cated that when dimethyl acetylenedicarboxylate reacted with dicyclopentadienyl nickel it did so in a typical Diels–Alder manner with one of the cyclopentadienyl rings leaving the remaining one intact. Supporting evidence for this type of addition was obtained from a study of the n.m.r. spectrum of the complex which revealed a single signal at −5.24 p.p.m. relative to tetramethylsilane and with an intensity signifying five equivalent hydrogens in the molecule. The entire n.m.r. spectrum consisted of signals at −6.55, −5.24, −3.7 and −2.18 p.p.m., with relative intensities in the ratio of 2:5:8:1, respectively. The triplet at −6.55 was assigned to the two free olefinic protons shown in Structure I. The group of bands at −3.7 was concluded to be a superposition of a singlet from the six methoxy hydrogens over a partially visible multiplet from the two tertiary type hydrogens. The small triplet at −2.18 p.p.m. was assigned to the lone hydrogen bonded to the carbon possessing a free pair of electrons bonded to nickel.

Complex I represents an example of a nonconjugated olefin electron pair system bonded to a metal. A most notable feature of the structure is that the double bond bonded to nickel arises from the incoming reagent, dimethylacetylene dicarboxylate, and not from the cyclopentadienyl ring originally bonded to nickel. The extension of this reaction to other acetylenes together with a more detailed discussion of the structure will be set forth in a future publication.

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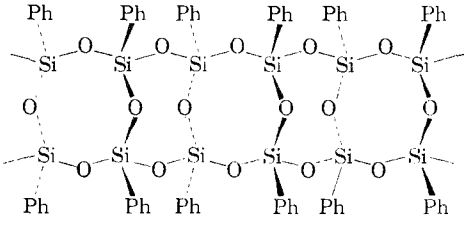
DOUBLE CHAIN POLYMERS OF PHENYLSILSESQUIOXANE

Sir:

We wish to report the synthesis of high molecular weight soluble polymers from a trifunctional monomer, along with evidence that they possess a stereoregular double chain structure. These polymers contain phenylsilsesquioxane (*i.e.*, "phenyl-T" or $C_6H_5SiO_{3/2}$) units joined together to form syndiotactic chains which are joined in turn through *cis*-fusion at each unit to give a "ladder" like linear network structure:



Soluble low polymers of phenylsilsesquioxane have been prepared by equilibrating the condensation products of phenylsilanetriol in a suitable solvent, such as toluene, xylene, or diglyme.[1] Thus, refluxing a mixture of the hydrolysate of phenyltrichlorosilane with 0.1% KOH and an equal weight of toluene through a distilling trap arranged for water separation for 16 hours, cooling, filtering off the small amounts of crystalline phenyl-T_8 and phenyl-T_{12} formed, and precipitating the product into ligroin or methanol resulted in approximately 99.9% condensation of the silanol and gave a polymer analyzing correctly for $(C_6H_5SiO_{3/2})_x$. We observed no tendency toward gelation in any such equilibration where enough solvent was present to give a liquid mixture. The polymer obtained, ($[\eta]$ = 0.12 dl./g. in benzene, $\bar{M}_n$ = 14,000, $\bar{M}_w$ = 26,000) showed a "most probable" molecular weight distribution, rather than the very broad distribution expected for a branched polymer and observed for methylsilsesquioxane copolymers.[2] Fractionation gave a little additional T_{12} and a series of polymer fractions which showed the steep, linear log $[\eta]$ *vs.* log $\bar{M}_w$ relation (a = 0.92) characteristic of linear, nearly rigid rod polymers, rather than the very low slope $[\eta]$ *vs.* $\bar{M}_w$ relations observed for micromicrogels.[2]

The soluble phenyl-T polymers prepared by Sprung and Guenther[3] *via* the base-catalyzed hydrolysis of phenyltriethoxysilane resemble the above materials in their infrared spectra and X-ray diffraction patterns, but are of somewhat higher molecular weight ($[\eta]$ = 0.14–0.26 dl./g.) and somewhat narrower molecular weight distribution.

Soluble polymers of much higher molecular weight have been obtained by equilibrating phenyltrichlorosilane hydrolysate, phenyl-T_{12}, or the above soluble low polymers with an alkaline rearrangement catalyst in the presence of lesser (*e.g.*, 5–30%) quantities of suitable solvents.[1] For example, a mixture of 0.50 g. of phenyltrichlorosilane hydrolysate, 0.5 mg. of KOH, 0.5 g. of benzene, and 0.13 g. of Dowtherm A was heated for one hour at 250° in a loosely stoppered testtube. The resulting tough, frothy mass was dissolved in benzene, neutralized with acetic acid, and precipitated into a large excess of methanol to give 0.33 g. of high polymer, $[\eta]$ = 4.0 dl./g., $\bar{M}_w$ = 4.1 × 10^6. However, curvature in the $[\eta]$-$\bar{M}_w$ relations indicated that some branching was present in such specimens where $\bar{M}_w > 2 \times 10^5$.

None of the phenylsilsesquioxane polymers obtained could be melted upon heating, but they did dissolve in benzene, tetrahydrofuran, and methylene chloride, and films of the higher polymers could be oriented by stretching in benzene vapor. The X-ray diffraction patterns of the crude polymerization products, the reprecipitated dry polymers, and of the oriented films indicated that all such polymer specimens were poorly crystallized (7–8 distinct reflections observed, none very sharp). Evidently, the direction of the polymerization process is not controlled by the formation of an extended crystalline phase.

The X-ray data (repeating distance 5.0 ± 0.5 Å., mean interchain spacing 12.5Å., whence four monomer units per repeating chain segment), detailed analyses of the ν_a(Si–O–Si) skeletal chain vibrational spectrum in the 1040–1160 cm.$^{-1}$ region of the infrared, and determinations of end

(1) General Electric Company, Belgian Patent 586,783, May 16, 1960.

(2) F. P. Price, S. G. Martin and J. P. Bianchi, *J. Polymer Sci.*, **22**, 41 (1956).

(3) M. M. Sprung and P. O. Guenther, *ibid.*, **28**, 17 (1958).

groups and other structural defects all support the *cis*-syndiotactic double chain structure, and indicate that 95–98% of the phenyl-T units in the higher polymers are in the *cis*-syndiotactic configuration. This arrangement of trifunctional units into a linear, double chain network is reminiscent of that found in DNA. Calculations of bond angles and examination of models show that the *cis*-syndiotactic ladder structure is the only extended, regular network of three-connected units which can accommodate the rigid, bulky phenylsilsesquioxane groups while maintaining tetrahedral bond angles on the silicons and the preferred bond angles of *ca.* 155°[4] on the oxygens.

The results show that the formation of an ordered one-dimensional network (double chain polymer) under equilibrium controlled conditions can be a spontaneously stereoselective process, probably for much the same reasons that the formation of ordered three-dimensional networks (crystals) can also be spontaneously stereoselective. In both cases the requirement that each structural building unit be at a bridgehead position, joined to three or more others in such a way as to avoid bond angle distortions or steric hindrance, places severe limitations upon the permissible modes of bond formation. It is suggested that this inherent stereoselectivity of network structure formation may help account for the evolution and operation of the network polymer systems which play such prominent roles in living organisms.

(4) R. F. Curl and K. S. Pitzer, THIS JOURNAL, **80**, 2371 (1958).

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THE POSSIBLE PARTICIPATION OF FLAVIN ADENINE DINUCLEOTIDE IN ADENOSINETRIPHOSPHATASE ACTIVITY[1]

Sir:

Recent reports of the effects of reducing agents[2] and flavin antagonists[3] on the ATPase[4] activity of mitochondria, and subparticles therefrom, indicate that a flavin derivative is possibly involved in the process. Because of the importance attached to ATPase as a manifestation of the system of oxidative phosphorylation, it was decided worthwhile to investigate the question of flavin involvement with the soluble ATPase of desiccated mitochondria.[5]

