

**Abstracts of the Papers Published in Other Journals
by the Staff Members of the Institute During 1967**

Nuclear Chemistry

Continuous Energy Spectra of Protons and Alpha Particles Emitted by the Deuteron and Alpha Particle Reaction. Kiyoji Fukunaga, Hitoshi Nakamura, Tetsumi Tanabe, Kazuhiko Hosono and Seishi Matsuki. *J. Phys. Soc. Japan*, **22**, 28 (1967).—Continuous energy spectra of protons and alpha particles have been studied in the deuteron-alpha particle scattering at the incident deuteron energy of 14.2 MeV. In the energy spectra of protons, the evidence for a final state resonance in the neutron and alpha particle system have been obtained and the energy spectrum is compared with the theory of final state interaction. There is a good agreement between the experiment and the theory. The angular dependence of the cross sections at peaks shows a stripping-like feature. The energy spectrum of the alpha particles at the higher energy is mainly affected by the effect of the final state interaction of the triplet S state in the neutron and proton system. The angular dependence of these alpha particles shows a forward peak in the laboratory system and it may be explained by an exchange process.

Electron Beam Extraction from INS AG synchrotron. Part II. Experiment. Kazuo Huke, Sunao Kawasaki, Tatsuya Yamakawa, Seitaro Yamaguchi, Kiyoji Fukunaga, Jun Kokame, Sukeaki Yamashita and Takuji Yanabu. *Japan. J. appl. Phys.* **6**, 242 (1967).—The electron beam has been extracted from the INS 750 MeV AG synchrotron. A Piccioni scheme was applied and the extraction efficiency obtained was 10 % at the electron energy of 540 MeV and 5 % at 700 MeV. The behaviour of the beam inside and outside of the synchrotron was studied in comparison with the theoretical analysis. The pulse duration of the extracted beam could be extended to the order of 700 μ s without any difficulty for the 21.5 cps operation of the synchrotron.

Excitation of Spin-Flip States of Light Nuclei in Inelastic Scattering of Alpha Particles. Hitoshi Nakamura. *J. Phys. Soc. Japan*, **22**, 685 (1967).—Angular distributions of inelastically scattered alpha-particles, leading to the $\Delta T=0$ spin-flip states of C^{12} at 12.7 MeV and B^{11} at 8.6 MeV, were observed. These angular distributions were found to show a unique pattern. Such characteristics of the angular distributions were also observed for the 10.4 MeV state of Mg^{24} and the 8.9 MeV state of Si^{28} . These four states were systematically interpreted as the $\Delta T=0$ spin-flip states by the j - j coupling shell model.

The excitation mechanism for these states is discussed and it is concluded

that a spin-orbit interaction between the incident alpha-particle and a nucleon in the target nucleus plays an important role.

The angular distributions for another unnatural-parity state of C^{12} at 11.8 MeV (2^-), Mg^{24} at 5.22 MeV (3^+) and Si^{28} at 6.27 (3^+) were also observed.

The 14.08 MeV collective state of C^{12} was found to be excited strongly.

Coulomb Excitation by Nitrogen Ions. Masakatsu Sakisaka, Fumio Fukuzawa, Nobutsugu Imanishi, Kunihiro Shima, Katsuhiko Tsuji, Tetsuo Yamazaki and Yoshiaki Uemura. *Genshikaku-Kenkyu*, **11**, 597 (1967), in Japanese.—The acceleration of triply charged nitrogen ions by the Kyoto University Cyclotron was performed. One to ten nanoamperes of nitrogen ion beam of about 11.5 MeV was extracted from the cyclotron. Laboratory techniques developed to accelerate and extract the nitrogen ions are described. Preliminary results of the coulomb excitation on odd nuclei such as ^{45}Sc , ^{75}As , ^{127}I and ^{138}Cs are also reported. B(E2) factors obtained for the $7/2^-$ state of ^{45}Sc , $3/2^-$ state of ^{75}As , $5/2^+$ state of ^{127}I and $7/2^+$ state of ^{138}Cs are listed in Table 2 in this report.

Cluster Structures of the Nucleus. Takuji Yanabu, Sukeaki Yamashita, Dai Ca Nguyen, Shigeru Kakigi, Ryutaro Ishiwari, Kiyohiko Takimoto, Kouya Ogino, Kazuhiko Hosono, Seishi Matsuki and Tetsumi Tanabe. *Genshikaku-Kenkyu*, **12**, 8 (1967), in Japanese.—Nuclear clusters such as deuterons, tritons and alpha particles in the nucleus, if any, were tried to be detected by the coincidence technique between these clusters and quasi-elastically scattered protons from these clusters. The incident proton beam was obtained from the INS cyclotron and the energy was about 55 MeV. Progresses in the detection techniques and logical circuits to discriminate such clusters are described. Preliminary results on the Be^9 ($p, p\alpha$) He^3 reaction are also reported.

Kyoto University Tandem Van de Graaff. Tsunahiko Sidei, Jiro Muto, Isao Kumabe, Hiroshi Ogata, Kiyohiko Takimoto, Yasuhiko Ōkuma, Makoto Inoue, Yoshinori Ogata, Yoshiaki Uemura, Sukeaki Yamashita, Gen Imamura, Takashi Takagi, Yasuhiro Yokota, Kōichi Inoue, Toshio Takabe and Taro Ohama. *Memoirs of the Faculty of Science, University of Kyoto, Series of Physics, Astrophysics, Geophysics and Chemistry*, **32**, 1 (1967).—A tandem type Van de Graaff accelerator at the Department of Physics in Kyoto University is described. Details of the accelerator, ion optical arrangement, structure of the columns, acceleration tubes, vacuum system, negative ion injection system, generation and control of the high voltage, beam analyzing magnet and switching magnet, high pressure gas system, building and general arrangement of the equipments are presented. The course of the construction and test of the machine is also described with the specifications of the machine and its performances.

Energy Spectra of Inelastic Scattering of 28.4-MeV Alpha Particles. Isao Kumabe, Hiroshi Ogata, Tong-Hyuk Kim, Makoto Inoue and Yasuhiko Ōkuma. *J. Phys. Soc. Japan*, **23**, 147 (1967).—Thin targets of ^{58}Ni , Cu, Ag, Ta and Au were bombarded with 28.4-MeV alpha particles and the energy spectra of emitted alpha particles were measured at several angles.

The experimental values of the peak energies in the energy spectra at 150° arising from the compound-nucleus process were found to be in good agreement with the values of the Coulomb barrier height for an optical model potential.

Prominent features of the energy spectra for Ag are as follows. The differential cross sections at a forward angle (30°) increase with alpha-particle energy, while those at backward angles (more than 90°) decrease with alpha-particle energy. At an intermediate angle (60°) between them, the energy spectrum is nearly flat. General features of the energy spectra for Ta and Au resemble those for Ag except for the low energy parts where the cross sections are decreased by the higher Coulomb barrier.

These features may be explained by a mechanism which takes account of the collective excitation of the residual nucleus.

Breakup of Deuteron by Alpha Particle Impact. Kiyoji Fukunaga, Tetsumi Tanabe, Sukeaki Yamashita, Noboru Fujiwara, Shigeru Kakigi and Takuji Yanabu. *Contributions to the International Conference on Nuclear Structure*, 39 (1967).—The $d(\alpha, p\alpha)n$ reaction was investigated by the p - α coincidence method. Alpha particle detector was fixed at angles of 11.2° and 10.0° , and the proton detector moved around the beam axis with constant polar angles of 30° and 40° respectively. The position of a broad peak in the energy spectrum of alpha particles agrees with that of zero momentum of neutron at large proton angles and shifts to that of the Li^5 ground state with the decrease of the proton angle. The experimental results deviates from the predictions of impulse approximation breakup theory.

The Structure of Li^6 and Li^7 in Excited States. Sukeaki Yamashita, Seishi Matsuki, Kiyoji Fukunaga, Dai Ca Nguyen, Noboru Fujiwara and Takuji Yanabu. *Contributions to the International Conference on Nuclear Structure*, 253 (1967).—Coincidence measurements were performed between alpha-triton and alpha-deuteron from the $Li^6(\alpha, \alpha d)\alpha$ and $Li^7(\alpha, \alpha t)\alpha$ reactions respectively. The incident alpha particle energy was 29.4 MeV. In the coincided alpha-particle spectrum, a strong peak was observed corresponding to the inelastic scattering leading to the 2.18 MeV state of Li^6 or to the 4.63 MeV state of Li^7 . In the case of Li^6 , the observed correlation is fairly well reproduced by the plane wave Born approximation theory except for the deviation of the symmetry axis. For Li^7 , however, the PWBA theory cannot reproduce the observed correlations.

Quasi-Free Proton-Alpha and Alpha-Alpha Collision in Be^9 and Other Light Nuclei. Takuji Yanabu, Sukeaki Yamashita, Shigeru Kakigi, Dai Ca Nguyen, Noboru Fujiwara, Kazuhiko Hosono, Seishi Matsuki, Tetsumi Tanabe, Kiyohiko Takimoto, Kouya Ogino and Ryutaro Ishiwari. *Contributions to the International Conference on Nuclear Structure*, 261 (1967).—The reactions $Be^9(p, p\alpha)He^5$ and $C^{12}(p, p\alpha)Be^8$ were studied with a 55.3 MeV proton beam from the INS synchrocyclotron of University of Tokyo. The summed energy spectrum of protons and alpha particles emitted in coincidence shows a peak corresponding to the ground resonance state of He^5 . The angular correlation between protons and alpha particles can be reproduced with parameters of the cluster structure of Be^9 .

The $(\alpha, 2\alpha)$ reactions on O^{16} and Ne^{20} at 28.5 MeV were studied with an α -

particle beam from the Kyoto University Cyclotron. Although the quasi-free scattering process takes place mainly in these reactions, the final state resonances between an emitted α -particle and the residual nucleus cannot be neglected.

Core Excitation of Light Odd Nucleus by (d, p) Reaction. Shigeru Kakigi, Kazuhiko Hosono, Hitoshi Nakamura, Dai Ca Nguyen, Noboru Fujiwara and Takuji Yanabu. *Contributions to the International Conference on Nuclear Structure*, 276 (1967).—In the $C^{12}(d, p)C^{13}$ reaction, it was observed that the transition probabilities to the 3.68 MeV, $3/2^-$ and 7.55 MeV, $5/2^-$ states of C^{13} are of the same order of that to the ground state of C^{13} . The transition to these excited states are forbidden by the spin-parity selection rule if the simple stripping process is assumed. The transitions can be explained with a two step process, *i. e.*, one step is the capture of a $1p\ 1/2$ neutron and the other is the C^{12} core excitation to its 4.43 MeV, 2^+ state by the inelastic scattering of deuterons or protons.

Inelastic Scattering of Alpha Particles by Be^9 at 28.5 MeV. Kiyoji Fukunaga, Hitoshi Nakamura and Noboru Fujiwara. *J. Phy. Soc. Japan*, 23, 911 (1967).—Differential cross sections of the elastic scattering and the inelastic scattering of alpha particles from Be^9 at the incident energy of 28.5 MeV are obtained. The angular distributions for the ground state and 2.43 MeV state show the clear diffractive nature. For the positive parity state, the phase relation of the experiment does not agree with the diffraction theory, and the interaction radius is smaller than those for the ground state and the collective state. The peak at 1.7 MeV in pulse height spectrum is considered to be caused by a final state interaction between the S wave neutron and the Be^9 nucleus.

Coulomb Excitation of ^{45}Sc , ^{75}As , ^{127}I and ^{133}Cs . Nobutsugu Imanishi, Fumio Fukuzawa, Masakatsu Sakisaka and Yoshiaki Uemura. *Nuclear Physics*, A101, 654 (1967).—The Coulomb excitation of ^{45}Sc , ^{75}As , ^{127}I and ^{133}Cs has been studied using 11.5 MeV nitrogen ions as bombarding particles. From the thick target yields of de-excitation gamma rays, the $B(E2) \uparrow$ values are obtained as ^{45}Sc : 378 KeV, 0.0086 ± 0.0017 ; ^{75}As : 280 and 199 KeV, 0.051 ± 0.012 and 0.015 ± 0.003 ; ^{127}I : 203 and 59 KeV, 0.072 ± 0.014 and 0.054 ± 0.011 ; ^{133}Cs : 160 and 81 KeV, 0.13 ± 0.03 and 0.022 ± 0.004 , respectively, in units of e^2b^2 . The results for ^{127}I and ^{133}Cs are compared with theoretical predictions.

