

(2 $\bar{1}1$) axes, which are quite different from those striations appearing on the surface of single-crystalline thin film of f.c.c. lattice assuming (111) orientation caused by lattice defects included in another three kinds of ($\bar{1}11$) planes. The dark field images of the same pattern show that the squamous pattern is also caused by diffraction effect owing to the microstructure of the crystal including various lattice defects, the origin of which seems to have a close relation to the growth mechanism of the crystal itself in the solution.

Infrared studies of rubber-filler system. I. Infrared absorption spectra of inorganic fillers. Eiji Suito and Masafumi Arakawa. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 291 (1962).

Infrared studies of rubber-filler system. II. Identification of rubbers compounded with fillers by infrared absorption spectra. Eiji Suito and Masafumi Arakawa. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 300 (1962).

Polymer Chemistry

Über den Lösungszustand des Polyvinylalkohols in Wasser. 1. Mitt. Metastabiler Zustand der Lösung. Togoro Matsuo und Hiroshi Inagaki. *Makromol. Chem.*, **53**, 130 (1962).—An gelösten, unter verschiedenen Polymerisationsbedingungen hergestellten Proben von Polyvinylalkohol wurden Streulichtmessungen ausgeführt. Es wurde besonders die Wirksamkeit von verschiedenen optischen Reinigungsmethoden berücksichtigt. Die Zimm-Diagramme für drei von fünf Proben zeigten anormale Kurven, was darauf hinweist, daß noch in verdünnter Lösung Mikrogelteilchen vorhanden sind, während die anderen zwei Proben normale Kurven aufwiesen. Diese ermöglichen, das Molekulargewicht des Gelösten zu bestimmen. Durch Stehenlassen der Lösung bei 30 °C trat eine zeitliche Zunahme der Streuintensität auf, die wahrscheinlich durch Bildung weiterer Mikrogelteilchen verursacht wird. Die Aufbewahrung bei 0 °C ergab jedoch keine merkliche Veränderung. Durch Erhitzen der Lösung auf 100 °C konnten die Mikrogelteilchen nur zum Teil zerlegt werden. Das besagt, daß die Teilchen aus einem parakristallinen und einem amorphen Bereich bestehen und daß nur der letztere Anteil bei 100 °C desintegriert wird. Um den Zusammenhang zwischen der Kristallinität einer Probe und deren Lösungsverhalten zu erkennen, wurde ein Präparat im festen Zustand bei verschiedenen Temperaturen vorbehandelt. Der Einfluß dieser Vorbehandlung auf den Lösungszustand wird im Zusammenhang mit der Röntgenkleinwinkelstreuung im festen Zustand diskutiert.

Über den Lösungszustand des Polyvinylalkohols in Wasser. 2. Mitt. Molekulargewichtsbestimmung durch Streulichtmessungen. Togoro Matsuo und Hiroshi Inagaki. *Makromol. Chem.*, **55**, 150 (1962).—Unter der Annahme, daß sich Polyvinylalkohol (PVA) bei 80 °C molekulardispers in wäßrige Lösung bringen läßt, wurde das Molekulargewicht für einige Fraktionen von PVA durch Streulichtmessungen

bestimmt. Zugleich wurde der Staudinger-Index $[\eta]$ für dieselben Proben bei 80°C gemessen. Durch beide Versuchsreihen stellte man fest: (1) die Beziehung zwischen $[\eta]$ und dem Molekulargewicht M_w stimmt mit derjenigen von Matsumoto und Ohyanagi überein, die mit Hilfe von Streulichtmessungen an Polyvinylacetatlösungen und polymeranalogen Umsetzungen zu PVA abgeleitet wurde; (2) der Staudinger-Index nimmt mit steigender Temperatur stark ab; (3) der zweite Virialkoeffizient wird mit Erhöhung der Temperatur merklich kleiner. Ferner diskutieren wir die Beziehung zwischen $[\eta]$ und M_w auf Basis der neuen Theorie von Kurata, Stockmayer und Roig für den Effekt des ausgeschlossenen Volumens in einer Polymerkette und errechnen den ungestörten Fadenendenabstand der Polymerkette im Wasser, welchen man nur bei der Θ -Temperatur messen kann.

Apparent specific volume of polymers in solution. Hiroshi Inagaki. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 364 (1962).

Application of the Archibald ultracentrifugal method for the study of dilute polymer solutions. I. Theory and some preliminary data on the system polystyrene-methyl ethyl ketone. Hiroshi Fujita, Hiroshi Inagaki, Tadao Kotaka and Hiroyasu Utiyama. *J. Phys. Chem.* **66**, 4 (1962).—The theory of Kegeles, Klainer and Salem for the Archibald ultracentrifugal method for polydisperse macromolecular solutes has been improved and extended. It is shown that the new theory allows determination of the weight-average molecular weight and the light scattering second virial coefficient of a given system from sedimentation experiments performed under conditions appropriate to the Archibald method. The validity of the derived equation has been tested with sedimentation and light scattering experiments on two polystyrenes of different molecular weights in methyl ethyl ketone at 25°. For both the molecular weights and the second virial coefficients fairly good agreements have been obtained between the data from these two different experiments.

