

**Abstracts of the Papers Published in Other Journals  
by the Staff Members of this Institute  
During the Year 1964**

**Nuclear Physics & Chemistry**

**Mono-Energetic Positron Emission in the Decay of  $^{152}\text{Eu}$**  Sakae Shimizu, Yasuyuki Nakayama, Haruyoshi Hirata and Hiromasa Mazaki *Nuclear Physics*, 54, 265 (1964)—The mono-energetic positron emission of the 1409 keV E1 transition in  $^{152}\text{Sm}$  has been measured using a Siegbahn-Slätis intermediate-image spectrometer. By comparing the intensity of the positron peak with that of the internal conversion line of the same transition the branching ratio for this process has been determined as  $(2.5 \pm 1.0) \times 10^{-7}$  positron per gamma transition, in reasonable agreement with that reported by Perdrisat *et al.* The mean life of the 1531 keV level of  $^{152}\text{Sm}$  has been estimated to be  $\tau = 5.7 \times 10^{-15}$  sec. From our experimental value and relative transition intensities it is found that the 1409 keV E1 transition is retarded, when compared with the single proton transition probability, by a factor of at least about 60.

**Direct Interactions and Compound Nuclear Process in Inelastic Scatterings of Low Energy Proton.** Jun Kokame. *Genshikaku Kenkyu*, 8, 405 (1964), in Japanese—An attempt was reported to estimate cross-sections of direct interactions and the compound nuclear process separately in  $\text{Al}^{27}(\text{p}, \text{p}')\text{Al}^{27*}$  scatterings in the energy range of 6.5 to 14 MeV, based upon some assumptions: (1) a similarity in yields of inelastic scatterings of protons and alpha-particles exciting collective levels by direct interactions. (2) the  $2J+1$  rule of the compound nuclear process. (3) a negligible effect of the interference between the both reaction mechanisms.

**Fundamental Studies on Heavy Ion Reactions. (I). The Acceleration of Heavy Ions with the Cyclotron of Kyoto University and the Preparation of Foil Stripper.** Study Group of Heavy Ion Reactions in Kyoto University. *Genshikaku Kenkyu*, 8 (5), 617 (1964), in Japanese—A description is given of the subharmonic acceleration of heavy ions with the 105 cm cyclotron of Kyoto University. The experiments were done by using He gas and CO gas, and the various subharmonic acceleration modes of ions were obtained in both cases. The preparations of thin  $\text{Al}_2\text{O}_3$  foils for electron stripping are also described in detail.

**Excitation of Unnatural-Parity States in  $(\alpha, \alpha')$  Scatterings on  $\text{O}^{16}$ ,  $\text{Ne}^{20}$ ,  $\text{Mg}^{24}$  and  $\text{Si}^{28}$  at 28.5 MeV.** Jun Kokame, K. Fukunaga, N. Inoue and H. Nakamura *Physics Letters*, 8, 342 (1964)—Angular distributions and cross-sections of  $(\alpha, \alpha')$  scatterings from unnatural-parity states in  $\text{O}^{16}$ ,  $\text{Ne}^{20}$ ,  $\text{Mg}^{24}$  and  $\text{Si}^{28}$  were measured. They show relatively clear diffraction patterns. The integrated cross-sections over  $15^\circ$  to  $80^\circ$  CM is about 6 mb in  $\text{O}^{16}$  and 1.2 mb in  $\text{Ne}^{20}$ ,  $\text{Mg}^{24}$  and  $\text{Si}^{28}$ . The most probable mechanisms for the scattering seem to be the exchange process and/or the successive multiple process.

**Fundamental Studies on Heavy Ion Reactions. (II). The extractions of 3 MeV He and 10 MeV C ions subharmonically accelerated with the Cyclotron of Kyoto University.** Study Group of Heavy Ion Reactions in Kyoto University. *Genshikaku Kenkyu*, **9** (3), 363 (1964), in Japanese—The 3.3 MeV He and 10 MeV C ions which were thirdsubharmonically accelerated with the 105 cm cyclotron were detected with a silicon solid state detector. The optimum values of the deflector voltage and the Q-magnet current are given. The effective charge of 8 MeV C ions during the passage of aluminum and silicon foils was measured as 4.2+. The nuclear plates were also used to detect the 10 MeV C ions.

**Alpha Emitting Reactions on Be<sup>9</sup>, B<sup>10</sup> and B<sup>11</sup> Induced by Protons, Deuterons and Alpha-Particles** Takuji Yanabu, Sukeaki Yamashita, Shigeru Kakigi, Dai-Ca Nguyen, Kiyohiko Takimoto, Yasumasa Yamada and Kouya Ogino. *Journal of the Physical Society of Japan*, **19**, 1818 (1964)—The angular distributions have been obtained for alpha-particles from the reactions Be<sup>9</sup> (*p,α*) Li<sup>6</sup> (ground state), Be<sup>9</sup> (*d,α*) Li<sup>7</sup> (ground, first and second excited states), B<sup>10</sup> (*p,α*) Be<sup>7</sup> (ground state), B<sup>10</sup> (*d,α*) Be<sup>8</sup> (ground state), B<sup>11</sup> (*p,α*) Be<sup>8</sup> (ground state) and B<sup>11</sup> (*d,α*) Be<sup>9</sup> (ground and second excited states), and from the elastic and inelastic (second excited state) scatterings of alpha-particles by Be<sup>9</sup>. Besides, the angular distribution of deuterons from the reaction Be<sup>9</sup> (*p,d*) Be<sup>8</sup> (ground state) was measured. The energies of incident beams were nearly 7 MeV for protons, 14 MeV for deuterons and 28 MeV for alpha-particles. The results, except for B<sup>10</sup> (*p,α*) Be<sup>7</sup> and B<sup>11</sup> (*p,α*) Be<sup>8</sup>, show forward and/or backward rises and may be interpreted by direct interactions. The integrated cross sections of the reactions (*p,α*) and (*d,α*) on Be<sup>8</sup> are larger than those on B<sup>10</sup> and B<sup>11</sup>.

**Al and Ni (*p,p'α*) Reactions by 55 MeV Protons.** Takuji Yanabu, Sukeaki Yamashita, Teruo Nakamura, Shigeru Kakigi, Dai-Ca Nguyen, Kiyohiko Takimoto, Koya Ogino, Makoto Inoue and Yasuhiko Okuma. *Genshikaku Kenkyu*, **9** (4), 421 (1964), in Japanese—Quasi-free proton-alpha scattering in Al and Ni were investigated by 55 MeV protons. Proton-alpha angular correlations were measured with a proton counter at 70° direction to the incident beam, together with an alpha counter at various position. Two dimensional pulse height analyzer was used. No peak was found in the add energy spectrum of protons and alpha particles corresponding to the ground state of the residual nuclei, either in Al or Ni.

In Al, vague angular correlation was found between protons and alpha particles which are in the energy range from ground to 7.5 MeV excitation of the residual Na nucleus. The cross section for the quasi-free scattering of this group is an order of 4 μb/sterad.

In Ni, also vague angular correlations were recognized in two groups of protons and alpha particles corresponding to the energy range from ground to 12.5 MeV excitation and from 12.5 MeV to 20 MeV excitation of the residual Fe nuclei. Cross sections of these quasi-free scattering phenomena are of the order of 90 μB/sterad and 130 μb/sterad, respectively.

These results are far from satisfactory, and more investigations are needed.

**Activation Analysis of Manganese with Pu-Be 1c Neutron Source.** Tsunenobu Shigematsu, Masayuki Tabushi, Shiro Goda, Kenzo Tamaki and Yasuharu Nishikawa. *Radioisotopes*, **13**, 13 (1964), in Japanese—Radioactivation analysis of manganese was studied with a low-level neutron source, (1c) Pu+Be, and the procedure designed was applied to the nondestructive analysis of the element in some mineral samples.

Paraffin was used as moderator, and the distribution of thermal neutron was measured by using In foil, MnO<sub>2</sub> and Au foil. The maximum thermal neutron flux of  $3 \times 10^8 \text{ n/cm}^2 \cdot \text{sec.}$  was obtained with 1~2.1cm thick paraffin.

The self-shielding effect and self-absorption effect were also studied; the both effects were observed when the amounts of sample exceeded 250 mg.

Two hundred and fifty milligrams of powdered sample (Ca. 200 mesh) was irradiated for 17 hours at the distance of 2.5 cm from the neutron source, and after cooling for 10 min, activity was measured with G-M counter.

The decay curve and the gamma scintillation spectrum indicated that the activity obtained was attributed to the decay of <sup>56</sup>Mn. The constituents of minerals such as O, Na, Mg, Al, Si, Ca, Fe etc., did not give any effect, when manganese content was more than 2%. Manganese in minerals can be determined within the relative error of 5%.