Observation of the Nuclear Raman Scattering by ^{181}Ta . Sakae Shimizu, Yasuhito Isozumi and Yasuyuki Nakayama. *Physics Letters*, 25B, 124 (1967).—An incoherent gamma-ray scattering by the nuclear optical anisotropy of the nuclei having large intrinsic deformations is known as the nuclear Raman scattering. The photon scattering by this process in the giant resonance region has been observed using $Li(p, \gamma)$ gamma rays as incident rays and ^{181}Ta as a deformed target nucleus. Only a Raman scattering to the 303 KeV level, one of three members of the ground-state rotational band of ^{181}Ta , was observed for the incident photons of 14.8 MeV and 17.6 MeV from the $^7Li(p, \gamma)^8Be$ reaction. The experimental total cross section obtained is $\sigma_{exp} = (9.6 \pm 3.9) \times 10^{-28}$ cm². A possible explanation is proposed for a considerable deviation of the experimental result

from the theoretical prediction by Fano.

Analytical Chemistry

Spectrophotometric Determination of Scandium with Pontacyl Violet 4BSN. Tsunenobu Shigematsu and Katsuya Uesugi. *Bunseki Kagaku*, **16**, 467 (1967), in Japanese. —A new spectrophotometric method for the determination of scandium was studied, using Pontacyl Violet 4BSN (Color index 16580) as a reagent. Scandium reacts with Pontacyl Violet 4BSN at pH 6.4~7.2 to form a colored complex with an absorption maximum at 630 m μ , which can be used for the determination of scandium. Beer's law was followed up to 1.2 ppm of scandium, and molar absorption coefficient was 13,700 at 630 m μ . Aluminum, iron(III), copper(II), nickel, chromium(III), beryllium and phosphate interfere with the determination of scandium. The mole ratio of scandium to the reagent was 1 : 2 at pH 6.8.

Fluorophotometric Determination of Aluminum and Gallium with Lumogallion. Yasuharu Nishikawa, Keizo Hiraki, Kiyotoshi Morishige and Tsunenobu Shigematsu. *Bunseki Kagaku*, **16**, 692 (1967), in Japanese.—Lumogallion reacts with aluminum or gallium to form a complex with reddish yellow fluorescence, and was used as a reagent for the fluorophotometric determination of aluminum and gallium. Several conditions for the emission of fluorescence, the effect of diverse ions, and the composition of fluorescent complexes were investigated. The maximum fluorescence intensity of aluminum complex was found at pH 5.0 when heated for 20 minutes at 80°C ; whereas that of gallium complex, at pH 3.0. The complexes were also extractable into amyl alcohol. The fluorescence of the complexes were stable at least for 2 hours either in water or in amyl alcohol solution. By using lumogallion, 0.1~2 μ g of aluminum and 0.5~5 μ g of gallium in 25 ml solution could be determined. Ferric iron, Ni²⁺, Co²⁺, Cu²⁺, Sc³⁺, Sn⁴⁺, Ti⁴⁺, V⁵⁺ and Cr⁶⁺ interfered.

The Synergistic Effect in Solvent Extraction. —The Correlation of the Ionic Radius of Rare Earth Elements with the Stability Constants of Rare Earth Benzoyltrifluoroacetate Adducts with *n*-Hexylalcohol, TBP and TOPO. Tsunenobu Shigematsu, Masayuki Tabushi, Masakazu Matsui and Takaharu Honjo. *Bull. Chem. Soc. Japan*, **40**, 2807 (1967).—The synergistic effect of *n*-hexylalcohol, TBP and TOPO on the extraction of rare earth ions with benzoyltrifluoroacetone in benzene was studied. The stability constants of the adducts were determined by means of the curve-fitting method.

The new fundamental equation based on the shift of $\text{pH}_{1/2}$ ($-\Delta\text{pH}_{1/2}$) was proposed to analyse the data.

The results were discussed in relation to the ionic radius of rare earth elements and summarized as follows :

- (1) The stability of rare earth benzoyltrifluoroacetates decreases but that of the adducts increases, as the ionic radius increases.
- (2) The maximum number of base molecules bonding to one molecule of the metal chelate is 2, except in the case of lutetium adduct with TOPO, where the

formation of secondary adducts is not observed.

(3) Although the overall stability constant of the adducts increases in the following order ; lutetium < terbium < europium < lanthanum, as mentioned above, the first stability constant does not show such a distinct sequence. Therefore the contribution of the second stability constants seems to be an important factor.

(4) Organic bases studied form stable adducts with rare earth benzoyltrifluoroacetates in the following order ; *n*-hexyl alcohol < TBP < TOPO. This order corresponds to the donating power of lone pair electrons of the oxygen atoms in these compounds.

Physical Chemistry

Infrared Spectra of Acetic Acid Adsorbed on Alumina in Tetrachloromethane. Soichi Hayashi, Tohru Takenaka and Rempei Gotoh. *Nippon Kagaku Zasshi*, 88, 133 (1967), in Japanese.—Infrared spectra of acetic and deuterioacetic acids adsorbed on alumina were measured at various concentrations in tetrachloromethane in order to investigate the adsorbed state at liquid-solid interfaces. The adsorption isotherm was of the Langmuir type at relatively low concentrations. When the initial concentration was low, both of the deuterated and undeuterated acetic acids adsorbed on γ -alumina took two kinds of ionic states, characterized by two pairs of absorption frequencies 1590~1465 and 1560~1420 cm^{-1} , while the molecular adsorption was found to proceed as the monomolecular saturation was approached. β -Alumina showed the similar behaviors although its adsorbing power was smaller than that of γ -alumina. These results were compared with those obtained by other authors for the adsorption from gaseous states. It was also found that the scattering of light by powder was reduced in the liquid phase, which revealed high accuracy of measurements in the case of liquid phase adsorption.

Electrocapillary Phenomena at Oil-Water Interfaces. Part II. The Counterion Binding at Oil-Water Interfaces. Akira Watanabe, Mutsuo Matsumoto, Hisako Tamai and Rempei Gotoh. *Nippon Kagaku Zasshi*, 88, 507 (1967), in Japanese.—The structure of electrical double layers at oil-water interfaces was investigated by measuring electrocapillary curves for surface active agent solutions in methylisobutylketone (oil phase) in contact with aqueous solutions of various inorganic electrolytes. In the case of potassium halides, ions of large crystallographic radii prevent interfacial tension suppression over the cathodic polarization range due to the adsorption of cetylpyridinium or cetyltrimethylammonium chloride. This shows that adsorbed surface-active agent ions are neutralized by the counterion binding. In the case of sodium dodecylbenzenesulphonate in oil phase, divalent cations were arranged in a sequence of increasing tendencies of the prevention of the interfacial tension suppression over the anodic polarization range, which was similar to that of the binding ability of these cations with chondroitin sulphate. It was also found that high valent cations showed strong binding tendencies. All these counterion bindings appear to support the concept of the orientation of surface-active agents with polar head groups immersed into the aqueous side of the in-

terface. The counterion binding is supposed to take place not only by the electrostatic attraction but also by the chemical affinity, and a rough estimation of free energies of binding was made.

Electrocapillary Phenomena at Oil-Water Interfaces. Part I. Electrocapillary Curves of Oil-Water Systems Containing Surface Active Agents. Akira Watanabe, Mutsuo Matsumoto, Hisako Tamai and Rempei Gotoh. *Kolloid-Z.u. Z. für Polymere*, **220**, 152 (1967).—The electrocapillary phenomena at oil-water interfaces, *i. e.* the change in the interfacial tension with an applied potential difference, take place over a moderate polarization range of ca. 20 to $-20V$, when the systems have sufficiently high electric conductance and contain surface active agents. Experiments were carried out in the presence of potassium chloride in the aqueous phase and ionic surface active agents in the oil phase, respectively. It was found that the interfacial tension was suppressed over the cathodic or anodic polarization range, depending on whether the surface active agent used was cationic or anionic, respectively. Here the sign of polarization was conventionally taken as that of the water phase with respect to the oil phase. It was then concluded by the use of the *Lippmann-Helmholtz* equation that the water side of the interface is charged positively or negatively in the respective case mentioned above. It appears that this charge is due to the counter ion layer which is formed corresponding to the adsorption of ionic surface active agents on the oil side.

Electrocapillary Phenomena at Oil-Water Interfaces. Part II. The Counterion Binding at Oil-Water Interfaces. Akira Watanabe, Mutsuo Matsumoto, Hisako Tamai and Rempei Gotoh. *Kolloid Z. u. Z. für Polymere*, **221**, 47 (1967).—In order to discuss the structure of the electrical double layer at the oil-water interface, we measured the electrocapillary curves for various inorganic electrolyte aqueous solutions (aq. phase) in contact with the oil phase containing surface active agents (oil phase). When the aqueous phase contained potassium halide, the depression of the interfacial tension over the cathodic polarization range due to the adsorption of the surface active agent, *i. e.* cetyl pyridinium chloride or cetyltrimethyl ammonium chloride, was suppressed strongly. The suppression was larger for the anion of larger crystal radius. This phenomenon indicated that the adsorbed surface active ion was neutralised by the binding of counterions. When the oil phase contained sodium dodecyl benzene sulphonate, the interfacial tension was depressed over the anodic polarization region. This depression was again suppressed by the counterion binding. The order of this suppression for various divalent cations agreed with that of the binding ability to chondroitin sulphate. Moreover, high valent cations had strong binding ability. These counterion binding support the idea of the penetration of polar groups of orientated surface active agents into the aqueous phase at the oil-water interface.

Slip Fracture of Bentonite Gels. Rempei Gotoh and Kiyoshi Shimizu. *Bentonite No. 8*, 2 (1967), in Japanese.—The hydrogel of Wyoming Bentonite shows a characteristic slip fracture under a critical shear stress, *i. e.* the shear strength. The shear strength and the shear modulus of the gel were measured by various methods over a wide range of bentonite concentration. The shear modulus in-

creasing concentration in the similar manner to the gels of linear polymers. The shear strength (σ_0) is related to the shear modulus (G), as shown by the equation :

$$\sigma_0 = \gamma_0 G$$

where γ_0 is the critical shear strain. γ_0 takes values ranging from 1/10 to 1/30, which are in fairly good agreement with the value predicted for an ideal crystal by Mackenzie.

Crystallization of Amorphous Selenium Films Prepared by Vacuum-Evaporation. Makoto Shiojiri. *Japan. J. appl. Phys.* 6, 163 (1967).—An electron microscopic study was made on the crystallization of amorphous selenium films prepared by vacuum-evaporation onto glass at room temperature. The films were crystallized by irradiation of an electron beam, and changed into metallic selenium. The crystals grew most prominently in their a-axes with the (01 $\bar{1}$ 0) surface planes. Small-angle-tilt and twist boundaries as well as twinning crystals were observed in the growing crystals. The generation of the twist boundaries and the twinning crystals are interpreted by mechanisms similar to those proposed in a previous paper (*J. Phys. Soc. Japan*, 21, 335 (1965)), and that of tilt boundaries is also interpreted by a modified mechanism.

Observation of Dissociated Dislocations in Lead Iodide. Makoto Shiojiri, Hiroshi Morikawa and Eiji Suito. *Japan. J. appl. Phys.* 6, 409 (1967).—Lamella single crystals of lead iodide grown from solution were examined by transmission electron microscopy. Dislocations in lead multi-ribbons, extended nodes and extended jogs were also observed.

Dielectric Properties of Polytetrafluoroethylene and Tetrafluoroethylene-Hexafluoropropylene Copolymer. Naokazu Koizumi, Shinichi Yano and Fukuju Tsuji. *J. Polymer Sci. Part C*, No. 21, (1967).—Precision measurements of dielectric properties of polytetrafluoroethylene and copolymers of tetrafluoroethylene and hexafluoropropylene were made over a temperature range of -40 to $+180^\circ\text{C}$ at frequencies of 10Hz to 300 kHz. Polytetrafluoroethylene exhibited the typical dielectric behavior of a nonpolar substance: no dielectric loss peak was found over the experimental range of temperature and frequency. The dissipation factor remained constant, being about 2×10^{-5} . Copolymers of tetrafluoroethylene and hexafluoropropylene showed two dielectric loss peaks: one occurred at about 100°C and the other at about -20°C . There was a break point, or an abrupt bend, near 60°C in the curve of dielectric constant versus temperature, indicating the existence of a transition point. The high- and low-temperature loss peaks correspond to the α and γ relaxation, respectively, which have been found for the mechanical behavior of this copolymer. The dielectric relaxation in the copolymer was attributed to the slightly polar nature of the perfluoromethyl side groups. The activation enthalpy and entropy are 80 kcal./mole and 180 eu for the α relaxation and 12 kcal./mole and 15 eu for the γ relaxation, respectively. The α and γ relaxations are discussed in connection with the molecular motion of the copolymer chain.

