ions on surfaces and may be useful in practical testing of surface cleanliness.

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RECEIVED AUGUST 13, 1948

SIDE-CHAIN CRYSTALLIZATION IN ALKYL POLYACRYLATES

Sir:

Rehberg and Fisher[1] synthesized and polymerized a series of *n*-alkyl acrylates from methyl up to hexadecyl. They reported that the brittle points of these polymers decrease with increasing length of side chain, up to octyl (−65°) after which further increase leads to higher brittle points (*e. g.*, +35° for hexadecyl polyacrylate). In the latter paper it is noted parenthetically that the higher alkyl polyacrylates are crystalline in character.

We have prepared polymers of tetradecyl, hexadecyl and octadecyl acrylate, and copolymers of hexadecyl acrylate with methyl acrylate, and have established the fact that the high brittle points of these polymers are due to crystallization of the *alkyl side chains*. At low temperatures these side chain crystallites bind the polymer into a firm, waxy structure. At a fairly sharp melting point the crystallites melt, and the polymer becomes rubbery. This phenomenon is distinct both from the second order transition phenomenon exhibited by the lower acrylates and from the usual type of polymer crystallization (alignment of the polymer chain itself).

A series of X-ray diffraction photographs were obtained from hexadecyl acrylate polymer which serve to confirm the side-chain crystallinity of these samples. Normal wide angle and small angle Debye–Scherrer patterns were taken. The wide angle diagrams showed the polymeric material to be crystalline, and exhibited a very strong line at 4.2 Å. Small angle patterns were obtained at film-to-specimen distances of 20 cm. with filtered Fe radiation. These diagrams exhibited two sharp diffraction lines at 50 and 150 Å., respectively.

A small angle diagram was also obtained from hexadecyl acrylate monomer. (This material is liquid at room temperature but the specimen was cooled so that it was crystalline.) This diagram showed a diffraction maximum at 28 Å. The length of the polymer side chain is somewhat less than this.

The 150 and 50 Å. spacings found in the polymer may be considered as the first and third orders of a fundamental 150 Å. spacing. If the suggested interpretation of these long spacings as due to a crystallization of side chains is correct, then it would appear that the periodicity in the crystalline side chain packing repeats every six side chain units.

An effort was made to obtain orientation by drawing fibers of the hexadecyl acrylate polymer. X-Ray diagrams of these fibers showed slight orientation effects. The maxima of the long spacings occurred on the equator of these diagrams, which agrees with the interpretation that the crystallization is that of the side chains.

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RECEIVED JULY 20, 1948

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[1] C. E. Rehberg and C. H. Fisher, THIS JOURNAL, **66**, 1203 (1944); *Ind. Eng. Chem.*, **40**, 1429 (1948).

[2] American Chemical Society Post-Doctoral Fellow 1947–1948.

POLAROGRAPHIC CURRENT TIME CURVES

Sir:

From theoretical considerations, Ilkovič[1] has shown that the average diffusion current for a dropping mercury electrode is given by

$$\begin{aligned} i_d &= knD^{1/2}Cm^{2/3}t^{1/6} \\ &= ICm^{2/3}t^{1/6} \end{aligned}$$

If the "diffusion current constant" (I) for a given ion in a given supporting electrolyte is independent of capillary constant, as required by the Ilkovič equation, the performance of practical polarographic analyses can be greatly simplified. Lingane and Loveridge[2] have shown that, for the range of capillaries generally used in analysis, I is not strictly constant. The author recently has shown[3] that it is not possible to properly correct a polarogram, obtained with a large series resistance, by simply subtracting the product of the observed average current and the series resistance from the applied e. m. f. In an attempt to compute the average current for a given applied e. m. f. and series resistance, he was unable to obtain agreement between the calculated and experimental values if he assumed the current during the life of a drop grew as the one-sixth power of the time.

It was, therefore, considered to be of importance both in practical analyses and theoretical studies to examine experimentally the current time relationship for individual drops.

The Brush Development Co. pen recorder, with which recordings can be made over a frequency range of d. c. to 100 c. p. s., was used to determine the relationship on the diffusion region for 0.001 M lead in 1 M potassium chloride (0.01% gelatin),

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[1] D. Ilkovič, *Coll. Czech. Chem. Commun.*, **6**, 498 (1934).

[2] J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **66**, 1425 (1944).

[3] H. A. McKenzie, unpublished work.

