophylline (20 g, 80 mmol) and poly(4-vinylpyridine) (6 g, 60 mmol) in dimethylformamide at 80°C for 24 hr in a nitrogen atmosphere. The solvent was then eliminated by heating *in vacuo*. The residue was dissolved in water (50 m*l*) and then precipitated in an ethanol—ether mixture (3:1). The

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dried product was a hygroscopic, slightly yellow powder. The degree of quaternization determined from the chloride ion analysis was 29%, and the yield was 85%. The maximum absorption of THPVP was at 273 nm in 0.2-*M* KCl aqueous media.

Adenine and thymine (Sigma) were used without further purification. Theophylline was purchased from Nakarai Chem. Co., Kyoto. Dimethylformamide was distilled under reduced pressure. Poly(4-vinylpyridine) was prepared by bulk polymerization of 4-vinylpyridine with benzoyl peroxide as the initiator.[5] The degree of polymerization was estimated to be 3800 by viscometry.[6]

It should be mentioned that, unlike other polymers containing nucleic-acid bases reported from other laboratories, the polycations described herein can have fairly large molecular weight. This is an advantage in many respects. Detailed studies on the spectroscopic, hydrodynamic and catalytic properties are now in progress in our laboratory.

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