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SHORT COMMUNICATION

Functional Monomers and Polymers. LI. On the Synthesis and Polymerization of Acryloylaminomethyl Derivatives of Nucleic Acid Bases*

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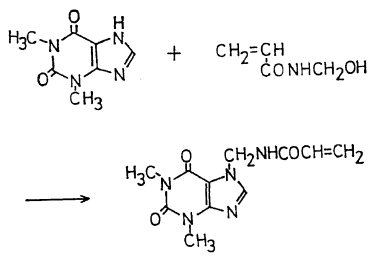
The syntheses of a series of monomeric compounds containing heterocyclic moieties of nucleic acid have been reported in previous papers.[1] The preparations for vinyl, dicarboxylic, propanediol, and amino acid esters derived from purine or pyrimidine bases were described in detail. This communication reports on the synthesis of *N*-(acryloylaminomethyl) derivatives of theophylline, to be used for the synthesis of new polymeric substances with both polyvinyl and polyamide linkages as the main chain.

N-(acryloylaminomethyl)theophylline (**1**) was provided by the reaction of theophylline with *N*-(hydroxymethyl)acrylamide in an aqueous 2-*N*HCl solution at room temperature for 60 h, and recrystallized from methanol to give colorless needles in a 38-% yield; mp, 201—202°C *Anal.* Calcd for $C_{11}H_{13}N_5O_3$: C 50.18, H 4.98, N 26.61 Found: C 50.08, H 4.82, N 26.47. UV, λ_{max} (in H_2O) 274 nm, ε 8600. Treatment of adenine and guanine with *N*-(hydroxymethyl)acrylamide in a manner similar to that used for theophylline afforded the corresponding monomers. However, the yields were quite low (5% and 2%, respectively). On the other hand, such monomers could not be obtained in the case of pyrimidine bases such as uracil and thymine, since these bases are preferentially protonated in acidic conditions.



1

1 was readily homopolymerized with AIBN in dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and pyridine solutions. These results are shown in Table I. The IR spectrum of the polymer did not show the presence of vinyl groups. In the NMR spectrum, new signals was found to appear at 1.5 and 2.1 ppm, corresponding to $-CH_2-$ and $>CH-$, respectively. The molecular weights of the polymers obtained seem to be influenced by the sort of solvents used for the polymerization. The lower molecular weight which occurred in the polymerization in DMF would be due to the low homogeneity of the reaction system. The polymer was soluble in acetic and formic acids, but insoluble in water and alcohols.

Table I. Free-radical polymerization of **1**[a]

Solvent	Conversion, %	M_n[b]
DMF	52.8	39,000
DMSO	94.8	74,000
Pyridine	85.0	67,000

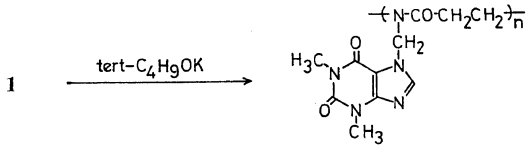
[a] At 60°C, for 7 h; [**1**], 0.2 mol/dm^3; [AIBN], 0.01 mol/dm^3.

[b] Determined by a high speed membrane osmometer; solvent, acetic acid—water (7: 3) mixture.

* For Part L of this series, see ref 3.

Hydrogen-transfer polymerization of **1** was carried out in DMF, pyridine, and chlorobenzene solution by using potassium *tert*-butoxide as a catalyst. The results are shown in Table II. The polymer was precipitated into methanol, and the methanol-insoluble part was separated from the soluble part.

The β-alanine-type structure of the polymers was confirmed from both IR and NMR spectroscopies. The IR spectrum (KBr) of the polymer did not show the N—H stretching vibration (3300 cm^{-1}) and the N—H deformation (1520 cm^{-1}), which were present in **1**; the carbonyl stretching vibration shifted from 1660 to 1650 cm^{-1}. The NMR spectrum in DMSO-d_6 solution at 150°C did not show the signal of amide protons, and suggested the presence of the β-alanine structure (broad signal at δ 2.8 ppm for $-N-CH_2-$ and at δ 4.6 ppm for $-CH_2-CO-$ in the $-CH_2-CH_2-CON\langle$ unit).



The molecular weight of the polymer obtained in DMF solution, determined from the NMR spectrum based on the terminal unsaturated units,[2] was 7400 for the methanol-insoluble part and 1800 for the methanol-soluble part. Both methanol soluble and insoluble polymers were soluble in water, DMSO, and acetic and formic acids, but insoluble in benzene, acetone, and ethyl acetate.

Table II. Hydrogen-transfer polymerization of **1**[a]

Solvent	Conversion, %	
	MeOH-insol part	MeOH-sol part
DMF	42.8	44.5
Pyridine	9.4	66.7
Chlorobenzene	2.3	69.4

[a] At 100°C for 20 hr. *N*-Phenyl-β-naphthylamine in a trace amount was present in the system: **[1]**, 0.4 mol/dm^3; [*tert*-C_4H_9OK], 0.08 mol/dm^3.

Further studies on more convenient ways to synthesize other monomeric nucleic acid base analogs and on their polymerization are now in progress.

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