

of a catalyst fragment, an active hydrogen, or other material present as an impurity to give a saturated hydrocarbon end group.

The reaction of hexamethylenedithiol and dibenzalicyclohexanone also produces a polymer of low molecular weight. However, it was not possible to extend the reaction to include dimercaptan addition to 3,3'-dinitrodibenzalacetone, diethyl 1,7-octadiene-1,8-dicarboxylate, 1,6-diphenyl-1,5-hexadiene-3,4-dione or dimethyl acetylenedicarboxylate.

Experimental

Preparation of Polymers from Dibenzalacetone and Hexamethylenedithiol.—A typical solution polymerization consisted of charging a four-ounce polymerization bottle with 1.981 g. (0.01349 mole) of hexamethylenedithiol and 3.088 g. (0.01348 mole) of dibenzalacetone in 15 ml. of dry benzene and adding 0.2 ml. of piperidine. The solution was protected by a nitrogen atmosphere and the bottle was tumbled in a 30° constant temperature bath for 24 hours. The polymer was precipitated with 25 ml. of methanol, dried and reprecipitated. The inherent viscosity⁴ as determined in benzene was 0.31 at 25°.

Anal. Calcd.⁵ for $C_{23}H_{23}S_2O$: C, 71.82; H, 7.34; S, 16.68. Found: C, 72.06; H, 7.58; S, 16.56.

Polymers from Dibenzalicyclohexanone and Hexamethylenedithiol.—A polymer was produced from these monomers by the same general method as shown above. The inherent viscosity in benzene at 25° was 0.14.

Anal. Calcd. for $C_{26}H_{32}S_2O$: C, 73.53; H, 7.60; S, 15.10. Found: C, 73.95; H, 7.66; S, 14.38.

Attempted Oxidation of Polymer End Groups.—To a solution of 1.015 g. of polymer from dibenzalacetone and hexamethylenedithiol (inherent viscosity 0.22) dissolved in 50 ml. of chloroform was added 0.1 g. of iodine. The solution was shaken at room temperature for 24 hours after which it was poured into a mixture of 100 ml. of methanol and 50 ml. of water containing 1 g. of sodium bisulfite. The polymer was isolated by decantation and was washed with two 100-ml. portions of methanol. The inherent viscosity was 0.06.

Effect of Monomer Balance.—The molar ratio of hexamethylenedithiol and dibenzalicyclohexanone in a typical polymerization was varied and the effect upon the viscosity of the polymer was noted. These experiments are recorded in Table I.

TABLE I

EFFECT OF MONOMER BALANCE ON INHERENT VISCOSITY OF POLYMER

Hexamethylene-dithiol, g.	Dibenzalicyclohexanone, g.	Molar ratio dithiol/ketone	Inherent viscosity
0.996	1.894	96/100	0.16
.990	1.863	97/100	.16
.991	1.846	98/100	.19
.987	1.820	99/100	.21
.975	1.780	100/100	.23
.991	1.791	100/99	.24
.987	1.766	100/98	.20
1.002	1.774	100/97	.18
0.989	1.733	100/96	.15
1.000	1.734	100/95	.16

Time Required for Polymer Formation.—At 30° a solution of 0.0067 mole of hexamethylenedithiol and dibenzalacetone in 10 ml. of benzene was polymerized and the reaction followed by noting the viscosity and yield of the polymer. The polymers were dried *in vacuo* until there was no further loss of weight. The results are reported in Table II.

(4) We are indebted to Messrs. Donald Janssen and Norbert Goeckner for all inherent viscosities reported.

(5) We are indebted to the Micro-Tech Laboratories, Skokie, Ill., and to Mr. Joseph Nemeth of the University of Illinois for the micro-analytical results.

TABLE II

TIME REQUIRED FOR POLYMER FORMATION

Time, hr.	Inherent viscosity	Yield, %	Time, hr.	Inherent viscosity	Yield, %
0.005	0.12	12	1	0.27	82
.083	.21	48	2	.26	75
.167	.33	68	6	.25	80
.250	.34	76	9	.24	72
.500	.29	71	24	.27	71
.750	.29	71	48	.20	71
			72	.21	54

Mercaptan Disappearance.—By amperometric titration⁶ the rate of disappearance of thiol end groups was followed in an emulsion polymerization.

