

A Reinvestigation of Parabanic Acid-Formaldehyde Polymerization

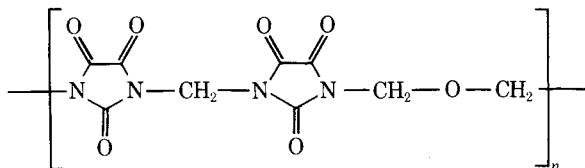
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Synopsis

An earlier paper reported the synthesis of derivatives of parabanic acid, mono- and dimethylol parabanic acid, and their polymerizations with themselves and with aqueous formaldehyde. The study is reported herein to clarify that work. The reported synthesis of monomethylol parabanic acid was not reproducible. Identical low-molecular-weight polymers were obtained from the condensation of parabanic acid with formalin and from the self-condensation of dimethylol parabanic acid. The final polymer contains a little of the original parabanic acid and a large amount of the condensation product from a ring opening byproduct. Commonly, two products are possible, a soluble one at lower reaction times and temperatures and an insoluble one at longer times and temperatures. Films cannot be formed by solvent casting or heat pressing. Elemental analyses and infrared spectra show that the actual products are not of the structure originally proposed.

INTRODUCTION

Several years ago a publication appeared which described the synthesis of monomethylol parabanic acid and dimethylol parabanic acid by the room temperature condensation of formaldehyde (formalin) with parabanic acid.¹ Further, this paper discussed several condensations of these materials in hot, aqueous formaldehyde. It was reported that the following reactions yielded polymer: (a) parabanic acid with formalin, (b) monomethylol parabanic acid alone, and (c) parabanic acid with dimethylol parabanic acid. These polymers (proposed structure I) were shown then to be useful for treating rayon for crease resistance:

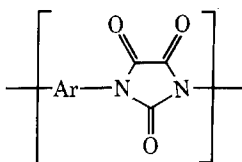


I

Other reports of polyparabanic acids are available in the literature.^{2,3} These materials, however, are not formed from the parabanic acid as monomer but from the hydrolysis of the poly(iminoimidazolidinedione). These materials (II) contain aromatic functions linking the parabanic acid nuclei and are known to

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be thermally stable film-formers.



II

The purpose of this study was to clarify the procedures and elucidate the polymer structure of that material reported in the earlier paper.¹

EXPERIMENTAL

General

Hydrolysis tests were carried out in 10% w/v sulfuric acid or 10% w/v NaOH. Samples (~100 mg) were placed in 250-mL erlenmeyer flasks with either 50 mL of acid or base and sealed with a rubber stopper. The flasks were placed on a power shaker and shaken continuously at room temperature (25–28°C). After five days, 1 mL of hydrolysate was removed to a test tube, 4 mL of pH 4.5 acetate buffer, and 1 mL of Nash's reagent⁴ was added. The mixture was shaken and heated at 37°C for 30 min of a water bath. The depth of yellow color that developed was dependent on formaldehyde concentration. The formaldehyde concentration in the hydrolysate solutions was estimated by comparison with standards made by diluting 0.1, 0.5, 1.0, and 2.0 mL of 37.3% formalin to 50.0 mL with distilled water and then taking 1.0 mL from each standard and treating exactly as for hydrolysate solutions. In several cases, the presence of formaldehyde was confirmed by mixing several drops of test solution with 2 mL of 6*M* H₂SO₄ and enough 1,8-dihydroxy-naphthalene-3,6-disulfonic acid to cover the tip of a micro-spatula. The mixture was warmed to 60°C and if formaldehyde was present a violet color developed after about 15 min.

Parabanic Acid (PBA)

This compound was made according to Murray's procedure.⁵ The yield was 62.5% and the melting point was 240–244°C. Several attempts to make PBA by the earlier procedure¹ were unsatisfactory because too little solvent for the reaction and too little acid for neutralization of the product were specified.

ANAL. Calcd for C₃H₂N₂O₃: C, 31.59%; H, 1.77%; N, 24.56%; O, 42.08%. Found: C, 31.47%; H, 1.66%; N, 24.59%; O, 42.48%.

