

Abstracts of the Papers Published in Other Journals by the Staff Members of this Institute During the Year 1965

Nuclear Physics and Chemistry

Effect of Chemical Binding on the Radioactive Decay Constant. Sakae Shimizu. *Kagaku to Kogyo*, **18**, 935 (1965), in Japanese.—Historical aspect of the development of the study on the chemical effect on the radioactive decay constant is reviewed. After describing principles of the measurement applicable to find minute difference of the decay constant between two different chemical compounds containing same radioactive nucleus, the works with ^7Be and $^{99\text{m}}\text{Tc}$ so far published by other workers are reflected with giving tables summarize the experimental results. The work with $^{235\text{m}}\text{U}$ in progress in the author's laboratory is reported by describing some details of experimental techniques. The observed result for metallic uranium ($^{235\text{m}}\text{U}$) and uranium atoms embedded in a carbon base ($^{235\text{m}}\text{UC}$) was found to be $[\lambda(^{235\text{m}}\text{UC}) - \lambda(^{235\text{m}}\text{U})] / \lambda(^{235\text{m}}\text{U}) = -3.2 \times 10^{-3}$ as preliminary one. Some discussions and future aspects of development of the study on this phenomenon are also given.

The Effect of Chemical State on the Decay Constant of a Nuclear Isomer, $^{235\text{m}}\text{U}$. Sakae Shimizu and Hiromasa Mazaki. *Physics Letters*, **17**, 275 (1965)—An experiment was performed to study the effect of the chemical state on the decay constant of $^{235\text{m}}\text{U}$. Details are given of the source preparation, the measuring system, and the experimental method. A least squares analysis applied to the observed results for metallic uranium (U) and uranium atoms embedded in a carbon base (UC) yielded $[\lambda(\text{U}) - \lambda(\text{UC})] / \lambda(\text{U}) = (3.2 \pm 0.05) \times 10^{-3}$.

Search for Radiationless Annihilations of Positrons. Sakae Shimizu, Takeshi Mukoyama and Yasuyuki Nakayama. *Physics Letters*, **17**, 295 (1965)—An experiment was performed in search for the radiationless annihilation of 300-keV positrons in a lead foil target, using a lithium-drifted silicon junction detector for the ejected bound electrons and a 400-channel pulse-height analyzer. A peak was observed in the electron spectra which is interpreted as the radiationless annihilation of positrons with a K- and/or L-shell electron. The cross section was found to be $(3.0 \pm 0.9) \times 10^{-26} \text{ cm}^2$, as a sum of those for KK, KL, KM, and LL pairs of bound electrons. The ratio of the number of radiationless annihilations to that of the two-quantum annihilation was found to be $1:6.8 \times 10^4$.

Incoherent Scattering of Gamma Rays by K-Shell Electrons. Sakae Shimizu, Yasuyuki Nakayama and Takeshi Mukoyama. *Physical Review*, **140**, A806

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(1965)—The differential cross section for the incoherent scattering of 662-keV gamma rays by the K-shell electrons of tin, tantalum, and lead was determined by experiment. The scattered photons were selected in coincidence with accompanying K x rays from the scatterer foil, using the NaI (Tl) scintillation detectors and the slow-fast coincidence method. The cross section $d\sigma_K/d\Omega$ was compared with that predicted by the Klein-Nishina formula, $d\sigma_F/D\Omega$, at scattering angles 20° , 35° , 50° , 65° , and 100° . The experimental results show that for all cases with these scatterer elements the cross-section ratio $d\sigma_K/d\sigma_F$ is less than unity for small scattering angles and approaches zero as the angle decreases to zero, as predicted by nonrelativistic calculation. For large angles, this ratio is greater than unity and at 100° it is found to be equal to about 1.2 for tin, 1.3 for tantalum, and 1.5 for lead. The experimental approximate dependence of the cross-section ratio on the binding energy of the struck K-shell electrons was also obtained for various gamma-ray scattering angles. On the bases of certain assumptions an attempt was made to calculate theoretical values to be compared with the experimental results for small and large scattering angles. The calculated values indicate the general behavior of the dependence of the ratio on the scattering angle.

Elastic and Inelastic Scatterings of Polarized Protons from Be⁹ and Al²⁷.

Kiyoji Fukunaga. *Journal of the Physical Society of Japan*, **20**, 1 (1965)—The angular dependence of the asymmetry of the polarized protons scattered from Be⁹ and Al²⁷ have been measured. The data of the elastic scattering at the energy of 7 MeV for both nuclei, and 12 MeV for Be⁹ are consistent with other published data.

The asymmetry of 7 MeV protons inelastically scattered from Be⁹ which remained to the excited state of 2.43 MeV has an opposite sign of the elastic scattering, and the maximum asymmetry is about 35% at the angle of 50 degrees in the center of mass system.

Elastic and Inelastic Scattering of 28.5 MeV Alpha-Particles from O¹⁶, Ne²⁰, Mg²⁴ and Si²⁸. Jun Kokame, Kiyoji Fukunaga, Hitoshi Nakamura and Nobuyuki Inoue. *Journal of the Physical Society of Japan*, **20**, 475 (1965)—Elastic and inelastic scattering of 28.5 MeV alpha-particles have been investigated.

Blair's phase rule is fairly well satisfied in forward angles ($<90^\circ$) with a few exceptions. Some anomalous diffractive patterns were obtained for 4⁺ states in O¹⁶, Ne²⁰ and Mg²⁴, which have some common feature with each other. A relatively large yield from a doublet at 6.88 MeV is Si²⁸ seems to contradict the current assignment of spin-parity of the doublet.

The inelastic scattering from unnatural-parity states in these nuclei shows a diffractive pattern and the relation between the phase and the angular momentum transfer is similar to the Blair's phase rule in spite of the reverse parity, except in the case of O¹⁶ where the relation is almost reverse. The reaction mechanism

is considered most probably to be a successive multiple excitation and/or an exchange process.

Estimation of Direct- and Compound- Nuclear Reaction Cross-Sections in $\text{Al}^{27}(p,p')\text{Al}^{27*}$ in the Energy Range of 6.5 to 14 MeV. Jun Kokame and Kiyoji Fukunaga. *Journal of the Nuclear Society of Japan*, **20**, 649 (1965).—An attempt was tried to estimate the cross-sections of direct interactions and the compound nuclear process separately, using the experimental data of $\text{Al}^{27}(p,p')\text{Al}^{27*}$ scattering. Under three assumptions, 1) the similarity of the probability of direct collective excitations by alpha-particles and protons, 2) the $2J+1$ rule for the yield of the compound nuclear process, and 3) a negligible effect of the interference between the both processes: the cross-sections of direct interactions, summed up the lower six proton groups, were estimated to be about 80 mb over the energy range of 8.5 to 14 MeV of incident protons. On the other hand, the compound part decreases exponentially from 140 mb to 30 mb in the same energy range.

Ionization Yield of the $\text{N}^{14}(n,p)\text{C}^{14}$ Reaction in Air. Ryutaro Ishiwari. *Journal of the Physical Society of Japan*, **20**, 658 (1965).—The ionization yield of the $\text{N}^{14}(n,p)\text{C}^{14}$ reaction produced by thermal neutrons in air was measured with a pulse ionization chamber. The uncorrected value of the reaction energy was obtained as 0.600 ± 0.006 MeV. This value was corrected for columnar recombination and for the variation of W , the average energy to produce an ion pair, with particle energies. For the variation of W_ω , the empirical formula obtained in the previous work was used. Assuming that W_p is equal W_ω for the same velocity and that the relative value of W_c with respect to Po alpha particles is 1.10, the corrected reaction energy was calculated as 0.621 ± 0.006 MeV in good agreement with the established Q value. This result indicates that W_p for about 600 keV is actually equal to W_ω for the same velocity in air. Some evidences, which suggest that the relative value of W_c is about 1.10 and W_ω for the same velocity as C^{14} is probably equal to this value, were also discussed.

