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Methylene-hydantoin and Related Compounds. II. Poly-5-methylene-hydantoin and Poly-α-aminoacrylic Acid

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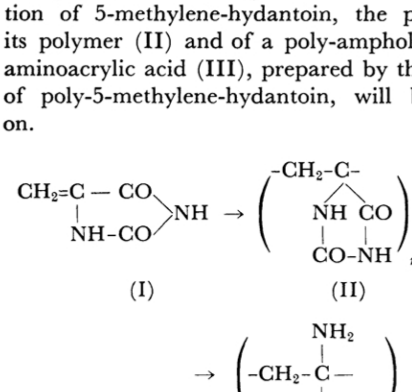
5-Methylene-hydantoin was polymerized easily by free radical initiators, and showed a higher reactivity in copolymerization with styrene. From the copolymerization of styrene (M_1) and 5-methylene-hydantoin (M_2), the monomer reactivity ratios, r_1 and r_2, were found to be 0.03 and 24, while the Q and e values in Alfrey-Price's Q-e scheme were found to be 21 and -0.23, respectively. As is shown by the large Q value, the high reactivity of 5-methylene-hydantoin is based on the high resonance stabilization of its radical, a stabilization which results from the conjugation system. This was also confirmed by a study of the ultraviolet spectrum. Poly-5-methylene-hydantoin showed electrolytic behavior in its solubility and solution viscosity. This property is due to the dissociation of NH at the 3 position of the hydantoin group. The polymers of 3-methyl-5-methylene-hydantoin and 3-phenyl-5-methylene-hydantoin were observed to show very weak acidities, resulting from the NH at the 1 position. Poly-α-aminoacrylic acid was obtained by the alkaline hydrolysis of poly-5-methylene-hydantoin. This polymer was soluble in water, and showed an unusual amphoteric behavior in solution viscosity.

In a previous paper,[1] the synthesis of 5-methylene-hydantoin (I) from pyruvic acid and urea was reported. This material is an exo-methylene compound, one which polymerizes easily in spite of having a bulky group at the double bond. In this paper, the investigations of the polymerization of 5-methylene-hydantoin, the properties of its polymer (II) and of a poly-ampholyte, poly-α-aminoacrylic acid (III), prepared by the hydrolysis of poly-5-methylene-hydantoin, will be reported on.



(I) (II) (III)

Results and Discussion

5-Methylene-hydantoin was polymerized in water and in acetic acid with free radical initiators. The polymerization was also carried out in situ with the monomer produced by the decomposition of dipyruvic triureide or by the reaction between pyruvic acid and urea without isolation. 3-Methyl- and 3-phenyl-5-methylene-hydantoin were polymerized in organic solvents with azobisisobutyronitrile. The results are shown in Table I.

The rate of the polymerization of 5-methylene-hydantoin was very fast. The precipitation of the polymer began immediately and was almost complete within one hour. The differences between the molecular weights of these polymers were shown by their solution viscosities. The smaller molecular weight of the polymer produced in water may be caused by the smaller solubility of the polymer in this solvent. It was found that the viscosities of polymers produced from the monomer in situ were almost the same as that obtained from the purified monomer.

The polymers were proved to be formed by the addition polymerization at the double bond in 5-methylene-hydantoin; there was a remarkable similarity between the infrared spectra of the polymer and of fused 5, 5-dimethyl-hydantoin, as is shown in Fig. 1.

It was found that 5-methylene-hydantoin did not copolymerize with vinyl acetate, but that it did copolymerize with styrene, methyl methacrylate and acrylonitrile when treated by a free radical initiator. Copoly-(acrylonitrile - 5 - methylene-hydantoin), containing a small amount of the latter monomer unit, showed good dyeing properties against a basic dyestuff such as Rhodamine 6G.

The copolymerization of styrene (M_1) and 5-methylene-hydantoin (M_2) was investigated in order

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[1] S. Murahashi, H. Yuki, K. Kosai and F. Doura, This Bulletin, **39**, 1559 (1966).

