

and their respective complexes show a small lengthening of the unit spacing only for the conversion of polyglycine I into the cobalt complex.

Meggy and Sims⁴ showed that polyglycine I absorbed orange II equivalent to only 42 per cent of the total terminal amino-groups, whereas polyglycine II absorbed the theoretical amount of dye on the terminal residues. In neither case was the X-ray diffraction pattern disturbed on absorption of dye. Earlier, Bamford and his co-workers⁵ had commented on the ready absorption of certain dyes on the amide groups of a β -polypeptide (DP about 100), although there was hindered access to a proportion of the terminal amino groups.

The observed uptake of cobalt by polyglycine I suggests a binding of 1 cobalt to 4 amide groups, comparing well with a ratio of 1 cobalt to 3–4 amide groups in a complex with diglycylglycine⁶. From model structures it would appear probable that the inter-chain cobalt ion is co-ordinated to 2 amide groups and 2 ammonia molecules.

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Copolymerization by Vapour Phase Chromatography

ALTHOUGH the polymerization of organic compounds has been known for more than 100 years, the simultaneous polymerization of two or more monomers was not investigated until about 1911, when copolymers of olefines and diolefines were examined and found to have rubber-like properties. For some time the investigation of the mechanisms of the reactions of copolymerization lagged behind that of the properties of copolymers.

During the 1930's it was observed that different monomers could differ markedly in their tendencies to enter copolymers, and that often the composition of the copolymer was very different from the composition of the monomer mixture used in its production.

Dostal and Mark¹ attacked the theoretical aspects of copolymerization in 1936 and assumed that the rate of addition of monomer to a growing free radical depended only on the nature of the end-group on the radical chain. Norrish and Brookman² considered the copolymerization of styrene and methylmethacrylate on the basis of the four chain growth steps but apparently erred in their assumptions concerning the concentration of the free radical species. In 1944 Lewis and Mayo³, Alfrey⁴ and Wall⁵ independently derived the equation now known as the copolymerization equation. This equation may be represented as:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left(\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \right) \quad (1)$$

where $[M_1]$ and $[M_2]$ are monomer concentrations and r_1 and r_2 are the monomer reactivity ratios defined as the ratios of pairs of rate constants for the propagation reaction (for details the reader is referred to Mayo and Walling's review of the subject⁶).

Equation (1) describes the composition of the copolymer being formed at any instant from a polymerizing mixture of the two monomers M_1 and M_2 and as such finds wide application in the predetermination of monomer concen-

trations necessary to produce a copolymer of particular composition.

Before making use of the copolymerization equation for systems involving novel catalysts it is generally necessary to determine the values of r_1 and r_2 , the monomer reactivity ratios. This can be accomplished using a variety of analytical techniques fully described in the literature^{6,7}. In general, one performs experiments using a variety of known monomer mixtures, allows the reaction to proceed until the monomers have partially polymerized, then isolates the polymer from the unreacted monomer and determines the composition by elemental analysis. Generally the total separation of polymer from unreacted monomer is difficult and the elemental analyses tedious and fraught with error. Some attempts have been made to use physical techniques in the copolymer analyses. Among these the use of index of refraction measurements has permitted the determination of the monomer reactivity ratios for the system styrene-butadiene⁸ and Marvel and co-workers⁹ have made use of ultra-violet absorption spectroscopy.

This communication describes the use of gas chromatography to follow the copolymerization of two gaseous olefinic monomers at a catalytic surface.

Using an automatic gas chromatograph previously described by us¹⁰ it was possible to sample, at regular predetermined intervals, from the polymerizing system, which was at sub-atmospheric pressure.

Mixtures of ethylene and propylene or ethylene and butene-1 at pressures of the order of 10 cm mercury were contacted with a catalytic surface prepared by the reaction of $\alpha\text{-TiCl}_3$ deposited on a surface and CH_3TiCl_3 . The TiCl_4 produced in the reaction was removed by pumping prior to the addition of the monomer mixture. The details of the formation of the catalyst are in the course of publication¹¹. Immediately on contacting the olefinic mixture with the catalytically active surface a small sample, 0.5 c.c. in volume, was taken from the reacting mixture, which had a volume of 400 c.c., that is, less than 0.15 per cent of the mixture is removed during each sampling. Subsequent samples were removed at intervals of 0.5 h and at the end of the experiment a record of the time variation of each of the polymerizing monomers was obtained. The chromatograph was calibrated for each of the reacting species and graphs representing the change in concentration of each of the monomers were obtained.

Selecting a time interval from the initiation of the reaction and noting the monomer concentrations at the beginning and end of the interval it was possible, using the methods of Lewis and Mayo³, to calculate the monomer reactivity ratios for the system. For the ethylene butene copolymerization, using the aforementioned catalyst system, the monomer reactivity ratios were determined to be $r_1 = 3.6$ and $r_2 = 0.16$.

In order to ascertain in a conclusive manner that the choice of the time interval did not affect the values of the monomer reactivity ratios, that is, that the degree of conversion did not affect the reactivity ratios if the composition of the polymerizing mixture was known over the time interval, the r_1 and r_2 values were calculated at a variety of time-intervals. Since the Lewis and Mayo procedure is extremely time-consuming and mechanically laborious the calculations were programmed for an I.B.M. 1620 computer and carried out using it. The computation of r_1 and r_2 was performed for time-intervals of a duration increasing in steps of one hour from one hour up until the cessation of the reaction after approximately nineteen hours. Variation of r_1 and r_2 over the increasing interval was slight and well within the precision of the experimental measurements.