**Decay of <sup>157</sup>Tb** Ichiro Fujiwara, Shiro Iwata, Tomota Nishi, Shiro Goda, Masayuki Tabushi and Tsunenobu Shigematsu. *Nuclear Physics*, **50**, 346 (1964)—A sample of Gd<sub>2</sub>O<sub>3</sub> enriched to 97.01% in the mass number 156 was bombarded with 38.5 MeV alpha-particles. The activity of <sup>157</sup>Dy produced by the ( $\alpha, 3n$ ) reaction was isolated chemically from the target material. The number of nuclei of <sup>157</sup>Dy was determined from the counting rate on the 330 keV photopeak. After the <sup>157</sup>Dy radioactivity ( $T_{1/2} = 8.2\text{h}$ ) had died out, terbium was separated from dysprosium. The scintillation spectrum of the terbium fraction showed only one photopeak at the energy of 43 keV X-rays of gadolinium when the source was situated inside a well-type crystal. The number of <sup>157</sup>Tb nuclei was determined from the counting rate of the K X-rays in the well-type crystal and by the measurement of the K and L orbital electron capture ratio with a thin NaI(Tl) crystal. From the number of nuclei of the parent and the daughter, the half life of <sup>157</sup>Tb was estimated to be  $150 \pm 30\text{y}$ . A decay scheme of <sup>157</sup>Tb is proposed.

## Analytical Chemistry

**Spectrophotometric Determination of Strontium in Sea Water using *o*-Cresolphthalein Complexone.** Katsuya Uesugi, Masayuki Tabushi, Toshiharu Murakami and Tsunenobu Shigematsu. *Bunseki Kagaku*, **13**, 440 (1964), in Japanese—A spectrophotometric method for strontium using *o*-cresolphthalein complexone was studied and applied to the determination of strontium in sea water and brine samples. Strontium reacted with the reagent at pH 11~12 to form a colored complex having an absorption maximum at 575 m $\mu$ . Beer's law was followed up to 3ppm of strontium and the molar extinction coefficient was 32,000.

In order to prevent the interfering effects of diverse ions, strontium was separated by coprecipitation with calcium oxalate and by cation exchange treatment, whereby 96~97% recovery of strontium was ascertained by using  $^{89}\text{Sr}$  as a tracer. Strontium in sea water samples was estimated to be 7~8mg/l, and in brine samples (15° Bé) to be 30 mg/l.

**Determination of Strontium in Shell-fish by *o*-Cresolphthalein Complexone.** Tsunenobu Shigematsu, Katsuya Uesugi, Toshiharu Murakami and Masayuki Tabushi. *Bunseki Kagaku*, **13**, 1032 (1964), in Japanese—The spectrophotometric method for strontium by *o*-cresolphthalein complexone was applied to the determination of strontium in shell-fish samples. The analytical results showed that strontium content in shell samples ranged from 0.1 to 0.27%, and in dry flesh samples 3.3 to  $8.7 \times 10^{-3}\%$ .

**The Determination of Titanium in Sea Water, Marine Organisms and Sediments.** Tsunenobu Shigematsu, Yasuharu Nishikawa and Tomio Kusakabe. *Nippon Engakukaishi*, **17**, 232 (1964), in Japanese—In this study, amounts of titanium contained in sea water, biomaterials and sediments were determined by a method using tiron (disodium-1, 2-dihydroxybenzene-3, 5-disulfonate).

Ferric iron was added to slightly acidified sample solution as a carrier for titanium, and pH was adjusted to 8.5–9.5 with ammonia. Ferric hydroxide was filtered and dissolved in sulfuric acid. The major portion of iron was removed by mercury cathode electrolysis, and then the absorbance of titanium-tiron complex formed at pH 4 in the presence of EDTA, was measured at 420 m $\mu$ .

After analyzing sea water and lake water samples, several kinds of biomaterials such as seaweed or shellfish, and sediments, the following results were obtained:

The content of titanium in sea water amounted to approximately 2 $\mu\text{g/l}$ , and that in several kinds of shellfishes and seaweeds amounted to  $2.5\text{--}6.9 \times 10^{-2}\%$  and  $2.5\text{--}6.5 \times 10^{-3}\%$  in ash samples, respectively. The titanium content in marine sediments was of the order of  $10^{-1}\%$ . In general, the sea samples contained less amount of titanium as compared with the similar land samples.

**Behavior of Strontium in Concentration of Sea Water.** Tsunenobu Shigematsu, Masayuki Tabushi, Toshiharu Murakami and Katsuya Uesugi. *Nippon Engakukaishi*, **17**, 1 (1964), in Japanese—A study was conducted on the behaviors of strontium and calcium in the concentrating process of sea water. In this study, sea water was gradually evaporated at 50~70°C or at the boiling temperature until it reached one twentieth of its initial volume, and the behaviors of strontium and calcium were traced by using radioactive isotopes,  $^{89}\text{Sr}$  and  $^{45}\text{Ca}$ . Strontium in sea water and brine was spectrophotometrically determined by *o*-cresolphthalein complexone method after it was separated from other elements by coprecipitation with calcium oxalate and by cation-exchange method.

The following conclusions were obtained from the experimental results:

1. In the early stage of concentration, the loss of strontium from the sample solution was negligible. When 85% (in volume) of sea water was evaporated, the concentration of strontium reached the maximum and was four times as much as

the concentration of sea water. Strontium indicated rapid precipitation after it reached the maximum point, and a trace of strontium was detected in the bittern.

2. The behavior of calcium was almost the same as that of strontium although the depositing tendency of strontium was a little more remarkable than that of calcium, and most of strontium was considered to be distributed in the gypsum deposit.

3. The ratios of strontium concentration in sea water and brine samples were in good agreement with the results obtained from the evaporation experiments.

**Determination of Zirconium in Sea-Water.** Tsunenobu Shigematsu, Yasuharu Nishikawa, Keizō Hiraki and Heishiro Nakagawa. *Nippon Kagaku Zasshi*, **85**, 490 (1964), in Japanese—Zr in sea-water was determined by the fluorometric method with morin. Into 20 l. of sea-water, 20 ml. of conc. HCl and 200 mg. of  $\text{Al}^{3+}$  as  $\text{AlCl}_3$  solution were added and pH of the solution was adjusted to 8. After standing overnight, the precipitate was filtered and dissolved in 50 ml. of  $3^N$  HCl and the solution was evaporated to dryness. The residue was treated with 10 ml. of  $2^N$  HCl and Zr was extracted with 10 ml. of 0.2 M TTA-benzene solution. Zr-TTA-complex was then decomposed with  $\text{HClO}_4$  and again evaporated to dryness. The residue was dissolved with  $1.8^N$  HCl and the solution was transferred to a 25 ml. volumetric flask. To the solution, 0.5 ml. of 0.02 % morin alcoholic solution was added. The solution was diluted to the volume with  $1.8^N$  HCl. The fluorescence intensity of the solution was measured. In this procedure, the recovery of zirconium was found to be about 95%.

Zr in sea-water collected at the offshore of Kuroshima, Wakayama Pref. and the coast of Misakicho, Osaka Pref., Japan was found to be 0.01~0.04  $\mu\text{g./l.}$

Zr content in several marine animals and plants was also determined and found to be in the order of  $10^{-4}\%$  in ash samples.

**The Solvent Extraction and Spectrophotometric Determination of Uranium Using Benzoyltrifluoroacetone as the Chelating Reagent.** Tsunenobu Shigematsu, Masayuki Tabushi and Masakazu Matsui. *Bulletin of the Chemical Society of Japan*, **37**, 1333 (1964).—The solvent extraction of uranium as a benzoyltrifluoroacetone chelate was investigated, and a procedure for the separation and spectrophotometric determination of uranium was proposed.

**The Coprecipitation of Yttrium with Calcium Oxalate.** Tsunenobu Shigematsu, Masayuki Tabushi and Masakazu Matsui. *Bulletin of the Chemical Society of Japan*, **37**, 1610 (1964)—The coprecipitation of yttrium with calcium oxalate was investigated. The effects of the pH value, the tracer component to the carrier ratio, the concentration of the buffer solution and several other variables on the distribution coefficient were investigated, using yttrium-91 as a tracer.

**Activation Analysis of Manganese with Pu+Be 1c Neutron Source.** Tsunenobu Shigematsu, Masayuki Tabushi, Shiro Goda, Kenzo Tamaki and Yasuharu Nishikawa. *Radioisotopes*, **13**, 13 (1964), in Japanese—Radioactivation analysis of manganese was studied with a low-level neutron source, (1c) Pu+Be, and the procedure

designed was applied to the nondestructive analysis of the element in some mineral samples.

Paraffin was used as moderator, and the distribution of thermal neutron was measured by using In foil,  $\text{MnO}_2$  and Au foil. The maximum thermal neutron flux of  $3 \times 10^8 \text{n/cm}^2 \cdot \text{sec}$  was obtained with 1~2.1cm thick paraffin.

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The decay curve and the gamma scintillation spectrum indicated that the activity obtained was attributed to the decay of  $^{56}\text{Mn}$ .

The constituents of minerals such as O, Na, Mg, Al, Si, Ca, Fe etc., did not give any effect, when manganese content was more than 2%. Manganese in minerals can be determined within the relative error of 5%.

## Inorganic Chemistry

**The Physical Properties of Fine Particles** Sukeji Kachi and Yoshichika Bando. *Hiyomen*, 2, 1 (1964). In fine particles, its morphological, crystallographic, magnetic properties and characteristics of phase transformation were in detail reviewed.