Inorganic Chemistry

Changes in Light Absorption Spectrum of the Cobalt-Containing Glasses Subjected to High Pressure. Megumi Tashiro, Tokuji Yamamoto and Sumio Sakka. *Yogyo Kyokai Shi (J. Ceram. Assoc. Japan)*, **75**, 201 (1967), in Japanese.—A pressure of 55 kilobars was applied to cobalt-containing glasses by the use of a high pressure apparatus of the simple squeezer type at room temperature. Light absorption spectra, in the visible range, of the powdered specimens before and after application of the pressure were determined with a microspectrophotometer. From the experimental results changes in ionic distance between the Co^{2+} ion and its neighboring O^{2-} ions and also changes in number of the O^{2-} ions coordinated around the Co^{2+} ion were calculated by the Ligand Field Theory. Changes in refractive index of the specimens before and after the compression were also measured to determine the residual shrinkage of the glass in bulk. The results obtained are summarized as follows; 1) The three absorption peaks characteristic for both the four- and six-fold coordinated Co^{2+} ions in all of the glass specimens were shifted toward the shorter wave length. 2) The local shrinkage of the glass structure in the neighborhood of the Co^{2+} ions calculated from the shift of the absorption peaks were 0.005 for the silicate glass, 0.07 for the alkali-borate glass, whereas the shrinkages of the glasses in bulk were 0.02~0.05 and 0.03~0.07 for the silicate and alkali-borate glasses, respectively. 3) Besides the shift of the absorption peaks, development of the new peaks which are probably attributed to the change in coordination number of the Co^{2+} ions from four to six, were observed for the high-alkali borate glass.

Effects of Addition of Glasses Containing BaO and TiO_2 on Properties of BaTiO_3 Ceramics. Toshio Maki and Megumi Tashiro. *Yogyo Kyokai Shi (J. Ceram. Asso. Japan)*, **75**, 278 (1967), in Japanese.—In order to extend the firing range of BaTiO_3 ceramics and also improve their dielectric properties, glass powders of the $\text{BaO-TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ system were added as the binding agent in a total amount of 5 to 15 wt% to BaTiO_3 crystal powders. The mixtures of crystal and glass powders were formed by drypressing, being subjected to the measurement of the firing range (the range corresponding to the water-absorption-zero temperature to the deformation temperature). Measurements of dielectric properties were made at room temperature with a frequency of 1Mc/sec. for the mixtures fired at 1200° to 1400°C for 60 min. The results obtained are summarized as follows: 1) The firing range of the pressed compacts extends by about 100° to 200°C by the addition of the glass powders rich in BaO and TiO_2 . 2) Dielectric properties of the sintered specimens become less sensitive to their firing temperature by the addition of the glasses. 3) The dielectric constant of the sintered specimens is much affected by the composition of the glasses added; the MgO component in glass is effective to increase the dielectric constant of the specimens. 4) The addition of the glass powders together with MgF_2 crystal powders most increases the dielectric constant of the specimens. 5) The effects of the addition of glass powders were explained on the basis of the electron-microscopic observation of the microstructure of the specimens.

On the Reaction between Petalite Crystals and Lithia-Containing Glass. Toshio Maki and Megumi Tashiro. *Yogyo Kyokai Shi (J. Ceram. Assoc. Japan)*, **75**, 359 (1967), in Japanese.—The bending strength of the petalite ceramics produced by firing petalite powders with addition of a small amount of lithia-containing glass is much affected by the chemical composition of the glasses added and also by the cooling schedule in the process of their firing. In order to explain these effects, the microstructures of the specimens produced with additions of the glasses of the $\text{Li}_2\text{O-SiO}_2$ system and the $\text{Li}_2\text{O-MgO-Al}_2\text{O}_3\text{-SiO}_2$ system under various firing conditions were examined with electronmicroscopic and x-ray diffraction techniques. For the specimens fired with the addition of the $\text{Li}_2\text{O-SiO}_2$ glass and then annealed the meta-lithium silicate ($\text{Li}_2\text{O}\cdot\text{SiO}_2$) crystallites were found to precipitate in the glass matrix surrounding large grains of spodumene crystals, whereas for those fired with the addition of the $\text{Li}_2\text{O-MgO-Al}_2\text{O}_3\text{-SiO}_2$ glass and then annealed no such crystals was observed. When quenched after firing, no crystals was observed in both of the specimens fired with the addition of the $\text{Li}_2\text{O-SiO}_2$ and $\text{Li}_2\text{O-MgO-Al}_2\text{O}_3\text{-SiO}_2$ glasses. Low bending strength of the specimens fired with the addition of the $\text{Li}_2\text{O-SiO}_2$ glass was attributed to the presence of microcracks produced by the big difference in thermal expansion coefficient between the meta-lithium silicate crystals precipitated and their surroundings.

Order-Disorder Transformation of Fe-Co Alloys in Fine Particles. Hajime Asano, Yoshichika Bando, Norihiko Nakanishi and Sukeji Kachi. *Trans. Japan Inst. of Metals*, **8**, 180 (1967).—The specific heat and the lattice constant of Fe-Co alloys in the bcc range have been measured. The specimens are prepared by the reduction of solid solution $\text{Fe}_{1-x}\text{Co}_x\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ in hydrogen at 800°C . It has been confirmed that the FeCo (CsCl type) superlattice exists over a wide range (30~75 at.% Co), and the so-called “550°C anomaly” of the $\text{Fe}_{0.5}\text{Co}_{0.5}$ superlattice has also been observed in the alloys containing 21~60 at.% Co. This anomaly appears at almost the same temperature in the composition range of 21~50 at.% Co ($555^\circ\sim 560^\circ\text{C}$), and its transition temperature falls abruptly when the cobalt content is greater than 50 atomic per cent. There is a broadpeak at about 550°C in specific heat curves of 21, 23, 25, 27 and 27.5 at.% Co alloys. These peaks have hitherto been considered due to the transition of the Fe_3Co superlattice. Judging from the composition dependence of its transition temperature and the shape of the specific heat curves, however, it is reasonable to consider that these peaks do not correspond to the Fe_3Co superlattice but to the extension of the 550°C anomaly.

The effect of ordering on the lattice constant causes an increase in cell size in the 40~60 at.% Co alloys and a decrease in the 23~40 at.% Co alloys.

The results of measurements by means of a neutron diffraction technique and the Mössbauer effect on a slow-cooled 25 at.% Co alloy have shown no evidence for the existence of the Fe_3Co superlattice.

The Preparation and Physical Properties of Fine Particles. Toshio Takada. *Bussei*, **8**, 525 (1967), in Japanese.—Recent experimental results on the preparation method and physical properties of oxide fine particle were outlined. Main descriptions are as follows. (1) Preparation method and particle shape of fine

particles, (2) Topotaxy, (3) Particle size and lattice constant of α -Fe₂O₃ and MgO, (4) Ion distribution of ferrite particles prepared by aqueous solution, (5) Characteristics of phase transformation and lattice imperfection in metallic fine particles, (6) On amorphous state, (7) Superparamagnetism of ferro- and antiferromagnetism.

Studies on Sintering Mechanism by Autoradiography. Terumi Oda, Toshio Takada and Sukeji Kachi. *Funtai Oyobi Funmatsuyakin (J. Japan Soc. Powder Met.)*, 14, 118 (1967), in Japanese.—The apparent self-diffusion coefficient of silver during sintering was determined by autoradiography. The coefficient is given by $D_{app}^{sintered} = 0.0084 \exp(-33000/RT) \text{ cm}^2 \text{ sec}^{-1}$. The activation energy lies between those for the self diffusion and for grain boundary diffusion in polycrystal. This fact may indicate that the sintered body has more vacancies in itself.

Mössbauer Effect Study of Magnetism in Fine Particles. Teruya Shinjo. *Funtai Oyobi Funmatuyakin, (J. Japan Soc. Powder Met.)*, 14, 248 (1967), in Japanese.—This paper reports the following three topics concerned with the magnetic properties of fine particles. They are recently obtained results by the author's group.

- 1) The spin flop temperature of α -Fe₂O₃ (Morin temperature) shifts to the lower with decrease of the particle size. This fact was ascertained by the Mössbauer effect analysis from the microscopic standpoint.
- 2) The Mössbauer effect of Co⁵⁷ doped into Cu-2%Co alloy was measured at various temperatures and the size distribution of precipitated Co particles was estimated using the Néel's relation for superparamagnetism. The result agreed well with electron microscopic observation.
- 3) Using the α -FeOOH samples of various particle sizes, the dependence of Mössbauer spectra on the fluctuating rate of the internal field was examined. The theoretically expected spectra calculated by Wickman were introduced for comparison. The ability of the Mössbauer effect for the study of dynamical phenomena was discussed.

The Effect of Impurities on Densification of Oxide During Sintering. Yoshi-chika Bando. *Funtai Oyobi Funmatsuyakin (J. Japan Soc. of Powder Met.)*, 14, 378 (1967), in Japanese.—The study was outlined that, during sintering of oxide containing minor amount of impurities, a liquid phase is formed and penetrates among the grains to form impurity layer. The mechanism of segregation of CaO and SiO₂ to the grain boundaries of oxide was discussed from the view point of liquid phase sintering. Densification proceeds by liquid phase sintering.

NMR Determination of Metal Ion Distribution in Manganese Ferrite Prepared from Aqueous Solution. Hiroshi Yasuoka, Akira Hirai, Teruya Shinjo, Masao Kiyama, Yoshichika Bando and Toshio Takada. *J. Phys. Soc. Japan*, 22, 174 (1967).—In order to determine the metal ion distribution in a new type manganese ferrite (MnFe₂O₄), which was prepared by precipitation from aqueous solution, the nuclear magnetic resonance (NMR) of Mn⁵⁵ was studied. In this ferrite, two separate resonance signals were observed, which were identified as associated

with Mn^{2+} ions located at the tetrahedral (*A*-) and the octahedral (*B*-) sites respectively. By integrating those NMR spectra, it was decided that about 10% of Mn^{2+} ions are present at *B*-sites. Using the ratio of the amount of the Mn^{2+} ions located at *A*-sites to that at *B*-sites and the value of saturation moment ($4.2\mu_B$), the metal ion distribution in this manganese ferrite was determined to be $Mn_{0.48}^{2+} Fe_{0.52}^{3+} (Mn_{0.06}^{3+} Mn_{0.46}^{3+} Fe_{1.02}^{3+} Fe_{0.46}^{3+})O_4$. From the temperature dependence of the resonance frequency, the Curie temperature was estimated to be 770°K. The high Curie temperature compared with that of ordinary manganese ferrite (573°K) is explainable by the above metal ion distribution. It was found that the metal ion diffusion between *A*- and *B*- sites occurs at about 250°C, and above 450°C the metal ion distribution accords with that of ordinary manganese ferrite.

Size Distribution of Co Particles Precipitated in Cu Determined by the Mössbauer Effect. Saburo Nasu, Teruya Shinjo, Yoji Nakamura and Yotaro Murakami. *J. Phys. Soc. Japan*, 23, 664 (1967).—According to Néel's estimation for superparamagnetism, the size distribution of Co particles precipitated in Cu-Co alloy was determined from the analysis of the Mössbauer spectra. For the gamma-ray source, Co^{57} was doped into Cu-2%Co alloy and measurements were made between 95°K and 335°K.

The obtained result was in good agreement with electron micrographic observation.

Mössbauer Effect of Fe^{57} in $Fe(OH)_2$. Hiroki Miyamoto, Teruya Shinjo, Yoshichika Bando and Toshio Takada. *J. Phys. Soc. Japan*, 23, 1421, (1967).—The Mössbauer effect of $Fe(OH)_2$ was measured in paramagnetic and antiferromagnetic region (4.2°K). At 90°K, quadrupole splitting $1/2e^2qQ$ and isomer shift were observed to be 3.00 mm/sec and 1.25 mm/sec respectively.

As for the spectrum at 4.2°K, four resonance lines were observed in contrast with usual six lines splitting. This spectrum is interpretable in terms of a uniaxial electric field gradient and a magnetic hyperfine field perpendicular to the axis of electric field.

An excellent agreement of experimental peak positions with calculated ones was obtained by assuming $\lambda = -0.75$, where λ is the ratio of the quadrupole interaction energy to the Zeeman one.

