Bull. Chem. Soc. Jpn., 64, 3438—3441 (1991) [Vol. 64, No. 11

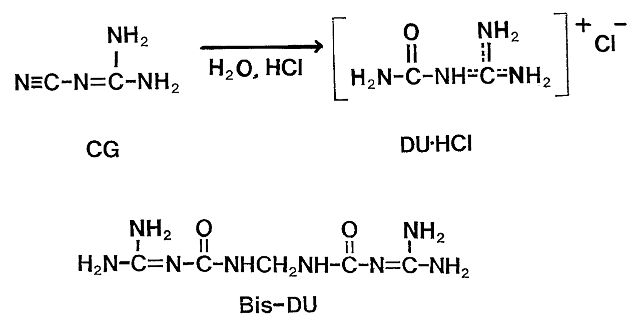
Reaction of Cyanoguanidine with Formaldehyde. V. Properties of Cyanoguanidine–Formaldehyde Resin as a Coagulating Agent of Anionic Colloidal Particles

Ryuichi Shiba,* Miyuki Takahashi, Toichi Ebisuno,†
Yoichi Shindou,† and Michiaki Takimoto†
Department of Applied Science, Faculty of Technology, Tokyo Denki University,
Kanda, Chiyoda-ku, Tokyo 101
† Department of Chemistry, Faculty of Science, Toho University,
Miyama 2-2-1, Funabashi, Chiba 274
(Received March 7, 1991)

The coagulation of anionic colloidal particles by the cyanoguanidine (CG)–formaldehyde resin has been reported to be caused by an electrostatic interaction of the (diaminomethylene)urea (DU) cation with an anionic surface charge of particles. Our results show that neither DU·HCl nor di-hydrochlorides of *N*,*N*′-methylenebis [*N*′-(diaminomethylene)urea] (Bis-DU·2HCl), itself, nor the resinous products of DU·HCl or Bis-DU·2HCl with formaldehyde, are such effective coagulating agents as the CG–formaldehyde resin and are not explicable only in terms of the electrostatic interaction. Gel-permeation chromatograms of the resins have revealed that the coagulation efficiency increased in proportion to the increase of the fraction of components having higher molecular weight, suggesting that components having higher molecular weight play an important role in coagulation due to the CG–formaldehyde resin.

The resinous products of cyanoguanidine (CG) with formaldehyde under acidic conditions are useful as commercial coagulating agents.[1] The reaction of CG with formaldehyde under acidic conditions is complicated, since the transform of CG into (diaminomethylene)urea (DU) is simultaneously accompanied by the hydroxymethylation and codensation of CG with formaldehyde, as well as the hydroxymethylation and condensation of DU with formaldehyde.[2–6] The coagulation of anionic colloidal particles by CG–formaldehyde resin (CG-resin) has since been explained to be due caused by neutralization of surface charge with cationic DU.[7] However, the detailed mechanism of coagulation has not yet been solved.

In order to elucidate the coagulation mechanism, the composition of the CG-resin was analyzed by gel-permeation chromatography under various conditions, together with those resinous products of DU·HCl and di-hydrochlorides of *N*,*N*′-methylenebis [*N*′-(diaminomethylene)urea] (Bis-DU·2HCl) with formaldehyde, which are hereafter referred to as the DU·HCl-resin and Bis-DU·2HCl-resin. The amounts of formaldehyde bound to DUs or released from the CG-resin by acid-hydrolysis were quantitatively measured, as well as the viscosity change, in order to confirm the reactions. The relationship between the distribution of the molecular weight of these resins and the coagulation efficiency was analyzed.



$$N{\equiv}C{-}N{=}\overset{NH_2}{\overset{|}{C}}{-}NH_2 \xrightarrow{H_2O,\ HCl} \left[H_2N{-}\overset{O}{\overset{\|}{C}}{-}NH{\cdots}\overset{NH_2}{\overset{\vdots}{C}}{\cdots}NH_2 \right]^{+} Cl^{-}$$

$$H_2N{-}\overset{NH_2}{\overset{|}{C}}{=}N{-}\overset{O}{\overset{\|}{C}}{-}NHCH_2NH{-}\overset{O}{\overset{\|}{C}}{-}N{=}\overset{NH_2}{\overset{|}{C}}{-}NH_2$$

Scheme 1.