TABLE I. POLYMERIZATION OF 5-METHYLENE-HYDANTOIN AND ITS ANALOGUES

Monomer or starting material	g.	Solv.,	ml.	Init.,	mg.	Temp. °C	Yield %	$\eta_{sp/c}$*1 ($c=1$)
5-Methylene-hydantoin	1.0	H_2O	15	$K_2S_2O_8$	20	60	100	0.51
5-Methylene-hydantoin	1.0	AcOH	25	AIBN	10	60	100	1.16
Pyruvic acid, urea	5.0, 3.4	AcOH	25	AIBN	100	80	37	1.12
Dipyruvic triureide	5.0	HCOOH	100	AIBN	50	60	72	1.19
3-Me-5-methylene-hyd.	1.0	MeOH	20	AIBN	10	60	100	0.45*2
3-Ph-5-methylene-hyd.	2.0	Me_2CO	35	AIBN	60	53	85	0.49*3

1* Solvent, 0.09 N NaOHaq; $c=1$ g./100 ml.; temp., 30.0°C.
2* Solvent, 0.04 N NaOHaq.
3* Solvent, THF.

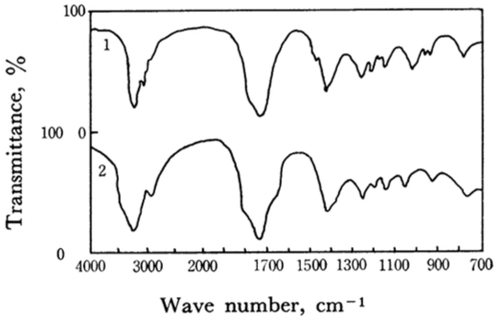

Fig. 1. Absorption spectra of: 1, fused 5,5-dimethyl-hydantoin; 2, poly-5-methylene-hydantoin in KBr disk.

TABLE II. COPOLYMERIZATION OF 5-METHYLENE-HYDANTOIN (M_2) AND STYRENE (M_1)

Total monomer 10^{-2} mol.	M_2*1	Time min.	Conv. %	Anal. N%	m_2*2
4.19	0.098	150	4.9	18.55	0.727
4.95	0.160	120	3.1	21.36	0.845
4.71	0.251	60	3.6	22.34	0.886
4.68	0.507	40	4.0	23.81	0.949
4.72	0.771	20	4.4	24.16	0.964
4.52	0.910	12	2.3	24.35	0.972

*1 M_2: Mole fraction of 5-methylene-hydantoin in monomer mixture.
*2 m_2: Mole fraction of 5-methylene-hydantoin in copolymer.

to obtain the monomer reactivity ratios of these two monomers. The copolymerization reaction was carried out in methanol at 70°C using azobisisobutyronitrile as the initiator. The results are shown in Table II. It was found that 5-methylene-hydantoin was incorporated predominantly in all the copolymers. The composition curve derived from the results in Table II is shown in Fig. 2. The curve shows a higher reactivity of 5-methylene-hydantoin than that of styrene; the monomer reactivity ratios, r_1 and r_2, were calculated to be 0.03 ± 0.02 and 24 ± 1 respectively. The Q and e values calculated from these r_1 and r_2 were 21 and -0.23 respectively.

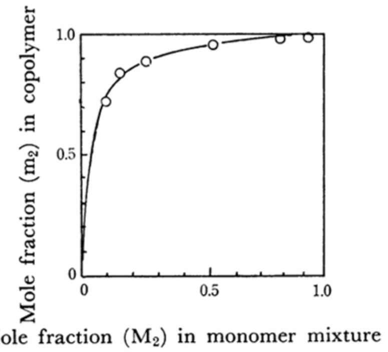

Fig. 2. Copolymer composition curve in the copolymerization of styrene (M_1) and 5-methylene-hydantoin (M_2).
Open circle: observed value
Full line: theoretical curve for $r_1=0.03$, $r_2=24$

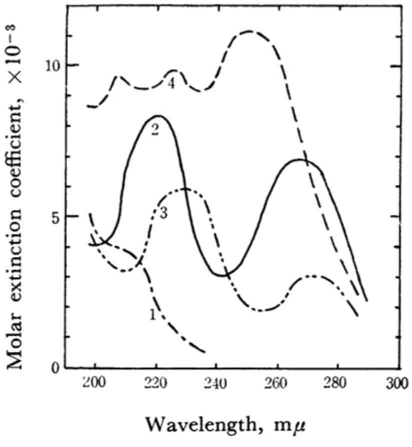

Fig. 3. Absorption spectra of: 1, 5-methyl-hydantoin in H_2O; 2, 5-methylene-hydantoin in H_2O; 3, 3-methyl-5-methylene-hydantoin in H_2O; 4, 3-phenly-5-methylene-hydantoin in EtOH.

