

69. Macropolymerization of Ethylene. (VI)

Copolymerization of the Ethylene with the Isobutylene.

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The ethylene containing 6.4% isobutylene was polymerized at 254–283°C under 1,400–1,600 atm. press. The products were found homogeneous with less quantity of isobutylene as remained unreacted. From these facts the copolymerization reaction was recognized. The molecular weights of the products were calculated from the usual formula :

$$\lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = K_m \times 0.94 \times 10^{-4}$$

Although this formula does not hold accurately for these copolymers, it was used approximately.

The molecular weights of the copolymers were found to be about one third of those of polyethylenes prepared under the same conditions. Furthermore, the reaction of copolymerization was found to proceed as a second order reaction. The rate constants calculated as a second order reaction were 1.2–1.5 times as large as those of polymerization reactions of ethylene alone, so that the velocity of the chain initiation and that of the chain termination must be 4–5 times as large in copolymerization as in ethylene polymerization.

A reaction mechanism with which these facts could be explained were derived. The apparent activation energy of the copolymerization reaction was about 38 Kcal.

70. X-ray Studies on the Aging of Poval-filaments.

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To obtain some clue on ageing phenomena in semi-molten povalfilaments, X-ray diagramatic studies were performed with two series of samples. The ones, "open system", were those allowed to stand in ordinary atmosphere without any treatment to avoid evaporation of water at various temperature (0°, 30°, 50°, 70°, 100°, 150° & 200°) and the others, "closed system" were the samples sealed in glass tubes.

The X-ray photographs thus obtained were examined regarding the changes of each principal spacing (R_1 , R_4) and the photometer curves.

Both series of samples showed not a super-position of crystalline and amorphous phase but a continuous change of lattice spacing to regular form. These tendencies