Quasi-Free Alpha-Alpha Collisions in Be^9 and C^{12} at 28 MeV. Takuji Yanabu, Sukeaki Yamashita, Kiyohiko Takimoto and Kouya Ogino. *Journal of the Physical Society of Japan*, **21**, 1303 (1965).—In the reactions $\text{Be}^9(\alpha,2\alpha)\text{He}^5$ and $\text{C}^{12}(\alpha,2\alpha)\text{Be}^8$ at 28 MeV, the single and summed energy spectra of emitted alpha-particles have been measured at several pairs of angle in order to investigate the quasi-free collision between incident alpha-particles and alpha-clusters in Be^9 and C^{12} . The summed energy spectrum of the alpha-particles from the reaction $\text{Be}^9(\alpha,2\alpha)\text{He}^5$ shows a peak corresponding to the ground state of He^5 at the angles at which the emitted particles come from the collision between incident alpha-particles and nearly zero-momentum alpha-clusters in Be^9 . The momentum spread of

the alpha-cluster in Be^9 coupled with He^{f} (ground state) is estimated to be 0.3 fm^{-1} from the angular correlation of the peak in the summed energy spectrum, and the probability of finding an alpha-cluster in this state is 0.12, if a plane wave impulse approximation is assumed. In the reaction $\text{C}^{12}(\alpha, 2\alpha)\text{Be}^8_{\text{g'nd}}$, the yield has a minimum at the angles expected from the quasi-free collision between incident alpha-particles and nearly zero-momentum alpha-clusters in C^{12} . The state in which an alpha-cluster is bound to Be^8 (ground state) in C^{12} seems to be very different from that for Be^9 .

(α, d) and (α, t) Reactions on Be^9 , F^{19} and Al^{27} at 28.6 MeV. Shigeru Kakigi. *Journal of the Physical Society of Japan*, **20**, 1967 (1965).—Momentum spectra were obtained at several angles for deuteron and triton groups from the (α, d) and the (α, t) reactions on Be^9 , F^{19} and Al^{27} at 28.6 MeV with a broad range magnetic analyzer and nuclear emulsions. The particles were identified by the measurement of the track length of the particles in the emulsions. The (α, d) reactions were found to be similar to the (d, p) reactions in the behaviour of the excitation of the residual nuclear states explained by the Nilsson model. For the single particle states, the higher l -value transition is favoured in the (α, t) reaction in contrast to the (d, p) reaction. In the (α, d) reaction the differential cross sections for the ground states of B^{10} and Si^{28} and for the first excited state of Ne^{20} are preferentially large and show forward rise.

The Excited Core Model of Light Nuclei in (α, α') Scattering. Jun Kokame, Kiyoji Fukunaga and Hitoshi Nakamura. *Physics Letters*, **14**, 234 (1965)—Elastic and inelastic scatterings of alpha-particles at 28.5 MeV from Al^{27} are compared with those from Si^{28} . The summed differential cross section for the five low-lying states of the former is quite resemble with that for the first excited state of the latter. This fact indicates that these five state of Al^{27} are a multiplet produced from the first excited state of the core nuclei Si^{28} by coupling it to one hole in the $1d_{5/2}$ orbit in core.

Fundamental Studies on Heavy Ion Reaction (III). Charge Changing Collisions of C Ions. Study Group of Heavy Ion Reactions in Kyoto University. *Genshikaku Kenkyu*, **10**, 303 (1965), in Japanese.—The equilibrium charge distributions of 9.7 MeV ^{12}C ions in formvar, C, Al_2O_3 , Ag and Au are measured. After traversing the foil the ions are separated according to charge by a 12000G magnetic field and recorded on a nuclear emulsion. Mean charges in these foils show a systematic dependence on the atomic number of foil materials: formvar 4.6; C 4.7; Al_2O_3 4.8; Al 4.8; Ag 4.7; Au 4.5.

Inorganic Chemistry

On the Precipitation Behavior of Strontium in Brine. Tsunenobu Shigematsu, Masayuki Tabushi, Toshiharu Murakami and Katsuya Uesugi. *Nippon Engaku Kaishi*, **18**, 227 (1965), in Japanese.—This paper describes the behavior of strontium in brine shown when the strontium is precipitated as carbonate, oxalate, and phosphate. In this study, sodium carbonate, sodium oxalate, sodium phosphate or sodium hydroxide was used as precipitant. The behavior of strontium was traced by using radioactive isotope ^{89}Sr , while calcium and magnesium were determined by EDTA titration.

When sodium carbonate and sodium oxalate were used as a precipitation agent, the behavior of strontium and calcium were almost the same. When sodium oxalate was used, the precipitation ratio of strontium was the most remarkable. In the case of adding sodium oxalate of 0.6 times as much to the equivalent quantity of calcium and strontium in brine, approximately 60% of them were deposited, but the precipitation ratio of magnesium was extremely small. When using sodium phosphate, on the other hand, the precipitation ratio of strontium was higher than those of calcium and magnesium. When sodium hydroxide was added to brine, a portion of strontium was considered to coprecipitate with magnesium hydroxide. After the deposition of magnesium in brine reached more than 90%, the deposition of calcium became rapid, and the precipitation ratio of strontium was about 56%.

Behavior of Phosphate Ion in Concentrating Process of Sea Water. Tsunenobu Shigematsu, Katsuya Uesugi and Masayuki Tabushi. *Nippon Engaku Kaishi*, **18**, 269 (1965), in Japanese.—A study was conducted on the behavior of phosphate in the concentrating process of sea water. The behavior of phosphate was traced by using radioactive isotope, ^{32}P . Phosphate in sea water was spectrophotometrically determined by phosphomolybdate method after it was separated from other elements by coprecipitation with ferric hydroxide.

When the evaporating temperature was kept below 80°C, the loss of phosphate from the sample solution was negligible in the early stage of concentration. On the other hand, the phosphate transferred rapidly into the deposit, when more than 70% (in volume) of sea water evaporated.

In the case of evaporation at temperatures more than 90°C, phosphate started to deposit in the early stage, but the precipitation rate was not so high as in the case mentioned above.

The depositing tendency of phosphate was more remarkable than that of strontium or calcium.

The Effect of Particle Size of $\gamma\text{-Fe}_2\text{O}_3$ on the Transformation from γ -Form to α -Form. Yoshichika Bando, Masao Kiyama, Toshio Takada

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and Sukeji Kachi. *Japanese Journal of Applied Physics*, **4**, 240 (1960).—Particles prepared by thermal decomposition of metallic salt consist of the smallest unit particles linked to form an aggregate similar in shape to the original crystal of the salt. Crystals of γ -FeOOH are thin and platelike with dimensions of 2 to $5\mu \times 0.2$ to $0.5\mu \times 0.01$ to 0.02μ . Particles of γ -Fe₂O₃ obtained by oxidation of Fe₃O₄, which directly precipitated in aqueous solution of iron salt, do not form an aggregate, but are separated. The transformation temperature was determined by D. T. A.. The transformation temperature decreases with decreasing unit particle size, and the temperature of aggregate is lower than that of separate particles, despite the same unit particle size. 3 figs. 5 refs.

