continued interest of Dr. A. J. Riker, Department of Plant Pathology, and Dr. W. H. Peterson, Department of Biochemistry, is acknowledged gratefully.

Summary

The polysaccharide produced by the crown-gall organism, *Phytomonas tumefaciens*, was partially methylated. Hydrolysis of this methyl derivative yielded 3,4,6-trimethylglucopyranose.

Oxidation of the trimethylglucose produced 3,4,6-trimethyl-δ-gluconolactone, and on treatment of this lactone with phenylhydrazine, the phenylhydrazide of 3,4,6-trimethylgluconic acid was obtained.

A 3,4,6-trimethylphenyl osazone was also prepared from the trimethylglucose, which proved to be identical with that obtained from the hydrolysis products of trimethylinulin.

These data show that a substantial proportion of the glucopyranose residues in the crown-gall polysaccharide are united through 1,2-glucosidic linkages.

BERKELEY 4, CALIFORNIA RECEIVED MARCH 27, 1950

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polyalkylene Sulfides. IV. The Effect of *p*H on Polymer Size[1,2]

BY C. S. MARVEL AND GENE NOWLIN

The primary purpose of the present work was to investigate the effect of *p*H on emulsion polymerization of dithiols and dimercaptans in the hope of finding optimum conditions for producing high molecular weight polyalkylene sulfides. Earlier work[3,4] in this Laboratory has shown that emulsion polymerization gives more satisfactory results than solution polymerization. However, the polymer size failed to reach the magnitude desired and the results were not consistent.

The emulsion polymerization of hexamethylenedithiol with biallyl (1,5-hexadiene) was studied in emulsions in which MP-189-EF[5] was used as an emulsifier and a persulfate was employed as the initiator with copper and bisulfite activators as previously recommended by Bacon[6] and Morgan[6] for the reduction activated polymerization of acrylonitrile.

In the first series of experiments the *p*H of the emulsifier solution, containing the initiator and activators, was varied within the range 3.0 to 8.6 by addition of proper amounts of sodium hydroxide solution. Duplicate runs were made in all polymerization studies reported here. The yields and inherent viscosities are summarized in Table I.

TABLE I

THE EFFECT OF *p*H ON POLYMER SIZE OF POLYHEXAMETHYLENE SULFIDE IN UNBUFFERED EMULSION

Number	0.1 *N* NaOH, ml.[a]	*p*H,[b] initial	*p*H, final	Conversion, %[c]	Inherent viscosity[d]
1	2.93	3.0	2.4	92	0.77
2	3.89	3.5	2.4	93	.74
3	4.27	4.3	2.5	91	.74
4	4.40	5.0	2.5	92	.66
5	4.70	6.0	2.5	93	.74
6	5.10	6.9	2.6	90	.70
7	7.30	8.6	6.4	75	.22

[a] This is the volume of hydroxide solution necessary to give the desired initial *p*H. [b] All *p*H determinations reported throughout this work were measured with a Beckman *p*H meter, model H2. [c] Based on recovery of polymer after one reprecipitation as described in the experimental. [d] All inherent viscosities reported throughout this paper were determined from solutions containing 0.4 g. of polymer/100 ml. of chloroform.

It can be seen that polymer size, as determined from inherent viscosities, is essentially constant when the polymers are prepared in emulsions initially in the *p*H 3.0–6.9, and per cent. conversions are approximately equal (90–93%); furthermore, the *p*H dropped to the same value, 2.4–2.6, at the end of the polymerization period. However, when the initial *p*H was 8.6, there was a smaller *p*H change (to 6.4), the conversion (75%) and polymer size (inherent viscosity, 0.22) were considerably decreased. This might be expected, since the oxidation of mercaptans to disulfides is a competing reaction in alkaline medium.[7,8] In a preliminary experiment it was found that the inherent viscosities of polymers prepared at a *p*H of 2.0 to 1.0 dropped appreciably (0.28 to 0.16).

