

interpret the dielectric behaviour of emulsions, theories of interfacial polarization are discussed with reference to a spherical dispersion system. The general solutions of the Wagner theory are discussed, being found to be insufficient quantitatively for the experimental results. A new theory applicable to a concentrated dispersion is developed on the assumption that the Wagner equation holds for an infinitesimally increasing process in concentration of disperse phase. Experimental results are interpreted quantitatively by this new theory. It is suggested by the new theory that, if the dielectric constant of oil phase is much larger, dielectric dispersion may be observed even in emulsions of o/w type. Such a suggestion was verified by dielectric measurements for nitrobenzene-in-water (n/w) emulsions. The shearing effect found in w/o emulsions may be caused by breaking up particle agglomerates.

Polymer Chemistry

Application of the Archibald ultracentrifugal method for the study of dilute polymer solutions. II. Examination of two solution systems near the Flory temperature. Hiroshi Inagaki, Shuji Kawai and Atsushi Nakazawa. *J. Polymer Sci.*, **A1**, 3305 (1963).—To test the validity of the generalized Archibald method developed previously, sedimentation experiments were made for two systems, polystyrene-cyclohexane and polymethyl methacrylate-n-butyl chloride, near the Flory temperature relevant to each. It was found that the slope of the resulting plot between the reciprocal of the apparent molecular weight M_{app} (extrapolated back to zero centrifugation time) and the concentration tends to zero at the Flory temperature, while this slope shows positive or negative values, depending on whether the temperature is higher or lower than the characteristic one. Thus the present method gives just the same information for dilute polymer solutions as does the light scattering. A further study was carried out to elucidate the time-dependent nature of $M_{app}(t)$, calculated at each centrifugation time, in terms of the thermodynamic nonideality of solution and of the fractionating action of the ultracentrifuge on a polydisperse solute.

Einige Bemerkungen über die Molekulargewichtsbestimmung nach dem Archibald-Verfahren unter besonderer Berücksichtigung der Arbeit von W. Scholtan und H. Marzolph. Hiroshi Inagaki. *Makromol. Chem.*, **64**, 215 (1963).—The apparent molecular weight M_a is determined from sedimentation data. The slope of the sedimentation diagram is discussed. The curve obtained by plotting $1/M_a(0)$ vs. polymer concentration c , where $1/M_a(0)$ is the value of $1/M_a(t)$ extrapolated to the time $t=0$, is discussed with regard to the cause of its curvature. The bending, for a given system, increases with better solvents. Also, for a given system, the bending of the curve increases with increasing molecular weight of the solute. Thus, the author interprets the molecular weight dependence on the second virial coefficient A_2 , namely the fact that the value of A_2 increases anomalously with increasing molecular weight, differently than was observed by Scholtan and Marzolph (*Makromol. Chem.* **57**, 52 (1962)).

Study on molecular structure of polymethyl isopropenyl ketone by X-ray diffraction method. Ryuzo Koyama. *Bull. Inst. Chem. Res., Kyoto Univ.*, **41**, 207 (1963).

Intrinsic viscosities and unperturbed dimensions of long chain molecules. Michio Kurata and Walter Stockmayer. *Fortschr. Hochpolym. Forsch.*, **3**, 196 (1963).— A new theory of the intrinsic viscosity of chain polymer solutions is developed on the basis of the Kurata-Stockmayer-Roig theory of the excluded volume effect (*J. Chem. Phys.* **33**, 151 (1960)). The presented theory predicts that the intrinsic viscosity becomes proportional to the molecular weight in the limiting case of very good solvent, even for a non-draining molecule. The unperturbed dimension of polymer chain is obtainable from good solvent data of intrinsic viscosity by a simple analysis of the viscosity-molecular weight relationship, without the aid of the theta-solvent data. For about 100 linear chain polymers, including 50 addition polymers, 15 amylosic and cellulosic chains, 25 condensation polymers, 5 polypeptides and 5 polynucleotides, their unperturbed dimensions and the effective bond lengths are evaluated from the existing data of viscosity, and the results are discussed in relation to the molecular structure of the chains. Some related problems such as the sedimentation constant and the osmotic second virial coefficient are also studied in the light of the presented theory of intrinsic viscosity. Viscosity constants appearing in the Mark-Houwink-Sakurada equation are given for 223 polymer-solvent systems.

Effects of gamma radiation on polymer in solution. 4. Crosslinking and degradation of poly (acrylic acid) in aqueous solution. Ichiro Sakurada and Yoshito Ikada. *Bell. Inst. Chem. Res., Kyoto Univ.*, **41**, 103 (1963).