These titrations showed that in the addition of hexamethylenedithiol to dibenzalacetone, the mercaptan groups disappeared very rapidly; nearly 70% in a minute, nearly 80% in seven minutes, 95% in an hour and 99% in twelve hours. Thereafter there appeared to be no further decrease in mercaptan groups and even possibly a slight increase.

(6) I. W. Kolthoff and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **18** 161 (1946).

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Equilibrium Sorption of Several Organic Diluents in Polyvinyl Acetate¹

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In the course of an investigation of the kinetics of vapor take-up by thin polymer films,² the equilibrium sorption has been determined for several organic diluents in polyvinyl acetate (viscosity average molecular weight approximately 170,000). Experiments have been made at 30, 40 and 50° with acetone, benzene and 1-propanol and at 40° with propyl chloride, allyl chloride, propylamine and isopropylamine. In all cases the solutions were concentrated in polymer; values of v_1 , the volume fraction of solvent, ranged from 0.02 to 0.20. In these experiments the diluent concentration in the swollen polymer in equilibrium with a given vapor pressure of diluent was determined gravimetrically using a quartz spiral balance. The procedure, apparatus, and materials used have been discussed in detail elsewhere.²⁻⁴ Results of the present experiments are summarized in Table I, which gives v_1 ⁵ as a function of p/p_0 , the ratio of diluent vapor pressure for the swollen polymer to that for the pure diluent. The systems studied, although polar, are relatively simple inasmuch as the polymer is non-crystalline and above its second-order transition temperature. It is of interest, therefore, to consider these data in the light of the Flory-Huggins^{6,7} theory of polymer solutions.

(1) Work supported by a grant from Office of Ordnance Research, U. S. Army.

(2) R. J. Kokes and F. A. Long, submitted for publication.

(3) S. Prager and F. A. Long, *THIS JOURNAL*, **73**, 4072 (1951).

(4) R. J. Kokes, F. A. Long and J. L. Hoard, *J. Chem. Phys.*, **20**, 1711 (1952).

(5) The volume fractions were calculated from the experimentally determined weight fractions assuming that solvent and polymer volumes were additive on mixing.

(6) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

(7) M. L. Huggins, *ibid.*, **9**, 440 (1941).

bution to χ_1 . With the pure polymer and at 40° the entropy for acetone (beyond the configurational) is approximately -2.5 e.u. and for propanol it is approximately 6 e.u. Thus for both systems the data indicate that the entropy contribution to χ_1 is comparable in size to the contribution from the heat of mixing. For both systems the entropy and heat terms give opposing contributions to χ_1 , a result which is in accord with an early discussion by Huggins.¹¹

(11) M. J. Huggins, *Ann. N. Y. Acad. Sci.*, **44**, 431 (1943).

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The Sakaguchi and Biacetyl Reactions for the Identification of Alkyl Guanidines

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Some representative mono-, di- and trialkyl-substituted guanidines have been prepared and their reactivity to the Sakaguchi¹ and biacetyl² tests has been determined (Table I). Of the compounds tested, only methylguanidine, in which the grouping $\text{RNHC}(=\text{NH})\text{NH}_2$ is present, gives a positive Sakaguchi test. Guanidine and the di- and trialkyl substituted compounds do not react even at levels 100-fold as great. These findings are contrary to the report of Poller³ who maintained that the symmetrically substituted di- and trialkyl compounds give positive reactions. Since this worker failed to characterize adequately his test compounds, it is impossible to determine whether these were authentic.

The most intense coloration in the biacetyl reaction for this series of compounds is given by *asym*-N,N-dimethylguanidine, in which the grouping $\text{RR}'\text{NC}(=\text{NH})\text{NH}_2$ is present. The compounds in which one or both of these alkyl groups are replaced by hydrogen show lower intensities and develop their color at a slower rate. Compounds in which two or three of the nitrogen atoms are substituted with alkyl groups fail to react even at levels 2000-fold as great.