In a variation of these experiments the *p*H of the emulsifier solution was adjusted to the desired value in the range 3.0–5.4 prior to introduction of the initiation and activators. On addition of the latter agents to the adjusted emulsifier solution the *p*H in each instance dropped to 2.6–2.7. At the conclusion of the

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] This is the fourth paper on Polyalkylene Sulfides; for the third, see Marvel and Baumgarten, *J. Polymer Sci.*, in press.

[3] Marvel and Chambers, THIS JOURNAL, **70**, 993 (1948).

[4] Marvel and Aldrich, *ibid.*, **72**, 1978 (1950).

[5] MP-189-EF is an electrolyte-free emulsifier which consists essentially of mixed alkanesulfonic acids. We are indebted to Dr. Stanley Detrick of Jackson Laboratory, E. I. du Pont de Nemours and Company, for this material.

[6] (a) Bacon, *Trans. Faraday Soc.*, **42**, 140 (1946); (b) Morgan, *ibid.*, **42**, 169 (1946).

[7] Hall and Reid, THIS JOURNAL, **65**, 1466 (1943).

[8] Gilman, "Organic Chemistry," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 835.

polymerization period the *p*H of each emulsion had dropped to 2.4–2.5. The conversions were of the same order (91–93%) as those for the preceding run listed in Table I, but the inherent viscosities were slightly higher and were approximately equivalent (0.79 to 0.83). The improvement in polymer size seems to be due to a lower alkali concentration in these latter runs.

The next series of experiments differed from the preceding in that the emulsions were buffered at the desired *p*H in the range 2.0–7.2. In three separate polymerization runs sodium acetate–acetic acid, potassium hydrogen phthalate–sodium hydroxide (or hydrochloric acid) and sodium citrate–sodium hydroxide (or hydrochloric acid) buffers were used for comparison. Data pertinent to these buffered *p*H polymerizations are given in Table II.

TABLE II

THE EFFECT OF *p*H ON POLYMER SIZE ON POLYHEXAMETHYLENE SULFIDE IN BUFFERED EMULSION

Number	Buffer	Buffer concn., *M*[a]	*p*H initial[b]	Conversion, %[c]	Inherent viscosity
8	Acetate	0.015	3.0	93	0.86
9	Acetate	.015	3.5	96	.91
10	Acetate	.036	4.0	92	.89
11	Acetate	.087	4.5	87	.57
12	Acetate	.171	5.5	82	.32
13	Acetate	.199	6.1	87	.28
14	Phthalate–HCl	.05	2.3	94	.56
15	Phthalate–NaOH	.05	3.0	95	.78
16	Phthalate–NaOH	.05	3.5	95	.86
17	Phthalate–NaOH	.05	4.0	95	.68
18	Phthalate–NaOH	.05	4.5	96	.65
19	Phthalate–NaOH	.05	5.5	93	.64
20	Citrate–HCl	.30	2.0	95	.39
21	Citrate–HCl	.40	3.0	95	.69
22	Citrate–HCl	.48	3.5	97	.66
23	Citrate–HCl	.55	4.0	93	.30
24	Citrate–HCl	1.00	5.0	92	.26
25	Citrate–NaOH	0.60	6.1	Negligible	<0.1

[a] Under this heading is given the molarity of the emulsifier solution with respect to acetate, phthalate or citrate concentrations. [b] The *p*H remained essentially constant during the polymerization; the final *p*H was within 0.1–0.3 of a *p*H unit of the initial value. [c] Based on recovery of polymer after one reprecipitation as described in the experimental.

Figure 1 shows the effect of *p*H in buffered emulsion on polymer size as determined from inherent viscosity measurements. It can be seen that there is an optimum *p*H lying in the approximate range 3.0–3.7 in each of the three buffered emulsion systems listed in Table II. The inherent viscosities of polymers obtained under optimum *p*H conditions were 0.91, 0.86 and 0.69 for the acetate, phthalate and citrate buffers, respectively. Apparently polymer size is dependent not only on the *p*H of the emulsion but also on the particular buffer employed.

