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

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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

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

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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(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

$$i_d = knD^{1/2}Cm^{2/3}t^{1/6}$$
$$= ICm^{2/3}t^{1/6}$$

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),

(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.