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The Anionic Polymerization of *n*-Butyraldehyde Azine

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Little is known concerning the polymerization of compounds with C=N bonds except for carbodiimides[1] and isocyanates.[2-6] We have already reported on the anionic polymerization of acetaldazine and have reported that the polymer thus obtained was a viscous oligomer.[7,8] The failure to obtain a high polymer from acetaldazine may be due to the proton transfer of the active hydrogens of the α,ω-methyl groups in the monomer. Thus, we are led to the polymerization of *n*-butyraldehyde azine, which has less active α-hydrogen than acetaldazine, and to the comparison of the molecular weight of the obtained polymer with those of formaldazine and acetaldazine under similar conditions.

The results of the polymerization of *n*-butyraldehyde azine by BuLi under various conditions are shown in Table 1. The oligomer was prepared in a good yield and was separated into a methanol-insoluble part (Oligomer 1) and a methanol-soluble part (Oligomer

TABLE 1. POLYMERIZATION OF *n*-BUTYRAZINE BY BUTYLLITHIUM[a]

Solvent	React. temp. (°C)	Total yield (%)	Oligomer 1 (%)	Molecular weight of Oligomer 1
Bulk[b]	−40	72.1	19.8	3130
	0	88.8	24.8	2890
	30	86.8	26.2	2870
Toluene[c]	−40	88.4	20.5	2870
	0	83.7	22.7	2670
THF[c]	−40	90.8	17.2	3030
	0	91.6	16.8	2990

a) Polymerization time 20 hr.
b) Monomer=28 mmol, BuLi=0.3 mmol.
c) Monomer=0.89 mol/l, BuLi=30 mmol/l.

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[1] G. C. Robinson, *J. Polymer Sci.*, *A-1*, **2**, 3901 (1964).
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[3] V. E. Shashoua, W. Sweeny, and R. F. Tietz, *ibid.*, **82**, 866 (1960).
[4] C. King, *ibid.*, **86**, 437 (1964).
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[6] T. Kashiwagi, M. Hidai, Y. Uchida, and A. Misono, *J. Polymer Sci.*, *B*, **8**, 173 (1970).
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[8] M. Kamachi and S. Murahashi, *Polymer J.*, **4**, 651 (1973).

2). In order to make it clear whether or not the addition polymerization occurs, the polymer thus obtained was characterized first.

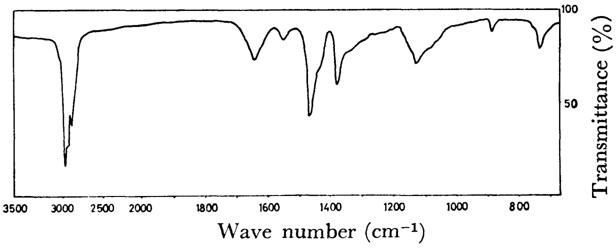


Fig. 1. The IR spectrum of oligomer 1 (KBr).

The IR spectrum of Oligomer 1 is shown in Fig. 1. It shows absorption bands at 1645 cm^{-1} ($\nu_{C=N}$) and 1555 cm^{-1} ($\nu_{N=N}$). The IR spectrum of Oligomer 2 is identical to that of Oligomer 1 except for its intensity. The UV spectrum of Oligomer 1 was measured in the range from 220 to 700 nm in a hexane solution; it showed an absorption maximum at 235 nm, a shoulder at 296 nm, and a weak absorption at 378 nm showing the –N=N– group.[12] The absorptions at 235 and 296 nm may be assigned to the n-π^* transition of the –C=N bond.[8] The NMR spectrum of Oligomer 1 is shown in Fig. 2. Each peak was assigned as is shown in Fig. 2, taking into account the conventionally available data. These assignments were consistent with the results of the IR spectra and the qualitative chemical tests. The product obtained from the treatment of the Oligomer, 1 or 2, with dilute aqueous hydrochloric acid was distilled into another ampoule containing an alcoholic solution of 2,4-dinitrophenylhydrazine by using a high-vacuum technique. An orange-yellow solid was thus formed (mp 118—122 °C). The product was identified as n-butyraldehyde hydrazone by a mixed-melting-point test with the authentic product, thus indicating the existence of pendant $-N{=}CH-CH_2-CH_2-CH_3$ groups.

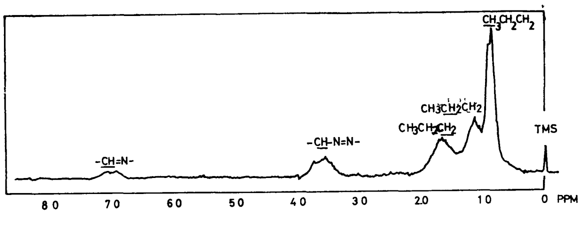
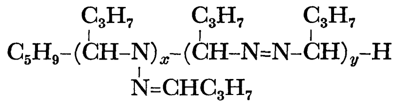


Fig. 2. The NMR spectrum of Oligomer 1 (CCl$_4$ 5% solution).

In order to establish the existence of the $-\underset{\substack{|\\R}}{C}H-N{=}N-\underset{\substack{|\\R}}{C}H-$ group, which is likely to cleave thermally at the C–N bonds and which evolves nitrogen molecule, the mild pyrolysis of Oligomer 1 at 200 °C was carried out under a high vacuum and the gaseous product thus obtained was collected into a vial for mass spectrometry. High-resolution mass spectrometry showed that the gas product was a nitrogen molecule (m/e 28.02).