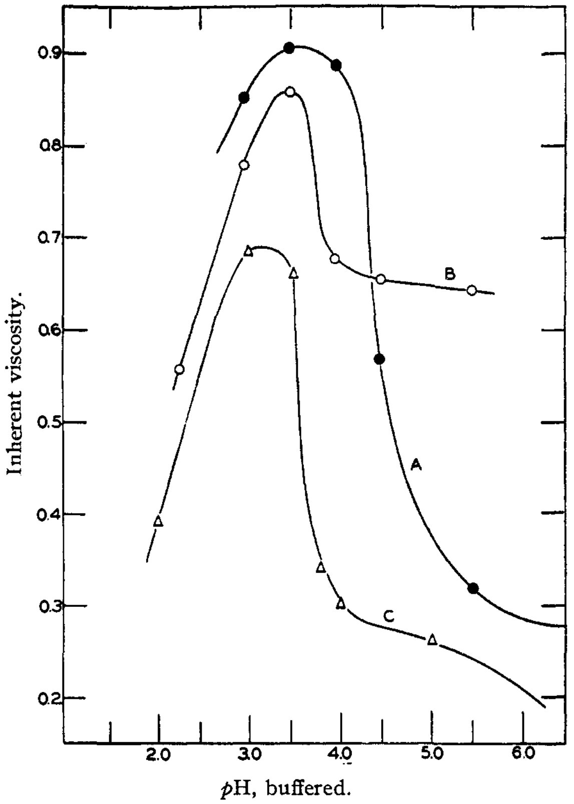

Fig. 1.—The effect of *p*H in buffered emulsion upon inherent viscosity: A, acetate buffer; B, phthalate buffer; C, citrate buffer.

Because of the greater effectiveness of the acetate, improvements were sought in emulsion polymerizations utilizing this buffer. In order to ascertain the optimum buffer concentration a series of polymerizations was made in emulsions buffered at the optimum *p*H 3.4, in which the buffer concentration was the only variable. The acetate concentration in the emulsifier solution was varied from 0.004 to 0.2 *M*. Polymers of approximately equal molecular weight were obtained in the range 0.004 to 0.04 *M*; the inherent viscosities varied only slightly, 0.93–0.88. When the buffer concentration was 0.1 *M* or greater, there was a marked decrease in inherent viscosity, 0.65–0.60. It is probable that this decrease is due to precoagulation of latices during polymerization. Precoagulation is not an unexpected consequence of increased ionic concentrations; therefore, retardation of polymer growth might be anticipated at high buffer concentrations. However, a comparison of these results, listed in Table III, with the acetate runs discussed previously in Table II indicates that *p*H is a predominant factor controlling polymer size and at high buffer concentrations precoagulation also has some effect.

The polyhexamethylene sulfides from biallyl and hexamethylenedithiol are tough, fibrous, white solids if their inherent viscosity is 0.48 or greater. Toughness and internal strength

TABLE III

THE EFFECT OF BUFFER CONCENTRATION ON POLYMER SIZE OF POLYHEXAMETHYLENE SULFIDES

Number	Sodium acetate,[a] *M*	*p*H initial	*p*H final	Conversion, %[b]	Inherent viscosity
26	0.000	3.5	2.4	90	0.81
27	.004	3.4	2.9	93	.93
28	.010	3.4	3.2	93	.91
29	.020	3.4	3.3	93	.89
30	.040	3.4	3.3	94	.88
31	.100	3.4	3.3	95	.65
32	.200	3.4	3.3	91	.60

[a] In this column is given the sodium acetate molarity of the emulsifier solution. [b] Based on recovery of polymer after one reprecipitation as described in the experimental.

increase as the inherent viscosity increases. At inherent viscosities of 0.10 to 0.30 the polymers are powdery, white crystals.

