SHORT COMMUNICATIONS

Poly(vinyldiaminotriazine) as Highly Selective Hydrogen Bonding Host in Methanol

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Molecular recognition of substrates by synthetic organic receptors attracts many chemists because of its potential utility for the artificial enzymes. Various well-designed receptors using complementary hydrogen bonding have been synthesized.^{1–3} However, most of these receptors satisfactorily functioned only in aprotic solvents such as carbon tetrachloride and chloroform, because protic solvents competitively destroy the hydrogen bonds.⁴ Thus, current attention is paid to molecular recognition in a protic environment, as is done in nature.

Kunitake *et al.*⁵ prepared Langmuir-Blodgett films of an amphiphile involving diaminotriazine (DAT) and successfully recognized nucleic acid bases and nucleosides at air–water interface. Nowick *et al.*⁶ showed that adenine–thymine base-pairing is formed in aqueous micellar solutions. These results strongly suggest that polymeric systems are useful for hydrogen bond formation in protic solvents. In the present communication, we report that poly(2-vinyl-4,6-diamino-1,3,5-triazine) (PVDT) recognizes nucleic acid bases through hydrogen bonds even in methanol, since an appropriate reaction field is provided by the polymer.

EXPERIMENTAL

Poly(2-vinyl-4,6-diamino-1,3,5-triazine) (PVDT) was prepared by radical polymerization of 2-vinyl-4,6-diamino-1,3,5-triazine (0.29 mol dm^{-3}) in dimethyl sulfoxide (DMSO) at 70°C with azobisisobutyronitrile (AIBN) (3.9 mmol dm^{-3}) as initiator.

Adsorption of nucleic acid bases was carried out by incubating fine powder of PVDT in 1 ml of a methanol solution of the guest at 25°C (The PVDT was insoluble in methanol). After 1 h of incubation with intermittent shaking to achieve a complete equilibrium, the solid was removed by centrifugation and the supernatant was analyzed with reversed-phase HPLC. As the internal standard, 4-hydroxypyridine, which shows no measurable interaction with PVDT, was added to the incubation mixture.

RESULTS AND DISCUSSION

When methanol solutions containing all of uracil, thymine, adenine, and cytosine (1 mM each) were incubated at 25°C with 50 mg of PVDT, the concentra-

tions of uracil and thymine in the liquid phase immediately decreased (Figure 1). The equilibrium was attained within 15 min. On the contrary, adenine and cytosine were hardly adsorbed. Thus, PVDT selectively binds uracil and thymine in methanol. On elevating the temperature, the adsorbed uracil and thymine were released to the liquid phase, confirming a reversibility of the adsorption. Adsorption experiment of guanine could not be conducted because of its poor solubility in methanol.

As shown in Table I, the adsorption activity (uracil, thymine $\gg$ cytosine, adenine) exactly coincides with the number of the hydrogen bonding sites of the guests toward the DAT residue in PVDT (see Figure 2 for the

Figure 1. HPLC patterns for a methanol solution of uracil/thymine/cytosine/adenine mixture (a) before and (b) after the contact with PVDT. One milliliter of the solution (concentration of each of the guests is 1 mM) was treated with 50 mg of PVDT at 25°C .

Table I. Adsorption of nucleic acid bases by PVDT in methanol and ethanol at 25°C

Guest molecule	Number of hydrogen bonding sites toward DAT	Adsorption activity ^a	
		In methanol	In ethanol
Uracil	3	0.30	0.04
Thymine	3	0.24	0.04
Cytosine	2	0.02	0.01
Adenine	2	0.03	0.02
Pyrimidine	1	0	0
Purine	1	0	0

^a The ratio of the decrease in the concentration of each of the guests, observed on the contact with 10 mg of PVDT, with respect to the initial concentration (1 mM). The amount of the solution is 1 ml (see Experimental section for detail).

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Figure 2. Hydrogen bond formation of PVDT with the guests.

Figure 3. Schematic illustration for the hydrogen bonding sites provided by PVDT.

hydrogen bonding patterns). Unsubstituted pyrimidine and purine, which possess only one hydrogen bonding site, are not adsorbed at all. Apparently, the complementary hydrogen bond formation is responsible for this selective recognition. The argument is further evidenced by the fact that 3-methyluracil, whose hydrogen bond formation is hindered by the methyl group on the N atom, was hardly adsorbed by PVDT.

In terms of the Langmuir adsorption isotherm, the binding constant of the DAT residue in PVDT with uracil was determined to be 270 M^{-1} at 25°C . This value

is greater than the corresponding value for the complex formation between 2,6-dibutyramidopyridine (a model compound of DAT) and 1-butylthymine (90 M^{-1})^{2c} in non-competitive chloroform. The remarkable hydrogen bonding activities of the DAT residues in the polymer are unequivocally substantiated. Assumedly, appropriate apolar microsphere is formed by the several DAT residues in PVDT even in protic environment (see Figure 3), and the selective recognition of nucleic acid bases through hydrogen bond formation is achieved there.

It is noteworthy that fine powder of 2-vinyl-4,6-diamino-1,3,5-triazine, which is almost insoluble in methanol, did not adsorb uracil to a measurable extent. The polymeric structure is strictly required for the recognition in methanol. When ethanol was used as the solvent (in place of methanol), the adsorption of the guests by PVDT was virtually nil (Table I). Assumedly, the apolar microsphere, required for the hydrogen bond formation, is not provided efficiently in ethanol.

In conclusion, PVDT reversibly and selectively adsorbs nucleic acid bases through hydrogen bond formation in methanol. Potentiality of synthetic polymers as hydrogen-bonding hosts, which are effective even in protic solvents, has been strongly indicated.

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