The method described here is at present under analytical examination with the aim of being able to calculate mathematically the monomer reactivity ratios from one experimental polymerization. It is hoped that in the very near future we shall be able to discuss the catalyst system

described here and several others which we have examined in more detail and to report the results of the mathematical analysis of the system which we are at present carrying out.

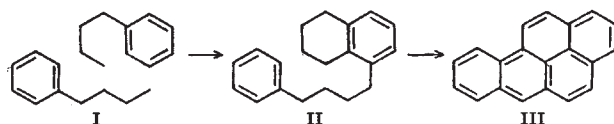
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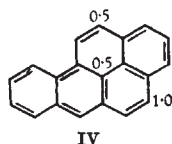
Mode of Formation of 3,4-Benzopyrene at High Temperatures

3,4-BENZOPYRENE (III) and other polycyclic aromatic hydrocarbons have been identified in coal tar, in soot, in the atmospheric dust of cities, in the exhausts of petrol and Diesel engines, in shale oil, in carbon black, in processed rubber, in coffee soots, in human hair wax, in smoked food, in snuff, in tobacco, and in cigarette and tobacco smoke¹. As 3,4-benzopyrene is a potent cancer-producing hydrocarbon, its mode of formation is clearly of importance. In 1958² it was suggested that 3,4-benzopyrene is formed by high-temperature reactions (incomplete combustion and the like) from simpler hydrocarbons, and that a C₁₂-C₁₄ compound (such as butylbenzene or tetralin) may be the critical intermediate. Two such molecules would be expected to give (II) which would suffer ready cyclodehydrogenation to 3,4-benzopyrene (III).



Subsequent work has tended to confirm this view. Pyrolyses of butylbenzene³, of tetralin⁴, or of *n*-decane⁵ at 700°, for example, have given tars which have been shown to contain significant quantities of 3,4-benzopyrene. The relative yields of the various hydrocarbons in these tars and in tars produced by the pyrolysis of simple related hydrocarbons are consistent with the suggested mode of formation of 3,4-benzopyrene (as I→III).

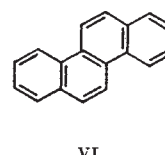
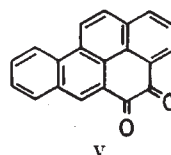
More recently, the pyrolyses of [1-¹⁴C]tetralin⁶ and of [δ-¹⁴C]butylbenzene (our unpublished results) have been undertaken; if the foregoing mode of formation is correct then the 3,4-benzopyrene formed should have activity corresponding to 2.0 labelled carbon atoms, distributed as in (IV).



Pyrolysis of [1-¹⁴C]tetralin has given a tar from which twenty-one compounds (or their derivatives) have been isolated in sufficient quantity and purity for radiochemical analysis. The 3,4-benzopyrene isolated from this tar was found to have an activity corresponding to 1.96 labelled

carbon atoms, in good agreement with the proposed mechanism.

In the same way the pyrolysis of [δ-¹⁴C]butylbenzene has given a tar from which eighteen compounds have been isolated for radiochemical assay. The 3,4-benzopyrene was found to have activity corresponding to 1.92 labelled carbon atoms, and its distribution has been determined by degradation as follows. Oxidation of the 3,4-benzopyrene gave 3,4-benzopyrene-6,7-quinone (V), which had 1.92 labelled carbon atoms. This was then further oxidized to crude chrysene-6,7-dicarboxylic acid which was decarboxylated. The resulting carbon dioxide had activity corresponding to 0.87 labelled atoms in reasonable agreement with the expected value (1.0). Moreover the chrysene (VI) obtained by the decarboxylation had 1.12 labelled atoms, again in reasonable agreement with the expected value (1.0).



It must be concluded therefore that the mode of formation represented by (I→III) is an important route for the formation of 3,4-benzopyrene at high temperatures.

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BIOCHEMISTRY

Composition of Spermaceti

SPERMACETI is the solid wax obtained mainly from the head of the sperm whale, *Physeter macrocephalus* L. (*P. catodon* L.). Sperm oil is present in a large head-cavity in a liquid state. On standing after removal from the whale a crystalline deposit forms in the oil. The deposit is separated by filtration, pressed, melted, purified from traces of oil with dilute alkali and finally freed from the soaps thus produced and from excess of alkali. Spermaceti is said chiefly to consist of cetyl palmitate together with a small proportion of esters of other fatty acids, including lauric, myristic and stearic^{1,2}.

As pure spermaceti has a very low iodine number and contains no free acids and alcohols, the saponification value which normally lies between 125 and 136 does not correspond well with the saponification value of cetyl palmitate, which is 116.7.

A very fine sample of spermaceti (iodine number 2.8, acid number 0.1 and saponification value 125.4) was saponified and the alcohol- and acid-fractions isolated. By gas chromatography the alcohol-fraction was shown to consist of 80 per cent cetyl alcohol, 12 per cent stearyl alcohol, 6 per cent myristyl alcohol and of 2 per cent hydrocarbons.

The acid-fraction was converted through the acid chlorides to methyl esters. By gas chromatography the percentage composition of the ester mixture was calculated by comparison with the pure methyl esters: