Preparation and Properties of Polyhexamethyleneguanidine[*1,*2]

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In previous studies,[1,2] we prepared alkylenedicyanamide in a pure state for the first time and studied its polymerization, which yielded a transparent, insoluble-infusible polymer. In the first paper,[1] it was also pointed out that alkylenedicyanamide reacted with alkylenediamine to give an anion exchange resin which might have the structure of polyalkyleneguanidine.

This is the first report on polyalkyleneguanidine and its properties. In regard to this problem, one previous patent[3] had indeed been granted. However, the polyhexamethyleneguanidine described in the patent was questionable because of the erroneous method used for the preparation of hexamethylenedicyanamide.

Preparation of Polyhexamethyleneguanidine. A methanolic or aqueous methanolic (or ethanolic) solution of a mixture of hexamethylenedicyanamide (I) and hexamethylenediamine dihydrochloride (II) was refluxed until no crystal was separated by cooling. The condensation was accelerated by adding a small amount of hexamethylenediamine. The removal of the solvent at a reduced pressure left a colorless, transparent gel which was in turn solidified by simple heating. The solubility of the resulting polymers in water varied with the molar ratio of the starting materials, as is shown in Table 1.

TABLE 1. SOLUBILITY OF THE POLYMERS IN WATER

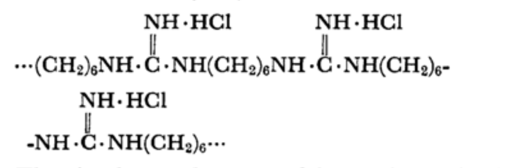
Starting materials		Solubility
I mole	II mole	
1	1	soluble
1	0.9	soluble
1	0.8	insoluble
1	0.7	insoluble
1	0.6	insoluble
1	0.5	insoluble

As is clear from the table, water-insoluble polymers could be obtained when 1 mol of I was reacted with less than 0.8 mol of II. The product obtained was a colorless, transparent glassy mass which was infusible and insoluble (in the case of water-insoluble polymers) in all common solvents.

Structure of the Polymer. The reaction of I with II may be supposed to proceed as follows:

$$n\,\mathrm{NCHN(CH_2)_6NHCN} +$$

$$n\,\mathrm{ClH\cdot H_2N(CH_2)_6NH_2\cdot HCl} \rightarrow$$



$$\cdots\mathrm{(CH_2)_6NH\cdot}\overset{\overset{\displaystyle \mathrm{NH\cdot HCl}}{\|}}{\mathrm{C}}\mathrm{\cdot NH(CH_2)_6NH\cdot}\overset{\overset{\displaystyle \mathrm{NH\cdot HCl}}{\|}}{\mathrm{C}}\mathrm{\cdot NH(CH_2)_6}\text{-}$$

$$\text{-}\mathrm{NH\cdot}\overset{\overset{\displaystyle \mathrm{NH\cdot HCl}}{\|}}{\mathrm{C}}\mathrm{\cdot NH(CH_2)_6}\cdots$$

That is, the result expected is a polymer having guanidine linkage. It is also supposed that the product obtained using a mixture of I and II in a molar ratio of 1 : 1 will have a simple polyguanidine structure, but that when a mixture of the

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[*1] Presented at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

[*2] Cyanamide Derivatives. LXXVI, Preceding papers of this series: LXXV. K. Sugino and T. Tanaka, "The Reactions of Acrylates and Acrylonitrile with Guanidine in DMF", submitted to *J. Org. Chem.* LXXIV: H. Nagasaka, E. Ichikawa and K. Odo, *Yuki Gosei Kagaku Kyokai Shi (J. Soc. Synth. Org. Chem. Japan)*, **25**, 1048 (1967).

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1) K. Sugino, K. Shirai and R. Kitawaki, *J. Org. Chem.*, **26**, 4122 (1961).

2) R. Kitawaki, K. Shirai and K. Sugino, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **67**, 1485 (1964).

3) E. K. Bolton *et al.* (Du Pont), U. S. Pat. 2325586 (1943).

same compounds in a molar ratio of 1 : less than 0.8 is reacted, the polymerization of I itself occurs simultaneously, resulting in the formation of insoluble polymers.

One piece of evidence for the presence of guanidine linkage in the polymer molecule is that when the resin was decomposed by digesting it with hot concentrated hydrochloric acid, the resulting solution gave a distinctly positive Sakaguchi test.

Another piece of evidence for the polyguanidine structure of the polymer is its infrared spectrum. It is shown in Fig. 1, along with that of hexamethylenediguanidine dihydrochloride[4] for comparison.