The Magnetic Properties of α -Fe₂O₃ Fine Particles. Yoshichika Bando, Naoichi Yamamoto, Masao Kiyama, Toshio Takada, Teruya Shinjo and Hideo Takaki. *Journal of the Physical Society of Japan*, **20**, 2086 (1965).—The spin flipping transition and the weak ferromagnetization of fine particles of α -Fe₂O₃ were experimentally investigated, with relation to particle size. Fine particles, having mean sizes ranging from 1μ to 200\AA , were prepared by precipitation from aqueous solution of ferric salts. The transition temperature which is about -15°C for the bulk specimen decreases with decreasing particle size. The weak ferromagnetization σ_0 of particles has a value lower than that of the bulk specimen, when particles were precipitated in aqueous solution kept in the temperature below 100°C .

Weak Association between Alkali Metal Ions and Mononegative Ions of Aromatic Hydrocarbons. Hiroaki Nishiguchi, Yasuto Nakai, Kazuo Nakamura, Kazuhiko Ishizu, Yasuo Deguchi and Hideo Takaki. *Molecular Physics*, **9**, 153 (1965).—Extra hyperfine splittings due to alkali metal cations have been observed in the electron spin resonance (E.S.R.) spectra of biphenyl, naphthalene, anthracene and pyrene mononegative ions. It is interpreted as being due to ion-pair association between the aromatic anions and the metal cations. The unpaired spin densities at the metal nuclei are estimated using the data from the atomic beam experiments. In the case of biphenyl-alkali metal systems the appropriateness of the model described in a previous paper has been checked by studying the temperature dependence of the cation hyperfine splittings and the E.S.R. spectra of some methyl substituted biphenylanions. The structure of the ion-pairs are discussed using Mulliken's theory of charge-transfer complexes.

Physical Chemistry

The Coalescence of Mercury Droplets in Aqueous Solutions in the Presence of Surface Active Materials. Akira Watanabe, Mutsuo Matsumoto and Rempei Gotoh. *Kolloid-Zeitschrift, Zeitschrift für Polymere*, **201**, 147 (1965).—The

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range of the electrical potential of coalescence of mercury droplets in solutions of surface active materials was measured by using the twin dropping mercury electrodes, developed by the present authors. It was thus hoped that the role of surface active materials in stabilizing emulsions in general was clarified by the present study. Experiments were carried out by using sodium dodecylsulphate, cetylpyridinium chloride, a polyvinyl alcohol and EPANs, a group of nonionic surface active copolymers of ethylene oxide and propylene oxide at various mole ratios, as the surface active materials. All these substances showed perfect protection; mercury droplets did not coalesce at any potential of mercury surfaces, when the concentration of these substances exceeded certain values characteristic of these materials. Moreover, in the case of EPANs, the logarithm of this concentration was found to be a linear decreasing function of the HLB value of the molecule; the stabilizing power increased with increasing hydrophilic character of the molecule. The adsorption behaviour of various EPANs on to the mercury surface was also studied by measuring differential double layer capacities. It was found that the stabilization was intimately related to the formation of films of the surface active materials at the mercury-solution interfaces.

Polarized Infrared Spectra of Succinimide. Soichi Hayashi. *Nippon Kagaku Zasshi*, **86**, 27 (1965), in Japanese.—Polarized infrared spectra of succinimide were observed with the electric vector along each of the three crystal axes. A new method was proposed for the determination of the direction of the transition moment associated with a given molecular vibration, which can generally be used for orthorhombic crystals consisting of molecules with a C_s , C_{2h} or C_2 symmetry. The directions of the transition moments of succinimide were determined by this method and compared with the assignment given by Uno and Machida. A good agreement was obtained except for a few points, that is, one of the bands which should be assigned to the CH_2 rocking vibration was assigned to the skeletal vibration by these authors and vice versa. It was also found that the influence of the molecular interaction on infrared active vibrations was negligible in the case of succinimide.

Polarized Infrared Spectra of Acetanilide. Soichi Hayashi. *Nippon Kagaku Zasshi*, **86**, 790 (1965), in Japanese.—Infrared spectra of acetanilide were observed with the electric vector along each of the three crystal axes in turn. The method, proposed previously for molecules with a C_s , C_{2h} or C_2 symmetry, was extended to include molecules with two C_s symmetry groups, and applied to acetanilide for the determination of the directions of the transition moments. By this method, absorption bands could be classified into those associated with the vibration of benzene ring and those with the vibration of amide group, each group of vibrations was subdivided into inplane and out-of-plane vibrations. Absorption bands were assigned in accordance with directions of the transition moments,

Transformation and Growth of Copper-Phthalocyanine Crystal in Organic Suspensions. Eiji Suito and Natsu Uyeda. *Nippon Kagaku Zasshi*, **86**, 969 (1965). in Japanese.—The growth processes of Cu-phthalocyanine ($C_{32}H_{16}N_8Cu$) accompanied by the crystal transformation into the stable form were studied with various organic suspension. The rate of formation of the stable modification turned out to follow the kinetic equation of the first order except for its earlier stages. As the results of X-ray diffractometry, the activation energy for the formation of the stable crystals in toluene suspension was evaluated to be about 14.0 Kcal/mol. The electron microscopy as well as the analysis of line profiles of the X-ray diffraction revealed that the preliminary growth of the metastable form took place at the earlier stages in advance of the actual transformation into the stable form.

Being treated in benzene, the vacuum-deposited micro-crystals gave rise to slender thin crystals of the metastable form which were as large as those of the stable form obtained by the ordinary treatment of the metastable powder in organic suspension. By the analysis of selected area electron diffraction patterns obtained from raft structures of these slender crystals, the molecular arrangement in the crystal as well as the crystal habit was revealed to be very similar to each other with regard to both crystal forms. The mechanism of the nucleation of the stable form was discussed on the basis of the similarity of the outward appearance as well as the lattice structure of two crystal forms.

Orientation Overgrowth of Condensed Polycyclic Aromatic Compounds Vacuum-Evaporated onto Cleaved Face of Mica. Natsu Uyeda, Michio Ashida and Eiji Suito. *Journal of Applied Physics*, **36**, 1453 (1965).—When Pt-, Cu-, and Zn-phthalocyanines are vacuum-evaporated onto cleavage faces of muscovite, single-directional orientation occurs at lower substrate temperature. At higher temperature ranges, Zn-phthalocyanine has a double-directional orientation while Pt- and Cu-phthalocyanines show triple-directional ones. High-resolution electron diffraction patterns, which were well-defined fiber diagrams, revealed that all three compounds showed conspicuous isomorphism with one another, and Zn- and Cu-phthalocyanines occurred in the metastable forms of their dimorphs. General crystal structures of metastable forms are discussed on the basis of the found isomorphism with Pt-derivative.

Evaporated films were composed of lamellar crystal strips, and the fiber diagrams showed that at least two kinds of lattice orientations were assumed by all three compounds, while the longitudinal crystal axis of individual strips always ran parallel to their b axes.

As to relative orientation of the evaporated films to the substrate, the b axis of the former was parallel to either of the two directions which made $\pm 60^\circ$ with the a axis of muscovite in the case of the single-directional orientation. When the

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evaporated films had double- or triple-directional orientations, the electron diffraction pattern showed twofold symmetries in spite of the apparent triangular configuration. It turned out that this axis of twofold symmetry also coincides with the same axis of muscovite as above. It is presumed that the unique orientation axis of the evaporated films coincides with the staggering direction of the two oxygen tetrahedron sheets in the top subcell of muscovite. Plausible origin of these orientations are also discussed in terms of lattice vibration near the surface.

Lattice imperfections of the evaporated films were directly observed in the lattice image obtained by the high-resolution electron microscopy. The dislocation density seems rather high when compared with other similar lamellar crystal strips of the same compounds formed by colloid chemical methods. This was ascribed to the crystal formation controlled by the epitaxial effect.

Infrared Studies of the Rubber-Filler System. I. Infrared Absorption Spectra of Inorganic Fillers. Eiji Suito and Masafumi Arakawa. *Rubber Chemistry and Technology*, **38**, 219 (1965).—Infrared spectra of 33 kinds of commercial reinforcing fillers were measured by use of the KBr pellet method in connection with studies of the filler effect in rubberfiller systems. Characteristic absorptions of individual fillers are discussed in relation to their method of preparation.

Infrared Studies of the Rubber-Filler System. II. Identification of Rubbers Compounded with Fillers by Infrared Absorption Spectra. Eiji Suito and Masafumi Arakawa. *Rubber Chemistry and Technology*, **38**, 227 (1965).—Infrared spectra of vulcanized rubbers compounded with fillers were studied on thin sections of samples made by a low temperature microtome technique. By this method, identification of fillers as well as rubbers is possible. The infrared absorption spectra of rubbers compounded with several types of fillers are described.

Effect of Particle Characteristics on the Static Properties of Powder. Masafumi Arakawa, Takao Okada and Eiji Suito. *Journal of the Society of Materials Science Japan*, **14**, 764 (1965). in Japanese—As an approach to reviewing the packing properties of fine powders, the relationships between particle characteristics such as particle size, shape, surface roughness and adsorbed matter, and static properties of powders have been studied.

In this experiment, the white alundum, zinc powder, calcium carbonate and mica powder were used as samples. The angle of repose, porosity and packing property were measured as static property of powders.

The results obtained are summarized as follows:

As particle size decreases, the angle of repose and porosity increases. But the value becomes constant under the critical size of the particles at hard coagulated powder. And it has little relation with the particles shape, surface roughness and

surface adsorbed layer at the fine powders.

The packing property has been studied by the tapping compressed method. The relationship between the apparent density of powder bed and the tapping frequency can be correlated to Kuno's equation.

The packing coefficient k_1 at the first stage of packing corresponds to the constant b of Kawakita's equation, that is related to the coagulation force of powder. The k_1 decreases with the particle size, and take minimum value at about 3μ , and then it increases again. These results suggest that the unit particles will build up the coagulated secondary particle, and the static properties of fine powders are influenced by the characteristics of the coagulated particles.

Electron Microscopy on the Crystallization Process of Titanium Dioxide Films. Eiji Suito and Makoto Shiojiri. *Proceedings of the Japan Academy*, **41**, 455 (1965).—Titanium dioxide films were amorphous when vacuum-deposited on rocksalt at room temperature. Crystallization took place with electron irradiation of the current density of the order of $10\text{-}10^2$ mA/cm², and rutile and anatase crystals were formed. The rutile crystallites were composed of fine granules and did not grow into large grains. The anatase crystals grew in large grains whose size was more than 10μ in length. The composition of the anatase and rutile crystals showed conspicuous difference from specimen to specimen, which seemed to be ascribed to the difference which was *a priori* implied in the original films. A process was also observed in which small angle grain boundaries were formed in the anatase crystals when they were grown from amorphous state.

Studies of the Crystallization of Lithium Silicate Glasses. Jiro Matsuda and Eiji Suito. *Kogyo Kagaku Zasshi*, **67**, 884 (1964), in Japanese.—In case of devitrification of lithium silicate glass, the crystals are not always produced as can be expected from the phase relations in the system of $\text{Li}_2\text{O-SiO}_2$ quite different crystal may often be formed under a little different condition for devitrification.

When $\text{Li}_2\text{O-2SiO}_2$ glass devitrifies, $\text{Li}_2\text{Si}_2\text{O}_5$ (lithium disilicate) is always formed as shown in the phase diagram of the binary system.

But when a little amount of K_2O (3 mole %), and Au (0.005 mole %) are added to glass, another crystal Li_2SiO_3 (lithium metasilicate) is formed.

To explain the cause for formation of such different crystals, a study was made on the devitrification of lithium silicate glass, the results being as follows:

1) In devitrification of $\text{Li}_2\text{O-SiO}_2\text{-K}_2\text{O}$ glass (32 mole % Li_2O , 65 mole % SiO_2 , 3 mole % K_2O), $\text{Li}_2\text{Si}_2\text{O}_5$ is formed from the plate-shaped glass, and Li_2SiO_3 from the powder glass.

2) When $\text{Li}_2\text{O-2SiO}_2$ glass devitrifies, if only it contains a small amount of K_2O , Li_2SiO_3 crystal is always formed on the surface and $\text{Li}_2\text{Si}_2\text{O}_5$ from the inside,

3) Rate of crystallization of lithium silicate glass is decreased by adding potassium ion to the glass.

4) Activation energy for the growth of $\text{Li}_2\text{Si}_2\text{O}_5$ in the powder glass ($\text{Li}_2\text{O} \cdot 2\text{SiO}_2$) is about 49 kcal.

Formation of Fine Particles. Eiji Suito. *Shikizai*, **38**, 126 (1965), in Japanese.—This paper describes the formation of fine particles associated with manufacturing industry of pigments. The crystal nucleation, crystal growth, phase transformation and aggregation of crystallites are interpreted in relation to their influence on the size, shape and surface state of particles.

Structure of Evaporated Films and Catalytic Actions. Eiji Suito. *Shokubai (Catalyst)*, **7**, 167 (1965). in Japanese.—Recent studies are reviewed on the structure of vacuum-evaporated films and catalytic actions. Image formations of electron microscope due to diffraction contrasts, crystal lattice images and moiré fringes are described with respect to crystal defects. The nucleation, coalescence, epitaxy and decoration of steps on the substrate crystal are shown concerning the growth of evaporated metal films. Several experiments of gas absorption and catalytic actions on evaporated metal films are illustrated.

Simultaneous Measurement of Stress and Infrared Dichroism on Polymers I. Stress Relaxation on Vulcanized Natural Rubber. Rempai Gotoh, Tohru Takanaka and Naomi Hayama. *Kolloid-Zeitschrift, Zeitschrift für Polymere*, **205**, 18 (1965).—A method for simultaneous measurements of stress and infrared dichroism as time-dependent behavior of polymer films was devised by using a double beam infrared spectrometer. The film sample held between clamps of a stretching device was placed just in front of the entrance slit of the spectrometer where the sample and reference beams came alternately. Two polarizers were used, one in the sample beam and the other in the reference beam. Thus the sample and reference beams were polarized to have the electric vectors parallel and perpendicular to the stretching direction of the sample, respectively. With this arrangement the spectrometer responded only to the difference in the transmittance of the two beams. Setting the spectrometer at one of the wavenumbers of the absorption band maxima, we could record continuously the change in its dichroism during mechanical treatments which gave rise to the molecular orientation in the sample. The stress was recorded automatically by means of a couple of strain gages pasted on the cantilever beam of the stretching device.

By theoretical considerations, a simple relationship was found to exist between the quantity recorded on the spectrometer by this method and the orientation function of transition moment of a vibrational absorption band with respect to the stretching direction.

The method was applied to the stress relaxation experiments of vulcanized natural rubber carried out at different elongations less than 600% and at the room temperature. Changes of infrared dichroism were measured for five absorption bands at 1664, 1380, 1361, 1129, and 844 cm^{-1} , of which the last one is a crystalline band. From the results of this study, it was concluded that the stress relaxation observed was ascribed mainly to the amorphous orientation rather than to the crystalline orientation, which was completed almost immediately after elongation.