Non-Newtonian flow and normal stress phenomena in solutions of polystyrene in toluene. Tadao Kotaka, Michio Kurata and Mikio Tamura. *Rheologica Acta*, **2**, 179 (1962).—Non-Newtonian flow and normal stress phenomena are studied with solutions of polystyrene in toluene with varying temperature, concentration and molecular weight. The temperature dependence of normal and shear stresses of a solution with fixed concentration can be described in terms of shift factor, a_T , which is commonly used in the study of linear viscoelastic phenomena of polymeric systems. From the measurements of normal and shear stresses the elasticity contribution to flow behavior of polymer solution can be evaluated, and its dependences on concentration and molecular weight are discussed. Each of the tested solutions shows more or less non-Newtonian viscosity behavior, especially very strongly in solutions with high concentration and high molecular weight. And these solutions are mainly "Hookean" in shear, but non-Hookean character appears in solutions with high concentration and with rather low molecular weight. The zeroshear viscosity versus concentration relationship is found to obey a c^0 -dependence in a certain range of concentration, while in the same concentration range the reciprocal

of steady shear compliance shows a $c^{3/2} \sim c^2$ -dependence. The zeroshear viscosity versus molecular weight relationship of solutions at a fixed concentration obeys the well-known $M^{3/4}$ -dependence above a certain critical value of molecular weight which is dependent on the concentration. While the reciprocal of compliance is almost independent of molecular weight above this value, and it seems to be somewhat affected by the type of polymers such as molecular weight heterogeneity and/or degree of branching of the polymer.

Properties and structure of polyvinyl alcohol film, grafted with styrene by γ -ray irradiation. Waichiro Tsuji, Ryoza Kitamaru and Terumichi Ichiba. *Kobunshi Kagaku*, **19**, 389 (1962), in Japanese.—The polyvinyl alcohol film pretreated with water was irradiated in styrene with Co^{60} γ -ray. Then the graft polymerization of styrene to polyvinyl alcohol film proceeded with the irradiation. The grafted film expanded almost evenly to the three dimensional directions. Styrene grafted polyvinyl alcohol film was cut into small pieces. Using those many small test pieces, specific gravity, degree of swelling in water and benzene, heat plasticity etc. were measured. It was found that there were little difference of properties between inner layer and surface layer of the film. The fact indicates that the graft copolymerization would proceed homogenously in the outer and inner parts of the film except extremely thick one.

The properties of graft polymerized polyvinyl alcohol fibers. Waichiro Tsuji, Ryoza Kitamaru and Terumichi Ichiba. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 86 (1962).

The softening of raw silk by treating with chemical compounds. Waichiro Tsuji and Masazo Imai. *Sen-i Gakkaishi*, **16**, 879 (1960), in Japanese.—The research for the softening of raw silk by treating with chemical compounds was carried out. It is found that raw silk is softened remarkably by the treating with chemical solutions, such as potassium rhodanate, calcium chloride, ammonium chloride, sodium bicarbonate and triethanolamine diluted with 10% of water. To evaluate the stiffness of the treated sample, the buckling force was measured using torsion balance and the stiffness was shown with the value of $P_{\max}$ of Euler's equation, relating to the buckling of long column,

$$P_{\max} = 4\pi^2 EI / l^2,$$

where $P_{\max}$ is buckling force, E is Young's modulus, I is moment of inertia and l is length of sample. Values of $P_{\max}$ of raw silks which were treated with 10% water solution of some chemical compounds above described were decreased as same as the wet raw silk. The mechanism of the softening was discussed, and it was deduced that raw silk was plasticized by such chemicals.

Studies on graft polymerization onto cotton. I. Grafting of styrene onto cotton by pre-irradiation with electron beams. Ichiro Sakurada, Toshio Okada and Fujiko Kimura. *Sen-i Gakkaishi*, **18**, 687 (1962), in Japanese.—The grafting of styrene onto

cotton fabric by pre-irradiation method has been studied. Cotton was irradiated in the presence of air by the use of electron beams from a van de Graaff accelerator, and then brought into contact with methanol solution of styrene which contained about 5% water at various temperatures in vacuo for the grafting. Styrene was found to be grafted readily onto cotton at a dose of the order of 1 Mrad. At a constant radiation intensity (2.0×10^4 rad/sec) the amount of styrene grafted increased with total dose and the grafting time. The optimum temperature of grafting was 50°C. So far as the total dose was constant the rate of grafting was independent of the intensity of irradiation between a dose rate of 2.0×10^3 and 1.0×10^5 rad/sec. Almost no grafting reaction was observed when it was carried out in air. Effect of the presence of ferrous ion in monomer solution on the grafting of styrene onto cotton was also studied. In the case of the grafting in vacuo, ferrous ion accelerated the process at lower temperatures, but it did not accelerate it at 50°C and 80°C. Grafting occurred to a considerable extent in air when monomer solution contained ferrous ion.