The ultraviolet spectra of 5-methylene-hydantoin, 5-methyl-hydantoin, 3-methyl-5-methylene-hydantoin and 3-phenyl-5-methylene-hydantoin are shown in Fig. 3. 5-Methyl-hydantoin showed only an absorption band at 215 mμ, but the three methylene-hydantoins gave strong absorption bands at 240—280 mμ, resulting from the π—π^* transition, besides the bands in the 200—240 mμ region. The high reactivity of 5-methylene-hydantoin represented by the *Q* value is apparently correlated with this spectroscopic observation, which shows a strongly conjugated structure in this monomer.

Poly-5-methylene-hydantoin was a colorless solid which was insoluble in water and in common organic solvents, but soluble in dilute aqueous solutions of bases such as sodium hydroxide, ammonia, pyridine, triethylamine and ethanolamine. The dissolution of the polymer in a basic aqueous solution suggests the ionization of hydrogen at the 3 position of the hydantoin group. The hydrogen is made considerably acidic by the inductive effect of two neighboring carbonyl groups, contrary to the very weak acidity of the hydrogen at the 1 position. The mono-sodium salt of poly-5-methylene-hydantoin was obtained by pouring a solution of polymer and a large excess of sodium hydroxide into methanol. The polymers of 3-methyl- and 3-phenyl-5-methylene-hydantoin, which have no hydrogen at the 3 position, were also soluble in a basic aqueous solution, but higher concentrations of the base were required for their dissolution. Poly-5-methylene-hydantoin was soluble in a 0.02 N sodium hydroxide solution, and 0.5 N was needed to dissolve poly-3-phenyl-5-methylene-hydantoin with a bulky hydrophobic phenyl group.

The electrolytic properties of the polymers were observed by means of their viscosities. These are shown in Figs. 4 and 5. The reduced viscosities of a solution of poly-5-methylene-hydantoin in aqueous sodium hydroxide were measured at a constant concentration of the polymer but with varying concentrations of the base (Fig. 5), and vice versa (Fig. 4). Each viscosity curve showed a maximum at the equivalent concentrations of the polymer and the base. On the other hand, the reduced viscosity of the polymer in a 0.045 mol. aqueous triethylamine solution increased with a decrease in the concentration of the polymer (Fig. 4, Curve 2). The higher viscosity at a lower concentration of the polymer, even in the presence of an excess of triethylamine, is probably due to the small ionization of this weak base.

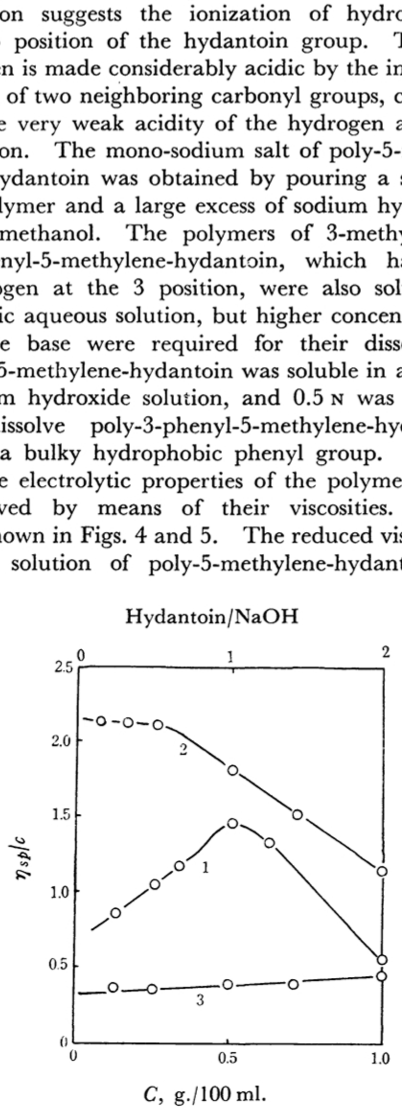

Fig. 4. Viscosities of poly-5-methylene-hydantoin and poly-3-methyl-5-methylene-hydantoin.
1 Poly-5-methylene-hydantoin in 0.179% aqueous NaOH solution
2 Poly-5-methylene-hydantoin in 0.460% aqueous Et_3N solution
3 Poly-3-methyl-5-methylene-hydantoin in 0.159 % aqueous NaOH solution
Temp., 30.0°C