Simultaneous Measurements of Stress Relaxation and Infrared Dichroic Change of Vulcanized Natural Rubber. Rempei Gotoh, Tohru Takenaka and Naomi Hayama. *Nippon Kagaku Zasshi*, **86**, 1137 (1965), in Japanese.

—An instrument for simultaneous measurements of stress and infrared dichroism of polymer films was constructed by using a double beam infrared spectrometer, and was applied to the study of the stress relaxation of vulcanized natural rubber.

The film sample held between clamps of a stretching device was placed just in front of the entrance slit of the spectrometer where the sample and reference beams came alternately. Two polarizers were used, one in the sample beam and the other in the reference beam, so that the sample and reference beams were polarized to have the electric vectors parallel and perpendicular to the stretching direction of the sample, respectively. Then, by setting the spectrometer at one of wavenumbers of the absorption band maxima, one could record continuously the change in its dichroism during the stress relaxation. From these records, the orientation functions of transition moments with respect to the stretching direction were calculated. The results of this study suggested that the stress relaxation observed was ascribed mainly to the orientation in the amorphous part rather than to the orientation in the crystalline part, which was completed almost immediately after elongation.

Die ungestörte Knäuelldimension von Polyacrylnitril unter Berücksichtigung des Einflusses der Polymerisationstemperatur. Hiroshi Inagaki, Katsuhiko Hayashi and Togoro Matsuo. *Makromolekulare Chemie*, **84**, 80 (1965).—

In order to study the influences of polymerization temperature upon the molecular conformation of polyacrylonitrile, two types of samples are prepared at two different temperatures using a redox system. By employing the Archibald ultracentrifugal procedure the molecular weight determination is made for seven fractions from a sample polymerized at -30°C . (“T”-series) and for six ones from that obtained at $+60^{\circ}\text{C}$. (“S”-series).

Between the intrinsic viscosity in dimethyl formamide (DMF) and the molecular weight the following relations are found:

$$[\eta]_{30^{\circ}}(\text{dl./g.}) = 2.09 \cdot 10^{-4} M^{0.75} \quad (\text{“S”-series})$$

$$[\eta]_{30^{\circ}}(\text{dl./g.}) = 2.96 \cdot 10^{-4} M^{0.74} \quad (\text{“T”-series})$$

The viscosity equation for the "S" -series is in good agreement with that of Cleland and Stockmayer.

These results are analysed with aid of the recent viscosity theory of Stockmayer and Fixman to evaluate the unperturbed dimension of these two homologous series. The $[\eta]$ - M -relation for the "S" -series in the Stockmayer-Fixman form is:

$$[\eta]_{30^\circ}(\text{dl./g.}) = 2.0 \cdot 10^{-3} M^{1/2} + 0.65 \cdot 10^{-5} M$$

The unperturbed dimension of the "S" -series is found to be smaller than that of the "T" -series. The steric factor σ , defined as the ratio of unperturbed dimension to that corresponding to the free rotation, is about 2.10 and 2.30 for the "S" -and "T" -series, respectively. This leads to the conclusion that the syndiotactic part in the chain of polyacrylonitrile will be increased by a lowering of the temperature of polymerization.

Preparation of Block Copolymers of A-B-A Type and its Behavior in Dilute Solution. Hiroshi Inagaki and Takeaki Miyamoto, *Makromolekulare Chemie*, **87**, 166 (1965).—Two block copolymer samples of styrene and methyl methacrylate were prepared by employing the procedure described by Bamford and Jenkins. The preparation, isolation, and characterization of these A-B-A type block copolymers are reported in detail. This paper further deals with the intrinsic viscosity data obtained in diethyl malonate and *n*-butyl chloride. The molecular conformation in these solvents is most likely to be of a random coil type differing from what the polymer chain would assume in toluene.

Intra-chain Interaction and Molecular Shape of Block Copolymer in Dilute Solution. Hiroshi Inagaki, *Makromolekulare Chemie*, **86**, 289 (1965).—Relationships between intrinsic viscosity $[\eta]$ and molecular weight M obtained for block copolymers of sandwich type of styrene and methyl methacrylate in toluene are collected from various publications and analyzed using the Stockmayer-Fixman equation:

$$[\eta]/M^{1/2} = K + B'M^{1/2}$$

According to this analysis, it is pointed out that intra-chain interactions between segments in sandwich block copolymers should be fairly larger than those for each of parent homopolymers. On the other hand, their unperturbed dimensions should be smaller than those for each of parent homopolymers. These features characteristic of sandwich block copolymers are subject to account in terms of the incompatible nature of these parent homopolymers.

Normal Stresses and Dynamic Moduli in Polymer Solutions. Kunihiro Osaki, Mikio Tamura, Tadao Kotaka and Michio Kurata. *Journal of Physical Chemis-*

try, **69**, 3642 (1965).—A method for separate determination of two normal stress differences, $\sigma_{11}-\sigma_{33}$ and $\sigma_{22}-\sigma_{33}$, in polymer solutions is presented on the basis of the Coleman and Noll theory of second order viscoelastic fluids. Here σ_{11} , σ_{22} and σ_{33} represent the normal stresses in the directions, 1, 2 and 3, of which 1 is parallel to the flow line, 2 is perpendicular to the plane of shear and 3 is perpendicular to the above both. The basic equations are:

$$-\frac{\partial p}{\partial \ln r} = \sigma_{11} - \sigma_{33} + \frac{\partial(\sigma_{22} - \sigma_{33})}{\partial \ln \kappa}$$

$$\left(\frac{1}{\kappa^2}\right)\left(-\frac{\partial p}{\partial \ln r}\right) - \frac{2G'}{\omega^2} = 3(\sigma_{22} - \sigma_{33})/\kappa^2,$$

where p is the pressure exerted normal to the fixed plate of a parallel plate rotational rheometer at a distance r from the axis of rotation, κ is the rate of shear and G' is the real part of the dynamic complex modulus as a function of the angular frequency. Application of the method is made to four systems, (i) polystyrene in toluene, (ii) poly(cis-butadiene) in xylene, (iii) cellulose trinitrate in butyl acetate, and (iv) poly(methyl methacrylate) (PMMA) in diethyl phthalate (DEP). In the first three systems, good agreement was found between two values, $(-\partial p/\partial \ln r)/\kappa^2$ and $(2G'/\omega^2)$. In the system of PMMA-DEP, a considerable discrepancy was found between two quantities $(-\partial p/\partial \ln r)/\kappa^2$ and $2G'/\omega^2$ in the observed range of κ and ω . But it was observed that this discrepancy had a tendency to vanish at the limit of very small κ and ω . Thus, it was concluded that in polymer solutions, $\sigma_{22}-\sigma_{33}$ component of the normal stress is, if not zero, no larger than 10% of $\sigma_{11}-\sigma_{33}$ component.