Studies on graft polymerization onto cotton. II. Effect of solvent on the grafting of styrene onto cotton. Ichiro Sakurada, Toshio Okada and Fujiko Kimura. *Sen-i Gakkaishi*, 18, 693 (1962), in Japanese.—Effects of solvent and atmosphere of irradiation on the grafting and stability of active center for grafting were studied. Cotton irradiated by electron beams in air was smoothly grafted by styrene in vacuo at 50°C in methanol solution without addition of water, and its grafting rate was rather high as compared to that in a monomer solution which contained water. Besides methanol, ethanol and propanol were effective for the grafting whereas butanol and amyl alcohol were not effective. Cotton irradiated in various solvents showed practically the same rate of grafting. The active center for grafting decayed more or less rapidly by heating in air or water. When irradiation was carried out with Cobalt-60 γ -rays, the rate of the grafting onto cotton irradiated in vacuo was twice as that irradiated in air, and it was deterred in the case of irradiation in benzene. Acrylic acid grafted readily onto cotton although a considerable amount of homopolymer was produced.

Studies on graft polymerization onto cotton. III. Graft polymerization onto dyed cotton fabric with pre-irradiation technique. Ichiro Sakurada and Fujiko Kimura. *Sen-i Gakkaishi*, 18, 698 (1962), in Japanese.—Dyed cotton fabric was pre-irradiated with electron beams and then subjected to graft polymerization in vacuo at 50°C with a grafting mixture of styrene-methanol or styrene-methanol-water. Although the degree of grafting of dyed cotton fabric was lower than that of undyed one, fabric dyed with Sirius Supra Yellow FRAL, Alcian Blue 8 GN and Sirius Supra Orange F 3 G were grafted with styrene smoothly without much fading. Almost no grafting was observed when fabrics were dyed with Indanthrene Brown G, Indanthrene Grey K or Sulphur Brown MC.

Effects of gamma radiation on polymer in solution. I. Poly (vinyl acetate). Ichiro Sakurada and Yoshito Ikada. *Bull. Inst. Chem. Res., Kyoto Univ.*, 40, 1 (1962).

Effects of gamma radiation on polymer in solution. II. Poly (vinyl methyl ether). Ichiro Sakurada and Yoshito Ikada. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 16 (1962).

Effects of gamma radiation on polymer in solution. III. Poly (vinyl alcohol) partially acetalized with glyoxylic acid. Ichiro Sakurada and Yoshito Ikada. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 25 (1962).

Shrinkproofing of wool by permanganate / sodium chloride treatment. Masao Horio, Chikaaki Sakai, Takashi Kondo and Ken'ichi Sekimoto. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 351 (1962).

Comparison between the effect of permanganate / sodium chloride and that of permanganate / water upon wool. Masao Horio, Chikaaki Sakai, Takashi Kondo and Ken'ichi Sekimoto. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 358 (1962).

Theory of multi-coordination centered catalyst. A proposed mechanism of stereoregular polymerization. Junji Furukawa. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 130 (1962).

Stereoregular polymerizations of acrylic ester and its related monomers. Teiji Tsuruta and Junji Furukawa. *Bull. Inst. Chem. Res., Koto Univ.*, **40**, 151 (1962).

Preparation of polyether. Junji Furukawa and Takeo Saegusa. *Bull. Inst. Chem. Res., Koto Univ.*, **40**, 171 (1962).

Study on vulcanization promoters. Junji Furukawa, Shinzo Yamashita and Ryuzo Yamamoto. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 197 (1962).

Preparation of active calcium carbonate for reinforcing SBR. Junji Furukawa, Shinzo Yamashita, Hiroshi Niwa, Minoru Fukuda and Teizo Kotani. *Bull. Inst. Chem. Res., Kyoto Univ.*, **40**, 211 (1962).

Organic Chemistry

New addition reactions. II. Addition of aliphatic epoxides to Schiff bases. Ryohei Oda, Masaya Okano, Shohei Tokiura and Akira Miyasu. *Bull. Chem. Soc. Japan*, **35**, 1216 (1962).—See, this Bulletin, **40**, 406 (1962).

New addition reactions. III. Addition of aliphatic epoxides to nitriles. Ryohei Oda, Masaya Okano, Shohei Tokiura and Fujio Misumi. *Bull. Chem. Soc. Japan*, **35**, 1219 (1962).—See, this Bulletin, **40**, 406 (1962).

New addition reactions. IV. The addition of Schiff bases to diketene. Ryohei Oda, Shunichi Takashima and Masaya Okano. *Bull. Chem. Soc. Japan*, **35**, 1843 (1962).—See, this Bulletin, **41**, 223 (1963).