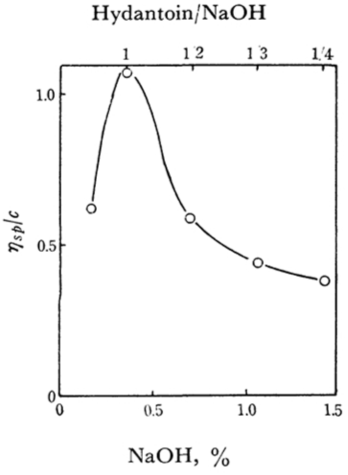

Fig. 5. Viscositiy of poly-5-methylene-hydantoin. Temp., 30.0°C; solvent, aq. NaOH; *c*=1 (g./100 ml.)

The solubility of poly-3-methyl-5-methylene-hydantoin in an alkaline solution suggests the electrolytic nature of this polymer. However, probably as a very weak poly-electrolyte, it gave only a linear relationship between the reduced viscosity and the polymer concentration in a 0.04 N aqueous sodium hydroxide solution.

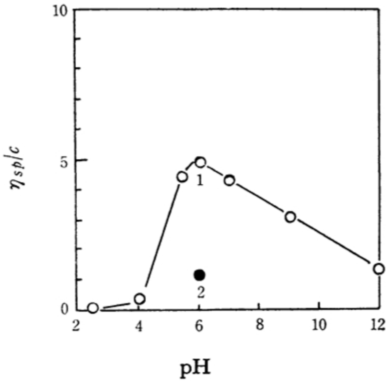

Fig. 6. Viscosity of poly-α-aminoacrylic acid.
1 Poly-α-aminoacrylic acid
2 Poly-5-methylene-hydantoin Na salt
Temp., 30.0°C; solvent, H_2O; *c*=1 (g./100 ml.)

Poly-5-methylene-hydantoin apparently behaved as a poly-acid upon the dissociation of the NH group at the 3 position. However, the changes in its viscosity with the variation in the circumstances were small in comparison with those of a typical poly-electrolyte, such as poly-acrylic acid or poly-methacrylic acid. This is probably due to the small degree of polymerization of the poly-5-methylene-hydantoin obtained. Furthermore, the bulky hydantoin group directly attached to the main chain may so largely prevent the internal rotation that the transformation of the polymer chain is restricted.

Poly-α-aminoacrylic acid is one of the most simple poly-ampholytes; several attempts to prepare it have been reported.[2-4] However, poly-α-aminoacrylic acid with quantitative amounts of free amino and acid groups has not been obtained. It has been found, though, that the neighboring amino and carboxyl groups easily reacted to form a lactam ring in strongly acidic media.

The hydrolysis of poly-5-methylene-hydantoin was carried out in aqueous sodium hydroxide at the boiling point. About fourteen days were necessary to complete the reaction. The careful neutralization of the reaction mixture gave a colorless polymer, which was soluble in water and dimethylformamide. The solubility in water was preserved not only in the alkaline region but also in the acidic region above pH 3. At pH 3 the polymer began to precipitate, but it was dissolved reversibly by the addition of aqueous alkali.

The elemental analysis showed the polymer to be poly-α-aminoacrylic acid and that it did not have a lactam ring in any appreciable amount. The number of free amino groups in the polymer was determined spectroscopically with the dinitrophenylated polymer. The amino-nitrogen content as calculated from the data was consistent with that of poly-α-aminoacrylic acid.