Physicochemical Studies on Isotactic Polystyrene. Hiroyasu Utiyama. *Journal of Physical Chemistry*, **69**, 4138 (1965).—An isotactic polystyrene sample prepared by using a Ziegler type catalyst has been fractionated by a stepwise separation of crystalline solid precipitate from a system, isotactic polystyrene-monochlorobenzene-cyclohexanol at 8°. Measurement of crystallinity of the films of the fractionated samples by an infrared spectroscopic method has shown that the fractions differ in their speed and degree of crystallization. Light scattering and viscosity measurements have been carried out at 25.3° on the fractionated samples using monochlorobenzene as solvent and 2, 4, 6-trimethyl phenol as antioxidant. One of the fractions (F-4), the films of which readily crystallize at relatively low temperature, has shown a negative initial slope and a minimum in the plot of the conventional reciprocal scattered intensity function versus $\sin^2(\theta/2)$. From theoretical consideration, it has been concluded that this anomaly is due to large optical anisotropy (an optical anisotropy as forty times as large as that of atactic polystyrene). This conclusion has been confirmed by a more direct measurement, of vertical and horizontal components of scattered light using vertically or horizontally polarized light. It has also been found that optical anisotropy of highly crystallizable sample

of isotactic polystyrene fraction decreases with the increase in temperature, while that of the conventional atactic polystyrene is very small and slightly increases with temperature. The second virial coefficient corrected for the effect of optical anisotropy of the sample F-4 is exceptionally small. From the analysis of the experimental results of dependence of limiting viscosity number on molecular weight combined with the results of $A_2M_w/[\eta]$, it has been concluded that as the degree of isotactic stereoregularity increases, the short-range parameter A increases and the long-range interaction parameter B decreases. A consideration on the estimated value of optical anisotropy of styrene monomer as function of the mode of rotation of benzene ring has led to the conclusion that the optical anisotropy is a good measure of the degree of the isotactic stereoregularity of polystyrene. The optical anisotropy increases as the degree of isotactic stereoregularity increases. This increase is due to the hindered rotation around the C-C bond connecting the benzene ring to the main chain. The hindrance is due to the larger interaction between neighboring benzene rings, which simultaneously decreases the flexibility of the chain.

Complex Modulus of Concentrated Polymer Solutions in Steady Shear.

Kunihiro Osaki, Mikio Tamura, Michio Kurata and Tadao Kotaka. *Journal of Physical Chemistry*, **69**, 4183 (1965).—Complex moduli of concentrated polymer solutions in steady shear were measured with a rheometer of the coaxial cylinder geometry. The outer cylinder was given a synthetic motion of pure rotation and sinusoidal oscillation, and the inner cylinder was suspended concentrically in the outer cylinder by a torsion wire. The oscillatory part of the inner cylinder motion was detected separately from the stationary part of the motion to determine the complex modulus $G_{\kappa}^*(\omega)$ as a function of angular frequency ω for various fixed values of the rate of the superimposed shear κ . Measurements of the complex modulus with superimposed steady shear, $G_{\kappa}^*(\omega)$, were performed at 30° on four polymer-solvent systems, i.e., 15% solutions of polystyrenes with molecular weight $M=1.95 \times 10^6$ and 2.51×10^6 in toluene; a 10% solution of poly(methyl methacrylate) with $M=1.60 \times 10^6$ in diethyl phthalate, and a 5% solution of poly(*n*-butyl methacrylate) with an extremely high molecular weight, 1.2×10^7 , in diethyl phthalate. From these measurements, the following results were found. (1) In the low-frequency range, both the real and imaginary parts of the complex modulus in steady shear, $G_{\kappa}'(\omega)$ and $G_{\kappa}''(\omega)$, decreased with increasing rate of shear κ . The effect was more remarkable in the real part than in the imaginary part, and at very low frequencies, $\log [G_{\kappa=0}'(\omega)/G_{\kappa}'(\omega)]$ was appreciably larger than $\log [G_{\kappa=0}''(\omega)/G_{\kappa}''(\omega)]^2$. (2) In the range of high frequency which corresponds to the rubbery plateau region of the relaxation spectrum, $G_{\kappa}'(\omega)$ still decreased with increasing rate of shear, whereas $G_{\kappa}''(\omega)$ increased. (3) The effect of superimposed shear on G_{κ}^* was practically negligible for Newtonian fluids. The molecular weight depen-

dence of the steady-shear viscosity was also studied on a series of polystyrene-toluene systems under various fixed values of κ . Based on the results obtained, a discussion is given of the entanglement couplings in concentrated polymer systems.

Unperturbed Dimensions of Poly(tetrahydrofuran). Michio Kurata, Hiroyasu Utiyama and Kensuke Kamada. *Markromolekulare Chemie*, **88**, 281 (1965).—Viscosity and light scattering measurements of poly(tetrahydrofuran) were carried out in various solvents, involving a mixed theta solvent. The intrinsic viscosity *vs.* molecular weight relationships obtained in the range of molecular weight from $3.5 \cdot 10^4$ to $1.1 \cdot 10^6$ were: $[\eta] = 1.31 \cdot 10^{-3} M_w^{0.60}$ in benzene (30°C.), $1.76 \cdot 10^{-3} M_w^{0.54}$ in cyclohexane (30°C.), $4.22 \cdot 10^{-4} M_w^{0.65}$ in ethyl acetate (30°C.), and $3.43 \cdot 10^{-3} M_w^{0.45}$ in a mixed theta solvent of ethyl acetate (22.7 wt.-%) and n-hexane (77.3 wt.-%) (31.8°C.), respectively. The recent α^2 -treatment of the viscosity data leads to the following values of the conformational parameter which was defined as the ratio of the end-to-end distance of the polymer in the unperturbed state to that in the freely rotating state: $\sigma = 1.85$ in benzene, 1.70 in cyclohexane, 1.58 in ethyl acetate, and 1.64 in the theta mixture. Effect of benzene, on the chain conformation was notable. This polymer was prepared by bulk polymerization at 0°C. with an aluminum triethyl and water catalyst and the ratio of the weight average to the number average molecular weight was about 1.04 as was determined by the sedimentation velocity analysis.

Chemical Treatment of Cotton by the Graft Copolymerization of Reactive Monomer and Cross-linking. Waichiro Tsuji and Tetsuo Ikeda. *Report of the Institute for Chemical Fiber, Kyoto Univ.*, **22**, 11 (1965), in Japanese.—The reactive monomers such as acrylamide and glycidyl methacrylate were graftcopolymerized onto cotton by high energy irradiation. A long chain crosslinking could be introduced to the cotton using the reactivities of the grafted contents.

The crease-recovery and some tensile properties of the grafted and crosslinked cottons were examined. Considerable improvements were obtained in some treated cottons without much lowering of the tensile properties.

Studies on the Nonwoven Fabric. (I). On the Laboratory Equipment for Making the Dry Process Nonwoven Fabric. Waichiro Tsuji, Masazo Imai, Koichi Sugita, Yoichi Kanayama and Toshio Hirata. *Journal of the Adhesion Society of Japan*, **1**, 34 (1965)-in Japanese.—At the beginning of the study on the nonwoven fabric the laboratory equipment for making the dry process nonwoven fabric was made. It is made up of three parts, i.e. rando-webber, saturator and heating unit. The webber is the air-lay random web machine with a built-in 14 in carding unit. In the saturator the web is sandwiched between tow stainless steel endless screens which convey it through the saturation bath. For the removing

of the excess binder liquor, either squeeze rolls of vacuum extraction system can be used. The heating unit is the infrared radiant heating system and the temperature is changed by the changing of the distance between the web and infrared tubes.

It was found that the nonwoven fabric with almost satisfactory uniformity could be made by this equipment using acrylic emulsion binder. Further, Tetoron or rayon nonwoven fabrics were made under various velocities through saturator or pressures of vacuum extraction, and their binder contents, tensile strengths and elongations were examined. It was found that the control of the binder content should be done by the change of pressure of the vacuum extraction.

Thus it was shown that this equipment could be satisfactorily used to make nonwoven fabric probe in our further work, and the data were obtained which would be required to determine the operating condition.

Dynamic Mechanical Properties of Drawn Polypropylene Films.

Hyeong-Dong Chu, Ryoza Kitamaru and Waichiro Tsuji. *Kobunshi Kagaku (Chemistry of High Polymers)*, **22**, 488 (1965), in Japanese.—The viscoelastic properties of drawn semicrystalline polypropylene films have been studied as a function of draw temperature, draw ratio and annealing time. The temperature dependency of dynamic modulus and loss tangent of the films drawn to several times under different conditions has been investigated in a wide range of temperature.

