dide treatment. The properties of some polymers are listed in the table.

TABLE I

Sample	Polymer of	Intrinsic Viscosity (dl./g.) (a)	(b)	Molecular weight	$[\alpha]^{25}D$
329	BG	1.19	4.10	(225,000)	$\sim 14^{b}$
365	BG	1.42	5.62	262,000^{b}	13.0^{b}
397	BG	1.87	7.56	336,000^{b} 358,000^{a}	13.0^{b}
245	MG	0.80	Insol.		−33.7^{a}
307	BG and MG^{d}	0.85	1.90	180,000^{b}	−22.5^{a} +13.5^{b}
361	GA^{e}	0.54^{c}	Insol.	62,000^{c}	−86.5^{c}
318	BG, MG and GA^{f}	0.42^{c}	Insol.	61,000^{c}	−54^{c}

[a] Dichloroacetic acid. [b] Chloroform–formamide. [c] 0.2 *M* Na_2SO_4, *p*H ≅ 7.3. [d] Calcd. for ratio 60% BG, 40% MG: C, 59.5; H 6.1; N, 7.7; benzyl, 24.6. Found: C, 59.6; H, 6.1; N, 7.5; benzyl, 25 (by ultraviolet absorption). [e] Prepared from 329: calcd. for polyglutamic acid: C, 46.5; H, 5.5; N, 10.8. Found: C, 46.6; H, 5.8; N, 10.5. [f] Prepared from 307: calcd. for ratio 16% BG, 28% MG, 56% GA: C, 50.7; H, 5.8; N, 9.8; benzyl, 6.5. Found: C, 50.6; H, 5.9; N, 9.5; benzyl, 6.4.

The molecular weights were obtained by light scattering measurements employing Zimm plots over the angular range 30 to 135°. The absence of association is demonstrated by the agreement obtained in dichloroacetic acid and chloroform–formamide solutions as well as the linearity of the concentration dependence down to the lowest measurable concentrations. The viscosities in chloroform–formamide solutions were found to depend upon the gradient; the intrinsic viscosities listed in the table are values obtained by extrapolation to zero gradient. The level of molecular weights obtained shows that in this system termination reactions which in other cases[5] may limit molecular weights do not do so here. The molecular weight of the water-soluble derivatives indicates that only about one or two bonds in the backbone of the molecules are broken during de-esterification. The action of the water-soluble polypeptides in biological systems is now being investigated.

We wish to thank Dr. A. Holtzer and Dr. J. H. Bradbury for valuable discussions and experimentation related to this work.

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(5) M. Sela and A. Berger, THIS JOURNAL, **75**, 6350 (1953).

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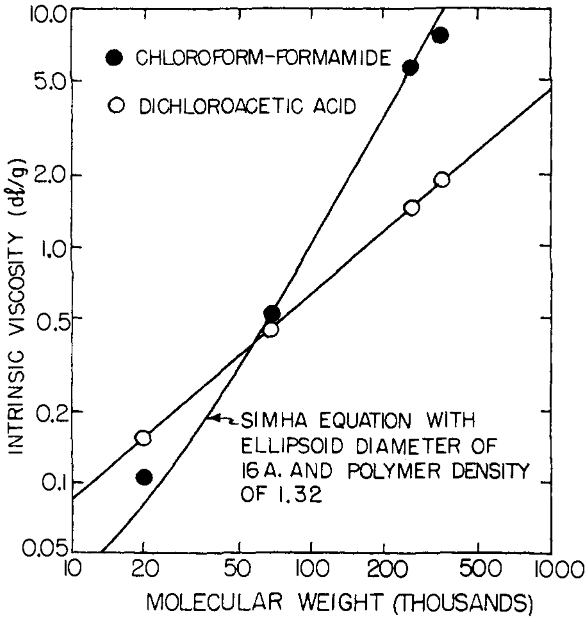
POLYPEPTIDES. II. THE CONFIGURATION OF POLYMERS OF γ-BENZYL-L-GLUTAMATE IN SOLUTION[1]

Sir:

The existence of two configurations, intramolecularly-bonded helical (α) and intermolecularly-bonded extended (β), for polypeptides in the solid state is well established.[2,3] We wish to report the existence of the counterpart of these two forms in solution as well as a solvated, randomly coiled form.