**The Morphological Properties and Magnetic Properties of Fine Particle Oxides.** Toshio Takada. *Journal of the society of Materials Science, Japan*, 13, 728 (1964), in Japanese—The magnetic properties of fine particles of oxides were investigated with relation to the morphological and crystallographic properties.

Coercive force of finely powdered  $\gamma\text{-Fe}_2\text{O}_3$  was measured and it was concluded that the shape and size of aggregate particle have a great effect on the coercive force. On the other hand, the magnetic properties of ultra-fine particles of anti-ferromagnetic substances i. e. NiO, CuO,  $\alpha\text{-Fe}_2\text{O}_3$ , were studied. It was discovered that the susceptibility shows the superparamagnetic character, when the unit particle size is very small ( $<100\text{\AA}$ ).

**The Magnetic Properties of Fine Particles.** Toshio Takada and Yoshichika Bando. *Kagaku*, 19, 322 (1964), in Japanese—The magnetic properties of oxides were reviewed with relation to the morphological and crystallographic properties of particles.

**Methods for Metal-Powder Production.** Sukeji Kachi and Yoshichika Bando. *Metal Physics*, 10, 112 (1964), in Japanese—Methods of production of small particles ( $<50\mu$ ) were reviewed. Morphological and crystallographic properties of fine particle were mainly described with relation to preparation method of particles.

**The Magnetization of Face Centered Cubic Ironnickel Alloys in the Vicinity of Invar region.** Yoshichika Bando. *Journal of the Physical Society of Japan*, 19, 237 (1964), in Japanese—The magnetization—composition curve of f. c. c. Fe-Ni alloy

in the neighborhood of 30% Ni was studied by using finely powdered alloys. In the particles, no trace of b. c. c. Fe-Ni alloys on cooling in liquid nitrogen was detected by the X-ray diffraction and magnetic measurement. The magnetization-composition curve (27.4~31.4% Ni) showed the abrupt decreasing of magneton numbers to 27.4% Ni. This result confirmly supports an idea that there are two electronic configuration in f. c. c. Fe, i. e. antiferromagnetic  $\gamma_1$ , and ferromagnetic  $\gamma_2$ .

**Mössbauer Study of  $\alpha$ -,  $\beta$ - and  $\gamma$ -FeOOH** T. Takada, M. Kiyama, Y. Bando, T. Nakamura, M. Shiga, T. Shinjo, N. Yamamoto, Y. Endo and H. Takaki, *Journal of the Physical Society of Japan*, **19**, 1744 (1964)—The magnetic studies on  $\alpha$ -,  $\beta$ - and  $\gamma$ -FeOOH were made by means of the Mössbauer effect.

$\alpha$ -FeOOH has a 6-line splitting due to antiferromagnetic ordering at 110°K and 300°K. Néel temperature was considered to be about 400°K. The spectrum of  $\beta$ -FeOOH shows a 6-line splitting at 110°K and only shows a doublet due to the quadrupole effect at 300°K. Therefore, the Néel temperature should lie between 110°K and 300°K.  $\gamma$ -FeOOH has no splitting caused by the internal field at 110°K and 300°K and is found to be paramagnetic down to 110°K.

**Fe<sup>57</sup> Mössbauer effect in ultra-fine particles of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.** T. Nakamura, T. Shinjo, Y. Endo, N. Yamamoto, M. Shiga and Y. Nakamura. *Physical Letters*, **12**, 178 (1964)—The Mössbauer effect was applied to the study of magnetic behaviour in ultra fine particles of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. When the particle size is very small (<100Å), the susceptibility shows the superparamagnetic character of antiferromagnetic particles. The spectrum of Mössbauer effect at 120°K, of a ultra-fine particle, has two characteristics in comparison with the peak position of normal  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at 120°K. One is that small particles have no Morin transition at least above 120°K and spins lie still in the basal plane. The other is that the internal field,  $H_i$ , is slightly reduced (about 5%) in the sample. The spectrum of the ultra-fine particle at 300°K had no more lines than two owing to the quadrupole interaction. This phenomenon can be interpreted as a motional narrowing due to the rapid relaxation of antiferromagnetic spins compared with the nuclear Larmor precession.

**Characteristics of Phase Transformation in Metallic Fine Particles (Martensitic transformation of Fe-Ni alloys, and ordering of CuAu and Cu<sub>3</sub>Au alloys)** Yoshichika Bando. *Transactions of the Japan Institute of Metals*, **5**, 135 (1964)—Effects of particle size upon the martensitic transformation of Fe-Ni alloys and the ordering of CuAu and Cu<sub>3</sub>Au alloys were studied. The specimens were prepared by the reduction of fine powdered solid solution of (Fe, Ni) C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, (Fe, Ni)<sub>3</sub>O<sub>4</sub> and (Cu, Au) CN in hydrogen at various temperatures. The Ms temperature decreases with decreasing particle size, and the particles (27.4% Ni) less than 0.7 $\mu$  do not undergo martensitic transformation even at the liquid nitrogen temperature. The rates of ordering in CuAu and Cu<sub>3</sub>Au increase with decreasing particle size. These phenomena were discussed from the viewpoint of the behaviors of crystal imperfections in fine particles.

**Elastic Constants of Ni-Fe and Ni-Cu Alloys** Junji Sakurai, Mitsuhiro Fujii,

Yoji Nakamura and Hideo Takaki. *Journal of the Physical Society of Japan*, **19**, 308 (1964)—Elastic constants of binary alloys, Ni-Fe and Ni-Cu, of their wide composition ranges having f.c.c. structure, were measured by means of a composite oscillator method in the frequency range from 1 to 5 Mc/s at room temperature. Elastic constants of Ni-Fe alloys vary quadratically as their compositions, while those of Ni-Cu vary linearly. These results can be interpreted in terms of the central and pair-like interactions between atoms of the alloys.

**Estimation of a Change of the Curie Temperature with Pressure for Gadolinium.** Tetsuo Nakajima and Hideo Takaki *Journal of the Physical Society of Japan*, **19**, 951 (1964)—A change of the Curie temperature with pressure for gadolinium has been estimated from the data of the temperature dependences of the magnetization and magnetostriction on the basis of thermodynamical theory of a phase transition of the second kind. This result is in good agreement with the experimental result.

**Fe<sup>57</sup> Mössbauer Effect in Fe<sub>2</sub>B, FeB and Fe<sub>3</sub>C.** Teruya Shinjo, Fumitake Itoh, Hideo Takaki, Yoji Nakamura and Naomoto Shikazono. *Journal of the Physical Society of Japan*, **19**, 1252 (1964)—We have made measurements of Mössbauer effect of Fe<sup>57</sup> in Fe<sub>2</sub>B and Fe<sub>3</sub>C.

As expected, all of these compounds have positive isomer shift but the difference among them is little and does not depend on assumed  $3d$  numbers. In these compounds, the quadrupole effect is smaller than 0.1 mm/sec and the variation of  $H_i/\mu_B$  is not large.

**Alkali Metal Hyperfine Structure in the ESR Spectra of Biphenyl Mononegative Ions.** Hiroaki Nishiguchi, Yasuto Nakai, Kazuo Nakamura, Kazuhiko Ishizu, Yasuo Deguchi and Hideo Takaki. *Journal of Chemical Physics*, **40**, 241 (1964)—The hyperfine splitting from the K<sup>+</sup> nucleus in the presence of a biphenyl anion in various solvents is discussed. Coupling consts. are tabulated for tetrahydrofuran, tetrahydropyran, 2,3-dihydropyran, and dimethoxyethane (no K<sup>+</sup> interaction). The Na<sup>2s</sup> population in the naphthalene anion is larger than that of K-biphenyl anion, and increased with decreasing temperature. This is explicable in terms of structure.

**Estimation of Pressure Effect on the Curie Temperature for Gold-Manganese Alloy and Mn-Zn Ferrite.** Takefumi Tsuboi, Tetsuo Nakajima and Hideo Takaki. *Journal of the Physical Society of Japan*, **19**, 768 (1964).—The heading problem is done using thermodynamical relations of a second order phase transition and the measurements of temperature- and field-dependences of the forced magnetization and the forced magnetostriction, and is compared in good accordance with the values which have been observed.

**On the Magnetic Transition in Cr-Rich Cr-Fe Alloys.** Takao Suzuki and Hideo Takaki. *Journal of the Physical Society of Japan*, **19**, 1241 (1964)—Magnetic susceptibilities and thermal expansivities have been measured on Cr-rich Cr-Fe alloys in order to know the magnetic phase boundary as a function of average number of

valence electrons. Transitions of the first kind were observed in  $\chi$  and  $\Delta l/l$  on the alloys of the content more than 2 at %.

Two possible interpretations were suggested, the one is that the first kind of magnetic structure transition corresponds to the change of the magnetic structure below  $T_N$  associated with the variation of average number of valence electrons, the other is attributed to the magnetothermomechanical effect.