The derived values of magnetic hyper fine field, $1/2e^2qQ$ and δ are 200 KOe, 3.06 mm/sec and 1.48 mm/sec respectively at 4.2°K. In consideration of the crystal structure of $Fe(OH)_2$, which is a hexagonal layer structure of CdI_2 type, spin axis of $Fe(OH)_2$ was concluded to be in the *c*-plane.

Neutron Diffraction of Manganese Ferrite Prepared from Aqueous Solution. Junji Sakurai and Teruya Shinjo. *J. Phys. Soc. Japan*, 23, 1426 (1967).—Neutron Diffraction Method was applied for manganese ferrite produced as the precipitates from aqueous solution in order to examine the cation distribution. Measurements were made in the high angle range where the magnetic scattering was negligibly small.

The obtained result was as follows; *A*-site ($Mn_{0.33} Fe_{0.67}$), *B*-site ($Mn_{0.67} Fe_{1.33}$).

Therefore, the ion distribution of this sample was found to be quite different from that of the usual samples prepared by the ceramic method, as had been suggested by the NMR study.

Production of Tin Single Crystal Foils from the Melt and Their Degrees of Perfection. Hideo Takaki, Masashige Koyama, Yoshikazu Tsujii and Shigeo Maeda. *Trans. Japan Inst. Metals*, 8, 195 (1967).—In order to investigate the relation between the thickness and the formation of striated subboundaries in the crystals grown from the melt and also to make a direct x-ray observation of dislocations in the similarly prepared thin single crystals, a technique has been devised for producing single crystal foils of tin from the melt: After vacuum melting and degassing, molten tin is thrust in a special type glass mould with a pressure of N_2 gas. Then, the production of tin single-crystal foils about 0.007 cm in thickness is successfully grown from the seed crystal. In this case, carbon is pre-coated on the inner walls of the glass mould to avoid direct contact between tin and glass. For the samples with the purity of 99.999 % or higher and the thickness of less than 0.01 cm, however, this carbon pre-coating technique was ineffective for suppressing of stress induced by the adhesion between glass and tin.

Improvements on the above disadvantages of this technique are now under investigation.

Magnetic Anisotropy in the *c*-Plane of Fe_2As . Norio Achiwa, Shuya Yano, Motoyoshi Yuzuri and Hideo Takaki. *J. Phys. Soc. Japan*, 22, 156 (1967).—The direction of magnetic moment and the magnetic anisotropy energy of Fe_2As in the *c*-plane were determined from measurements of magnetic anisotropy and field dependence of magnetizations on a single crystal disk of Fe_2As at liquid nitrogen temperature. The magnetic moment is in the $\langle 100 \rangle$ direction. The magnetic anisotropy energy is estimated to be 7×10^2 erg/g from saturation of torque amplitude.

Electrical Resistivity of Chromium Alloys. Hideo Ohno, Takao Suzuki and Hideo Takaki. *J. Phys. Soc. Japan*, 23, 251 (1967).—In order to clarify the degree of localization of the impurity state, electrical resistivities of dilute chromium alloys with Mn, Fe and Co were measured from 1.2°K above to their transition temperatures. The resistivity due to the potential scattering by the impurity atom was separated empirically and it was found that the resistivity due to impurity scattering of Mn alloy is at most $0.8 \mu\Omega$ cm per 1 at. % of Mn and is extremely small compared with those of Fe and Co. This supports the view that the impurity state of Mn in Cr is not localized, while those of Fe and Co are considerably localized. No resistance minimum was observed in these alloys and even in very dilute alloys within the experimental errors.

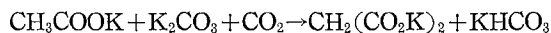
Organic Chemistry

Reactions of Allenes. I. The Synthesis of Unsaturated Monocarboxylic Esters by the Carboxylation Reaction of Allenes; Reaction Conditions and Products. Sango Kunichika, Yasumasa Sakakibara and Tadashi Okamoto. *Bull. Chem.*

Soc. Japan, **40**, 885 (1967).—The carboxylation reaction of propadiene and 1, 2-hexadiene with carbon monoxide and methanol in the presence of a catalyst was studied. Propadiene was carboxylated to give methyl methacrylate in a fairly good yield (62% based on the propadiene consumed) by the use of a catalyst composed of nickel carbonyl and methacrylic acid or water under a relatively low pressure. A small amount of methyl vinylacetate was also present. The predominant side reaction was a polymer formation reaction. The carboxylation of 1, 2-hexadiene, however, did not proceed smoothly, and a great amount of tarry materials was obtained. The carboxylation products obtained in low yields (max. 15%) were exclusively the materials formed by a carbonyl attack on the central carbon of the allenic structure, that is, methyl *trans*-2-methyl-2-hexenoate and methyl 2-butyl-2-propenoate.

Reaction of Anisole with Carbon Monoxide under High Pressure. Yoshimasa Takezaki, Akira Inoue, Nobuyuki Sugita, Hiroshi Teranishi and Kiyoshi Kudo. *Bull. Japan Petrol. Inst.*, **9**, 45 (1967).—A kinetic study has been made of the synthesis of *o*- and *p*-anisaldehyde from anisole-BF₃ complex and CO in hydrogen fluoride solution. In the preliminary investigation a new white complex was obtained below -60°C, the composition of which was 1 mole anisole-2 moles BF₃-1 mole HF with a m. p. of -60°C. The apparent equilibrium constant for the complex formation has been determined to be 219 at 0°C on the assumption of the existence of *o*- and *p*-complex of σ -type. As to the reaction of anisole with CO, the conditions enabling the liquid phase reaction rate-determining were found to be: a charge ratio of Anisole/HF < 30, a stirring speed above 750 rpm and an operational temperature below 60°C; the latter being essential to prevent side reactions leading to the formation of tarry matter. The rate of each *o*- and *p*-aldehyde formation is of the first order with respect to the dissolved CO and the complex respectively. The apparent rate constants are 6.67×10^{-3} (kg⁻¹ cm². min⁻¹) for *o*- and 4.23×10^{-3} for *p*-aldehyde formation at 40°C and the apparent activation energies 9 kcal·mole⁻¹ for both products. Compared with the rates of the same reaction with toluene and *m*-xylene, the rate constant of anisaldehyde formation is much smaller.

Synthesis of Alkali Malonates from Alkali Acetates, Carbonates and Carbon Dioxide under High Pressure. Kiyoshi Kudo and Yoshimasa Takezaki. *Kogyo Kagaku Zasshi*, **70**, 2147 (1967), in Japanese.—Reaction of alkali acetates with carbon dioxide and alkali carbonates to produce alkali malonates has been studied under high pressure:



The optimum conditions for the synthesis of malonate have been decided as follows: charge mole ratio of potassium acetate to potassium carbonate is 2 or higher; reaction temperature, 250~260°C; pressure of carbon dioxide, 400 atm or higher; and reaction time, 2 hours or longer. Under these conditions the yield of the malonate is 50~60 mole % based on the charged acetate. Only potassium carbonate can give a good result, but as for acetate sodium salt is also as effective as potassium salt. The reaction course must consist of the following steps: at

first the reaction takes place between solid reactants and gaseous carbon dioxide, but when a small amount of malonate is produced it is then dissolved in the neighboring acetate and liquefy the mass owing to the reduction of melting point, and on the later stage the reaction proceeds in the molten liquid phase to the final equilibrium. The apparent equilibrium constant for the over-all reaction in the liquid phase reaction has been determined to be 7.9×10^{-4} (atm⁻¹) at 250°C.

The Reaction of Enamines with Aromatic Isothiocyanate. Ryohei Oda, Akira Miyasu and Masaya Okano. *Nippon Kagaku Zasshi*, 88, 96 (1967), in Japanese.—Pyrrolidino- and piperidinoenamines react with aromatic isothiocyanates at 120°C for 5~25 hr. without solvent to give the corresponding amidines, probably arising from the decomposition of cyclic 1 : 1-adducts. Under appropriate conditions in which the reaction time is limited to a few hours and, if necessary, an excess amount of isothiocyanate is used, a cyclic 1 : 2 enamineisothiocyanate adduct is successfully isolated in addition to amidine. It is also found that the 1 : 2-adduct yields amidine, not the original enamine, and isothiocyanate by heating at 120°C. Based on these results, a probable reaction path has been proposed.

Addition Cyclization of Vinyldiazomethane with Dimethyl Fumarate and Fumaronitrile. Iwao Tabushi, Kunihiro Takagi, Masaya Okano and Ryohei Oda. *Nippon Kagaku Zasshi*, 88, 353 (1967), in Japanese.—The addition cyclization of vinyldiazomethane with dimethyl fumarate and fumaronitrile was investigated. The fumarate gave dimethyl 5-vinyl-*D*²-pyrazoline-3, 4-dicarboxylate quantitatively, as maleate did, but the pyrazoline from fumarate consisted of cis(70%) and trans(30%), while that from maleate was exclusively trans.

Both of the pyrazolines gave the same known carboxylic acid, 5-vinyl-*D*²-pyrazoline-3-carboxylic acid on alkaline hydrolysis.

Fumaronitrile gave 5-vinyl-3-cyanopyrazole which seems to be derived from 5-vinyl-3, 4-dicyano-*D*²-pyrazoline through spontaneous de-hydrogencyanidation. The cyanopyrazole was converted to the known pyrazole-1, 3-dicarboxylic acid.

Interpretation was given for the stereochemistry of the addition cyclization of fumarate and for predominant 1, 3-addition cyclization of electronically symmetric acceptor olefins with vinyldiazomethane.

The Formation of A Poly-S-Ylide. Shigeo Tanimoto, Jiro Horikawa and Ryohei Oda. *Kogyo Kagaku Zasshi*, 70, 1269 (1967), in Japanese.—*p*-Vinylbenzylmethyl sulfide was prepared from *p*-chlorostyrene via the corresponding Grignard compound, and it was polymerized with divinylbenzene in bulk using AIBM as initiator. The copolymer was then treated with methyl iodide to achieve the conversion of sulfide groups in it into sulfonium groups. When a mixture of the above resin and benzaldehyde was treated with potassium *t*-butoxide in DMSO, the starting sulfide resin and styrene oxide were obtained. This transformation can be rationalized by assuming the intermediate formation of the corresponding poly-S-ylide.

Synthesis of Polyamidebenzimidazoles. Jiro Horikawa, Shigeo Tanimoto and Ryohei Oda. *Chemistry of High Polymers*, 24, 501 (1967), in Japanese.—Some

polyamidebenzimidazoles were prepared in 80~90% yield by solution polycondensation of 1, 2, 4-triaminobenzene dihydrochloride with dicarboxylic acid in polyphosphoric acid.

In these polycondensation reactions, polyphosphoric acid acts as condensing agent as well as solvent.

Their preparation and physical properties, such as thermal stabilities, and solubilities, are described.

In comparison with polybenzimidazoles, it was observed that polyamide benzimidazoles have the same excellent thermal stabilities and less solubilities in solvents such as N, N-dimethylformamide and dimethylsulfoxide.

Reactions of P-Ylides with Sulphenese. Yoshihiko Ito, Masaya Okano and Ryohei Oda. *Tetrahedron*, **23**, 2137 (1967).—The reactions of stable P-ylides with sulphonyl chlorides in the presence of triethylamine have been investigated. P-ylides bearing an α -hydrogen such as carbethoxymethylene- and benzoylmethylene-triphenylphosphoranes react with methanesulphonyl chloride to yield α -sulphonated P-ylides (A). On the other hand, if P-ylides having no α -hydrogen are used, episulphones (B) or their decomposition compounds, olefins (C), and (alkanesulphonyl)methylene P-ylides (the sulphene insertion compounds) (D), are obtained. The ratio of B and D is 4 : 1 in the reaction with fluorenylidetriphenylphosphorane, but D is usually the principal product in the reaction with a series of α -carboalkoxy (or carbophenoxy)ethylenetriphenylphosphoranes.

The α , β -Addition of Amide Chlorides to Various Unsaturated Bonds and the Chemistry of the Adducts. Yoshihiko Ito, Seiichi Katsuragawa, Masaya Okano and Ryohei Oda. *Tetrahedron*, **23**, 2159 (1967).—It has been found that the reactions of amide chlorides with various unsaturated compounds such as enamines, benzalamines, carbodiimides, phenyl isocyanate and sulfurylaniline proceed in the manner of α , β -addition to give the corresponding 1 : 1-adducts in fair yields. These adducts can be effected by water, amines, alcoholates, malonate, LAH, phenyl magnesium bromide, and active zinc-copper complex, as well as by heating. Some results on these transformations are given.