High molecular weight samples of poly-γ-benzyl-L-glutamate (PBG) were prepared[4] covering the molecular weight range of 20,000 to 350,000. In the solid state and in solutions such as chloroform and dioxane only the characteristic 1650 ± 2 cm.$^{-1}$ band is observed in the carbonyl amide region.[5] The specific rotation is +13.0° ($CHCl_3$), −14° (dichloroacetic acid, DCA) and independent of concentration. The molecular weight–intrinsic viscosity relation is shown as a log–log plot in the figure. It is seen that in chloroform–formamide (CF) solution the slope has the unusually high value of 1.7. Moreover, it is found that these data can be fitted with the theoretical relation for ellipsoids of revolution.[6] The line drawn in the figure is based on lengths equal to 1.5 Å. times the degree of polymerization (DP) and a (solvated helix) diameter of 16 Å. Furthermore, the scattering envelopes suggest a rod-like shape for the molecules of high molecular weight with lengths equal to 1.5 Å. times DP. The behavior in DCA is quite different: the slope in the figure is 0.87, typical of coiled molecules, and the size determined from light scattering for the higher DP samples is much smaller and consistent with that required of a randomly coiled polymer exhibiting the observed intrinsic viscosities.



Low molecular weight polypeptides which show

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[1] Supported by Office of Naval Research and Office of the Surgeon General, Department of the Army.

(2) (a) E. J. Ambrose and A. Elliott, *Proc. Roy. Soc.* (*London*), **205A**, 47 (1951); (b) C. H. Bamford, L. Brown, A. Elliott, W. E. Hanby and I. F. Trotter, *Nature*, **169**, 357 (1953); (c) A. Elliott, *Proc. Roy. Soc.* (*London*), **221A**, 104 (1953); (d) C. H. Bamford, W. E. Hanby and F. Happey, *ibid.*, **206A**, 407 (1951).

(3) L. Pauling and R. B. Corey, *Proc. Natl. Acad. Sci.*, **37**, 241 (1951)

(4) E. R. Blout, R. H. Karlson, P. Doty and B. Hargitay, THIS JOURNAL, **76**, 4492 (1954).

(5) The existence of an intramolecularly bonded form in solution has been suggested previously on the basis of infrared evidence (references 2a and 2c) and on the basis of a correlation between the optical rotation in cresol solution and the fraction of this form present in the solid state (C. Robinson and M. J. Bott, *Nature*, **168**, 325 (1951)).

(6) R. Simha, *J. Phys. Chem.*, **44**, 25 (1940).

the β-configuration in the solid state were prepared by initiating with hexylammonium hydroxide to very low DP. We take as an example PBG prepared by initiating to DP 5.2. Solid films cast from different solvents show a single C=O amide frequency at 1628 ± 2 cm.$^{-1}$ characteristic of the β-form.[2] In solution, however, an additional C=O band is observed at 1658 cm.$^{-1}$ (chloroform), 1670 cm.$^{-1}$ (dioxane). This band appears to be associated with a solvated form since its frequency is solvent dependent. Both the 1628 and the higher frequency band appear at high concentrations ($\sim$20%) but upon dilution the 1628 band becomes progressively weaker until at 0.5% concentration only the higher frequency C=O band remains. The specific rotation in chloroform changes continuously with concentration from +18 at 5% to +2 at 0.75%, but in DCA shows a constant value of −14. The intrinsic viscosity is low: $[\eta]_{\text{DCA}} = 0.056$.

The following conclusions may be drawn from these observations. (1) The α-helical configuration is the stable form of high molecular weight poly-γ-benzyl-L-glutamate dissolved in weakly interacting solvents such as chloroform. (2) In strongly interacting solvents such as dichloroacetic acid the configuration is that of a randomly coiled polymer: this is presumably due to strong solvation and is independent of molecular weight. (3) With very low molecular weight polymers in weakly interacting solvents, however, two forms exist. One of these is believed to be a solvated form because of the solvent dependence of the C=O amide frequency. The other form is the intermolecularly bonded β-form which upon dilution is converted to the solvated form.