Dimethylol Parabanic Acid (DPBA)

Parabanic acid (11.4 g, 0.1 mol) was added to 50 mL H₂O at 25°C in a covered 150-mL beaker fixed with a magnetic stirrer. Formalin (14.9 mL of 37.3%, 0.2 mol) was added dropwise to the mixture. During addition of formalin the parabanic acid slowly went into solution. After addition was complete, the reaction mixture was evaporated to dryness by allowing it to stand ~12 days in a vacuum desiccator. The resulting white solid was recrystallized from methyl alcohol to give a 30% yield of DPBA; mp 130–135°C C; lit. 130°C.¹

ANAL. Calcd for $C_5H_6O_5N_2$: C, 34.49%; H, 3.47%; N, 16.09%. Found: C, 34.34%; H, 3.41%; N, 16.27%.

Note. On subsequent syntheses of DPBA, it was found that solvent removal could be effected more conveniently by gentle warming ($\sim 35^\circ\text{C}$) and overnight rotary evaporation.

Attempted Synthesis of Monomethylol Parabanic Acid (MPBA)

Synthesis was unsuccessfully attempted in two ways:

(1) PBA (11.4 g, 0.1 mol) was added to 50 mL of H_2O at $5-7^\circ\text{C}$ in a covered 150-mL beaker equipped with a magnetic stirrer. Formalin solution (7.45 mL, 37.3%, 0.1 mol) was then added dropwise, and the reaction mixture stirred for 15 min. The solvent was removed by allowing the reaction mixture to stand in a vacuum desiccator under water aspiration for ~ 12 days. The white solid residue was recrystallized from water. A white crystalline product (<10 mg) separated from the concentration, viscous, mother liquor upon prolonged (~ 2 weeks) refrigeration at $\sim 5^\circ\text{C}$, mp $240-246^\circ\text{C}$. MPBA was reported to melt at 142°C .¹

(2) PBA (11.4 g, 0.1 mol) was dissolved in 70 mL of H_2O at 50°C in a covered 250-mL beaker. The formalin solution (7.38 mL) was cooled to about 5°C before it was added dropwise to the rapidly stirred reaction mixture. After addition was complete, the reaction mixture was allowed to warm to room temperature and the solvent was rotary evaporated overnight with minimal heat to yield a white solid, mp $127-248^\circ\text{C}$, after one recrystallization from water. After a second recrystallization, a very small quantity of white product melting at $241-245^\circ\text{C}$ was obtained and assumed to be PBA.

Polymerizations

Polymers were made by aqueous reaction of equimolar amounts of PBA and formaldehyde, DPBA was itself, and equimolar amounts of PBA and DPBA, by following the previous procedure.¹

Table I lists specific reaction conditions for the various polymerizations. A white solid precipitated, usually during the first 8 h. All reactions were terminated by filtering the reaction mixture hot. The residue was washed with several portions of distilled water and then dried under gentle heat (infrared lamp).

The filtrates from polymerization reactions were cooled at $\sim 5^\circ\text{C}$. A flocculent, translucent precipitate usually formed. The precipitates were collected by filtration, washed with distilled water and dried.

Example 1: Polymerization of parabanic acid and formaldehyde (RXN no. 1, Table I): PBA (25.01 g, 0.2194 mol) in a 500-mL beaker was dissolved in 300 mL of distilled water with gentle warming and magnetic stirring. When dissolution was complete, the solution was cooled to room temperature. Formalin (37.38, 16.4 mL, 0.219 mol) was added dropwise with stirring at room temperature. The beaker was covered and the temperature was brought to 90°C and then slowly reduced to 50°C over a period of several hours. The solution was stirred for a total of 15 h, at the end of which time a small amount of white precipitate was present. This was collected, washed and dried to give 0.75 g, mp $245-246^\circ\text{C}$ with decomposition. The infrared spectrum was not identical to PBA. The filtrate was reacted for 7.25 h more at 90°C . A considerable quantity