Results and Discussion

Since CG was easily converted into DU·HCl by reacting it with equimolar H_2O and HCl, the CG-resin was considerd to have an analogous structure to that of the DU·HCl-resin. However, the reaction patterns of CG+HCl and DU·HCl with formaldehyde were different from each other. Figure 1 shows the time courses of the reaction of formaldehyde with CG- and DU·HCl-resins, respectively. A linkage of $-CH_2-O-CH_2-$ was scarcely formed in both resins. The amont of formaldehyde reacted tended to be underestimated when determined through iodometry, due to the formation of an insoluble product. More formaldehyde reacted with CG than with DU·HCl, and was incorporated to the methylene moiety of resious products. The amounts of the bound formaldehyde in the CG-resin increased for 2—3 h and were nearly saturated at 3 h. Gel-permeation chromatograms of CG- and DU·HCl-resins, as shown in Fig. 2, revealed that the CG-resin was enriched with components having higher molecular weight, compared with that of other resins. This was supported by the fact that the solution of the CG-resin is more viscous than that of the DU·HCl-resin. The distribution of molecular weight ranges from 200 to 1200 for the CG-resin which is wider than 150—400 for the DU·HCl resin. A similar result was also obtained when a Shodex Q801 column was used instead of TSK gel columns.

The results concerning the coagulation measurement

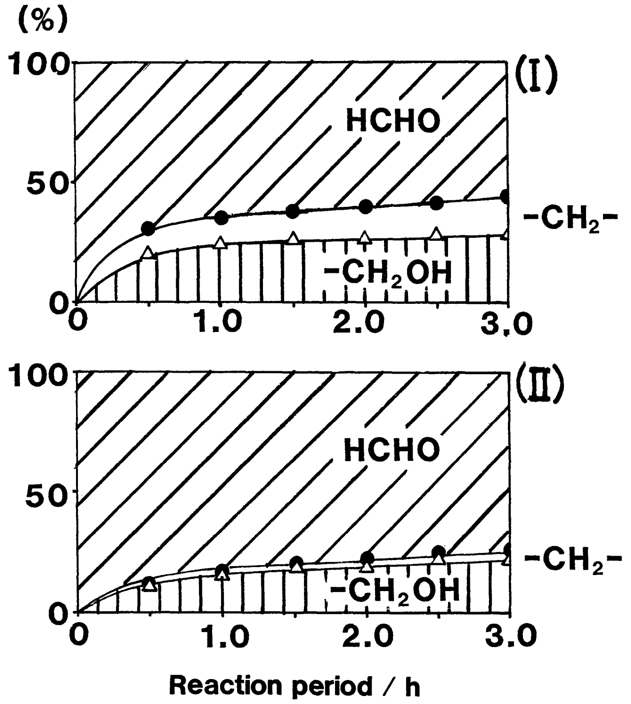


Fig. 1. Time courses of the reactions of cyanoguanidine (CG) and hydrochloride of (diaminomethylene)urea (DU·HCl) with formaldehyde at 70 °C. (I) CG+Formaldehyde+HCl=(1/2/1), (II) DU·HCl+Formaldehyde=(1/2). At 30-min intervals, aliquots of the reaction solutions were withdrawn, and the amounts of several types of formaldehyde were analysed by the Na_2SO_3 method (A) and the iodometry (B). ▨: HCHO=(A), ▥: $-CH_2OH$=(B)−(A), ☐: $-CH_2-$= (initial amount of formaldehyde)−(B).

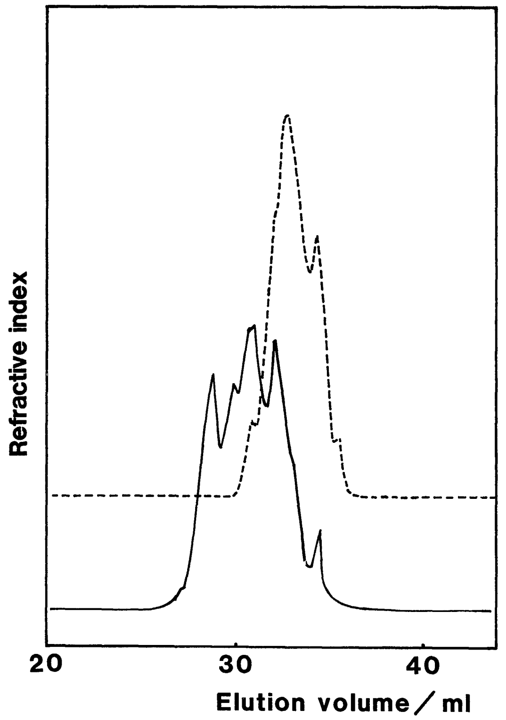


Fig. 2. Gel-permeation chromatograms of the CG- and DU·HCl-resins on combination columns comprising TSK gel G2500PW$_{XL}$ and G3000PW$_{XL}$. The resinous products of CG+Formaldehyde+HCl=(1/2/1)(——) and DU·HCl+Formaldehyde=(1/2)(-----), were eluted by a mixed solution of 0.5 mol dm^{-3} acetic acid and 0.5 mol dm^{-3} sodium acetate (1:1) at 40 °C.

are summarized in Fig. 3. Neither DU·HCl nor Bis-DU·2HCl, itself, nor the DU·HCl- or Bis-DU·2HCl-resin was such an effective coagulating agent as the CG-resin. Particles of Kaolin having anionic charges were also coagulated by these resins, which were virtually idnetical to polystyrene latex. These results were not explicable in terms of only the mechanisms hitherto presented, that the DU and/or Bis-DU cations should play decisive roles in the coagulation process of latex particles by the CG-resin. This suggests that the components having higher molecular weight in the CG-resin play an important role in the coagulation (flocculation) of latex particles. This was supported by the fact that the flocculation efficiency is improved with an increase of the fraction of components having higher molecular weight, that is, the flocculation efficiency of the CG-2.0F-HCl resin is superior to that of the CG-1.0F-HCl or CG-0.5F-HCl resin.

In order to obtain a clue for elucidating the structure of the CG-resin, its absorption spectrum in the UV region and ^{13}C NMR spectrum were measured. The CG-resin was acid-hydrolyzed under the same conditions as described in the experimental section. While the spectrum of the solution of CG was not affected by the pH, that of DU·HCl was different between acidic and alkaline pH. The spectrum of a solution of the CG-resin resembled that of DU (Fig. 4), suggesting that CG might be transformed into DU during the early stage of resinification. The ^{13}C NMR spectrum of the CG-resin also elucidated an early transformation of CG into DU, since the signal of $\delta=115.9$ (−CN) disappeared and a new signal of $\delta=150.9$ ($-CO-NH_2$) appeared during the early stage of resinification.

As shown in Fig. 5, the released formaldehyde molecules were classified into three categories, as described in the experimental section. The CG-resin has three types of methylene moieties, such as $=C(NHR)-NH-CH_2-NH-C(NHR)=$, $-CO-NH-CH_2-NH-CO-$, and $=C(NHR)-NH-CH_2-NH-CO-$.

These results suggested that the CG-resin has the structure of DU as the mother structure, and comprises a mixture of various condensates having three types of the methylene moieties. Our results suggest that the coagulation of anionic colloidal particles by the CG-formaldehyde resin is not explicable only in terms of its cationic charge, and that the components of the CG-formaldehyde resin having higher molecular weight are considered to play an important role in coagulation (fluocculation).

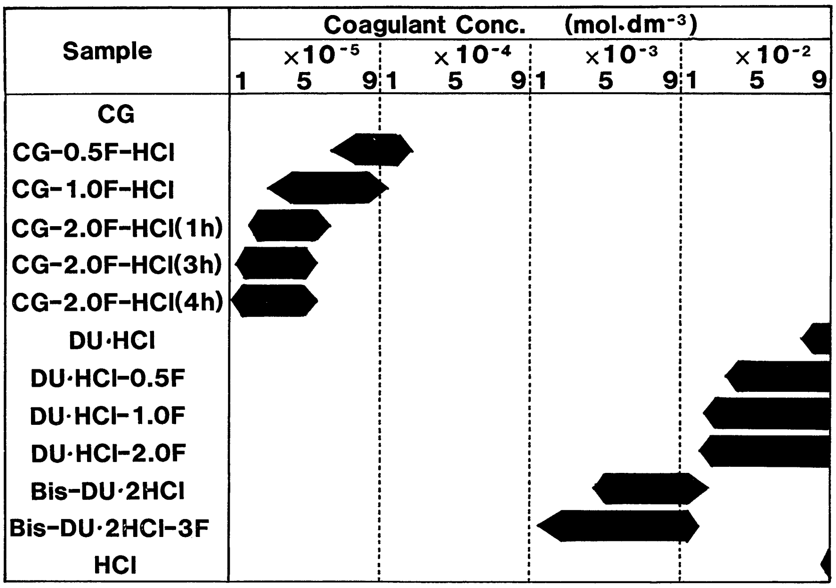


Fig. 3. Coagulation of polystyrene latex by CG, DU·HCl, Bis-DU·2HCl, and their resinous products with formaldehyde. Polystyrene latex: radius, 0.8—1.0 μm; final concentration 0.1%. The length and width of the band simultaneously represent the range of the concentration and the strength of the coagulating activity. CG-0.5F-HCl, CG-1.0F-HCl and CG-2.0F-HCl represent the resinous products of CG with formaldehyde (F) under acidic conditions (the feed mole ratios: CG/F/HCl=1/0.5/1, 1/1/1 and 1/2/1, respectively). DU·HCl-0.5F, DU·HCl-1.0F, DU·HCl-2.0F, and Bis-DU·2HCl-3.0F are the resinous products of DU·HCl/F=0.5, 1/1, and 1/2 and Bis-DU·2HCl/F=1/3, respectively. These products were obtained from the reactions for 4 h, unless otherwise noted.