Optically Active Organotin Compounds. Preparation and Reaction of (1-Methyl-2, 2-Diphenylcyclopropyl) Trimethyltin. Keiiti Sisido, Sinpei Kozima and Kôiti Takizawa. *Tetrahedron Letters*, **No. 1**, 33 (1967).—A synthesis of a compound with tin atom attached to an asymmetric carbon was carried out and the cleavage of the tin-carbon bond with hydrochloric acid and iodine was performed in order to examine the reaction mechanism.

Synthesis of Boshnia-Lactone and the Stereoisomers. Keiiti Sisido, Takao Kageyama, Hiroshi Mera and Kiitirô Utimoto. *Tetrahedron Letters*, **No. 16**, 1553 (1967).—In continuation of the preparation of cyclopentane derivatives, syntheses of all stereoisomers of lactone of 2-hydroxymethyl-3-methyl-cyclopentylacetic acid. One of the isomers was identified as the (\pm)-form of the natural product (boshnia-lactone). Stereochemistry of the synthesis was discussed.

Fragrant Flower Constituents of Osmanthus Fragrans. II. Keiiti Sisido,

Seizi Kurozumi, Kiitirô Utimoto and Tyûzô Isida. *Perfumery Essent. Oil Record, London*, 58, 212 (1967).—Comparison of the fragrant flower constituents of *osmanthus fragrans* Lour. var. *aurantiacus* Makino (in Japanese: Kinmokusei) collected on the campus of Kyoto University with a concrete imported from Mainland China was carried out. Except that the Chinese concrete is lacking in the lower boiling fractions and contains oxidized products, the essential parts of the constituents were similar. The main ingredients were found to be: ethyl caproate, β -phellandrene, *n*-hexanol, γ -hexenol (leaf alcohol), nonanal, (–)-linalool and the oxidized products, nerol, geraniol, dihydro- β -ionone, α -ionone, β -ionone, (+)- γ -decalactone.

Fragrant Flower Constituents of *Daphne Odora* Thunberg. Keiiti Sisido, Seizi Kurozumi and Kiitirô Utimoto. *Perfumery Essent. Oil Record, London* 58, 528 (1967).—Gas chromatographic examination of the essential oil *Daphne odora* Thunberg (in Japanese, Zintyôge) collected in early spring from two trees planted in the home garden of one of the authors (S.) showed that the constituents were:

β -phellandrene, *n*-hexanol, γ -hexenol(leaf alcohol), nonanal, *trans*-linalool oxide, *cis*-linalool oxide (–)-linalool, citronellyl acetate, neral, geraniol, (–)-citronellol, nerol and geraniol.

An oil prepared by mixing the constituents exhibited a fairly similar odor.

Direct Synthesis of Organotin Compounds. IV. Reaction of Benzyl Chloride with Metallic Tin. Keiiti Sisido, Sinpei Kozima and Tuneo Hanada. *J. Organometal. Chem.* 9, 99 (1967).—By the investigation of the solvent effects in the reaction of benzyl chloride and tin powder, it was elucidated that dibenzyltin dichloride was formed at first, and the conversion into tribenzyltin chloride occurred in polar solvents. In water, bis(dibenzylchlorotin) oxide was an intermediate in the conversion. Catalytic effects in the reaction was also studied.

Direct Synthesis of Organotin Compounds. V. Di- and Trialkyltin Chlorides and Bromides. Keiiti Sisido, Sinpei Kozima and Takao Tuzi. *J. Organometal. Chem.* 9, 109 (1967).—Di- and trialkyltin chlorides were prepared in good yields by the direct reaction of alkyl chloride with metallic tin when organic ammonium halides or a mixture of organic base and iodine-compound was used as the catalysts. Distribution of di- and trialkyltin chlorides varied with the kind and the amount of organic base, and reaction conditions. In the presence of a large amount of organic base, pure trialkyltin chloride was obtained. For the direct synthesis of alkyltin bromides, iodine source was not necessary.

Asymmetric Synthesis in Methoxy-mercuration of α , β -Unsaturated Esters. Junichi Oda, Tsutomu Nakagawa and Yuzo Inouye. *Bull. Chem. Soc. Japan*, 40, 373 (1967).—The methoxy-mercuration of (–)-menthyl crotonate, cinnamate and β -methylcinnamate resulted in partial asymmetric syntheses of the corresponding β -methoxylated derivatives, (–)-(*R*)- β -methoxybutyric acid, (–)-(*S*)- β -methoxy- β -phenylpropyl alcohol and (–)-(*S*)- β -methoxy- β -phenylbutyl alcohol. The results suggested an ionic mechanism involving a cyclic mercurinium ion as an intermediate which formed by electrophilic attack of mercuric acetate from the least hindered side of the double bond in the Cram-Prelog model of the systems, followed

by the attack of the methoxide ion from the opposite side. The reaction mechanism leading to the predominant enantiomers was discussed.

Optical Rotatory Dispersion of *trans*-Cyclane-1, 2-dicarboxylic Acid Thionamide. Yuzo Inouye, Seizi Sawada, Minoru Ohno and H. M. Walborsky. *Tetrahedron*, **23**, 3237 (1967).—Anomalous rotatory dispersion curves of thionamides derived from optically active *trans*-cyclane-1, 2-dicarboxylic acids involving 3, 4, 5 and 6-membered rings were investigated. The thionamides showed pronounced Cotton effects associated with their $n \rightarrow \pi^*$ absorption bands. The (*R*:*R*)-acid derivatives of the 3, 5 and 6-membered rings exhibited negative Cotton effects and on the basis of this empirical correlation, (–)-*trans*-cyclobutane-1, 2-dicarboxylic acid has been assigned the (1*R*:2*R*)-configuration.

Blätteralkohol XVI. Über Reaktionsmechanismus der Blätteralkohol-Reaktion. Akikazu Hatanaka, Tadahiko Kajiwara and Minoru Ohno. *Agr. Biol. Chem.*, **31**, 964 (1967), in German.—2-Methyl-4, 6-cyclohexadienaldehyde and *n*-butylaldehyde were treated with sodium in *p*-xylene to yield the aromatized “leaf alcohol reaction” product, 2-methylbenzyl alcohol, in a better yield than that with the cyclohexadienaldehyde alone. *n*-Butylic acid isolated from the reaction mixture unequivocally corroborated the operation of the crossed Cannizzaro disproportionation in this reaction, aliphatic aldehyde serving as the hydride donor. 2-Propyl-5-ethyl-4, 6-cyclohexadienealdehyde obtained by the NaOH-catalyzed Michael-Aldol condensation, gave 2-propyl-5-ethylbenzyl alcohol along with caproic acid under a similar condition in the presence of *n*-hexylaldehyde.

Blätteralkohol XVII. Über Blätteralkohol-Reaktion zwischen Blätteralkohol und Crotylalkohol. Akikazu Hatanaka, Tadahiko Kajiwara and Minoru Ohno. *Agr. Biol. Chem.*, **31**, 969 (1967), in German.—The leaf alcohol reaction with a mixture of leaf alcohol and crotyl alcohol under the standardized condition gave four kinds of the cross-bred products, 2-methyl-, 2-propyl-, 2-methyl-5-ethyl-, and 2-propyl-5-ethyl-benzyl alcohols, in accordance with the expectation from the previously proposed reaction mechanism.

Solvent Effect in Asymmetric Synthesis (Short Communication). Yuzo Inouye, Shuji Inamasu and Michio Horiike. *Chem. Ind. (London)*, 1967, 1293.—The *cis/trans* ratio as well as *trans*-(*R*:*R*)/(+)-(*S*:*S*) ratio of cyclopropane products in the NaH-catalyzed Michael type condensation of (–)-menthyl chloropropionate with methyl methacrylate, conducted in media of continuous dielectric constant, unequivocally showed the dependence of stereochemistry of the reaction on solvent polarity. The solvent effect was also correlated fairly well in quantitative terms by the Kirkwood-Onsager theory.

Optically Active Aromatic Chromophore VII. Evidence for the Optically Active ¹La Transition. Lawrence Verbit and Yuzo Inouye. *J. Am. Chem. Soc.*, **89**, 5717 (1967).—Evidence was presented for the direct observation of the optically active ¹La transition of phenyl group, by means of the UV and CD spectra of a series of structurally related cyclopropane derivatives of established absolute con-

figuration : (-)-(1*R*: 2*R*)-*trans*-2-phenylcyclopropanecarboxylic acid (I), (-)-(1*R*: 2*R*)-*trans*-1-methyl-2-phenylcyclopropane (II) and (-)-(1*R*: 2*R*)-*trans*-2-methylcyclopropanecarboxylic acid (III). The isotropic absorption spectrum of (I) exhibited a peak at 222 nm and the CD spectrum possessed a negative Cotton effect corresponding to this peak. The 222-nm Cotton effect was also present in II. The negative sign of this Cotton effect is characteristics of a phenyl ring attached to a disubstituted cyclopropane derivative. Assignment of the 222-nm peak in the isotropic absorption spectrum of II to the ¹La transition of the phenyl ring was substantiated by the absence of a corresponding peak in the spectrum of III.

The Progress of the Chemistry of Natural Products and a View for the Future. Eiichi Fujita. *Kagaku no Ryoiki, Zokan 80 : Tennen-butsu Kagaku '67*, 188 (1967), in Japanese.

On the Constituents of *Nauclea orientalis* L. I. Noreugenin and Naucleoside, A New Glycoside. (Terpenoids V). Eiichi Fujita, Tetsuro Fujita and Toyoko Suzuki. *Chem. & Pharm. Bull. Tokyo* 15, 1682 (1967).— β -Sitosterol, noreugenin, palmitic acid, and naucleoside, a new triterpene glycoside, have been isolated from *Nauclea orientalis* L. The direct isolation of 2-methyl-5, 7-dihydroxychromone (noreugenin) from natural source has never been published, although it has been synthesized and also derived from eugenin by demethylation.

Upon acidic hydrolysis, naucleoside gave quinoic acid as the aglycon, together with D-xylose and L-rhamnose as the sugar moiety. The order of linkage is shown to be represented by D-xylose—L-rhamnose—(C-3)-quinoic acid.

Terpenoids. VI. Isolation of Enmein and its 3-Acetate from *Isodon japonicus* Hara. Eiichi Fujita, Tetsuro Fujita and Masayuki Shibuya. *Yakugaku Zasshi*, 87, 1076 (1967), in Japanese.—Enmein is aditerpenoid bitter principle which has been isolated from *Isodon trichocarpus* Kudo. This paper deals with isolation of enmein and a related diterpene from *Isodon japonicus* Hara. The latter proved to have the structure of enmein 3-acetate on the basis of spectral and chemical evidence.

Studies on the Constituents of the Stems of *Isodon trichocarpus* Kudo. Eiichi Fujita, Tetsuro Fujita and Nozomu Ito. *Yakugaku Zasshi*, 87, 1150 (1967), in Japanese.—Constituents of stems of *Isodon trichocarpus* Kudo were investigated. The presence of stigmaterol and β -sitosterol was recognized on the vapor phase chromatogram. Ursolic acid was converted to its methyl ester acetate and identified with the authentic sample. Oleanolic acid was identified as a minor component through the conversion into its methyl ester and purification of the methyl ester with column chromatography. As diterpene components enmein and oridonin were isolated.

Studies on the Constituents of *Ophiorrhiza japonica* Bl. Eiichi Fujita and Akihisa Sumi. *Yakugaku Zasshi* 87, 1153 (1967), in Japanese.—An attempt was made to investigate the ethereal extract of *Ophiorrhiza japonica* Bl. and harman, fridelin and β -sitosterol were isolated. The methanolic extract gave also harman as a sole alkaloid.

The Structure and Stereochemistry of Trichokaurin, a New Diterpenoid from *Isodon trichocarpus* Kudo. Eiichi Fujita, Tetsuro Fujita and Masayuki Shibuya. *Chem. Commun.* 1967, 148.—The authors isolated a new kaurene-type diterpenoid, which was given the name trichokaurin, from the leaves of *Isodon trichocarpus* Kudo. Periodate oxidation of tetraol which was obtained by treatment of trichokaurin with lithium aluminum hydride afforded a hemiacetal lactone. The latter or hydrogenation using Adams' catalyst followed by oxidation with Jones' reagent yielded dihydro-1-*epi*-3-deoxydehydroenmein. This and the other reactions and spectral data led to an assignment of the structure including its stereochemistry to trichokaurin.