**Hall Effect of the Solid Solutions of  $TiC_xN_{1-x}$  and  $Ti_xV_{1-x}C$ .** Fumitake Itoh, Takashi Tsuchida and Hideo Takaki. *Journal of the Physical Society of Japan*, **19**, 136 (1964)—In the previous paper the authors had the result that the monocarbides of the fourth group transition metals with light valence electrons have the conduction electron much less than one per chemical formula, whereas those of the fifth group with nine valence electrons have about one conduction electron. In order to develop the result, the Hall coefficients have been measured on the two types of solid solutions, i. e.  $TiC-TiN$  and  $TiC-VC$ , and their electronic structures have been discussed.

**Change in Refractive Indices of Glasses under High Pressure.** Megumi Tashiro, Sumio Sakka and Tokuji Yamamoto. *Yogyo Kyokaishi*, **72**, 108 (1964), in Japanese—H.M. Cohen and Rustum Roy reported the silica glass densified under ultrahigh pressures with the opposed anvil apparatus shows no relaxation effects even when heated at 600°C (J. Am. Ceram. Soc., **44** [10] 523 (1961)). J. D. Mackenzie, however, has found recently that marked relaxation occurs at the beginning of reheating at above 300°C for silica glass densified with the high-pressure "Belt" apparatus (J. Am. Ceram. Soc., **46** [10] 461, 470 (1963)). In the present work Mackenzie's result has been confirmed for silica glass and a borosilicate glass both densified with the same opposed anvil type pressure apparatus as used by Cohen *et al.*

Samples of the silica glass were taken from a commercial clear grade silica glass rod. The borosilicate glass with the composition of  $Na_2O$  7.5,  $B_2O_3$  22.5, and  $SiO_2$  70% in weight, was melted in a platinum crucible. The glasses were pulverized to 40~50 $\mu$ , pelleted into a disc of approximately 6-mm diameter and 0.2-mm thickness, wrapped in a platinum foil, and pressed between two opposed anvils of the high-pressure apparatus at temperatures ranging from 25°C to 300°C for various periods. The pressure was released after the temperature of the sample was lowered to room temperature. The annealing of the densified glasses was made by reheating under atmospheric pressure at temperatures ranging from about 130°C to 900°C for various periods. Refractive indices of the reheated glasses were measured as the indication of relaxation.

The results showed that the relaxation becomes noticeable by reheating above approximately 300°C for the silica glass and at much lower temperatures than 300°C for the borosilicate glass. In both cases the relaxation completes almost in a few minutes at the beginning of reheating.

The activation energies of the relaxation process calculated from the initial changes in refractive indices were approximately 10 and 3 kcal/mol for the silica- and borosilicate-glasses respectively, which were both much lower than the activa-

tion energy of viscous flow in these glasses.

**Slip Casting of Petalite Ceramics. Studies of Thermal Shock Resisting Ceramics of the  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  System, IV.** Toshio Maki and Megumi Tashiro. *Yogyo Kyokaishi*, 72, 105 (1964), in Japanese—The firing range of petalite ceramics can be extended markedly by the addition of powdered lithia glass ( $\text{Li}_2\text{O}$  10.7,  $\text{MgO}$  8.9,  $\text{Al}_2\text{O}_3$  8.9,  $\text{SiO}_2$  71.5 wt.%) to petalite powders in a weight ratio of 1 : 9 (M. Tashiro and T. Maki, *J. Ceram. Assoc. Japan*, 70, 8 (1962); M. Tashiro and T. Maki, *J. Ceram. Assoc. Japan*, 71, 65 (1963); T. Maki and M. Tashiro, *J. Ceram. Assoc. Japan*, 71, 196 (1963)). In the present study, slip preparation most feasible for this nonplastic mixture was studied. The most stable slip composition determined was petalite 90, lithia glass 10, bentonite 5, and carboxymethyl cellulose (CMC) 0.02 in weight ratio. The raw materials were ball-milled in water to the fineness of almost less than  $5\mu$  in diameter. The optimum water content was 35% (wt.) of the wet base. When the bentonite content exceeded the above value, slip-cast specimens shrunk more than 27% in volume on firing. CMC was effective not only as a floating agent but for increasing the mechanical strength of dried slip-cast specimens. The modulus of rupture of 900 kg/cm<sup>2</sup> was attained in the slip-cast specimen fired at 1250°C for one hour.

**Magnetic Materials Obtained from Silicate Melts in the System  $\text{Fe}_2\text{O}_3-\text{MnO}-\text{Alkali Oxide}-\text{Al}_2\text{O}_3-\text{SiO}_2$ .** Megumi Tashiro, Sumio Sakka and Tadashi Kokubo. *Yogyo Kyokaishi*, 72, 92 (1964), in Japanese—Most commercial products of ferrites are made by firing preformed powder mixtures of raw materials. This conventional method, however, is not adapted for obtaining products of the special shapes such as fiber and film. In this study we undertook to examine the possibility of obtaining magnetic materials from melted silicates containing  $\text{Fe}_2\text{O}_3$  and  $\text{MnO}$  and of forming the melts into desired shapes by the ordinary glass-forming technique.

The compositions of the melts studied were of 7.5~20%  $\text{Fe}_2\text{O}_3$ , 7.5~20%  $\text{MnO}$  (or  $\text{CoO}$  and  $\text{NiO}$ ), 0~5%  $\text{Li}_2\text{O}$  (or  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ ), 0~15%  $\text{Al}_2\text{O}_3$ , and 55~70%  $\text{SiO}_2$  (mole). The raw materials were ferrous oxalate, manganese dioxide, cobaltic oxide, nickel oxide, lithium-, sodium- and potassium carbonates, aluminium hydroxide and potter's flint powders. Their mixtures to yield about 50 gram of melts were heated in sintered- alumina crucibles in an electric furnace at temperatures from 1300°C to 1400°C. Their melting behaviors and the workability of their melts into shapes of fiber or plate during cooling were investigated. X-ray diffraction analysis and magnetic measurement were made on materials quenched in air.

The results obtained are as follow :

1) The melts of the compositions, 7.5~15%  $\text{Fe}_2\text{O}_3$ , 7.5~20%  $\text{MnO}$ , 0~5%  $\text{Li}_2\text{O}$  (or  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ ), 5~15%  $\text{Al}_2\text{O}_3$ , 55~70%  $\text{SiO}_2$  (mole) were fluid at temperatures 1300°~1400°C, and were able to be formed into desired shapes during cooling.

2) The intensity of magnetization of quenched specimens reached up to 18 gauss/g at the field of 10,000 oersteds. Magnetization increased with increasing the content of  $\text{Fe}_2\text{O}_3$  or  $\text{Fe}_2\text{O}_3+\text{MnO}$ , and decreased with increasing the content of  $\text{Al}_2\text{O}_3$ . The specimens of high  $\text{Fe}_2\text{O}_3$  content saturated magnetically at a fairly weak magnetic field whereas the specimens of  $\text{Fe}_2\text{O}_3$  content less than 15 mole%

did not saturate even at the field as strong as 5,000~10,000 oersteds. The followings are some examples of the composition which showed high magnetization and magnetic saturation at a weak magnetic field.

Compositions (mole)	Intensity of magnetization at 5,000~10,000 oersteds
17.5Fe <sub>2</sub> O <sub>3</sub> ·17.5MnO·5Li <sub>2</sub> O·10Al <sub>2</sub> O <sub>3</sub> ·50SiO <sub>2</sub>	18 gauss/g
20Fe <sub>2</sub> O <sub>3</sub> ·10MnO·5Li <sub>2</sub> O·10Al <sub>2</sub> O <sub>3</sub> ·55SiO <sub>2</sub>	12.5 "
15Fe <sub>2</sub> O <sub>3</sub> ·15MnO·5Na <sub>2</sub> O·10Al <sub>2</sub> O <sub>3</sub> ·55SiO <sub>2</sub>	8.5 "

3) Separation of fine crystallites of spinel-type ferrites was confirmed by X-ray analysis in some of quenched specimens containing high amount of Fe<sub>2</sub>O<sub>3</sub>. The average size of the crystallites estimated from the broadening of X-ray diffraction peaks was 60~150Å.

4) Reheating quenched specimen generally increased the intensity of magnetization and also accelerated magnetic saturation at weak magnetic field.

**New Glasses.** Megumi Tashiro. *Kagaku to Kogyo*, 17, 502 (1964), in Japanese—Review Article.

**New Glasses.** Sumio Sakka. *Yogyo Kyokaishi*, 72, C61 (1964), in Japanese—Review Article.

## Physical Chemistry

**Influence of Surface Active Materials on the Coalescence of Mercury Droplets in Aqueous Solutions.** Akira Watanabe, Mutsuo Matsumoto and Rempei Gotoh. *Nippon Kagaku Zasshi*, 85, 730 (1964), in Japanese—The range of the electrical potential of coalescence of mercury droplets in solutions of surface active materials was measured by using the twin dropping mercury electrodes, developed by the present authors. It was thus hoped that the rôle of surface active materials in stabilizing emulsions in general was clarified by the present study. Experiments were carried out by using sodium dodecylsulphate, cetylpyridinium chloride, a polyvinyl alcohol and EPANs, a group of nonionic surface active copolymers of ethylene oxide and propylene oxide at various mole ratios, as the surface active materials. All these substances showed perfect protection; mercury droplets did not coalesce at any potential of mercury surfaces, when the concentration of these substances exceeded certain values characteristic of these materials. Moreover, in the case of EPANs, the logarithm of this concentration was found to be a linear decreasing function of the HLB value of the molecule; the stabilizing power increased with increasing hydrophilic character of the molecule. The adsorption behaviour of various EPANs on to the mercury surface was also studied by measuring differential double layer capacities. It was found that the stabilization was intimately related to the formation of films of the surface active materials at the mercury-solution interfaces.