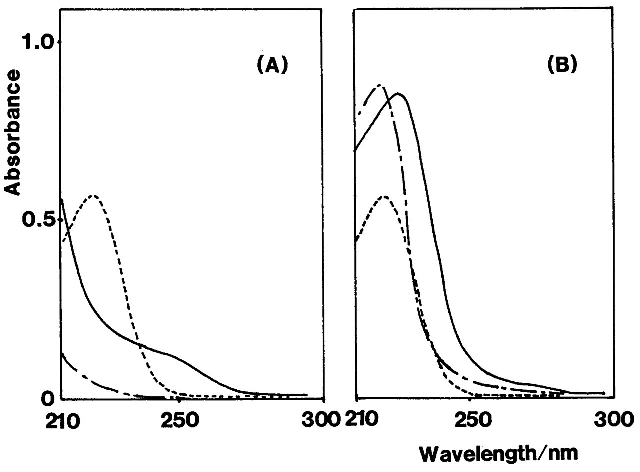


Fig. 4. UV spectra of CG, DU·HCl and the CG-resin under acidic and alkaline conditions. (A) Acidic: in 0.1 mol dm^{-3} HCl soln. (B) Alkaline: in 0.1 mol dm^{-3} aq NaOH soln. CG, ----: DU·HCl, —·—·: the CG-resin, ——. The CG-resin was prepared from CG and formaldehyde (CG/F/HCl=1/2/1) at 70 °C for 4 h.

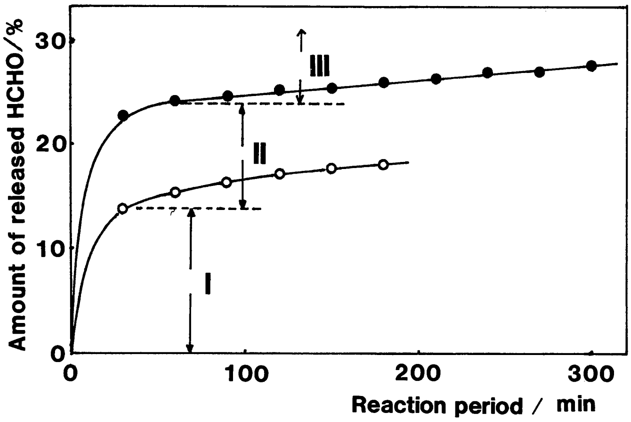


Fig. 5. Acid-hydrolysis of the CG-resin. The CG-resin used was the same as described in Fig. 4. The amounts of the released formaldehyde molecules were determined colorimetrically by the use of acetylacetone. The aq 1% solution of the CG-resin was hydrolyzed in 1.0 mol dm^{-3} HCl at 50 °C (—○—) and in 1.0 mol dm^{-3} H_2SO_4 at 90 °C (—●—). The numerals, I, II, and III each represents the type of released formaldehyde. I, the hydroxymethyl group: II, the methylene moiety in =C(NHR)-NH-CH_2-NH-C(NHR)= and/or in =C(NHR)-NH-CH_2-NH-CO-: III, the methylene moiety in -CO-NH-CH_2-NH-CO-.

Experimental

Preparation of Bis-CG, Bis-DU, and Resins. Bis(*N'*-cyanoguanidino)methane (Bis-CG) and Bis-DU were prepared by the same procedures already described.[8–10] Various CG-, DU·HCl-, Bis-DU·2HCl-resins were prepared by varying the reaction conditions, such as the feed mole ratios of CG, DU·HCl, Bis-DU·2HCl/formaldehyde, reaction temperature, and reaction periods. The typical preparations for CG- and DU·HCl-resins were as follows.

CG-resin: Forty two grams (0.5 mol) of CG were added to a mixture of 75 ml of 37% formalin (neuralized) (1.0 mol formaldehyde) and 66.3 ml of distilled water. After CG was thoroughly dissolved, 85.2 ml of 6 mol dm^{-3} HCl were added dropwise to the solution, the temperature of which was kept at 70 °C for 4—6 h.