Oridonin, a New Diterpenoid from *Isodon* Species. Eiichi Fujita, Tetsuro Fujita, Hajime Katayama and Masayuki Shibuya. *Chem. Commun.* 1967, 252.—The authors isolated a new diterpenoid, oridonin, from *Isodon japonicus* Hara and *I. trichocarpus* Kudo. The carbon skeleton and the functional groups were established by converting oridonin into dehydrotetrahydroisodocarpin by a series of reactions. Further chemical reactions and spectral investigations led to the establishment of the structure and absolute configuration of oridonin.

Acyloin Condensation with Some γ -Lactone Esters. Eiichi Fujita, Tetsuro Fujita, Hajime Katayama and Sonoko Kunishima. *Chem. Commun.* 1967, 258.—The reaction of a lactone ester derived from enmein, a diterpene of *Isodon* species, with sodium in liquid ammonia gave an oily abietane derivative, 6-hemiketal-7-ol derivative, as a major product, but the use of a large excess of sodium resulted in an increase of the yield of a triol and a diol. Subsequently, a new lactone diester was prepared from enmein, and it was allowed to react with sodium in liquid ammonia to give two acyloin products, both of which proved to have 6-hemiketal-7-ol structure. Thus, in either case, the major product was found to be the thermodynamically more stable hemiketal, in agreement with a study of stereomodels.

On the Stereochemistry of the Acetoxy-group at C-15 in Trichokaurin. Eiichi Fujita, Tetsuro Fujita and Masayuki Shibuya. *Chem. Commun.* 1967, 466.—Recently, we isolated a new kaurene-type diterpene from *Isodon* species and named trichokaurin. A structure for trichokaurin was suggested and the S-configuration of the acetoxy-group at C-15 was tentatively assigned on an assumption. But now, we reached the conclusion that the assignment was incorrect and trichokaurin has the R-stereochemistry at C-15. The evidence was based on the spectral data and chemical conversions.

The Chemical Conversion of Trichokaurin into (-)-Kaurene, Atisine, Garryine, and Veatchine. Eiichi Fujita, Tetsuro Fujita and Masayuki Shibuya. *Chem. Commun.* 1967, 468.—This communication deals with the chemical conversion of trichokaurin into (-)-16-keto-10-carboxy-17, 20-bisnorkaurane. A keto-diacetate which was derived from trichokaurin through four steps of reactions was allowed to react with calcium in liquid ammonia to afford an alcoholic ketone and triol. Subsequently, Nagata's modification of the Wolff-Kishner reduction

was applied to the triol. The product was hydrogenated and oxidised with Jones' reagent at room temperature to afford (-)-16-keto-10-carboxy-17, 20-bisnor-kaurane. Since the latter has been converted into (-)-kaurene, atisine, garryine, and veatchine, this transformation means the chemical conversion of trichokaurin into (-)-kaurene and those diterpene alkaloids.

Synthesis of Abietane and Transformation of Enmein into *enantio*-Abietane. Eiichi Fujita, Tetsuro Fujita and Hajime Katayama. *Chem. Commun.* **1967**, 968. —We converted abietic acid into abietane: catalytic hydrogenation of abietic acid or dihydroabietic acid gave all-*trans* tetrahydroabietic acid, whose methyl ester was reduced to an alcohol with lithium aluminum hydride. The alcohol, on oxidation with Jones' reagent at 0°, gave an oily aldehyde, which was subjected to a modified Wolff-Kishner reduction to give abietane. This means a total synthesis of abietane.

We also carried out the conversion of enmein into *enantio*-abietane. The route contains acyloin condensation of the lactone ester derived from enmein and the reductive elimination of its oxygenated functional groups.

The Structures of Lythranine, Lythranidine, and Lythramine, Novel Alkaloids from *Lythrum anceps* Makino. Eiichi Fujita, Kaoru Fuji, Kiyoshi Bessho, Akihisa Sumi and Shigetake Nakamura. *Tetrahedron Letters*, **1967**, 4595.—We isolated three new alkaloids, lythranine, lythranidine, and lythramine from *Lythrum anceps* Makino and investigated their structure.

Many spectral data and chemical evidence led to the assignment of the structures to these alkaloids. They are characteristic in structure having diphenyl moiety and a macro ring containing one piperidine molecule.

Polymer Chemistry

Studies on the Structure and Physical Properties of Crystalline Polystyrene. (II). Effects of Stereoregularity and Molecular Orientation on the Physical Properties of Isotactic Polystyrene. Fumio Sakaguchi, Ryoza Kitamaru and Waichiro Tsuji. *Sen-i Gakkaishi*, **23**, 18 (1967), in Japanese.—The mechanical properties of crystalline polystyrene (IPS) with different tacticities were studied as a function of crystallinity and molecular orientation.

It was found that both tensile strength and Young's modulus of crystalline isotactic polystyrene decrease, but its impact strength slightly increases by annealing sufficiently at 180°C, independent of the degree of crystallinity and molecular weight ($\bar{M}_v = 3.4 \sim 24.40 \times 10^5$). In this case, the ratio of the tensile strength to the modulus is a constant value of 0.01, regardless of draw ratio. These results may be well interpreted in accordance with Buchdahl's consideration for glassy state of polymer.

The intrinsic birefringence, Δn_c° for a model crystal of polystyrene with perfect *c*-axis orientation was calculated as -0.080 and -0.133 respectively with use of Denbigh's and Bunn's values for the bond principal polarizabilities. The birefringence is generally recognized to increase with draw ratio, approaching

an equilibrium value at about 400% of drawing. The contributions of crystalline and amorphous phases to the birefringence are estimated separately under an assumption of additivity of the contribution of both phases. The total birefringence, Δn may be expressed as $\Delta n = X\Delta n_c + (1-X)\Delta n_a$, and $\Delta n_c = fn_c^0$, where Δn_c and Δn_a are birefringences of crystalline and amorphous phases per unit volume, X the volume fraction of crystalline phase, and f the orientation parameter. Using the values of X and f obtained from x-ray study, each term of the equation is discussed. As a result, it was found that $X\Delta n_c$ increased monotonously with draw ratio, while $(1-X)\Delta n_a$ approached a maximum value at about 350% drawing.

It is recognized by studying the dynamic mechanical properties of the samples that in a plot of loss tangent versus temperature, the temperature where the loss tangent through a maximum due to molecular mobility in amorphous phase is independent of either the degree of crystallinity, or the draw ratio.

Studies on the Structure and Physical Properties of Crystalline Polystyrene.

(III) Mechanical Properties of Copolymers of Styrene with α -Olefins. Fumio Sakaguchi, Ryoza Kitamaru and Waichiro Tsuji. *Sen-i Gakkaishi*, 23, 25 (1967), in Japanese.—Mechanical properties of copolymers of styrene with some α -olefins produced with stereospecific catalysts are studied in relation to the kind of the opponent comonomers and the copolymerization ratios. As the opponent comonomers, such linear α -olefins as pentene-1 heptene-1 and decene were used.

It was found that for all the copolymers examined the tensile modulus and tensile strength were varied as a function of the density, irrespective of the comonomer sorts, whereas the tensile elongation depended on the composition of the copolymer and on the character of the comonomers. The results may indicate that the mechanical properties of the copolymers are not in a simple relation to the composition ratio and the natures of the comonomers, but greatly dependent on the crystallizability of the comonomers. This is in good accordance with the results reported by R. W. Ford for the copolymers of ethylene and linear α -olefins.

It was also found that the brittleness of crystalline polystyrene is much reduced by incorporating small amount of heptene-1 or decene-1 as comonomers without much lowering of the melting temperature. The difficulties of drawing process of crystalline polystyrene fiber after melt-spinning may be overcome by using such copolymers.

Mechanical Properties of Polypropylene-Styrene Graft Copolymer. Waichiro Tsuji and Hyong-Dong Chu. *Sen-i Gakkaishi*, 23, 145 (1967), in Japanese.—Static and dynamic mechanical properties of polypropylene-styrene graft copolymer were studied in comparing with those of polypropylene-polystyrene blend and each homopolymer. These properties were interpreted in relation with their structure.

Yield stress and strength at break of graft copolymer were increased with the increase of styrene content, but Young's modulus did not change remarkably and elongation at break decreased with grafting more than the value of polypropylene homopolymer but was still greater than the value for polystyrene homo-

polymer and blend.

In stress-strain curve, a yield point was observed in graft copolymers and for polypropylene, but not observed in blend and polystyrene.

The shape of loss modulus-temperature curve and the peak position of the absorption curve for the graft copolymer are different from that in the blend. Moreover, the curve for the graft copolymer whose powder or small pieces of the film was mixed and melt pressed was different from the curve for the original graft copolymer film, annealed after grafting. The absorption curve for the graft copolymer and blend showed two peaks; one at about 10°C and another at 110~120°C. The former absorption indicates the α_a -absorption of polypropylene which is due to the segmental motion of amorphous chains of the polymer and the latter absorption indicates the main dispersion of polystyrene.

The peak temperature of the absorption curve at the higher temperature region for the original graft copolymer and blends agrees with the temperature for polystyrene, but the peak temperature for which was melt pressed and annealed graft copolymer shifted about 10°C to higher temperature side from the peak temperature for polystyrene. This shift suggests that the molecular mobility of polystyrene branches in the graft copolymer may be restricted by the crystallites of polypropylene. In other words, polystyrene branches exist in the circumstance where crystallites of polypropylene may affect the molecular motions of the polystyrene branches.

In the case of blends polystyrene molecules must be excluded from crystallites, and in the original graft copolymer the grafting must take place only on the amorphous chains of polypropylene.

Dynamic Mechanical Properties of Polypropylene-Polyethylene Blend. Waichiro Tsuji and Hyong-Dong Chu. *Sen-i Gakkaishi*, 23, 152 (1967), in Japanese. —Static and dynamic mechanical properties of the blend of polypropylene and low density polyethylene were studied.

Tensile strength and Young's modulus of the blends increases with the increased weight content of polypropylene component, but the elongation at break of the blend which contains 50 wt. % of polypropylene or polyethylene is smaller than the value for each homopolymer and other blends. Also the elongation at break diminishes to a very small value by a heat treatment at a high temperature.

In the viscoelastic absorption curves (dynamic loss vs. temperature curves) for blends only one apparent peak is observed in the vicinity of room temperature for samples whose content of polypropylene are more than 50 wt. % and annealed at low temperature such as 90°C, but two peaks are separated for a sample containing 25 wt. % of polypropylene. The one peak for samples containing large amount of polypropylene separates into two peaks by an annealing at a high temperature such as 120°C or by a slow cooling from the melt.

These mechanical properties are interpreted in relation with the fine structure of blends and it is concluded that the change of the mechanical properties with a heat treatment must arise from the phase separation by proceeding crystallization.

Crystalline Transformations and Mechanical Properties of Polyolefin Fibers.

(I) Properties of Polybutene-1 and its Copolymers. Fumio Sakaguchi, Waichiro Tsuji, Takashi Yamazaki, Toshio Kitao and Shogo Oya. *Sen-i Gakkaishi*, 23, 254 (1967), in Japanese.—Mechanical properties of fibers and films of isotactic polybutene-1 and its copolymers were studied in relation to the crystalline transformation of the Form II to Form I.

No difference in the tensile strengths of fibers and films was recognized for the both crystalline forms, but there is a remarkable difference in the tensile elongation. Polybutene-1 fiber of the Form II shows much more drawability than that of the Form I. It is known that molecular and crystalline orientations in polybutene-1 fiber are more affected by drafting in melt-spinning than by drawing after spinning on account of accelerated transition due to drafting of the Form II to Form I.

An interesting feature of the copolymers of butene-1 with 3-methyl-1-butene or 4-methyl-1-pentene is an ability to cocrystallize in type of the Form II of polybutene-1. Though it is known that the Form II of butene-1 homopolymer is less stable at room temperature than the Form I, it was found that the Form II of those copolymers is stabilized owing to incorporation of those comonomer units into the crystal lattice of the Form II. Therefore, it is expected to improve the adverse properties such as the difficulty of drawing after spinning and the devitrification caused by crystal transition of polybutene-1 without lowering of its melting point, tensile strength and flexibility.

Crystalline Transformations and Mechanical Properties of Polyolefin Fibers

(II) Properties of Polypentene-1 and its Copolymer with 3-Methyl-1-Butene. Fumio Sakaguchi and Waichiro Tsuji. *Sen-i Gakkaishi*, 23, 306 (1967), in Japanese.—Physicochemical and mechanical properties of crystalline polypentene-1 and its copolymer with 3-methyl-1-butene were studied. The Form II, one of the two crystalline modifications of polypentene-1 was stable at room temperature and transformed gradually to another modification, Form I, by annealing at temperature range from 50°C to 80°C.