Effects of gamma radiation on polymer in solution. 5. Intramolecular crosslinking of poly(acrylic acid) in dilute solution. Ichiro Sakurada and Yoshito Ikada. *Bell. Inst. Chem. Res., Kyoto Univ.*, **41**, 123 (1963).

Effects of gamma radiation on polymer in solution. 6. Radiation protection and promotion on aqueous of poly (vinyl alcohol). Ichiro Sakurada and Yoshito Ikada. *Bell. Inst. Chem. Res., Kyoto Univ.*, **41**, 123 (1963).

Radiation induced graft copolymerization to cellulose. VII. Effect of pretreatment on grafting. Ichiro Sakurada, Norio Okada, Fujiko Kimura and Namiko Minekawa. *Bonded Materials*, **1**, 39 (1963), in Japanese.

Estimation of molecular weight distribution of polystyrene standard samples by diffraction method. Ichiro Sakurada and Masao Hosono. *Bull. Inst. Chem. Res., Kyoto Univ.*, **41**, 179 (1963).

Effect of Gamma irradiation upon wool fibers. Masao Horio and Kazuo Ôgami. *Bull. Inst. Chem. Res., Kyoto Univ.*, **41**, 1 (1963).

Polymerization of styrene, methyl methacrylate and acrylonitrile onto wool by gamma irradiation. Masao Horio, Kazuo Ōgami, Takashi Kondo and Ken'ichi Sekimoto. *Bull. Inst. Chem. Res., Kyoto Univ.*, **41**, 10 (1963).

Effect of gamma-irradiation upon cellulose. Masao Horio, Rikizo Imamura and Hideya Mizukami. *Bull. Inst. Chem. Res., Kyoto Univ.*, **41**, 17 (1963).

Two-step blockcopolymerization of acetaldehyde with propylene oxide. A synthesis of block-copolymer. Hiroyasu Fujii, Tadayasu Fujii, Takeo Saegusa and Junji Furukawa. *Makromol. Chem.*, **63**, 147 (1963).—A blockcopolymer of acetaldehyde with propylene oxide was prepared by using the two-step blockcopolymerization technique. In the first step, propylene oxide alone was polymerized with the triethylaluminum-water (1:1) system as a catalyst at room temperature for a fixed time. Then, the second step of the copolymerization was carried out by addition of acetaldehyde at -78°C . The two-step copolymerizate was separated into three fractions, i. e., the methanol-soluble (I), the methanol-insoluble and chloroform-soluble (II), and the chloroform-insoluble (III) fraction. The formation of blockcopolymer was confirmed by the hydrolysis of the two soluble fractions, (I) and (II), with hydrochloric acid. The methanol-insoluble fraction and chloroform-soluble fraction (II) was found to consist mainly of blockcopolymer of acetaldehyde with propylene oxide. Moreover, it was found that these two soluble fractions had a better thermal stability than the homopolymer of acetaldehyde.

Polymerization of 3-substituted oxazolidines. Masaya Okano, Akira Miyasu, Hakusei Hamada and Ryohei Oda. *Kobunshi-Kagaku*, **20**, 557 (1963). in Japanese.—In the presence of various acid catalysts the ring-cleavage polymerization of 3-aryl- and 3-alkyloxazolidines has been investigated. Monomeric oxazolidines were prepared by condensation or addition methods. 3-Phenyloxazolidine and its derivatives (e. g., 4-methyl-3-phenyl-, 5-methyl-3-phenyl-, and 2,3-diphenyloxazolidine) were easily polymerized by heating with a small amount of dimethyl aniline hydrochloride to give the corresponding poly (ether-imines), though their molecular weights were not so high. Under the same conditions, the polymerization of 3-alkyloxazolidines was unsuccessful, probably due to their strong basicities. In the case of the oxazolidines having a chloromethyl group on the ring, the polymerization could be carried out even in the absence of the catalyst, but the structure of polymers seemed to be somewhat complicated.

Studies of isocyanides. I. The formation of urethanes and ureas from isocyanides. Masaya Okano, Yoshihiko Ito, Tatsuya Shono and Ryohei Oda. *Bull. Chem. Soc. Japan*, **36**, 1314 (1963).—The reactions of isocyanides with alkyl hypochlorite, N-bromoamides and hydroxylamine have been investigated. Cyclohexyl and phenyl isocyanides give t-butyl carbamates (urethanes) by the zinc chloride-catalyzed reaction with t-butyl hypochlorite, followed by treatment with water. An analogous reaction with N-bromosuccinimide or N-bromoacetamide in the presence of a small amount of water gives the corresponding acylureas. On treatment with hydroxylamine hydrochloride and zinc chloride, cyclohexyl isocyanide affords N-cyclohexylurea.