**Studies on the Electrical Double Layer. (III). On the Adsorption Kinetics of Nonionic Surface Active Agents at a Dropping Mercury Electrode.** Akira Watanabe, Fukuju Tsuji and Shizuo Ueda. *Kolloid-Zeitschrift*, 198, 87(1964)—The differ-

ential double layer capacity of a dropping mercury electrode in contact with 1 N sodium sulphate solutions containing various concentrations  $c$  of nonionic surface active agents is strongly dependent on the time  $t$  which has passed after the mercury drop started to grow. The suppression of the capacity value over the zero polarization range increases with  $t$ , the time constant of this slow adsorption process being independent of the frequency of the ac bridge and decreasing from 175 msec for  $c=2.5 \times 10^{-5} M$  to almost zero for  $c=10^{-3} M$ . It is supposed that the slow diffusion process is the governing factor in this case. The kinetic capacity peaks, both anodic and cathodic, also increase with  $t$  in general, the time constants being of the order of msec. These time constants decrease with decreasing frequency  $f$ . The time constants for the anodic peaks decrease, while those for the cathodic peaks increase, with increasing concentration  $c$ . Under certain conditions anomalous behaviours are observed, e. g. the kinetic peaks decrease with increasing  $t$  for  $c=10^{-3}$  at  $f=3,900$  cps. This can be explained by the decrease with  $t$  in the fractional interfacial area newly formed, where the kinetic process can take place. If the adsorption exchange process can not take place at the old part of the total interface, the capacity per unit area of the mercury drop decreases with  $t$ .

**The Coagulation of Colloidal Powders.** Akira Watanabe. *Funtai oyobi Funmatsu Yakin*, 11, 17 (1964)—The stability of hydrophobic colloids is mainly governed by the magnitude of the potential energy of repulsion due to the superposition of electrical double layers and van der Waals attraction between approaching particles. In the absence of potential barriers, every collision between particles leads to adhesion (rapid coagulation), and in the presence of potential barriers, the probability of collision is decreased, thus leading to slow coagulation. A quantitative theory was given by Reerink and Overbeek to describe the influence of the double layer thickness at constant Stern potential on colloid stability, a situation which occurs when indifferent inorganic electrolytes are added to sols. While, Ottewill, Rastogi and the present author gave a theory which treated the case where the change in the Stern potential occurs due to adsorption. An extended theory of coagulation was also given which treated the general case of changing ionic strength and potential.

The experimental verification of the theory thus obtained was carried out by measuring the coagulation kinetics of positively charged silver iodide sols spectrophotometrically. Electrokinetic measurements were also made by using ultramicroelectrophoresis. The agreement between the theory and experiments was very good and a reasonable value of the van der Waals constant was obtained. Experiments were also shown which were carried out by employing the twin dropping mercury electrodes polarized at various potentials in electrolytic solutions. The condition of coalescence of the mercury droplets, i. e. the relation between the ionic strength and the critical potential of coalescence, was proved to be in excellent agreement with the theory of coagulation of colloid particles. Thus, the interaction between finely dispersed particles in hydrophobic colloids is essentially the same as that acting between macroscopic mercury droplets.

**Polarized Infrared Spectra of Benzene Derivatives.** Soichi Hayashi. *Nippon Kagaku Zasshi*, 85, 186 (1964), in Japanese—The polarized infrared spectra of highly

oriented crystals of *m*-dinitrobenzene, acetanilide and *p*-dimethoxybenzene were measured. Characteristic bands observed in the region  $2000\sim 1600\text{cm}^{-1}$  were assigned in accordance with Kakiuchi's result to the combination bands of hydrogen out-of-plane vibrations of benzene ring. Frequencies of the hydrogen out-of-plane fundamental vibrations, calculated from combination tones, were in good agreement with observed values.

The directions of transition moments of the fundamentals and their combination tones were calculated from dichroic ratios, and were compared with the results of X-ray analysis.

The agreement was satisfactory in the case of *m*-dinitrobenzene which has approximate  $C_{2v}$  symmetry. For acetanilide, some differences were found between the infrared results and those of X-ray analysis when its benzene ring was assumed to have  $C_{2v}$  symmetry. However, when  $C_s$  symmetry was assumed, a good agreement was obtained.

**Vibrational Spectra of Tetracyanoethylene.** Tohru Takenaka and Soichi Hayashi. *Bulletin of the Chemical Society of Japan*, 37, 1216 (1964)—The polarized infrared spectrum of a highly oriented crystal of TCNE have been measured, together with the Raman spectrum of a sample consisting of several lumps of the crystals. The infrared spectra of the powdered solid, solution, and vapor have also been observed for comparison. Under the assumption of the  $V_h$  symmetry, the normal vibrations of TCNE have been calculated for the in-plane modes by the use of the  $GF$  matrix method. The basic UBFF, as well as the modified one containing cross terms between the C=C and C—C bonds, has been used as the potential function for this molecule. The frequencies calculated with the modified UBFF agree well with the observed values. The potential energy distributions have also been calculated, and the nature of the in-plane fundamental vibrations has been elucidated. The tentative assignments have been made to the out-of-plane fundamental vibrations and to the overtone and combination vibrations.

**The Structure of Vacuum-deposited Films of Cadmium Telluride.** Makoto Shiojiri and Eiji Suito. *Japanese Journal of Applied Physics*, 3, 314 (1964)—Electron diffraction and electron microscopic studies were made on the structure and epitaxial growth of CdTe films deposited on a heated surface of cleaved mica. The epitaxy occurred at about  $70^\circ\text{C}$ . The epitaxial relation is  $(111)_{\text{CdTe-cub}}// (001)_{\text{Mica}}$  and  $[110]_{\text{CdTe-cub}}// [100]_{\text{Mica}}$ . Extra spots and streaks appeared in the transmission electron diffraction patterns. They are explained on the basis of a model that wurtzite type crystals grow on the  $\{111\}$  planes of a zinc-blende type crystal. In addition twinnings and stacking faults occur on these planes. The origin of stacking faults in the films is also discussed.

**Surface Area Determination Apparatus by Gas Chromatography.** Masafumi Arakawa. *Funtai Kogaku Kenkyukaishi*, 1, 3 (1964), in Japanese—A new apparatus has been devised for determining surface area of powders by the measurement of various gases and vapors adsorption. A known mixture of adsorbate and an inert carrier gas, helium, is flown through a packed column of sample at a constant rate. After saturation of the sample, the adsorbed vapor is eluted by the carrier

gas, and the concentration of the adsorbate in the effluent gas is measured by gas chromatograph apparatus. The measurement is easy and rapid to perform. Applications to carbon black, kaolinite and titan white are described.

**Experimental Studies on Sedimentation Balance.** Masafumi Arakawa and Takako Kobayashi. *Funtai Kogaku Kenkyukaiishi*, 1, 80 (1964), in Japanese—Some problems to be considered as the causes of error in the particle size measurement with sedimentation balance were discussed and the results were applied to the experiments.

Boyscott effect caused by weight pan was considerably large in certain conditions. To avoid the effect, it is effective to make large the ratio of the diameter of pan to that of settling vessel and to make short the distance between the bottom of the vessel and weight pan. However, the particle size measured by the special vessel in which the Boycott effect was negligible was rather large. And, comparative test between the apparatus used common type vessel and the other method give a full coincidence of the measured results within the limits of measuring accuracy.

The agitating effect by the vertical movement of weight pan was negligibly small.

**A New Automatic Recording Instrument for the Determination of Particle Size Distribution by Sedimentation Method.** Eiji Suito, Masafumi Arakawa, Hideo Mishima, Shozo Yano and Nobuyuki Okamoto. *Zairyo*, 13, 825 (1964), in Japanese—The sedimentation velocity of a particle is in proportion to the square of the particle size. Therefore, the particle size distribution can be determined from the changes of concentration with the depths of the suspension at the time selected according to the sample. In this instrument, the concentration gradient with depth is measured by means of specific gravity balance, and the cumulative curve of the particle size distribution is automatically recorded as the detection of the change of buoyancy with the square root of the depth that is in proportion to the particle size. The measurement is rapid, simple and reproducible. A few samples were measured, the results agreeing with those obtained by other methods.

**Shapes and Structures of Particles of Fine Powders.** Eiji Suito. *Kagaku*, 19, 312 (1964), in Japanese—Review Article.

**Particle Size Measurement of Powders.** Eiji Suito. *Nippon Kikai Gakkaishi*, 67, 1684 (1964), in Japanese—Review Article.