The amphoteric nature of the polymer was observed by means of a study of its solution viscosity. The effects of acid and base on the reduced viscosity are shown in Fig. 6. The viscosity of natural protein usually shows a minimum at the isoelectric point. Contrary to the usual poly-ampholyte, however, the viscosity of this polymer showed a maximum at pH 6, and decreased on both sides of that point almost symmetrically. This peculiar behavior of this polymer may be considered to be due to its intermolecular association in the neutral region and to its dissociation on the acidic and basic sides. The crowded amino and carboxyl groups along the main chain of this polymer seem to form zwitter-ions not only intramolecularly but also between the polymer molecules. This is also suggested by the viscosity of poly-α-aminoacrylic acid, which is very much higher than that of its parent polymer, poly-5-methylene-hydantoin.

Experimental

The Preparation of Poly-5-methylene-hydantoin.—a) The solution of 5-methylene-hydantoin (1.0 g.) and azobisisobutyronitrile (0.01 g.) in acetic acid (25 ml.) was sealed in an ampoule under nitrogen, and then left to stand at 60°C for 20 hr. The polymer thus precipitated was filtered, washed with methanol, and dried in vacuo at 100°C for one day. Poly-5-methylene-hydantoin (1.0 g.) was obtained. It was a colorless solid which decomposed above 300°C and was soluble in aqueous alkali, and was insoluble in water and in common organic solvents.

Found: C, 42.80; H, 3.74; N, 24.74. Calcd. for $C_4H_4N_2O_2$: C, 42.86; H, 3.60; N, 25.00%.

Its infrared spectrum is shown in Fig. 1.

b) Pyruvic acid (5.0 g.) and urea (3.4 g.) were dissolved in acetic acid (25 ml.) containing a small amount of hydrochloric acid, and the solution was heated at 100°C for 20 min. Then azobisisobutyronitrile (0.1 g.) was added to the cooled solution, and the solution was left to stand at 80°C for 20 hr. Poly-5-methylene-hydantoin (2.3 g., 37%) was obtained by the treatment described above.

c) A suspension of dipyruvic triureide (5.0 g.) in 80% formic acid (100 ml.) was heated at 100°C for 20 min.; after it had then cooled, the resultant clear solution was left to stand at 60°C for 20 hr. with azobisisobutyronitrile (0.05 g.). Poly-5-methylene-hydantoin (2.5 g., 72%) was obtained such as in the above-described treatment.

The Polymerization of 3-Phenyl-5-methylene-hydantoin.—The monomer was prepared according to Bergmann.[5] It melted at 200°C and polymerized immediately. (Lit.[5] 270°C (decomp.)).

A solution of 3-phenyl-5-methylene-hydantoin (2.0 g.) and azobisisobutyronitrile (0.06 g.) in acetone (35 ml.) was heated at 53°C for 20 hr. and then poured into methanol. The precipitates were washed with methanol and dried. The colorless polymer thus obtained (1.9 g.) was reprecipitated from tetrahydrofuran and methanol, and then dried. Poly-3-phenyl-5-methylene-hydantoin (1.7 g.) was thus obtained; yield, 85%. It was decomposed above 300°C; it was soluble in tetrahydrofuran, pyridine, dimethylformamide and dimethyl sulfoxide, and insoluble in water, alcohol, benzene and ether.

Found: C, 63.83; H, 4.54; N, 14.22. Calcd. for $C_{10}H_8N_2O_2$: C, 63.82; H, 4.29; N, 14.89%.

The Polymerization of 3-Methyl-5-methylene-hydantoin.—The monomer was prepared as has been described in the previous paper.[1] The polymerization was carried out in the same manner as that of 3-phenyl-5-methylene-hydantoin. Poly-3-methyl-5-methylene-hydantoin was thus obtained in a 78% yield. It was decomposed above 270°C; it was soluble in tetrahydrofuran, pyridine, dimethylformamide and

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2) R. Adams, J. L. Johnson and B. Englund, *J. Am. Chem. Soc.*, **72**, 5080 (1950).

3) E. Katchalski, I. Grossfeld and M. Frankel, ibid., **70**, 2094 (1948); M. Frankel and M. E. Reichmann, *J. Chem. Soc.*, **1952**, 289.

4) S. Sakakibara, This Bulletin, **32**, 13 (1959); **33**, 814 (1960); **34**, 171, 205 (1961).