Marvel and Baumgarten[2] obtained a polymer with rubber-like characteristics from a monomers mixture consisting of biallyl, 2,6-diallylphenol, bimethallyl (2,5-dimethyl-1,5-hexadiene) and hexamethylenedithiol in the ratio 1:1:2:4. In an unbuffered emulsion polymerization they obtained a polymer with an inherent viscosity of 0.60; this was increased to 1.16 by fractionation after the polymer had been exposed to air for several months. The *p*H studies have now been extended to include this mixture of monomers in the hope of producing an improved rubber-like polymer. From an emulsion buffered at a *p*H of 3.5 (the apparent optimum) with sodium acetate–acetic acid there was obtained a polymer whose inherent viscosity was 0.56. A simultaneous polymerization in unbuffered emulsion (initial *p*H, 5.1; final *p*H, 2.2) produced a polymer whose inherent viscosity was only 0.33. Thus, in agreement with the biallyl–hexamethylenedithiol polymerizations, it was again demonstrated that emulsions buffered at the proper *p*H yield larger polyalkylene sulfide molecules than do unbuffered emulsions.

It was possible to increase the inherent viscosity of the biallyl–hexamethylenedithiol polymer, by fractionation, to 1.04 (from 0.91) by three additional reprecipitations. A similar fractionation of the biallyl–diallylphenol–bimethallyl–hexamethylenedithiol polymer increased the inherent viscosity from 0.56 to 0.65 and yielded a sticky, rubbery substance of low internal strength possessing little "snap." Oxidation (by prolonged exposure to air) may be necessary in order to obtain a polymer with an inherent viscosity of 1.16 as reported by Marvel and Baumgarten.[2]

The use of a trace of *p*-*t*-butylcatechol as an inhibitor in the monomers mixture necessitated an investigation of the effect, if any, that this agent has upon the polymers produced in emulsion polymerization of biallyl and hexamethylenedithiol. The purpose of the first series was to determine if traces of the substituted catechol (0.05% of the weight of biallyl) retarded polymer growth. Emulsions were buffered at a *p*H of 3.9–4.0 (slightly above the optimum). Significant data are listed in Table IV. A comparison of run 55–56 with run 73–74 shows that better results were obtained if *p*-*t*-butylcatechol was present when the acetate buffer was employed. A comparison of runs 49 through 54 (all in phthalate-buffered emulsions) indicates that better polymers were obtained in the presence of both *p*-*t*-butylcatechol and initiator-activator than in the absence of either one or both of these agents. It is likely that the catalytic effect of the *p*-*t*-butylcatechol was due to its destruction of organic peroxides present in the biallyl.[9]

TABLE IV

THE EFFECT OF *p*-*t*-BUTYLCATECHOL ON THE POLYMERIZATION OF HEXAMETHYLENEDITHIOL AND BIALLYL

Run	Buffer	*p*-*t*-Butylcatechol	Initiator–activator solution	Conversion, %	Inherent viscosity
49–50	Phthalate	Present	Present	93	0.79
51–52	Phthalate	Present	Absent	91	.59
53–54	Phthalate	Absent	Absent	89	.30
55–56	Acetate	Absent	Present	95	.65
73–74	Acetate	Present	Present	92	.89

Because *p*-*t*-butylcatechol enhanced polymer growth, a second series of polymerizations was initiated. It was designed to show the optimum amount of *p*-*t*-butylcatechol and also to show the effects of replacing all, or part, of the oil-insoluble reducing agent, sodium bisulfite, with an equivalent amount of an oil-soluble reducing agent, *p*-*t*-butylcatechol. The polymerizations were carried out in emulsions buffered at a *p*H of 3.5 with sodium acetate–acetic acid, the usual amounts of persulfate and copper were used and the amounts of bisulfite and *p*-*t*-butylcatechol

