69. Macropolymerization of Ethylene. (VI)

Copolymerization of the Ethylene with the Isobutylene.

Shinjiro Kodama, Isoji Taniguchi and *Tadashi Zenbutsu.*

(Kodama Laboratory)

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 :

$$\lim_{c\to 0} \frac{\eta^{sp.}}{c} = K_m \times 0.94 \times 10^{-4}$$

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.

Kiyoshi Hirabayashi and *Fumihide Fujimoto.*

(Sakurada Laboratory)

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

were more evidently emphasised by observing photometer curves.

From the above mentioned results, we were obliged to recognize that the aging process in semi-molten poval-filaments was not a crystal growth as in ordinary low molecular substances, but a change of state to approach regular crystalline structure from non-crystalline structure.

71. Aging Phenomena in Poval-filaments.

Kiyoshi Hirabayashi and *Yasuo Sone.*

(Sakurada Laboratory)

Aging phenomena in semi-molten poval-filaments were persued by means of change of its ability of swelling and tolerance to hot water, etc. The swelling degree was represented in percentage of total weight by measuring the maximum water absorption at 30°C. and the ability of tolerance to hot water was measured by softening temperature of filaments hanged in water with constant load and constant temperature elevation. The experiments performed were as follows, (1) Time dependency upon swelling and softening temperature. (2) Effect of temperature, elongation and water contents upon aging. (3) Dilatometric measurement. It was found that there exists a linear relationship between swelling and softening temperature and the temperature facter was more pronounced than other effects. In addition to these facts, some volume contraction (57% P. V. A. 10 days. V. C. 0.256%) during aging were observed.

A relation between velocity of aging and heat-treatment were proposed as follows from theoretical point of view.

$V = AT^{\frac{1}{2}} e^{-E/RT}$, where V=velocity, T=abs. temperature,

E=activation energy.

From the experiments of swelling, it was deduced that the activation energy was 20–30 kcal/mol.

We are now discussing on the numeral deviation from the former report (A. E. 10–12 kcal/mol.), however, anyway it was proved that aging process should take place in the semi-molten poval-filaments.

72. Crystal Structure of Polyvinyl Alcohol.

Ichiro Sakurada, Keiroku Fuchino and *Noboru Okada.*

(Sakurada Laboratory)

It has been said[1] that the molecular repeat distance of polyvinyl alcohol 2.52 Å