5) M. Bergmann and D. Delis, *Ann.*, **458**, 82 (1929).

dimethyl sulfoxide, and insoluble in alcohol and benzene.

Found: C, 45.70; H, 5.07; N, 21.17. Calcd. for $C_5H_6N_2O_2$: C, 47.62; H, 4.80; N, 22.21%.

Sodium Salt of Poly-5-methylene-hydantoin.—A solution of poly-5-methylene-hydantoin (0.1 g., 0.89 mmol.) in 1 N sodium hydroxide (5 ml., 5.0 mmol.) was left to stand at room temperature for 30 min. Colorless precipitates were then produced by pouring the solution into methanol, filtering it, washing it with methanol, and drying it. Mono-sodium salt of poly-5-methylene-hydantoin (0.12 g.) was thus obtained. The salt was dissolved in water, and the original polymer was recovered by the addition of dilute hydrochloric acid.

Found: N, 20.2; Na, 16.0. Calcd. for $C_4H_3N_2O_2Na$: N, 20.9; Na 17.2%.

The Copolymerization of 5-Methylene-hydantoin with Styrene.—5-Methylene-hydantoin, freshly distilled styrene and azobisisobutyronitrile (about 5 mol% against the total of monomers) were dissolved in purified methanol (8 ml.). The copolymerization was carried out in a sealed glass tube under nitrogen at 70°C. The polymer composition was calculated from the results of a nitrogen analysis (Table II).

The Hydrolysis of Poly-5-methylene-hydantoin.—The solution of poly-5-methylene-hydantoin (1.5 g.) in 15% sodium hydroxide (100 ml.) was refluxed under a nitrogen stream. The evolution of ammonia ceased after 14 days. Hydrochloric acid was then added to the cold solution, and the pH was adjusted to about 6. The silicic acid produced from the glass vessel was precipitated, filtered off, and washed with water. The filtrate and washings were combined and concentrated in vacuo. To the residual solution (50 ml.), dilute hydrochloric acid was added, the pH of the solution was adjusted to 3, and the polymer was precipitated. The polymer was filtered, washed with 0.001 N hydrochloric acid and methanol, and dried in vacuo at 100°C for one day. A Beilstein test showed no chloride ion to be present. Poly-α-aminoacrylic acid (0.8 g.) was obtained; yield, 60%; colored above 250°C; soluble in water and dimethylformamide, and insoluble in common organic solvents.

Found: C, 40.7; H, 5.5; N, 16.0. Calcd. for $C_3H_5NO_2$: C, 41.4; H, 5.8; N, 16.1%.

The Determination of the Free Amino Group in Poly-α-aminoacrylic Acid.—The dinitrophenylation of the polymer was carried out according to Levy.[6] Poly-α-aminoacrylic acid (20.00 mg.) was dissolved in a solution of sodium carbonate (84.4 mg.) in water (30.0 ml.). 2, 4-Dinitrofluorobenzene (200 mg.) was then added to the solution, and it was stirred vigorously at 40°C for 2 hr. The excess reagent and the phenol thus produced were extracted off with ether from the acidified reaction mixture. The solution was neutralized with sodium bicarbonate. The ultraviolet spectrum of the solution of poly-α-(N-2, 4-dinitrophenyl)-aminoacrylic acid was measured with a Hitachi Perkin-Elmer type S 12-B spectrophotometer. The solution showed a λ_{max} at 360 mμ; the content of the dinitrophenyl group in the polymer was estimated using N-2, 4-dinitrophenyl glycine ($\lambda_{max}=360$ mμ, $\varepsilon_{max}=16.5\times10^3$; Lit.[7] $\lambda_{max}=360$ mμ, $\varepsilon_{max}=16.6\times10^3$) as the standard substance. The calculated amount of the free amino group for poly-α-aminoacrylic acid was 98 per cent of the theoretical amount.

We wish to express our deepest thanks to Mr. Heihachiro Kawaguchi for his active collaboration in the experiments.

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6) A. L. Levy and D. Chung, *J. Am. Chem. Soc.*, **77**, 2899 (1955).

7) C. Hashimoto, This Bulletin, **28**, 385 (1955).