Though mechanical properties of films or fibers of the both crystalline forms are affected by the degree of crystallinity, there is no essential difference in the tensile properties. It was found that copolymer of pentene-1 with 3-methyl-1-butene can cocrystallize in the Form II of polypentene-1 over the whole range of composition, and their melting points change continuously from 80°C of polypentene-1 to 300°C of poly(3-methyl-1-butene) according to the composition.

Although the crystalline copolymer of pentene-1 with minor 3-methyl-1-butene composition has almost the same poor tensile properties as pentene-1 homopolymer, the melting point of polypentene-1 increases by the copolymerization.

It is also recognized that the copolymerization of major 3-methyl-1-butene with pentene-1 is effective to decrease the characteristic brittleness of poly(3-methyl-1-butene).

Modification of Synthetic Fiber by the Graft Copolymerization of Reactive Monomer. 1. Graft Copolymerization of Acrylic Acid onto Polypropylene Fiber. Waichiro Tsuji, Tetsuo Ikeda, Yoko Kurokawa and Noboru Nakatani. *Sen-i Gak-*

kaishi, 23, 327 (1967), in Japanese.—Acrylic acid was graft copolymerized onto polypropylene fiber and fabric using Co^{60} γ -ray preirradiation method.

As the grafted polypropylene has reactive groups such as carboxyl groups in the grafted side chains, some aftertreatments including cross-linking can be achieved using these reactive groups.

Some properties of the acrylic acid grafted and aftertreated polypropylene fiber and fabric were examined.

The results are summarized as follows :

(1) Tensile properties such as dry, wet and knot tenacity and elongation of the grafted and aftertreated fibers are equal to that of original polypropylene fiber.

(2) Heat shrinkage of the fibers decreases considerably by acrylic acid grafting and the fiber grafted by 62 % shows heat shrinkage of 5~7 % and does not melt till 300°C.

(3) The effects of aftertreatment of the grafted fiber on the heat shrinkage are also remarkable. For example, greater heat stability is obtained by Ca-salt, NH_4Cl and epoxy treatments. Melting temperature of the polypropylene monofilament is not improved by acrylic acid grafting, but elevates to as high as above 300°C by the aftertreatment with inorganic salts of some metals such as Na and Ca.

(4) Tensile properties of the grafted and aftertreated fibers at elevated temperature do not improve as expected from the melting property.

(5) Moisture regain of polypropylene fabric increases by acrylic acid grafting and metal salts treatments. Especially in the case of Na-salt treatment the moisture regain is about 10 % in the 35.8 % grafted sample.

(6) It was found that the polypropylene fabric which is 20.5 % grafted with acrylic acid and converted into Na-salt has excellent dyeability for cationic dye and heat settability.

(7) Frictional static electricity of the acrylic acid grafted polypropylene monofilament and fabric decreases to about one half of the original polypropylenes. Conversion of the grafted acrylic acid to a hydrophilic Na-salt shows more remarkable decrease of frictional static electricity.

Modification of Synthetic Fiber by the Graft Copolymerization of Reactive Monomer. 2. Graft Copolymerization of Acrylic Acid onto Polyvinyl Chloride Fiber. Waichiro Tsuji, Tetsuo Ikeda and Yoko Kurokawa. *Sen-i Gakkaishi*, 23, 335 (1967), in Japanese.—Acrylic acid was graft copolymerized onto polyvinyl chloride (PVC) multifilament yarn using Co^{60} γ -ray irradiation and some properties of the fibers grafted and aftertreated were examined. The results are summarized as follows :

(1) Tensile properties of fibers such as dry and wet tenacity and elongation are almost unchanged by the grafting or aftertreatment.

(2) Heat shrinkage of the PVC fibers is decreased by acrylic acid grafting. The original PVC fiber shows the heat shrinkage up to about 60 % of its original length, while that of the 60.5 % grafted PVC fiber is below 10 %.

(3) The effects of the aftertreatments of the grafted fibers on the heat

shrinkage are remarkable. For instances, about 25 % grafted PVC fiber after-treated with $\text{Ca}(\text{CH}_3\text{COO})_2$ or APO shows heat shrinkage of only 10 % or below under 300°C.

(4) No improvement is resulted in tensile properties of the grafted and aftertreated PVC fibers at higher temperature in spite of their excellent heat stability.

Dynamic Mechanical Properties of Poly(4-methyl-1-pentene) Fractions. Fumio Sakaguchi, Waichiro Tsuji and Ryoza Kitamaru. *Kobunshi Kagaku*, **24**, 318 (1967), in Japanese.—The dynamic mechanical properties of poly(4-methyl-1-pentene) fractions were studied in relation to the fine structural heterogeneity which was estimated with various physicochemical properties. Some samples prepared by Ziegler-Natta catalytic system were fractionated by successive solvent extraction method with a series of solvents at their boiling points.

It was found that the stereoregularity of the fractions increased with higher extracting temperature, while the molecular weight of the fractions with higher stereoregularity remained approximately unaltered. The stereoregularity of the fractions was evaluated by making use of Miller's equation and it was concluded that the polymer could be regarded as a block copolymer composed of isotactic and atactic sequences.

By the measurements of the temperature dependence of dynamic mechanical properties in the temperature range from 0°C to 200°C, at the frequency of 110 c/s, it was found that the peak temperatures in $\tan \delta$ corresponding to the primary absorption for the undrawn slowly cooled crystalline films shifted to the lower temperatures as the degree of crystallinity of the samples increased, while for the drawn samples the primary absorption temperatures manifested in the maximum of the loss modulus shifted to the higher temperatures with increase of the stereoregularity. Furthermore, the effect of thermal history during the preparation of the films on the viscoelastic properties, and the secondary dispersion of E'' for samples probably caused by the crystalline phase were also investigated in relation to the stereoregularity. The characteristic bulk of this polymer indicated by the various experimental results may be interpreted in relation to the anomalous feature of the packing density of the polymer chains in the amorphous phase.

Crystallization of Copolymers of 3-Methyl-1-Butene with Olefins Produced by Ziegler-Natta Catalysts. Fumio Sakaguchi, Waichiro Tsuji and Ryoza Kitamaru. *Kobunshi Kagaku*, **24**, 493 (1967), in Japanese.—Copolymerizations of 3-methyl-1-butene with olefins such as butene-1, pentene-1, decene-1 and 4-methyl-1-pentene were carried out by using Ziegler-Natta catalytic systems.

In order to study the so-called isomorphism or cocrystallization phenomena between different comonomer units in the crystalline structures of the olefin copolymers crystallized from melt, the molecular and fine structures of the crystalline copolymers were investigated by the experimental information and discussion in relation to, 1) the chain conformations in crystalline structures of each olefin homopolymer, 2) dependence of the size of crystal lattice and phys-

icochemical properties such as crystallinity and melting point on the composition in the copolymer, 3) statistical analysis of the distribution of the sequence length of each comonomer unit in the copolymeric chains from the data of monomer reactivity ratios and 4) the constitution of the copolymeric chains in the amorphous phase by the measurement of viscoelastic properties.

All the copolymers cited here more or less indicated an evidence of the isomorphism or cocrystallization phenomena, in particular the copolymers with pentene-1 and 4-methyl-1-pentene showed strong tendency of it owing to the similarities of the molecular structure and the crystalline structure of each homopolymer, though in the copolymeric systems expect the copolymer with 4-methyl-1-pentene each comonomer unit was not always distributed at random but rather in blockwise. Furthermore, it was found that comonomer units of large size such as decene-1 having a steric hindrance due to the long side chain could not be incorporated into the crystal lattice as a crystallizable unit but only as a non-crystallizable defect.

The Physical Properties of Some Crystalline Olefin Copolymers. Waichiro Tsuji, Ryoza Kitamaru and Fumio Sakaguchi. *Annual Rep. Inst. Chemical Fibers, Kyoto Univ.*, 24, 15 (1967), in Japanese.—Various kinds of crystalline homo- and copolymers were synthesized from butene-1 pentene-1, 3-methyl-1-butene, 4-methyl-pentene, styrene and others with use of Ziegler's or Natta's catalyzer systems. And it is investigated whether the disadvantage properties of those homopolymers can be compensated or not by such copolymerizations.

In the copolymers of butene-1 with 3-methyl-1-butene or 4-methyl-1-pentene, as the result that the transformation in the crystalline from Form II to I characteristic of butene-1 homopolymers is prevented owing to the occurrence of the so-called isomorphism, the crystallinity can be hold over whole range in the copolymer components, and the low extensibility and the whitening of the fibers of butene-1 homopolymers could be improved without lowering their high melting temperature by the copolymerizations.

It is also found that both disadvantages of the extremely low melting temperature of homo-poly-pentene-1 as well as of the brittle property of homo-poly-3-methyl-1-butene could be compensated by the copolymerization of the monomers of these two homopolymers also owing to the isomorphism phenomenon in such copolymers.

Furthermore, the occurrence of isomorphism is also confirmed in the copolymers of 4-methyl-1-pentene and 3-methyl-1-butene and it is recognized that the negative temperature coefficient particularly above 50°C of the mechanical properties of poly-4-methyl-1-pentene could be relieved by copolymerization with 3-methyl-1-butene.

In addition it is also found that the brittleness of isotactic polystyrene can be alleviated by copolymerizing small amounts of pentene-1 or decene-1.

The Crystalline Structure of a Slightly Crosslinked Polyethylene Crystallized in the Stretched State. Ryoza Kitamaru, Hyong-Dong Chu and Waichiro Tsuji. *J. Polymer Sci.*, 5, 257 (1967).—An evidence has been first confirmed from the

birefringency study that by stretching in the completely molten state of a slightly crosslinked polyethylene, only closed chains terminated by two crosslinked units are stretched, while free chains belonging to the soluble fraction in the system or chains having one free end if belonging to the gel fraction can not be stretched. Based on this concept established, studies have been made of the crystalline structure of the sample crystallized from the molten and stretched state with x-ray techniques. As the result it is concluded that under such crystallization condition closed chains corresponding with the macroscopic stretching are first crystallized to result the so-called *c*-axis oriented crystallites whose chain axis is parallel to the stretching direction and an substantially isotropic crystallization in which the unstretched free chains involve will follow the foregoing oriented crystallization to result mostly the so-called *a*-axis oriented crystallites.

Broadening of Carbonyl Stretching Vibration Bands Appearing for Acrylate Copolymers. Fumio Kamiyama, Hisayuki Matsuda and Hiroshi Inagaki. *J. Phys. Chem.* **71**, 4153 (1967).—This communication deals with a preliminary result that the 1730 cm^{-1} band characteristic of C=O groups in methyl acrylate (MA)-styrene (ST) copolymers exhibited broadening with increase in the acrylate content without any shift of the band peak position. The half band width ($\Delta\bar{\nu}_b$ in cm^{-1}) decreases regularly with decreasing the MA content and was linearly proportional to the probability for finding the connection MA-MA-MA in the chain, P_3 , which was evaluated from the reactivity ratios for ST (1) and MA (2); $r_1=0.75$ and $r_2=0.20$ at 70°C [T. Alfrey *et al.*, *J. Polymer Sci.*, **1**, 37 (1946)].

Viscosity-Molecular Weight Relationships and Unperturbed Dimensions of Linear Chain Molecules. Michio Kurata, Masamichi Iwama and Kensuke Kamada. *Polymer Handbook* (edited by J. Brandrup and E. H. Immergut, Interscience Pub.), IV-1 (1967).—About 1000 relationships between intrinsic viscosity and molecular weight and 400 values of unperturbed dimensions of linear chain molecules were compiled from 450 references in the form of numerical table.