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THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE SOLUTIONS BY COMPLEX METAL AMMINES ADSORBED ON SILICA GEL

Sir:

The catalytic effect of cobalt and nickel sulfate adsorbed on the surface of silica gel upon the decomposition of a hydrogen peroxide solution has been reported to be only slight.[1]

Some of our recent work revealed that the complex metal amines of cobalt(II), copper(II), or nickel(II) adsorbed on the surface of iron-free silica gel very effectively catalyzed the decomposition of hydrogen peroxide solutions. When 1 g. of silica gel with its adsorbed metal ammine was placed in contact with 25 ml. of a 3% hydrogen peroxide solution, with or without its preservative, the decomposition was complete in 15 minutes at room temperature. A steady evolution of oxygen could be observed.

The complex metal ammines of silver(I), zinc(II), cadmium(II), or cobalt(III) adsorbed on the surface of silica gel failed to catalyze the decomposition of hydrogen peroxide solutions. Ammonia itself adsorbed on the surface of silica gel failed to effect any observable decomposition. It is of special interest to note that only those metal ammines characterized by unpaired electrons, hence paramagnetic, effected the decomposition of hydrogen peroxide solutions.

The adsorbed metal ammines that catalyzed the decomposition did not lose their activity with use. Samples of each were used on a fresh 3% hydrogen peroxide solution daily for a period of one month and were as active at the end of that period of time as they were at the beginning. The amount of the metal ammines adsorbed ranged from one to two millimoles per gram of silica gel. The metal ammines were prepared from metal nitrate solutions and concentrated ammonium hydroxide.[2]

Aqueous solutions of the nitrates of copper(II), cobalt(II) and nickel(II) produced little or no decomposition of 3% hydrogen peroxide, nor did aqueous ammonia solution itself. However, aqueous solutions of the complex ammines of copper(II), cobalt(II) and nickel(II) did produce rapid decomposition of the peroxide.

The same metal ions—cobalt, copper, nickel, silver, zinc and cadmium—coördinated with ethylenediamine or diethylenetriamine and adsorbed on the surface of silica gel, failed to give any noticeable catalytic decomposition of hydrogen peroxide solutions. Steric considerations and the stronger bonding of the metal ion to the ligand in these series may make it difficult for contact to be established between the hydrogen peroxide and the central metal ions of the adsorbed entity. The adsorption in these series ranged from 0.5 to 1.5 millimoles per gram of silica gel.

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(1) L. A. Nickolaw and Kobazeo, *J. Phys. Chem. U.S.S.R.*, **20**, 145–150 (1946).

(2) G. W. Smith, *J. Phys. Chem.*, **43**, 638 (1939).

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THE SYNTHESIS OF TERTIARY NITROPARAFFINS[1]

Sir:

While tertiary nitroparaffins have been known for a long time they have in no case been obtained by reactions which can be regarded as useful preparative methods.[2] We wish to describe the first practical synthesis of *t*-nitroparaffins, namely, the oxidation of *t*-carbinamines, $RR'R''C{-}NH_2$, to

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(1) This research was supported by the United States Air Force under Contract No. AF 18(600)-310 monitored by the Office of Scientific Research, Air Research and Development Command.

(2) In liquid phase nitrations, small amounts of hydrocarbon are heated with dilute nitric acid (generally around 130–150°) in sealed tubes which have to be opened for "periodic relief of pressure." Large numbers of sealed tubes are required, complex mixtures are produced, and the yields of *t*-nitrocompounds are poor [see, *e.g.*, S. S. Nametkin and K. S. Zabrodina, *Doklady Akad. Nauk S.S.S.R.*, **75**, 395 (1950); *C.A.*, **45**, 6998 (1951)]. Despite its great commercial importance, Hass' vapor phase nitration process can hardly be regarded as a laboratory synthesis, the more so since it gives rise to complex mixtures. And the reaction of silver nitrite with *t*-alkyl halides gives 0 to 5% yields of *t*-nitro compounds. B. Taub, Ph.D. Thesis, Purdue University, 1952.