DU·HCl-resin: The preparation procedure for DU·HCl-resin was virtually identical with that for CG-resin except for 69.4 g of DU·HCl and 75.7 ml of distilled water were used instead of 42 g of CG and 66.3 ml of distilled water.

Determination of Amounts of Formaldehyde. (I) Formaldehyde in the Reaction Solution. At 30 min intervals, aliquots of the solution were withdrawn, and the amounts of formaldehyde were determined by the Na_2SO_3 method (A) and iodometry (B). Residual amounts of formaldehyde (HCHO in Fig. 1)=(A); the amounts of formaldehyde in hydroxymethyl groups ($-CH_2OH$ in Fig. 1)=(B)−(A); the amounts of formaldehyde incorporated into the form of methylene moiety ($-CH_2-$ in Fig. 1)=(the initial amount of formaldehyde)−(B) were calculated.

(II) Formaldehyde in the Acid Hydrolysates. In order to obtain a clue to the structure of resins, a few standard samples (Bis-CG, Bis-DU and their hydroxymethyl derivatives) and resins were acid-hydrolyzed with 1.0 mol dm^{-3} HCl at 50 °C or 1.0 mol dm^{-3} H_2SO_4 at 90 °C and the amounts of formaldehyde were determined colorimetrically by the use of acetylacetone.[11] Further details were the same as described in our previous paper.[8] From the results on the standard samples the released formaldehyde molecules were classified into three categories, as follows: The most easily released formaldehyde (type I), from the hydroxymethyl groups; the moderately released ones (type II), from the methylene moiety in $=C(NHR)-NH-CH_2-NH-C(NHR)=$; and the ones hard to release (type III), from the methylene moiety in $-CO-NH-CH_2-NH-CO-$.

The Measurement of the Coagulation Efficiency. To carry out the coagulation measurement, 10 ml of a colloidal solution of 0.1% of polystyrene latex of 0.8—1.0 μm radius (or 25 ml of 600 mg dm^{-3} of Kaolin having anionic charges) and the resinous products solution containing 10^{-6}—10^{-2} mol dm^{-3} (the final concentration) were introduced to a stoppered test tube; the total volume was then adjusted to 20 ml (or 50 ml). The depth of the supernatant over the suspended layer was measured at 10-min intervals for 2 h. The coagulation efficiency of the resinous products was evaluated in terms of their minimum concentration in which the most rapid coagulation occurred.

Gel-Permeation Chromatography. A chromatographic separation of an aliquot of the resinous products was carried out on a combination columns comprising TSK gel G2500PW$_{XL}$ and G3000PW$_{XL}$, eluting by the mixed solution of 0.5 mol dm^{-3} acetic acid and 0.5 mol dm^{-3} sodium acetate (1 : 1) at 40 °C. The molecular weight of the components of the resins were estimated by calibration curves with polyethylene glycol.

^{13}C NMR Spectrometry. The NMR spectra of the products were measured in a D_2O solution with dioxane as the internal standard at 90 MHz on a JOEL FX 90Q instrument.

The authors wish to thank Dr. Takaaki Arai of Nihon University for generous gift of polystyrene latex.

References

1) S. Sakai, *Kobunshi,* **8**, 612 (1959).
2) M. Hamada, *Rep. Lab. Toho Reiyon,* **1**, 28 (1954).
3) U. Miyaoka and T. Matsui, *Rep. Fac. Tech. Fukui Univ.,* **2**, 85 (1955).
4) E. Yamada, *Kogyo Kagaku Zasshi,* **62**, 1161 (1959).
5) M. Hamada, *Rep. Lab. Toho Reiyon,* **2**, 85 (1955).
6) M. Takimoto, T. Ebisuno, and R. Shiba, *Bull. Chem. Soc. Jpn.,* **56**, 3319 (1983).
7) M. Nakajima and K. Kuwahara, *Kogyoyosui,* **1975**, 54.
8) R. Shiba, M. Takahashi, T. Ebisuno, and M. Takimoto, *J. Thermosetting Plast., Jpn.,* **10**, 141 (1989).
9) W. -D. Spiethoff, *Chem. Ber.,* **100**, 4050 (1967).
10) R. Shiba, M. Takahashi, T. Ebisuno, and M. Takimoto, *Bull. Chem. Soc. Jpn.,* **61**, 2197 (1989).
11) B. J. Comption and W. C. Purdy, *Anal. Chim. Acta,* **119**, 349 (1980).