TABLE I
 Polymerizations

RXN no.	Reaction Conditions			Products							
	Reactants (mol)	Water (mL)	Temp (°C)	Time (h)	Isolation ^a	Solubility ^b	m_p^d (°C)	n^c	Elemental analysis ^e		
									C	N	
1	PBA (0.2194) CH ₂ O (0.2194)	300	90-50 ^d	15	R	i	286-288	—	33.39	2.98	24.40
2	PBA (0.2194) CH ₂ O (0.2194)	300	85	27	F	i	220-230	—	31.87	3.28	21.02
3	PBA (0.2194) CH ₂ O (0.2413)	300	85	27	F	δDMF	264-265				
4	DPBA (0.05) PBA (0.05)	137	85	26	R	i	273-275		33.90	3.10	25.58
5	DPBA	—	140/vacuo	4	F		220-225				
6	PBA (0.2194) CH ₂ O (0.2194)	300	48-60	7	R	i	239-241		33.16	3.74	28.47
7	DPBA (0.00511)	7	50-60	16	F	δDMF	235-237	0.28	33.32	3.31	25.12
8	PBA (0.167) CH ₂ O (0.167)	228	55-60	7	F	δDMF	260-263				
					R	i	267-269				
					F	δDMF	250-253				
					F	δDMF	253-258	0.06			

^a R = product precipitated during reaction, granular. F = product was recovered from reaction filtrate, gummy.

^b Solvents tried = DMF, acetone, MEK, acetic acid, pyridine, methanol, ethyl acetate, xylene, toluene, wtaer, petroleum ether, butyl cellosolve, and *N*-methylpyrrolidone.

^c Inherent viscosity in dL/g at 25°C and 0.5 g/100 mL DMF.

^d Temperature was reduced to 50°C after initial reaction at 90°C; CH₂O was evolved.

^e Calcd for proposed¹ structure: C₉H₆O₇N₄; C, 38.29%; H, 2.09%; O, 39.54%; N, 20.08%.

of white matter precipitated with most of its clinging to the sides of the beaker. The reaction mixture was filtered hot. A flocculent white precipitate began forming in the filtrate as it cooled. The residue was washed with 300 mL of water in portions, collected by filtration, and dried. A white product (4.42 g, product no. 1-R, Table I) was obtained, which turned yellow at 283°C, brown at 286°C, and melted with decomposition at 286–288°C. The filtrate was refrigerated overnight. The flocculent precipitate that formed was collected by filtration to give 4.41 g of white product (product no. 1-F, Table I) softening at 215°C, turning yellow, then deep amber at 220–235°C.

Example 2: Polymerization of dimethylol parabanic acid with parabanic acid (RXN no. 4, Table I). PBA (0.0500 mol) and DPBA (0.0400 mol) were heated together at 85°C in 137 mL of water with magnetic stirring in a 250-mL erlenmeyer flask covered with a watch glass. After 26 h, the white precipitate that had formed was collected by filtration while hot, washed with water, and dried under gentle heat to give 5.00 g of product, mp 273–275°C decomp (product no. 4-R, Table I).

The filtrate from the above reaction was cooled several days at ~5°C. A product consisting of large transparent crystals and opaque granular solid separated. This was collected by filtration and washed and dried under gentle heat to give 3.86 g (product no. 4-F, Table I), mp 220–225°C decomp.

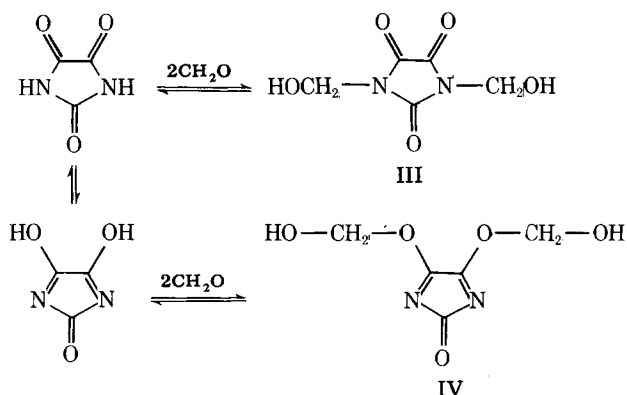
RESULTS AND DISCUSSION

Monomer Synthesis

Dimethylol parabanic acid (DPBA) was synthesized by the reported procedure albeit in only 60% yield compared to the 91% yield reported earlier.¹ Also, a quite tedious procedure was given in the earlier paper, that of slow evaporation of the water from the reaction mixture in a vacuum desiccator requiring at least 1 week. This process was modified by performing the drying and isolation on a rotary evaporator with gentle warming (below 35°C). Temperature limitation is critical because DPBA will slowly revert to formaldehyde and PBA by heating it in the dry state or by simply letting it stand in distilled water at room temperature.