Dilute Solution Properties of Poly(α -substituted methyl acrylates). Part I. Poly(methyl ethacrylate) and Poly(methyl *n*-butacrylate). Masamichi Iwama, Hiroyasu Utiyama and Michio Kurata. *J. Macromol. Chem.* **1**, 701 (1967).—Viscosity and light-scattering measurements were carried out on poly(methyl ethacrylate) (PMEA) and poly(methyl *n*-butacrylate) (PMBA) in various solvents, including diisobutyl ketone (11.4°C , theta solvent for PMEA) and *n*-butanol (13.0°C , theta solvent for PMBA). Both polymers were prepared with a diethylzinc-calcium complex catalyst, and the measurements were performed on ten fractions of each polymer, which were obtained by means of the elution column method. Values of M_w/M_n (the ratio of weight-average to number-average molecular weights) of these fractions were about 1.05, as determined by the sedimentation velocity analysis. The intrinsic viscosity versus molecular-weight relationships were $[\eta]=4.29\times 10^{-5}M_w^{0.75}$ (methyl ethyl ketone, 30°C), $2.35\times 10^{-5}M_w^{0.82}$ (benzene, 30°C), and $6.76\times 10^{-4}M_w^{0.50}$ (diisobutyl ketone, 11.4°C) for PMEA in the range of M_w of 4.61×10^4 to 1.91×10^6 , and $[\eta]=5.43\times 10^{-5}M_w^{0.73}$ (methyl ethyl ketone, 30°C) and $5.59\times 10^{-5}M_w^{0.50}$ (*n*-butanol, 13.0°C) for PMBA in the range of M_w of 7.52×10^4 .

to 4.28×10^6 , respectively.

The unperturbed dimensions were essentially the same either in theta solvents or in good solvents. The ratio δ of the root-mean-square end-to-end distance of the unperturbed chain to that of the freely rotating chain was 2.15 for PMEA and 2.28 for PMBA. On the basis of a comparison of these σ values with those of poly(alkyl acrylates) and poly(alkyl methacrylates) it was suggested that in the α -substituted acrylic chains the preferred rotational angle may deviate from the typical trans and gauche angles.

Some Recent Aspects in Polymer Solution Theory. Michio Kurata. *Pure App. Chem.* **12**, 587 (1967).—A review on the theory of polymer solutions was given with emphasis on the significance of the "third-power" law for the excluded volume effect. The end-to-end distance, spherical statistical radius and hydrodynamic properties of flexible linear polymers were discussed. The hydrodynamic properties of poly-electrolytes was also discussed in the light of the "third-power" law theory.

Diffusion of Ethyl Methyl Ketone in Atactic Polystyrene Above the Critical Concentration. Hisashi Odani. *J. Polymer Sci. : Part A-2*, **5**, 1189 (1967).—Integral absorption and desorption of ethyl methyl ketone in atactic polystyrene were studied as a function of film thickness at 25 and 45°C with concentrations above the critical concentration of system. In all cases investigated, the reduced absorption and desorption curves for films of different thickness did not give a single curve though the individual absorption and desorption curves appeared to have the shape expected from the Fickian diffusion mechanism. The initial slopes of the reduced curves increased with increasing film thickness for both absorption and desorption. The quantity R_0 , the value of the reciprocal of the half-time for absorption or desorption extrapolated to zero concentration increment, provides a measure of absorption rate at a given initial concentration. The dependence of R_0 on film thickness was almost unaltered in the concentration region concerned at both temperatures. The values of the mutual diffusion coefficient, D , of the system were calculated by assuming absorption and desorption processes for hypothetical film of infinite thickness are controlled by the purely Fickian mechanism. The values of D evaluated by this method agreed quite well with those deduced by Kishimoto from steady-state permeation measurements.

Electron Microscopic Texture of A-B Type Block Copolymers of Isoprene with Styrene. Takashi Inoue, Toshiichi Soen, Hiromichi Kawai, Late Masaaki Fukatsu and Michio Kurata. *J. Polymer Sci. : Part B*, **6**, 75 (1967).—A-B Type block copolymers of isoprene with styrene were synthesized by a "living polymerization" technique. The relative proportions of A and B sequences was varied while the total chain length was held almost constant. The electron microscopic texture of the bulk copolymer, cast from toluene solution, was investigated by means of osmium tetroxide fixation. This revealed a systematic change of the texture, from spheres of polyisoprene component "floating" in a matrix of polystyrene to an alternating lamellar arrangement of the two components, with increase of the

fraction of isoprene sequences up to about 60% by weight.

Ellipsoid Model for Polyelectrolytes. Michio Kurata. *J. Polymer Sci. : Part C, No. 15*, 341 (1967).—The expansion factor of polyelectrolytes is calculated by using an equivalent ellipsoid model which is essentially the same as that used by Kurata, Stockmayer, and Roig in the theory of excluded volume effect of non-ionic polymers. The Donnan-Kimball approximate solution of the Poisson-Boltzmann equation is used for evaluating the electric free energy of a chain. The result is applied to the calculation of the intrinsic viscosity $[\eta]$ as a function of the molecular weight M and salt concentration ρ_s . As a consequence, $[\eta]$ is predicted to be expressible in the form

$$[\eta] = KM^{1/2} + 0.51\phi_0[B_n + B_e(\rho_s)]M$$

over a wide range of the variables. Here K , B_n and ϕ_0 are constants independent of M and ρ_s . In a limited range of large ρ_s values, for example 0.1~1 mole l^{-1} for a 1:1 added salt, the parameter $B_e(\rho_s)$ is proportional to ρ_s^{-1} ; but in the range of lower values of ρ_s , for example 0.005~0.1 mole l^{-1} , $B_e(\rho_s)$ becomes proportional to a lower inverse power of ρ_s . For still lower values of ρ_s , the above equation is no longer valid, because $B_e(\rho_s)$ becomes a function of M rather than of ρ_s . In this range, the polyelectrolyte chain is in an extended rodlike form.

Mechanical Properties of Polyethylene Crystals. II. Deformation Process of Spherulite. Keinosuke Kobayashi and Toshio Nagasawa. *J. Polymer Sci. : Part C, No. 15*, 163 (1967).—Optical and electron microscopy of the plastic deformation process of polyethylene spherulitic film revealed the variation of the process with the temperature. Even within a single spherulite the mode of deformation differs with the relative position in the overall deformation; hence it is hard to represent with a simple affine model. The morphological change can be classified by dividing a spherulite into a few zones by conical boundaries which incline 45° to the direction of stretching and pass the center of the spherulite. At 20°C , the unfolding of molecules takes place in two sectors; the concentric extinction patterns are disturbed, probably due to rotation or bending of lamellae. At 95°C , the necking or the unfolding of molecules is not detected in any sector but the deformation with the slip between or within lamellae occurs preferentially in two side sectors. The anisotropic parameters corresponding to the tensile and shear compliances of simple lamellar structures are estimated from mechanical properties of tubular extruded film in which lamellae pile up along the machine direction. Applying these values of parameters to the structure model of spherulite, the mechanism of its deformation is analyzed. One of these parameters which relates to shear deformation inducing the "slip" between or within lamellae is most sensitive to temperature and varies widely with the irradiation dose (number of crosslinkings).

Metals and High Polymers. Masao Horio. *Sen-i to Kogyo (Textiles and Textile Industry)*, 23, S 128 (1967), in Japanese.—The present state of knowledge on the structure and physical properties of high polymers is discussed in comparison

with those of metals. The characteristics of these two materials are treated in various aspects including mechanical properties, crystalline structures and deformation mechanisms.

Biochemistry

The Apparent Binding of DDT to Tissue Components. Akikazu Hatanaka, B. D. Hilton and R. D. O'Brien. *J. Agr. Food Chem.*, **15**, 854 (1967).—Sephadex chromatography of tissue homogenates incubated with C¹⁴-DDT provided apparent evidence of binding of DDT with cockroach nerve cord and rat liver, muscle and brain. Binding was not localized in any particular subcellular fraction of brain. The non-toxic analogs DDE and 1, 1, 1, 2-tetrachloro-2, 2-bis(*p*-chlorophenyl)-ethane were equally effective in such binding. Triton X-100 was more effective than tissue homogenates in permitting passage of DDT through Sephadex. Electrophoresis of brain preparations showed no migration of DDT with any fraction. Apparently, evidence for binding based on Sephadex is inadequate in the case of DDT and related compounds.

A Spectrophotometric Microdetermination of Keto Acids with 3-Methyl-2-Benzothiazolone Hydrazone. Kenji Soda. *Agr. Bio. Chem.* **31**, 1054 (1967).—Various keto acids react sensitively with 3-methyl-2-benzothiazolone hydrazone to form the azine derivatives, which give the characteristic ultraviolet absorption spectra. The effect of pH, temperature, reaction period, buffer and the concentration of the reagent on the reaction and the spectra were investigated. Optimal conditions for the microdetermination of keto acids were established. Microamounts of keto acids (0.02~0.3 or 0.4 μ mole) were determined rapidly by this simple method with satisfactory results. Amino acids, fatty acids and most inorganic salts did not interfere with the determination of keto acids.

Enzymatic Racemization of Leucine and α -Aminobutyrate. Kenji Soda and Takaharu Osumi. *Agr. Biol. Chem.* **31**, 1097 (1967).—The occurrence of a new amino acid racemase catalyzing the conversion of either D- or L-isomer of α -aminobutyric acid and leucine to the racemate was found in a cell-free extract of *Pseudomonas striata* which was isolated from soil and identified. The extract failed to oxidize or deaminate either isomer of the substrates, and the balance value showed that no net gain or loss of total substrates occurred during the course of racemization. The racemization reactions were confirmed not to be catalyzed by the combined reactions of alanine racemase and D- and L-amino acid transaminases, but by the specific racemase. Effect of the inhibitors and cofactors on the enzyme activity were investigated.

Occurrence of Arginine Racemase in Bacterial Extract. Kenji Soda, Takamitsu Yorifuji and Koichi Ogata. *Biochim. Biophys. Acta*, **146**, 606 (1967).—*Pseudomonas graveolens* IFO 3460 could utilize D-arginine as a sole nitrogen source. The sonic extract of this bacteria possessed the activity to racemize D- and L-arginine. It was shown that the extract failed to catalyze transaminase reactions between

D- and L-arginine and pyruvate or α -keto-glutarate, and that these keto acids had no effect on the reaction. Although the extract exhibited alanine racemase activity, these results exclude the possibility of racemization via the combined reactions of D- and L-amino acid transaminases and alanine racemase or another amino acid racemase, and allow to conclude that this racemization reaction is catalyzed by a single enzyme racemizing arginine *i. e.* arginine racemase.

Electrophoretic Separation of Complexes between Aminoacyl RNA Synthetase and Transfer RNA. Toshio Okamoto and Yoshimi Kawade. *Biochim. Biophys. Acta*, 145, 613 (1967).—Stable complexes of *t*-RNA and aminoacyl RNA synthetase were demonstrated and isolated from the bulk of unbound protein by sucrose density gradient electrophoresis, using a crude enzyme preparation from thermophilic bacteria. Glycyl RNA synthetase formed a stable complex with *t*-RNA from both the homologous and a heterologous species. Valyl and arginyl RNA synthetases also complexed with homologous *t*-RNA, but not, or only weakly, with yeast *t*-RNA, in spite of the cross reactivity of the valine enzyme with latter. Periodate-oxidized homologous *t*-RNA formed complexes with glycyl and valyl RNA synthetases, but not with arginyl RNA synthetase. That the binding between the enzyme and *t*-RNA is specific was shown by the use of two *t*-RNA fractions, enriched and depleted with respect to glycine-accepting activity.

Nucleotide Sequences at the 5'-termini of *E. coli* Ribosomal RNA. Mituru Takanami. *J. Mol. Biol.* 29 323 (1967).—Procedures for the determination of the 5'-terminal nucleotide sequences of high molecular weight RNA were developed, and by means of those procedures, the structure at the 5'-termini of *E. coli* ribosomal RNA was studied. It was found that the major components of the two *E. coli* ribosomal RNA's had the following unique sequences at their 5'-termini; 16s RNA: ${}_pA_pA_pA_pU_pG_p$ ---, 23s RNA: ${}_pG_pG_pU_p$ ---.

Analysis of the 5'-terminal Nucleotide Sequences of Ribonucleic Acids II. Comparison of the 5'-terminal Nucleotide Sequences of Ribosomal RNA's from Different Organisms. Masahiro Sugiura and Mituru Takanami.—*Proc. Natl. Acad. Sci., U. S.*, 58, 1595 (1967).—The 5'-terminal nucleotide sequences of ribosomal RNA's from one yeast and four bacterial species were analysed by aid of a method based on an enzymatic phosphorylation of the terminal 5'-hydroxyl group. All ribosomal RNA's examined were found to be phosphorylated at the 5'-termini, so they were first treated with alkaline phosphatase to remove the terminal phosphoryl group, and then rephosphorylated with highly radioactive orthophosphate by using polynucleotide kinase. They were hydrolysed by alkali, T1 RNase and pancreatic RNase, and the resulting radioactive fragments were analysed. Each of the ribosomal RNA's examined showed considerable homogeneity with respect to the 5'-termini, and the major components in each class of ribosomal RNA's started with unique, but different sequences.