**X-Ray Analysis.** Eiji Suito and Makoto Shiojiri. *Nippon Gomu Kyokaishi*, 37, 875 (1964), in Japanese—Review Article.

## Polymer Chemistry

**Elastic Moduli of Polymer Crystals for the Chain Axial Direction.** I. Sakurada, T. Ito and K. Nakamae. *Makromolekulare Chemie*, 75, 1 (1964)—Some experiments were carried out to prove the validity of the assumption of a simple series model

for the calculation of the elastic modulus of crystalline regions in oriented linear polymers from X-ray determination of lattice extension. Various specimens such as filaments, fibers, and films were prepared from polyethylene, polyvinyl alcohol, polypropylene, polyoxymethylene and cellulose, stress-strain curves constructed under the assumption of a simple series model, and calculated values of modulus compared. In spite of the differences of microstructures of these specimens, nearly the same value for the lattice modulus was obtained for each polymer. A large difference of specimen moduli had no effect on the lattice modulus. Lattice moduli of dry and water-swollen polyvinyl alcohols or cellulose did not differ from each other. These results are a strong support for the above assumption.

Extensibility of various polymer molecules was also discussed.

**Dilute Solution Properties of Partly Urethanized Polyvinyl Alcohol.** Ichiro Sakurada, Akio Nakajima, and Kyoichiro Shibatani. *Journal of Polymer Science*, Part A, 2, 3545(1964)—Partly urethanized polyvinyl alcohol samples, in a range of degree of urethanization up to about 10 mole-%, were prepared by treatment of polyvinyl alcohol with urea. These were fractionated in a water-*n*-propanol system into fractions, each having nearly the same nitrogen content. The degree of polymerization of the partly urethanized polyvinyl alcohol was estimated from the intrinsic viscosity of polyvinyl alcohol obtained by hydrolysis of the corresponding urethanized polymer. The effects of introduced urethane residue on solubility and dissolved state of polymer were investigated in water and theta solvents. Further, some thermodynamic parameters in water were discussed in relation to those of partly acetylated polyvinyl alcohol.

**Experimental Determination of Elastic Moduli of the Crystalline Regions in the Direction Perpendicular to the Chain Axis in Oriented Polymers. (II). Isotactic Polypropylene.** Ichiro Sakurada, Taisuke Ito and Katsuhiko Nakamae. *Kobunshi Kagaku*, 21, 197 (1964), in Japanese—Elastic moduli of the crystalline region in the direction perpendicular to the chain axis ( $E_t$ ) for isotactic polypropylene (Isot. PP) were determined by means of an X-ray diffraction method with the same experimental technique described in Part I. Based on a simple series model the  $E_t$ -values for Isot. PP were calculated for the following two different equatorial planes.

$$\begin{aligned} \text{Isot. PP: (110) } E_t &= 2.9 \times 10^4 \text{ kg/cm}^2 \\ \text{(040) } E_t &= 3.2 \times 10^4 \text{ kg/cm}^2 \text{ (28}^\circ\text{C)} \end{aligned}$$

As the modulus parallel to the chain direction was found in our previous paper to be  $42 \times 10^4 \text{ kg/cm}^2$ , there is a remarkable anisotropy of the modulus in the parallel and perpendicular directions to the chain axis. This may reasonably be attributed to the different extension mechanisms of the polymer crystal in the two directions. In view of the experimental error importance may not be placed on the difference between the  $E_t$ -values obtained for two different planes. It was shown that the crystal moduli in the perpendicular direction are of the same order of magnitude as for the specimen modulus ( $Y_t = 2.3 \times 10^4 \text{ kg/cm}^2$ ). This seems to mean that the extension of crystalline and amorphous regions in the direction perpendicular to the chain axis occurs by a similar mechanism. It should further be noted that the  $E_t$ -values for Isot. PP have a magnitude just comparable to those for polyethylene

(PE) ( $3\sim 4 \times 10^4 \text{ kg/cm}^2$ ) described in I, Since, in an essential meaning, the crystals of both polymers are composed of saturated paraffine chains, the interchain cohesion forces may be compared by comparing the closeness of the packing of the atoms in the crystal. Thus the similarity of the  $E_t$ -values for the two polymers seems to be explained from the similar values of the mean effective volume per carbon atom calculated for their crystal structures ( $23.1 \text{ \AA}^3$  and  $24.8 \text{ \AA}^3$  for PE and Isot. PP, respectively, neglecting the hydrogen atoms).

**Experimental Determination of Elastic Moduli of the Crystalline Regions in the Direction Perpendicular to the Chain Axis in Oriented Polymers. (III). Polyoxymethylene** Ichiro Sakurada, Taisuke Ito and Katsuhiko Nakamae. *Kobunshi Kagaku*, **21**, 197 (1964), in Japanese—Elastic modulus of the crystalline region corresponding to the perpendicular direction to the chain axis ( $E_t$ ) was determined by an X-ray diffraction method. The crystal strain was obtained under constant load by measuring the spacing strain of an equatorial plane ( $10\bar{1}0$ ) which gave a very sharp and strong reflection. The crystal modulus was calculated as follows based on a simple series model:

$$\text{POM: } (10\bar{1}0) \quad E_t = 8.0 \times 10^4 \text{ kg/cm}^2 \quad (28^\circ\text{C})$$

The  $E_t$ -value is about 1/7 of the  $E_l$ -value, the modulus corresponding to the chain direction, i. e.  $54 \times 10^4 \text{ kg/cm}^2$  (this Journal **19**, 292 (1962)). The value is of the same magnitude as that for polyvinyl alcohol,  $9 \times 10^4 \text{ kg/cm}^2$ , while, two to three times as large as those for polyethylene ( $3\sim 4 \times 10^4 \text{ kg/cm}^2$ ) or isotactic polypropylene ( $3 \times 10^4 \text{ kg/cm}^2$ ). Those  $E_t$ -values seem to have some relation, in a qualitative meaning, with the crystalline densities or the closeness of packing of the atoms in the crystals. The specimen modulus was found to be  $E_t/1.7$ .

**Experimental Determination of Elastic Moduli of the Crystalline Regions in Oriented Polymers. (IV). Isotactic Polystyrene** Ichiro Sakurada, Taisuke Ito and Katsuhiko Nakamae. *Kobunshi Kagaku*, **21**, 206 (1964), in Japanese—Elastic modulus of the crystalline region parallel to the chain axis ( $E_l$ ) for isotactic polystyrene (Isot. PSt) was determined by an X-ray diffraction method with the same experimental technique as previously described in Part I. The modulus was found to be as follows:

$$\text{Isot. PSt:} \quad E_l = 12 \times 10^4 \text{ kg/cm}^2 \quad (23^\circ\text{C})$$

The result essentially agrees with that reported by Newman and Miller ( $E_l = 9.2 \times 10^4 \text{ kg/cm}^2$ ). The value is the smallest among those we have so far obtained for several crystalline polymers.

The crystal modulus for Isot. PSt was compared with that for isotactic polypropylene (Isot. PP), namely,  $42 \times 10^4 \text{ kg/cm}^2$  (See Part II). It is calculated, from the consideration of the effective cross-sectional area of the chain in the crystal, that "the modulus per chain" for Isot. PSt is 1/1.7 of that for Isot. PP. As both the chain skeletons in the two crystals are found by Natta to take the same type of the helical configuration, the difference of the chain elastic moduli for the two crystals should be explained in terms of the contribution of the intra- and intermolecular cohesion forces to the skeleton extensions in the chain direction.

**Saponification of Polyvinyl Acetates Prepared by Various Procedures.** Ichiro Sakurada, Yasuyoshi Sakaguchi, Zenya Shiiki and Jun Nishino. *Kobunshi Kagaku*, **21**, 241 (1964), in Japanese—Isotactic polyvinyl acetate (iso-PVAc) derived from isotactic polyvinyl ether and syndiotactic polyvinyl acetate (synd-PVAc) derived from polyvinyl trifluoroacetate were saponified in a mixture of acetone-water (7:3 by volume) using NaOH as a catalyst. Iso-PVAc showed a lower initial rate and a larger autocatalytic effect of the saponification compared with synd-PVAc. The differences between the both polymers were not so large as those between polymethyl acrylates of different steric configurations. The saponification rates of polyvinyl acetates prepared by radical polymerization of vinyl acetate or vinyl benzoate under various conditions were compared, but practically no difference was observed. The value was nearly the same as that of synd-PVAc. Therefore, these samples seemed to have nearly the same steric configuration. Some discussions on the results were described.

**Polymerization of Methacrylic Anhydride.** Ichiro Sakurada, Takehisa Iwagaki and Yasuyoshi Sakaguchi. *Kobunshi Kagaku*, **21**, 270 (1964), in Japanese—Methacrylic anhydride was polymerized in various solvents (dimethyl formamide, benzene, toluene, n-hexane) at various monomer concentrations (1~10 wt%) and temperatures (5~100°C) with a radical initiator. All polymers were soluble, and their IR-spectra showed the characteristic absorption bands of the six-membered ring of anhydride, and no characteristic band of five-membered ring of anhydride and of unsaturated double bonds were detected. From the above results, the polymers seem to be linear and have the head-to-tail structure. Degrees of polymerization of polymethacrylic acids (PMAA) derived from the polymethacrylic anhydrides were about 100. The PMAA's were esterified to polymethyl methacrylates (PMMA) and their IR-spectra were examined. The spectra of the polymers prepared by polymerization at relatively low temperature were nearly the same as those of conventional PMMA, and the spectra of the polymers prepared by polymerization at higher temperature and lower monomer concentration were nearly the same as those of isotactic PMMA.