These results suggest the following structure for the Oligomer 1:



$$C_5H_9-(\underset{\substack{|\\N=CHC_3H_7}}{\overset{\substack{C_3H_7\\|}}{C}H}-N)_x-(\overset{\substack{C_3H_7\\|}}{C}H-N{=}N-\overset{\substack{C_3H_7\\|}}{C}H)_y-H$$

It was proved by the results of the IR spectra that Oligomer 1 is similar to Oligomer 2 except in its molecular weight.

The structure of the oligomer was consistent with that of the acetaldazine. Evidence for the hydrazone rearrangement, which was pointed out in the case of acetaldazine,[8] was found in the IR spectrum of Oligomer 2, which was allowed to stand, but not in Oligomer 1. This indicates that the rearrangement of Oligomer 1 is more difficult than that of Oligomer 2.

TABLE 2. COMPARISON OF THE MOLECULAR WEIGHTS OF THE POLYMER OBTAINED FROM VARIOUS AZINES

Substance	State	Molecular weight (Degree of polym.)
Formaldazine[a]	Solid	$\eta_{sp/c}=0.25$[b]
Formaldazine[c,d]	Solid	Insoluble polymer
n-Butyrazine[c]		
Oligomer 1	Solid	2990 (21)
Oligomer 2	Tacky solid	1440 (10)
Acetaldazine[c]	Tacky solid	900 (10)

a) Formaldazine was polymerized by a trace of water at 0 °C.
b) H$_2$O Solution at 30 °C.
c) Monomer=0.89 mol/l, BuLi=30 mmol/l. Solvent, THF. Polym. temp. 0 °C.
d) Molar concentration of formaldazine was calculated by assuming that its density is the same as that of acetaldazine, because that of formaldazine was not determined.

The degree of polymerization of the oligomer of n-butyraldehyde azine was a little larger than that of the acetaldazine which was obtained under similar conditions, as is shown in Table 2, in spite of the increase in the bulkiness of the substituent group. This might be due to the decrease in the number of active hydrogens in α,ω-alkyl groups of n-butyraldehyde azine. In order to make this point clear, formaldazine, which has no active hydrogen, was polymerized to a solid polymer by a trace of water at room temperature and then explosively by butyllithium at −78 °C.[9] The intrinsic viscosity of the former was found to be 0.25 in an aqueous solution, but the latter polymer was insoluble in water as well as in common organic solvents. The degree of polymerization of the formaldazine polymer may be much larger than that of n-butyraldehyde azine. Thus, it is shown that high polymers can be anionically obtained from the C=N–N=C bond as well as from the diene bond.

These facts suggest that a cause of oligomerization in α,ω-disubstituted azine might be a proton transfer of active hydrogen.

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[12] H. H. Jaffe and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley (1964), p. 186.

[9] M. Kamachi and S. Murahashi, to be published.

Experimental

Reagents. The *n*-butyraldehyde azine was prepared from hydrazine hydrate and *n*-butyraldehyde according to the procedure of Curtius;[10] it was purified by reduced-pressure distillation through a Widmer column under nitrogen. The tetrahydrofuran was refluxed over metallic sodium and distilled into an ampoule on a high-vacuum system. The *n*-butyllithium was prepared in *n*-heptane by the method of Ziegler, and the concentration was determined by double titration.[11]

Polymerization. A 10 ml polymerization ampoule equipped with a nitrogen inlet with a stopcock was connected to a high-vacuum system, evacuated, and flushed with nitrogen by opening the stopcock. The ampoule was then removed under nitrogen flushing, after which a solution of butyllithium in heptane was injected by means of a hypodermic syringe into the ampoule under nitrogen. The ampoule was again connected to a high-vacuum system, the heptane was evaporated, and then the solvent and the monomer, which has previously been dried and degassed, were distilled into it. After being sealed off, the ampoule was placed in a thermostat at a given temperature. The polymerization system gradually turned orange-red in bulk polymerization, but immediately colored in a tetrahydrofuran solution.

The polymerization system became a red gel in the bulk polymerization and a red viscous solution in the solution polymerization. The reaction system was added to an excess of methanol to separate a methanol-insoluble polymer (Oligomer 1) and a methanol-soluble polymer (Oligomer 2). Oligomer 1 was filtered, washed with methanol, and dried. Oligomer 1 was a pale yellow solid, softening at 82—92 °C, which was soluble in petroleum benzine, benzene, toluene, and tetrahydrofuran.

Found: C, 69.18; H, 11.16; N, 19.83%. Calcd for C_8H_{16}-N_2: C, 68.57; H, 11.43; N, 20.00%.

Oligomer 2 was isolated by evaporating the filtrate, and it was freed from inorganic salt by washing its ether solution with a small amount of distilled water. Oligomer 2 was a pale yellow to yellow viscous liquid (or tacky solid), soluble in aliphatic hydrocarbon, acetone, benzene, methanol, and tetrahydrofuran.

Found: C, 69.84; H, 10.99; N, 18.83%. Calcd for C_8H_{16}-N_2: C, 68.57; H, 11.43; N, 20.00%.

The number-average molecular weights of these oligomers were determined by means of a vapour-presure osmometer (Mechro lab. 301A) in benzene.

The structure of the polymer was determined by studying its IR spectrum and NMR spectrum (Varian A 60) and by qualitative chemical tests for functional groups. The mass spectrum of the gas product obtained from the mild pyrolysis of the polymer was determined by means of a Hitachi model-10Z mass spectrometer.

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