As results it was found that the maximum $\tan \delta$ value in the α_a -absorption region decreased in accordance with 1) the increase of draw ratio; 2) the decrease of draw temperature; and 3) the decrease of annealing time of the drawn film.

The peak temperature T_w , in $\tan \delta$ -temperature curve shifted to a higher temperature also in accordance with the above-mentioned three conditions.

The experimental results suggest that if polypropylene film is either annealed for a short time after a drawing at a lower temperature or drawn to a high ratio over 10 times even at a higher temperature, some amounts of internal stress are stored in the molecular segments of the amorphous region so that the micro-brownian motion of the segments is restricted.

Temperature Variation of Unperturbed Chain Dimension of Stereoregular Polyvinyl Alcohols from Thermoelasticity Measurements in Diluents.

Ichiro Sakurada, Akio Nakajima and Kyoichiro Shibatani. *Makromolekulare Chemie*, **87**, 103 (1965).—The thermoelastic measurements were carried out on isotactic, syndiotactic, and atactic polyvinyl alcohol samples in ethylene glycol-water mixtures as a function of temperature from 20 to 90°C. The energy and entropy components of the retractive force, and the temperature variation of the unperturbed mean-square end-to-end distance $\langle R_0^2 \rangle$ were determined by thermodynamic analysis of the stress-temperature experimental results. It was found that $\partial \ln \langle R_0^2 \rangle / \partial T$ is negative for all samples and their absolute values are

in the order of *iso* > *ata* > *syn*. These results were discussed by considering the effects of stereospecific configurations on the chain conformation associated with bond rotations.

The Cationic Polymerization by p-Methoxystyrene under Electric Potential. Ichiro Sakurada, Norio Ise and Takao Ashida. *Makromolekulare Chemie*, **82**, 284 (1965).—The cationic polymerizations of p-methoxystyrene with iodine in ethylene dichloride were carried out under strong electric field. It was found that the polymer conversion was larger in the presence of the electric field than in its absence. The field effect was suggested to be due to the field-facilitated dissociation of ion-pairs at growing chain ends on the assumption that the rate constant of propagation of free ions was larger than that of ion-pairs.

Ring-Opening Copolymerization of Tetrahydrofurfuryl Acrylate and Methacrylate. Kaishi Noma, Yoshio Ohfuji and Ichiro Sakurada. *Kobunshi Kagaku (Chemistry of High Polymers)*, **22**, 69 (1965), in Japanese.—Ring-opening copolymerizations of tetrahydrofurfuryl acrylate (TA) and tetrahydrofurfuryl methacrylate (TMA) with epichlorohydrin (ECH) catalyzed by borontrifluoride-etherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) were carried out. Copolymers, almost perfectly soluble in acetone, were obtained in the copolymerizations of all systems. The apparent monomer reactivity ratios were $\gamma_{TA} = 0.56 \pm 0.05$ and $\gamma_{ECH} = 0.12 \pm 0.01$ for the copolymerization of TA and ECH at 0°C , and $\gamma_{TMA} = 0.72 \pm 0.15$, $\gamma_{ECH} = 0.14 \pm 0.01$ for the copolymerization of TMA and ECH at 0°C . For all of the copolymers obtained, the observed values of the double bond content were much smaller than the calculated ones. The latter were calculated from the polymer compositions by assuming that each of the TA or TMA monomer unit in the copolymers had one double bond. It seems that the cyclic polymerization mechanisms, in which not only the tetrahydrofuran rings, but also the C=C double bonds of TA or TMA take part, are comparatively important in the copolymerizations. Copolymerization of TA and tetrahydrofuran was also examined.

Radical Polymerization of β -Allyloxyethyl Acrylate. Kaishi Noma, Ryutoku Yosomiya and Ichiro Sakurada. *Kobunshi Kagaku (Chemistry of High Polymers)*, **22**, 166 (1965), in Japanese.—Radical polymerization of β -allyloxyethyl acrylate was carried out in benzene at 50°C or 60°C . The relationships between initial concentrations of the monomer and limiting viscosity numbers $[\eta]$ of the initial polymers, conversions and $[\eta]$ of the polymers, initial concentrations of the monomer and gel-points, initial rates of polymerization and initial concentrations of the monomer or the initiator, and initial concentrations of the monomer and compositions of the polymers were interpreted by assuming the mechanism of cyclopolymerization.

The Structure of Polyvinyl Alcohol Derived from Polydivinyl-*n*-butyral.

Ichiro Sakurada, Yasuyoshi Sakaguchi, Jun Nishino, Kozo Fujita and Koichi Inoue. *Kogyo Kagaku Zasshi*, **68**, 847 (1965). in Japanese.—Divinyl-*n*-butyral was synthesized and polymerized in bulk at 50°C in the presence of α, α' -azo-bisisobutyronitrile. The polymer (PVB) was soluble and its acetal content was in good agreement with the calculated value. The PVB was hydrolysed to polyvinyl alcohol (PVA) with hydroxylamine hydrochloride. The PVA obtained had nearly the same chemical structure as usual PVA derived from polyvinyl acetate (PVAc) but had a lower degree of polymerization (about 50). The PVA showed a somewhat different infrared spectrum and a much lower reactivity for the acetalization compared with usual PVA. The PVAc derived from the PVA showed at an alkaline saponification in an acetone-water mixture a somewhat higher initial rate of saponification and a much less autocatalytic acceleration effect than usual PVAc. These results seem to indicate that the PVA derived from the PVB may have a different steric structure than usual PVA. Some discussions were given for the steric structure of the PVA.

Graft Polymerization of Styrene and Vinyl Acetate onto Polyvinyl Chloride Fibers Imbibing Catalysts.

Ichiro Sakurada and Yasuyoshi Sakaguchi. *Sen-i Gakkaish-i*, **21**, 131 (1965), in Japanese.—Polyvinyl chloride (PVC) fibers imbibing solutions of various catalysts ($K_2S_2O_8$, $(NH_4)_2S_2O_8$, H_2O_2 , BPO and AIBN) were heated with pure styrene, styrene-methanol and styrene-petroleum benzene mixtures in the air in sealed tubes. Solvents in imbibing solutions were water (for $K_2S_2O_8$, $(NH_4)_2S_2O_8$ and H_2O_2), water-methanol mixtures (for $(NH_4)_2S_2O_8$, H_2O_2 and AIBN), methanol (for AIBN and BPO) and a methanol-benzene mixture (for AIBN and BPO); concentrations of the catalysts were 0.3~2%. About 2g of styrene was added per g-fiber, and heated at 30~90°C.

The grafting was affected by the composition of styrene solutions, the order of the ease of the grafting was pure styrene > styrene-methanol mixture (1 : 1 by volume) > styrene-petroleum benzene mixture (2 : 1 by volume). Among the catalysts AIBN was the most effective in contrast with cases of cellulose and polyvinyl alcohol fibers, and the degree of grafting of about 140% was obtained under favorable conditions. Increase of methanol contents in the imbibing solutions accelerated the grafting. These facts may be attributed to the greater affinity of methanol than that of water to PVC fiber.

Some experiments were also carried out with dry PVC fiber imbibing catalysts; PVC fiber was at first dipped in catalyst solutions, the solvents of the imbibing solutions were evaporated at room temperature, then the dry fiber was heated with pure styrene. Contrary to the cases of cellulose and polyvinyl alcohol fibers the graft polymerization proceeded rather smoothly. This may be due to the high affinity of styrene to dry PVC fiber.