0.001 *M* cadmium in 0.1 *M* potassium chloride (0.01% gelatin), and oxygen in 0.1 *M* potassium chloride (0.01% gelatin). A hand fabricated capillary (1.63 mg.$^{2/3}$ sec.$^{-1/2}$) and marine barometer tubing (2.05 mg.$^{2/3}$ sec.$^{-1/2}$) were used. The current time curves were approximately one-third order parabolas with a slight discontinuity after about the first 0.3 sec. (drop time 0.4 sec.). The log *i* *vs.* log *t* plot was approximately a straight line in each case. The average slope was 0.29 and not 0.17 as required by Ilkovič. The ratio of maximum current to average current (determined graphically) had a mean value of 1.29 instead of 1.17. It is of interest to note that Schulman, Battey and Gelatis[4] using a much slower recorder obtain a value of 1.25 for this ratio. Assuming the new current time relationship, the author was now able to accurately calculate the average current for a given applied e. m. f. and large series resistance.

In this preliminary communication, it is not possible to discuss the theoretical aspects of this study.

The author is deeply indebted to B. V. Hamon and the Electrotechnology Division of this Council for assistance. Grateful acknowledgement is due J. J. Lingane, M. C. Taylor and J. K. Taylor.

The above work forms part of the programme of Food Preservation Investigations of the Council.

(4) J. H. Schulman, H. B. Battey and D. B. Gelatis, *Rev. Sci. Instruments*, **18**, 226 (1947).

COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH
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RECEIVED AUGUST 21, 1948

PHOTOBROMINATION OF METHYLSILOXANE FILMS ON GLASS SURFACES

Sir:

Methylchlorosilanes[1] are used for the production of hydrophobic films on glass and ceramic surfaces. It is supposed that molecules of the type $Si(CH_3)_2Cl_2$ are hydrolyzed to form a coating consisting of one or several layers of $—Si(CH_3)_2—O—Si(CH_3)_2—$ chains with an exposed surface of $—CH_3$ groups.[2]

We have speculated that it should be possible to bring about photobromination, photochlorination or other reactions of the $—CH_3$ groups on the surface. Following halogenation still different functional groups might be introduced by processes such as the Friedel–Crafts reaction, thus altering the surface properties to meet specific requirements.

Our initial tests have demonstrated that the silicone surface can be photobrominated.

Test samples consisted of Pyrex and soft glass surfaces rubbed with the liquid silicone on a cotton swab. These specimens were exposed to radiobromine[3] vapor at a pressure of about 10 mm. The air pressure in the flask was less than a millimeter; some water vapor was present. The samples were illuminated for one hour by a 1000-watt Mazda bulb placed about two inches from the flask. The surfaces treated with silicone picked up ten to thirty times the amount of bromine required for the monobromination of each methyl group in an estimated monolayer.[3] Very little pickup occurred in the absence of illumination or with glass which was not coated. Rubbing with a dry towel after exposure reduced the bromine on the surface to a difficultly removable residue equivalent to approximately one monobrominated monolayer, but prolonged washing with water or carbon tetrachloride had relatively little effect. Illumination in the presence of chlorine gas for one hour removed a large fraction of the bromine. Dilute sodium hydroxide solution removed 50% of the bromine from some samples in fifteen minutes but showed much slower attack when the equivalent of only one or two monobrominated monolayers was left on the surface.

These results suggest the potentialities of radiohalogens as tools for investigating silicone films and furnish preliminary evidence that it may be possible to alter siloxane surfaces to meet specific requirements by substitution reactions, after the application of the silicone to the surface.[4]

This work was supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

(1) Obtained for this work from the General Electric Co. under the designation Dri-Film 9987.

(2) Francis J. Norton, *Gen. Elec. Rev.*, **47**, no. 8, 6 (1944); Eugene G. Rochow, "Introduction to the Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1946.

(3) Item No. 11 United States Atomic Energy Commission Radioisotopes Catalog No. 2. The specific activity when received was sufficient to give 20,000 counts per minute from one square inch of sample covered by an estimated monomolecular film of 5×10^{-9} moles of silicone[2] if each of the $—CH_3$ groups was converted to a $—CH_2Br$ group.

(4) A more complete discussion of these experiments is contained in the senior thesis of G. L. Vandervort filed with the library of the University of Wisconsin in June, 1948.

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RECEIVED AUGUST 7, 1948

THE CONFIGURATION OF STREPTOSE

Sir:

Crystalline ethyl N-acetyldihydrothiostreptobiosaminide[1] was demercaptalated with aqueous mercuric chloride and the product hydrogenated with Raney nickel catalyst at 95° and 100 atm. for seven hours to yield the crystalline N-acetyltetrahydrostreptobiosamine, m. p. 78–80°, $[\alpha]^{26}_{D}$ $-104°$ (*c* 0.838, water).

(1) F. A. Kuehl, Jr., E. H. Flynn, N. G. Brink and K. Folkers, THIS JOURNAL, **68**, 2096 (1946).