TABLE V

THE EFFECT OF VARYING AMOUNTS OF *p*-*t*-BUTYLCATECHOL ON POLYMER SIZE OF POLYHEXAMETHYLENE SULFIDE

Run	*p*-*t*-Butylcatechol soln., ml.[a]	$NaHSO_3$ soln., ml.	*p*-*t*-Butylcatechol in biallyl, %	Conversion, %	Inherent viscosity
113–114	0.0	1.0	0.00	93	0.90
71–72	.0	1.0	0.05	96	.91
101–102	.1	1.0	.05	93	.86
103–104	.2	1.0	.05	94	.70
105–106	1.0	1.0	.05	94	.47
107–108	1.0	0.5	.05	91	.39
109–110	2.0	0.0	.05	94	.31
111–112	4.0	0.0	.05	Negligible	<0.01

[a] The concentration is such that 2 ml. of the *p*-*t*-butylcatechol solution contains the same number of gram equivalents as 1 ml. of the sodium bisulfite solution (which contains the usual amount of bisulfite used in previous polymerizations).

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(9) Although the presence of peroxides in biallyl has not been proved definitely, preliminary colorimetric tests have indicated their presence.

were varied. The results of the second series are listed in Table V.

From these results it appears that 0.05% *p*-*t*-butylcatechol (by weight in biallyl) has a slight enhancing effect, but any further increase of this material retards polymer growth markedly. Furthermore, it can be seen that replacement of any part of bisulfite by an equivalent amount of the oil-soluble reducing agent, *p*-*t*-butylcatechol, has an adverse effect; therefore it is not practical to substitute the persulfate–*p*-*t*-butylcatechol oxidation-reduction system for the persulfate–bisulfite system.

Experimental

***p*H Studies.**—The emulsion polymerization techniques were essentially the same as those employed in earlier work by Marvel and co-workers.[2,4] The recipe in a typical polymerization was:

Monomers mixture	5 ml. (*ca.* 4.3 g.)
Emulsifier (1% MP-189-EF solution)	50
Ammonium persulfate	0.0215 g.
Sodium bisulfite	.0108
Cupric sulfate	.0011
p-*t*-Butylcatechol	.007

Monomers Mixture. **(A) Biallyl–Hexamethylenedithiol.**—Into a flask containing nitrogen was weighed rapidly 37.576 g. (0.25 mole) of hexamethylenedithiol and 20.535 g. (0.25 mole) of freshly distilled biallyl, which contained 0.05% (by weight) of *p*-*t*-butylcatechol.[10] The flask was stoppered, swirled and chilled in an ice-bath. Five-milliliter aliquots (*ca.* 4.3 g.) of this solution were used in the polymerizations.

(B) Biallyl–Diallylphenol–Bimethallyl–Hexamethylenedithiol.—Into a flask containing nitrogen was weighed rapidly in the order listed 15.030 g. (0.1 mole) of hexamethylenedithiol, 5.510 g. (0.05 mole) of bimethallyl, which contained 0.05% (by weight) of *p*-*t*-butylcatechol, 4.356 g. (0.025 mole) of 2,6-diallylphenol and 2.054 g. (0.025 mole) of biallyl, which contained 0.05% (by weight) of *p*-*t*-butylcatechol. The procedure from this point was identical to that described above. The 5-ml. aliquots used in the polymerizations weighed approximately 4.55 g. and contained 0.00071 g. of *p*-*t*-butylcatechol.

Emulsifier Solutions. **(A) Unbuffered.**—One per cent. solutions of MP-189-EF were made from water (redistilled from glass). The *p*H was adjusted with the proper amount of 0.1 *N* sodium hydroxide solution, or 0.1 *N* sulfuric acid, as indicated by a Beckmann *p*H meter.

(B) Buffered.—One per cent. solutions of MP-189-EF were made from solutions previously buffered at the desired *p*H by use of the acetate, phthalate or citrate buffers whose concentrations are given in Table II. Fifty-milliliter portions of these solutions were used in the polymerizations.