Materials and Methods.—Livers of adult, male Sprague–Dawley rats were the source of mitochondria isolated by conventional procedures. The mitochondria were converted to acetone powders immediately after isolation. Extracts of the powders were obtained by homogenizing in 0.25 *M* sucrose, and retaining that portion of the solution unsedimented by centrifugation at 105,000 *g* for 60 min. For maximal utilization, the extracts were lyophilized and reconstituted in water as needed. Enzyme activity was determined by the Martin and Doty procedure.[6] The FAD was of 99% purity.[7]

Results.—Previous work had shown that the ATPase of these preparations was greatly stimulated by dithionite and agents such as $NaHSO_3$ and NaHS. This effect indicated a possible requirement for a reducible cofactor or functional group. Oxidized and reduced DPN, TPN and cytochrome c had no effect on ATPase activity. However, experiments with FMN and FAD yielded rather dramatic results.

Figure 1 shows the effects of FAD on the ATPase activity in the presence of Mg^{++} or DNP. Pi formation with either activator is definitely elevated in the presence of added FAD over a range of FAD concentrations. In both cases the stimulation is maximal at 4.4×10^{-4} *M* FAD, and can be detected at the lowest concentration used (3.6×10^{-5} *M*). In contrast, FMN at these and higher concentrations has no discernible effect. Control experiments indicate that FAD causes no Pi formation in the absence of ATP.

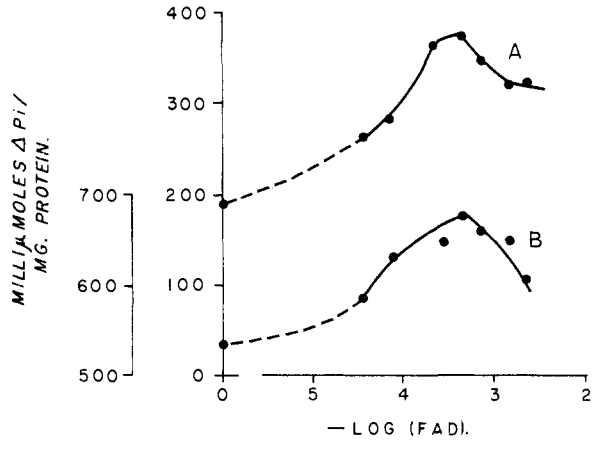

Fig. 1.—Stimulation of ATPase by added FAD—conditions: 6×10^{-2} *M* Tris buffer; 0.75 mg. protein; 1.2×10^{-2} *M* ATP; in volume 0.5 ml.; incubation temp. is 27°; curve A, 1×10^{-3} *M* DNP, *p*H 8.5, 10 min. incubation; curve B (accessory ordinate), 6×10^{-3} *M* Mg^{++}, *p*H 9.0, 4 min. incubation.

Table I shows that this phenomenon is reproducible with this type of preparation. In each of the four extracts tested, there is a definite stimulation by FAD which may be as great as 100%. One problem encountered with the soluble ATPase is loss of the DNP and Mg^{++} responses, particularly the former, under a variety of storage conditions. It was hoped that this process could possibly be due to dissociation or destruction of FAD.

(1) Supported in part by a National Science Foundation Grant (G-7490); North Carolina Heart Association; Institutional Grant of American Cancer Society; UNC University Research Council.

(2) (a) D. K. Myers and E. C. Slater, *Biochem. J.*, **67**, 558 (1957); (b) H. Löw, *Biochim. Biophys. Acta*, **32**, 1 (1959).

(3) (a) H. Löw, *ibid.*, **32**, 11 (1959); (b) M. J. R. Dawkins, J. D. Judah and K. R. Rees, *Biochem. J.*, **76**, 200 (1960).

(4) Abbreviations: ATPase, adenosinetriphosphatase; DNP, 2,4-dinitrophenol; DPN and TPN, di- and triphosphopyridinenucleotide; FMN, flavin mononucleotide; FAD, flavin adenine dinucleotide; Pi, inorganic phosphate; ATP, adenosinetriphosphate.

(5) H. A. Lardy and H. Wellman, *J. Biol. Chem.*, **201**, 357 (1953).

(6) L. Ernster, in "Methods of Biochemical Analysis," Interscience Publishers, Inc., New York, N. Y., **3**, 1 (1956).

(7) Obtained from California Corp. for Biochemical Research.