**Intramolecular Reactions of Polyvinyl Alcohols Prepared by Various Procedures.** Ichiro Sakurada, Yasuyoshi Sakaguchi and Zenya Shiiki. *Kobunshi Kagaku*, **21**, 289 (1964), in Japanese—Isotactic polyvinyl alcohol (isot-PVA) derived from isotactic polyvinyl ether and syndiotactic polyvinyl alcohol (synd-PVA) derived from polyvinyl trifluoroacetate were acetalized with acetaldehyde. Isot-PVA showed a larger reactivity than synd-PVA, however synd-PVA and PVA's derived from polyvinyl acetate prepared by radical polymerization under various conditions showed nearly the same reactivity to each other. The reactivities of isot-PVA with boric acid and borax were also larger than those of the other PVA's. From these results and the previously reported one for the saponification of polyvinyl acetate samples, PVA's derived from polyvinyl esters prepared by radical polymerization seem to have similar steric structures. Short branches in the polymer molecule may be the chief reason for the difference of the crystallinity of these PVA samples.

**Saponification Reaction of Polymethyl Acrylates Prepared by Various Methods**

**of Radical Polymerization.** Ichiro Sakurada, Yasuyoshi Sakaguchi, Takehisa Iwagaki and Yasuya Mikuzu. *Kobunshi Kagaku*, **21**, 426 (1964), in Japanese—Polymethyl acrylates prepared by radical polymerization of acrylic acid, methyl acrylate, tetrahydrofurfuryl acrylate and acrylic anhydride were saponified in a acetone-water mixture (7:3 by volume) using NaOH as a catalyst. Polymethyl acrylate, which differed markedly from the others in potentiometric titration behaviors and seemed to be more syndiotactic, showed a much higher initial rate of saponification (about 20 times) than the others, and the apparent rate constant of the sample decreased with conversion contrary to those of the other samples. Methyl acrylate polymers prepared by radical polymerization at various compositions of polymerization mixtures and temperatures showed nearly the same reaction rate to each other; therefore it seems that they have nearly the same steric configuration. Some discussions were given for the results.

**Effects of Polymer Concentration on the Rate of Acetalization of Polyvinyl Alcohol and Saponification of Partially Acetylated Polyvinyl Alcohol.** Ichiro Sakurada, Yasuyoshi Sakaguchi, Shuji Yoshida and Yasuhiro Ōmura. *Kobunshi Kagaku*, **21**, 517 (1964), in Japanese—Polyvinyl alcohol (PVA) was acetalized with acetaldehyde in water or a water-dioxane mixture using *N*/200 sulphuric acid or hydrochloric acid as a catalyst. The rate of acetalization was almost independent of polymer concentration (0.05~0.20 base mol/l). The rate of deacetalization of partially acetalized PVA was also investigated in a water-dioxane mixture using *N*/100 sulphuric acid as a catalyst, and it was found that addition of PVA to the reaction mixture decreased the reaction rate. These results are provoking contrast to those obtained by Smets and Petit. Rate of saponification of partially acetylated PVA in water or a water-dioxane mixture with *N*/200 hydrochloric acid was almost independent of polymer concentration and of addition of PVA. Some discussions were given for the results.

**Maximum Conversions of Acetalization of Polyvinyl Alcohol with Aldehydes Containing Sulfonic Acid Groups.** Ichiro Sakurada, Yasuyoshi Sakaguchi and Yasuhiro Ōmura. *Kobunshi Kagaku*, **21**, 564 (1964), in Japanese—Polyvinyl alcohols were acetalized with aldehyde sulfonic acids such as  $\beta$ -butyraldehyde sulfonic acid, *o*-benzaldehyde sulfonic acid and 2,4-benzaldehyde disulfonic acid in solution. The maximum conversions of the reactions were generally much lower than the calculated value from Flory's theory, and dependent on the steric configurations of polymer and the compositions of the reaction mixtures. Steric hindrance and/or electrostatic effects by acetals introduced into the polymer chains seem to be the reasons for these results. Statistical calculations were given for the maximum conversions.

**Effects of Sodium Chloride on Acetalization of Polyvinyl Alcohol in Water.** Ichiro Sakurada, Yasuyoshi Sakaguchi and Shuji Yoshida. *Kobunshi Kagaku*, **21**, 620 (1964), in Japanese—Polyvinyl alcohol (PVA) and some low molecular weight polyhydric alcohols were acetalized with various aldehydes (acet-, propion- and *n*-butyr-aldehyde) in water, using acid catalysts (hydrochloric acid, methanesulfonic

acid and toluenesulfonic acid), and the effects of addition of sodium chloride on the initial rate of the reactions were investigated. Sodium chloride (0~0.7*M*) generally accelerated acetalization of polyhydric alcohols, and the order of the acceleration effects was PVA>pentaerythritol>1,3-butanediol>1,3-propanediol. For example, by addition of 0.7*M* sodium chloride the acetalization rate of PVA increased nearly twice. The acceleration effect was nearly independent on the reaction temperature (5~70°C) in the case of the PVA, but increased with decreasing reaction temperature in the cases of the other alcohols. In the cases of the any alcohol the acceleration effect was nearly independent on concentration ( $[\text{OH}]=0.05\sim 0.02M$ ) of the alcohol and the kind and concentration (*N*/200 and *N*/10) of catalysts. Hydrolysis of ethyl acetate under the similar conditions was accelerated only slightly by addition of sodium chloride.

**Studies on Graft Polymerization onto Cotton. (X) Graft Polymerization of Styrene Emulsions Containing Non-ionic Emulsifiers to Cotton Imbibing Catalysts.** Ichiro Sakurada and Yasuyoshi Sakaguchi. *Sen-i Gakkaishi*, 20, 392 (1964), in Japanese—Cotton fabric imbibing aqueous solutions of  $\text{K}_2\text{S}_2\text{O}_8$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and  $\text{H}_2\text{O}_2$  or methanol solutions of  $\alpha$ ,  $\alpha'$ -azo-bisisobutyronitrile and benzoyl peroxide was heated with styrene emulsions containing non-ionic emulsifiers (polyethylene glycol oleate and laurate) in sealed tubes. The quantity of used styrene was about 1.4g per g-cotton. The effects of various factors on the grafting were examined.

In contrast to the cases of graft copolymerization with pure styrene, the effects of quantities (0.100%) and concentration (0.2~3%) of imbibing catalyst solution are relatively small. For the graft polymerization with pure styrene,  $\text{K}_2\text{S}_2\text{O}_8$  is generally more effective than the other catalysts, but  $\text{H}_2\text{O}_2$  is also as effective as  $\text{K}_2\text{S}_2\text{O}_8$  in the present cases. The atmosphere (air and nitrogen) at the polymerization had a little effect on the grafting as in the cases of grafting with pure styrene. Polymerization temperature (60, 90°C) has a greater effect on the grafting rate, but a less effect on the graft efficiency. The behaviors of the both emulsifiers are similar. The concentration (0.1~2%) of the emulsifier in emulsions has a greater effect on the grafting, and the highest grafting is obtained at the highest concentration of the emulsifier. The degree of grafting of about 70% may be obtained under suitable conditions.

**Studies on Graft Polymerization onto Cotton. (XI). Graft Polymerization of Styrene Emulsions Containing Cationic Emulsifiers to Cotton Imbibing Catalysts.** Ichiro Sakurada and Yasuyoshi Sakaguchi. *Sen-i Gakkaishi*, 20, 392 (1964), in Japanese—Cotton fabric imbibing aqueous solutions of  $\text{K}_2\text{S}_2\text{O}_8$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and  $\text{H}_2\text{O}_2$  or methanol solutions of  $\alpha$ ,  $\alpha'$ -azo-bisisobutyronitrile and benzoyl peroxide was heated with styrene emulsions containing cationic emulsifiers (lauryl pyridinium chloride, cetyl pyridinium bromide and lauryl trimethyl ammonium chloride) in sealed tubes. The quantity of used styrene was about 1.4g per g-cotton. The effects of various factors on the grafting were examined.

The effects of quantities (0.100%) and concentration (0.2~3%) of imbibing catalyst solutions and atmosphere (air and nitrogen) at the polymerization are generally small.  $\text{K}_2\text{S}_2\text{O}_8$  and  $\text{H}_2\text{O}_2$  are more effective than the other catalysts. Poly-

merization temperatures (60, 90°C) have a great effect on the rate of grafting, but the less effect on the graft efficiency. These behaviors are similar to those of the emulsions containing non-ionic emulsifiers. However, the behaviors of grafting depends considerably on the kinds of cationic emulsifiers used and the highest grafting was obtained at a relatively low concentration of the emulsifier in contrast to the emulsions containing non-ionic emulsifiers. Some abnormalities were found in the lauryl ammonium chloride 0.5%-K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system. The degree of grafting of about 60% is obtainable under suitable conditions.