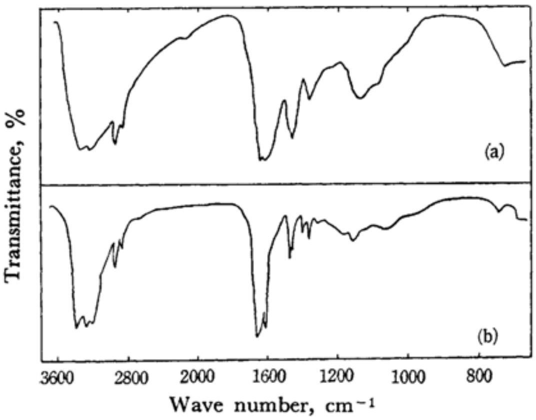

Fig. 1. Infrared spectra of the polymer and hexamethylenediguanidine 2HCl. (KBr pellet method)

(a) The polymer

(b) Hexamethylenediguanidine

The two spectra may be seen to be very similar to one other. Moreover, the spectrum of the polymer indicates the presence of methylene-group bands at 2920 cm^{-1}, 2860 cm^{-1}, and 1470 cm^{-1}, of imino-group bands at 3220—3240 cm^{-1}, and of C=N band at 1650 cm^{-1}.

Ion-exchange Property of the Polymer. When the polymer was pulverized into particles and treated with an aqueous solution of sodium hydroxide, it swelled and released the chloride ion into the solution. After it had been allowed to stand, it was collected, washed with water, and dried, resulting in a resin of the OH$^-$ type. The resin thus obtained was found to have a strong anion-exchange property, as was expected from its guanidine structure. Figure 2 shows the rate of the adsorption of hydrochloric acid by the resin.

The exchange capacities of this resin were found to be 7.68 mmol/g and 3.34 mmol/g for Cl$^-$ in a 0.5 N hydrochloric acid and in a 1 N sodium chloride solution respectively.

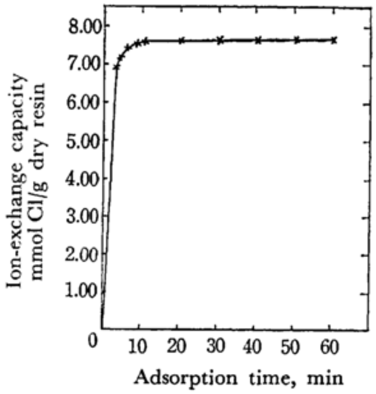

Fig. 2. The rate of adsorption of 0.5 N HCl by the resin.

Experimental

Hexamethylenedicyanamide (I). It was prepared by the procedure described earlier.[1,2] Mp 64—65°C.

Hexamethylenediamine Dihydrochloride (II). A commercially available reagent was used after recrystallization. Mp 248°C.

Preparation of Polyhexamethyleneguanidine Hydrochloride. *Water-soluble Polymer:* A mixture of 8.3 g of I, 8.5—9.6 g of II, and 0.2 g of hexamethylenediamine (III) was dissolved in 40 cc of 50% aqueous ethanol, and the solution was refluxed on a water bath for 2—5 hr. After the reaction, the ethanol and water were removed by distillation at reduced pressure, leaving a colorless, transparent gel-like mass. It was solidified by being heated at 100—110°C for 2—5 hr, resulting in a water-soluble resinous product.

Water-insoluble Polymer: A mixture of 16.6 g of I and 9.6 g of II was dissolved in 60 cc of methanol or 60 cc of 50% aqueous methanol, and the solution was refluxed on a water bath for 3 hr in the presence of III. After the reaction, the methanol (and the water) were removed by distillation at reduced pressure, leaving a colorless, transparent gel-like mass. It was solidified by being heated at 100—110°C for 2 hr, resulting in a water-insoluble resinous product.

Preparation of an Anion-exchange Resin. The water-insoluble polymer was softened with swelling by treating it with hot water at 80—90°C. Then it was pulverized, dried, and sieved into particles of 50—60 mesh. The resulting powdered resin was agitated with a 1 N sodium hydroxide solution for 2 hr. Then it was collected by filtration, thoroughly washed with water, and dried at 60—70°C.

Measurement of the Exchange Capacities of the Resin. 4.000 g of the OH$^-$-type resin thus obtained, after being completely dried in an air bath, was placed in a flask containing 200 cc of 0.5 N hydrochloric acid, and the mixture was stirred by magnetic stirrer. The concentration of hydrochloric acid was determined by using a 5 cc sample every 10 min.

2.000 g of the same resin were placed in a flask contaiaing 200 cc of a 1 N sodium chloride solution, and the mixture was stirred by magnetic stirrer. The pH of the solution reached a constant value of 11.86 after 2 hr. The concentration of Cl$^-$ in the solution was then determined.

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[4] K. Odo and K. Sugino, *Nippon Kagaku Kaisi (J. Chem. Soc. Japan)*, **63**, 336 (1942); see also Ref. 2.

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