PVC fibers imbibing solutions of various catalysts were also heated with pure vinyl acetate and its solutions, but the degree of grafting greater than about 15% could not be obtained. When dried PVC fibers imbibing AIBN or BPO were heated with a vinyl acetate-petroleum benzene mixture (2 : 1 by volume), the degree of grafting of about 35% was obtained, whereas when the dry fibers were heated with a vinyl acetate-methanol mixture (1 : 1 by volume), no desirable results were obtained. These results may be explained by the high affinity of vinyl acetate to dry PVC fiber and the retarding effect of methanol to the grafting.

Graft Polymerization of Styrene and Vinyl Acetate onto Polyester Fibers Imbibing Catalysts.

Ichiro Sakurada, Yasuyoshi Sakaguchi and Yasui Sakai. *Sen-i Gakkaishi*, **21**, 136 (1965), in Japanese.—Polyethylene terephthalate fibers (Tetoron) imbibing solutions of various catalysts ($K_2S_2O_8$, $(NH_4)_2S_2O_8$, H_2O_2 , BPO and AIBN) were heated with styrene in the air in sealed tubes. When the solvent of $K_2S_2O_8$ and $(NH_4)_2S_2O_8$ was water the grafting proceeded only slightly, but when solvent was a water-methanol mixture the grafting proceeded to a considerable extent. In the cases of H_2O_2 the grafting proceeded smoothly even when the imbibing solvent was water. The fibers imbibing methanol solutions of AIBN could also be grafted with relatively high efficiencies.

Dried fibers imbibing catalysts were heated with pure styrene or styrene-methanol mixtures, but the degree of grafting was low. Generally the graft efficiency of styrene onto the polyester fiber was lower than those onto cellulose, polyvinyl alcohol, nylon and polyvinyl chloride fibers. Behaviors of the grafting onto Vycron fiber were similar to those onto Tetoron fiber.

The graft polymerization of vinyl acetate onto the polyester fibers was also investigated, but no desirable results were obtained. The difficulty of the grafting onto the polyester fibers may be mainly due to difficulty of penetration of the catalysts and/or the monomers into the fibers.

Graft Polymerization of Acrylonitrile onto Various Fibers Imbibing Catalysts.

Ichiro Sakurada and Yasuyoshi Sakaguchi. *Sen-i Gakkaishi*, **21**, 141 (1965), in Japanese.—Various fibers imbibing solutions of several catalysts ($K_2O_2S_8$, $(NH_4)_2S_2O_8$, H_2O_2 , AIBN and BPO) were heated with pure acrylonitrile in sealed tubes. The heating was carried out for 50 hrs, at 60°C or for 20 hrs, at 80°C in air. Solvents for catalyst to be imbibed were water, water-methanol mixtures, methanol and benzene-petroleum benzene mixtures. Concentrations of the catalysts were 0.3~2%.

The grafting onto cellulose fibers proceeded smoothly in the presence of persulphates, but with difficulty in the presence of H_2O_2 , AIBN and BPO. The efficiency of grafting onto viscose rayon was greater than that onto cotton. The grafting onto unheat-and heat-treated (at 200°C) polyvinyl alcohol fibers proceeded

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easily when the catalyst was $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or H_2O_2 , but with difficulty when the catalyst was AIBN or BPO. The grafting onto nylon fibers proceeded to a considerable extent only in the case of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ catalyst.

In contrast to the above mentioned fibers the grafting onto polyvinyl chloride fibers took place more smoothly in the presence of AIBN and BPO than in the presence of $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The grafting of acrylonitrile onto polyester fibers was difficult throughout the experiments.

Instead of pure acrylonitrile an acrylonitrile-dimethyl formamide mixture (1:1 by volume) or 20% aqueous solution of acrylonitrile was used for the grafting, but the degree of grafting was always lower than that obtained with pure acrylonitrile. The grafting onto dried fibers imbibing catalysts was also difficult.

Generally the behaviors of grafting of acrylonitrile lay between those of styrene and vinyl acetate, and were rather near to those of vinyl acetate.

Organic Chemistry

Mechanism of Deoxymercuration with Hydrochloric Acid. Katsuhiko Ichikawa, Kotaro Nishimura and Shinichi Takayama. *Journal of Organic Chemistry*, **30**, 1593 (1965).—The deoxymercuration rates of oxymercurials derived from various olefins have been determined in 75% ethanol. The relative rates for β -ethoxy- α -chloromercuri compounds obtained from ethylene, propylene, 2-butene, isobutylene, cyclohexene, styrene, and *m*-methyl-, *p*-methyl-, *m*-chloro-, *p*-chloro-, *m*-bromo-, and *p*-bromostyrene are 1.00, 14.4, 86.3, 1560, 106, 72.1, 140, 415, 10.5, 36.6, 7.58, and 30.4, respectively, at 0° with hydrochloric acid. The *p*-value of the Hammett plot is -2.93 for the styrene derivatives. On the basis of these results, the mechanism of deoxymercuration is discussed.

Blätteralkohol. (XIV). Synthese des 2-Propyl-5-äthyl-benzylalkohols. Akikazu Hatanaka, Tadahiko Kajiwara und Minoru Ohno. *Agricultural and Biological Chemistry*, **29**, 662 (1965).—2-Propyl-5-ethyl-benzylalcohol was synthesized by an unequivocal route from propylbenzene, thereby establishing the previous deduction tentatively assigned to the leaf alcohol reaction product. This benzyl alcohol surmises one of a lemon-like flavor characteristic of manufactured black tea and an attempted search for this compound in the essential oil obtained by steamdistillation of manufactured black tea was made, but its existence has not so far been confirmed with a neutral fraction examined.

The Structure and Total Synthesis of Takatonine. Seiju Kubota, Takehiko Masui, Eiichi Fujita and S. Morris Kupchan. *Tetrahedron Letters*, No. 40, 3599 (1965).—Total syntheses of takatonine iodide and tetrahydrotakatonine by unequivocal routes show that takatonine iodide should be assigned the 1-(4'-methoxybenzyl)-5,6,7-trimethoxyisoquinoline methiodide structure, rather than

the isomeric 6,7,8-trimethoxy structure considered earlier.

Tumor Inhibitors. (VI). Cissampareine, New Cytotoxic Alkaloid from Cissampelos pareira. Cytotoxicity of Bisbenzylisoquinoline Alkaloids. S. Morris Kupchan, A. C. Patel, and Eiichi Fujita. *Journal of Pharmaceutical Sciences*, **54**, 580 (1965).—A preliminary study of *Cissampelos pareira* Linn. from Peru yielded a new alkaloid, cissampareine. Evidence is presented for assignment to cissampareine of the empirical formula, $C_{37}H_{38}N_2O_6$. Cissampareine and four other bisbenzylisoquinoline alkaloids isolated from menispermaceous plants were found to show significant and reproducible inhibitory activity against human carcinoma of the nasopharynx carried in cell culture (KB).

The Absolute Configuration of Enmein. Transformation of Enmein into (-)-Kaurane. Eiichi Fujita, Tetsuro Fujita, Kaoru Fuji and Nozomu Ito. *Chemical and Pharmaceutical Bulletin*, **13**, 1023 (1965).—Enmein, a diterpene bitter principle isolated from *Isodon trichocarpus* KUDO, was converted into (—)-kaurane, the absolute configuration of which had been established, *via* several steps without any changes of the stereo chemistry. Thus, the absolute configuration of enmein was established by chemical method.

Oxo Reaction and Carboxylation Reaction. Yasumasa Sakakibara and Tadao Nakamura. *Yuki Gosei Kagaku Kyokai-shi*, **23**, 757 (1965), in Japanese.—A review with 76 references.