Evidence for the replacement of the acidic hydrogens in PBA rests in the disappearance of the 2,740-cm⁻¹ band of PBA and the appearance of a band for the methylol structure at 1050 cm⁻¹ in the infrared spectrum.

Some question remains as to the exact structure of this dimethylol derivative. It is plausible that the methylol groups did not attach to the nitrogen (as in structure III) but instead to the oxygen from the enol form of PBA (as in structure IV):



An nmr spectrum was therefore taken to DPBA to clarify this structure. This technique was not conclusive; however, the CH_2 protons do appear far downfield ($\delta = 5.19$). Such a chemical shift is more easily explained by a methylene flanked by two oxygens rather than by one oxygen and one nitrogen, i.e., structure IV may be favored.

DPBA is readily hydrolyzed in water at room temperature over 5 days and is also unstable to base. In either case formaldehyde and PBA are the products as is the case when pure DPBA is heated at 80°C under vacuum.

The synthesis of monomethylol parabanic acid (MPBA) was attempted as published¹ and with several modifications thereon (more water and higher temperatures). This monomer was never isolated. One of the anomalies which appeared was in the experimental procedure requiring 0.1 mol of PBA to be dissolved in 50 mL of water at $5-7^\circ\text{C}$. However, the solubility of PBA is such that this is not possible. Further, even though 37% formalin solution was added in an attempt to react the heterogeneous mixture, the monomeric PBA never did dissolve.

Polymers

Several polymerizations were run and low-molecular-weight products were obtained from the reactions of: (a) equimolar amounts of PBA and formaldehyde, (b) DPBA alone, and (c) equimolar amounts of PBA and DPBA. All reactions were carried out by heating the monomers in aqueous solution. The original procedure called only for heating the reactants without specifying volume, time, or temperature. The last two factors were found to be important in determining the properties of the product. That is, increased time or higher temperatures resulted in a larger fraction of the product being insoluble in any solvent tried.

In general, the polymerizations gave a white precipitate during the reaction and this precipitate was filtered from the hot reaction mixture. When the filtrate was then cooled, a second product was formed. The first precipitate (type R in Table I) was insoluble in all solvents. The second precipitate (type F in Table I) was soluble initially in DMF. The earlier authors¹ then called for purification of products by precipitation from a DMF solution into benzene. When the soluble product was so treated, it was rendered insoluble in all solvents. A short (7-16 h) reaction time at a relatively low temperature ($50-60^\circ\text{C}$) tended to result in soluble polymers in DMF (before reprecipitation with benzene). Data from various reactions are summarized in Table I.

The polymers cannot be considered to be thermally stable in that they decomposed in melting point capillaries beginning usually at 200°C and the decomposition was essentially complete at 288°C . Reaction conditions caused some variation in the decomposition temperature.

All polymers produced here were unstable in 10% NaOH and H_2SO_4 upon agitation at room temperature for 5 days. Formaldehyde was produced and the infrared spectra demonstrated gross changes.

Except as noted above, the polymers were insoluble in DMF, acetone, methyl ethyl ketone, glacial acetic acid, pyridine, methyl alcohol, ethyl acetate, xylene, toluene, water, butyl cellosolve, and petroleum ether.

In an attempt to form a film directly from monomer, DPBA was pressed at

120°C and 20,000 psi for 30 min. A very weak, brittle, powdery, semitransparent film resulted. Attempts at film deposition from a DMF solution of the polymer yielded powdery deposits.

Because of the instability of DPBA (owing to facile reversion to PBA and formaldehyde) all polymerizations were essentially reactions of formaldehyde with parabanic acid in water. Therefore, it is not surprising that all products were quite similar regardless of starting materials. Furthermore, owing to the ring opening character of PBA, yet further structural differences from those reported are certain to occur and constitute the major portion of the backbone. The facts that polymers obtained were mostly insoluble, suggesting crosslinking, and that polymer solubility was sensitive to reaction time and temperature, suggesting hydrolysis, strongly support the notion that the parabanic acid ring opens during polymerization in hot water.

In an effort to clarify this structure, elemental analyses were compared to the calculated values for the structure originally proposed and to several other plausible structures proposed as a result of this work. Elemental compositions were not reported in the original paper. It is obvious that the real structure is quite far from that originally proposed and, in fact, there must be considerable contribution from other structures including urea-formaldehyde condensation products.

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