The alkyl guanidines used in this work were prepared by established methods already described in the literature. They were identified by m.p., elementary analysis and alkaline hydrolysis which produced carbon dioxide and volatile amines in the theoretical amounts.⁴ The volatile amines were identified by paper chromatography.⁵ Since these well-characterized compounds were available, potentiometric titrations were carried out to determine their base strengths. All of these compounds were found to have dissociation constants greater than pK_a 11.4 and the titrations did not differ within the experimental accuracy from the values for a water

blank. These results dispute the earlier findings of Davis and Elderfield⁶ that symmetrically substituted dialkyl guanidines are weaker bases than other types of alkyl substituted guanidines. The present work is in agreement with the findings of Neivelt, *et al.*,⁷ and of Angyal and Warburton.⁸

TABLE I

SAKAGUCHI AND BIACETYL REACTIONS OF ALKYL GUANIDINES

Compound	Sakaguchi reaction ^a		Biacetyl reaction ^b	
	Amt. tested, $\mu\text{g.}$	Intensity of color ^c	Amt. tested, $\mu\text{g.}$	Intensity of color ^d
Guanidine	100	0	6	1.0
Methylguanidine	630	1600	5	1.0
<i>asym</i> -N,N-Dimethylguanidine	362	0	0.5	1.0
<i>sym</i> -N,N'-Dimethylguanidine	414	0	1000	0
<i>sym</i> -N,N'-Diethylguanidine	100	0	1000	0
<i>sym</i> -N,N'-Dibutylguanidine	100	0	1000	0
<i>sym</i> -N,N',N'-Triethylguanidine	100	0	1000	0

^a The procedure used was identical to that described by A. A. Albanese and J. E. Frankston, *J. Biol. Chem.*, **159**, 185 (1945), with the exception that 3.5 min. was allowed after the addition of the hypochlorite reagent instead of 1.0 min. as used by these authors. ^b This reaction was carried out according to the directions of P. Eggleton, S. R. Elsdon and N. Gough, *Biochem. J.*, **37**, 526 (1943). ^c Known concentrations of arginine monohydrochloride (Eastman Kodak Co. Anal.) were used to standardize the procedure. Color intensities were determined with a Coleman colorimeter using a 530 m μ filter. The intensity is given in terms of $\mu\text{g.}$ of arginine base. The minimum amount of arginine that could be detected was 1 $\mu\text{g.}$ ^d Color intensities were determined by comparison with the color produced by known concentrations of creatine hydrate (Eastman Kodak). The intensity is given in terms of $\mu\text{g.}$ of creatine hydrate. The minimum amount of creatine hydrate that could be detected was 0.5 $\mu\text{g.}$

Experimental⁹

Guanidine Hydrochloride (Eastman Kodak Co.).—*Anal.* Calcd. for $\text{CH}_5\text{N}_3\text{Cl}$: N, 44.00. Found: N, 44.52, 44.26.

Methylguanidine Sulfate.—This compound was prepared¹⁰ from dicyanodiamide and methylamine hydrochloride by the procedure of Traube and Gorniak,¹¹ m.p. 238° (lit. m.p. 238°, 239–240°, 240°, 238–239°¹²).

Anal. Calcd. for $\text{C}_4\text{H}_{16}\text{N}_6\text{SO}_4$: C, 19.67; H, 6.60. Found: C, 19.64, 19.67; H, 6.55, 6.55.

***asym*-N,N-Dimethylguanidine Sulfate**.—S-Methylisothiourea sulfate was treated with aqueous dimethylamine according to the procedure of Phillips and Clarke,¹² m.p. 278–279° (lit. m.p. 285–288°, 295–297°, 285–287°¹³).

Anal. Calcd. for $\text{C}_6\text{H}_{20}\text{N}_6\text{SO}_4$: C, 26.46; H, 7.40. Found: C, 26.32, 26.47; H, 7.20, 7.35.

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