Initiator–Activator Solution.[6]—A solution of 2.150 g. of ammonium persulfate, 1.108 g. of sodium bisulfite and 0.110 g. of cupric sulfate pentahydrate in water (redistilled from glass) was prepared and diluted to a volume of 100 ml. One-milliliter aliquots of this solution were used in the polymerizations.

Polymerization Procedure.—Standard 4-oz. screw-cap bottles were flushed for two minutes with nitrogen to remove air. The bottles were charged successively with emulsifier solution, initiator–activator solution and monomers mixture. The bottles were capped and tumbled end-over-end in a 30° constant-temperature bath for five and one-half days. The *p*H of each emulsion was measured at the end of this time. Latices were coagulated by addition of 20-ml. portions of alum coagulant,[11] collected by filtration and dried in a vacuum desiccator. The polymers were dissolved in 75-ml. portions of chloroform and reprecipitated by pouring the resulting solutions into 300-ml. portions of methanol. Solvents were removed by filtration and the polymers were dried in a vacuum desiccator. Per cent. conversions listed in the Tables are based upon the amount of polymer recovered at this stage.

Polymers were fractionated by three additional reprecipitations from the chloroform–methanol solvent. The largest polymer obtained in this manner was from the biallyl–hexamethylenedithiol polymerization, number 9; the inherent viscosity of this polymer after fractionation was 1.04 and the recovery was 50%. The polymer melted at 75–77°.

Anal.[12] Calcd. for $C_6H_{12}S$: C, 62.00; H, 10.41; S, 27.59. Found: C, 61.79; H, 10.22; S, 27.45.

The largest biallyl–diallylphenol–bimethallyl–hexamethylenedithiol polymer obtained by a similar fractionation possessed an inherent viscosity of 0.65; nevertheless, this substance was the most rubber-like polymer produced in the present work.

Anal. Calcd. for $C_{58}H_{108}S_8O$: C, 64.62; H, 10.10; S, 23.80. Found: C, 64.61; H, 9.70; S, 22.62.

***p*-*t*-Butylcatechol Experiments.**—The monomers mixture of biallyl and hexamethylenedithiol and buffered emulsifier solution (*p*H 3.5) were prepared as previously described. The initiator–activator solutions were prepared in three portions:

Persulfate–Copper Solution.—A solution of 2.150 g. of ammonium persulfate and 0.110 g. of cupric sulfate was prepared in redistilled water and diluted to a volume of 100 ml. One-milliliter aliquots of this solution were used in each polymerization (nos. 101 to 114).

Bisulfite Solution.—A solution of 1.108 g. of sodium bisulfite was prepared in redistilled water and diluted to 100 ml. Aliquots as indicated in Table V were used in the polymerizations.

***p*-*t*-Butylcatechol Emulsion.**—*p*-*t*-Butylcatechol (1.755 g.) was emulsified with enough distilled water to make the total volume 100 ml. Aliquots listed in Table V were used in the polymerizations.

The procedure for these polymerizations was the same as that described under the *p*H study.

Summary

The emulsion polymerization of hexamethylenedithiol and 1,5-hexadiene gives the largest molecules when carried out at a *p*H of 3.0–3.7. Acetate buffers give better results than phthalate or citrate buffers.

The presence of a trace of *p*-*t*-butylcatechol in the monomers mixture also leads to better polymers but this reducing agent will not take the place of the bisulfite activator.

URBANA, ILLINOIS RECEIVED FEBRUARY 17, 1950

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[10] The *p*-*t*-butylcatechol was added to inhibit polymerization of the monomers mixture prior to charging the polymerization bottles. We wish to express thanks to Dr. H. L. Rice for this suggestion.

[11] This coagulant was prepared by dissolving 200 g. of aluminum potassium sulfate dodecahydrate in a solution of 200 ml. of concentrated hydrochloric acid in 2 l. of water.

[12] The microanalyses reported in this paper were done by Clark Microanalytical Laboratory, Urbana, Illinois.