**Studies on Graft Polymerization onto Cotton. (XII). Graft Polymerization of Styrene Emulsions Containing as Anionic Emulsifier of Cotton Imbibing Catalysts.** Ichiro Sakurada and Yasuyoshi Sakaguchi. *Sen-i Gakkaishi*, 20, 392 (1964), in Japanese—Cotton fabric imbibing aqueous solutions of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and H<sub>2</sub>O<sub>2</sub> or methanol solutions of  $\alpha$ ,  $\alpha'$ -azo-bisisobutyronitrile and benzoyl peroxide was heated with styrene emulsions containing sodium lauryl sulphate as an emulsifier in sealed tubes. The quantity of used styrene was about 1.4 g per g-cotton. The effects of various factors such as compositions of imbibing catalyst solutions and styrene emulsions, and temperature, time and atmosphere of polymerization on the grafting were studied. The degree of grafting of about 30% is obtained only when concentration of the emulsifier is 0.03~0.1%, and the catalyst is H<sub>2</sub>O<sub>2</sub>.

There is an intimate relationship between the degree of grafting and the rate of homopolymerization of styrene emulsion, and almost all plots of the degree of grafting vs. the rate of homopolymerization under the same conditions lie, independent of the nature of the emulsifiers, on the same curve. The degree of grafting becomes highest when the rate of homopolymerization has a medium value.

Furthermore, the secondary graft-polymerization of styrene to dry styrene grafted cotton fabric imbibing K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was studied and it was found that the graft-polymerization proceeded smoothly in the absence of water. Therefore, the acceleration effect of water on the grafting is due mainly to its swelling effect on the fabric.

**Studies on Graft Polymerization onto Cotton. (XIII). Graft Polymerization of Styrene to Viscose Rayons Imbibing Catalysts.** Ichiro Sakurada, Yasuyoshi Sakaguchi and Yasui Sakai. *Sen-i Gakkaishi*, 20, 454 (1964), in Japanese—Fabric from viscose rayon filament and crimped viscose rayon staple fibers imbibing aqueous solutions of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and H<sub>2</sub>O<sub>2</sub> or methanol solutions of  $\alpha$ ,  $\alpha'$ -azo-bisisobutyronitrile were heated in sealed tubes with pure styrene or with styrene emulsions containing various emulsifiers such as polyethylene glycol oleate and laurate, lauryl pyridinium chloride, cetyl pyridinium bromide, lauryl trimethyl ammonium chloride and sodium lauryl sulphate. The effects of various factors such as compositions of imbibing solutions and temperature, time and atmosphere of polymerization on the grafting were examined, and the results were compared with those for cotton. Proportionality was found between the degrees of grafting of cotton and those of rayons, and the degree of grafting of rayon was higher than that of cotton.

Dry rayons imbibing K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were also heated with styrene-methanol mixtures.

The grafting to rayons proceeded more smoothly than to cotton under conditions studied here.

**Studies on Graft Polymerization onto Cotton. (XIV). Graft Polymerization of Vinyl Acetate to Cellulose Fibers Imbibing Catalysts.** Ichiro Sakurada, Yasuyoshi Sakaguchi and Yasui Sakai. *Sen-i Gakkaishi*, **20**, 454 (1954), in Japanese—Cotton fabric, fabric from viscose rayon filament and crimped viscose rayon staple fibers imbibing aqueous solutions of  $K_2S_2O_8$ ,  $(NH_4)_2S_2O_8$  and  $H_2O_2$  or methanol solutions of  $\alpha$ ,  $\alpha'$ -azo-bisisobutyronitrile and benzoyl peroxide were heated with vinyl acetate in sealed tubes. The effects of various factors such as compositions of imbibing solutions, quantities of vinyl acetate, temperature, time and atmosphere of heating on the grafting were examined.  $K_2S_2O_8$  and  $(NH_4)_2S_2O_8$  are more effective than the other catalysts. The higher the concentration of catalysts and the temperature of heating, the higher the rate and the efficiency of the grafting. Such behaviors differ considerably from those of grafting of styrene. Grafting to rayons was easier than to cotton. The degree of grafting of about 140% was obtained under suitable conditions.

Dry cellulose fibers imbibing catalysts were also heated with vinyl acetate-organic solvent mixtures. Methanol, acetic acid, petroleum benzene and ligroin were used as solvents, but no desirable results were obtained. The secondary grafting of vinyl acetate to dry vinyl acetate grafted cellulose fibers imbibing  $K_2S_2O_8$  was also examined, but the grafting proceeded slightly in the absence of water. Vinyl acetate markedly differs from styrene in these points.

**Studies on Graft Polymerization onto Cotton. (XV). Graft Polymerization of Vinyl Acetate Emulsions to Cellulose Fibers Imbibing Catalysts.** Ichiro Sakurada and Yasuyoshi Sakaguchi. *Sen-i Gakkaishi*, **20**, 454 (1964), in Japanese—Cotton fabric and fabric from viscose rayon filament imbibing  $K_2S_2O_8$  and  $H_2O_2$  were heated with vinyl acetate emulsions containing various emulsifiers in sealed tubes. The effects of various factors such as kinds and concentration of catalysts and emulsifiers, temperature, time, and atmosphere of heating on the grafting were examined.

The grafting to rayon proceeded smoothly when emulsions contain non-ionic emulsifiers, namely polyethylene glycol oleate, and laurate, but no desirable results were obtained when emulsions contain cationic or anionic emulsifiers. In contrast to the grafting with pure vinyl acetate,  $H_2O_2$  is more effective than  $K_2S_2O_8$ . The grafting to cotton is generally difficult; vinyl acetate differs considerably from styrene in this point. A similar relationship to the grafting of styrene emulsions was found between the degree of grafting to rayon and the rate of homopolymerization of vinyl acetate emulsions. The result may be interpreted from the view points of the homopolymerization rate, penetration of monomers into fibers and chain transfer of catalysts.

**Graft Polymerization of Styrene onto Polyvinyl Alcohol Fibers Imbibing Catalysts.** Ichiro Sakurada and Yasuyoshi Sakaguchi. *Sen-i Gakkaishi*, **20**, 548 (1964), in Japanese—Untreated and heat-treated (at 180°C or 225°C) polyvinyl alcohol (PVA) fibers imbibing solutions (1 g/g-fiber) of various catalysts were heated with styrene

(1.8 g/g-fiber) in sealed tubes for graft polymerization. When potassium or ammonium persulfate were used as catalysts, the grafting generally proceeded smoothly, and the graft efficiencies of about 90% were obtained under suitable conditions. The graft efficiencies were affected only a little by catalyst concentrations (0.3~3%), solvents (water, water 15-methanol 85, water 30-acetone 70) of the imbibing solutions, and heating temperatures. In the cases of hydrogen peroxide, the graft efficiencies were generally lower than those in the cases of persulfates, but the efficiencies of about 80% were obtained under favorable conditions. The graft efficiencies increased with decreasing catalyst concentrations and heating temperatures, and increasing water contents of the imbibing solutions. In the cases of  $\alpha$ ,  $\alpha'$ -azo-bisisobutyronitrile and benzoyl peroxide, the grafting did not proceed so smoothly as in the cases of persulfates; the efficiencies were only about 55% even under favorable conditions, and the efficiencies were affected considerably by catalyst concentrations and heating temperatures.

The grafting was affected only a little by previous heat treatment of the fiber so far as the water contents of imbibing solutions were high, but considerably affected when the water contents were lower.

As the other series of experiments, dry PVA fibers imbibing catalysts were heated with styrenemethanol mixtures for the grafting, and it was found that the reaction proceeded as smoothly as with fibers imbibing catalyst solutions. But, the grafting scarcely proceeded when dry fibers were heated with pure styrene.

Graft polymerization of styrene in emulsion states onto PVA fibers were also investigated, The grafting of high efficiencies could be obtained using 2% polyethylene glycol oleyl ether as an emulsifier.

The grafting behaviors of the PVA-styrene system were generally similar to those of the cellulose-styrene system, but some small differences were found between them.

**Graft Polymerization of Vinyl Acetate onto Polyvinyl Alcohol Fibers Imbibing Catalysts.** Ichiro Sakurada and Yasuyoshi Sakaguchi. *Sen-i Gakkaishi*, 20, 555 (2964), in Japanese—Untrated and heat-treated (at 180°C or 225°C) polyvinyl alcohol (PVA) fibers imbibing solutions (1 g/g-fiber) of various catalysts were heated with vinyl acetate in sealed tubes for graft polymerization. When potassium or ammonium persulfate were used as catalysts, the grafting proceeded smoothly under suitable conditions, but the efficiencies were generally lower than those in the case of styrene, and were affected by heating temperatures and solvents of the imbibing solutions. In the cases of hydrogen peroxide, the grafting proceeded with some ease when water contents of the imbibing solutions were high, but the efficiencies were generally lower than those in the case of persulfates. In the cases of  $\alpha$ ,  $\alpha'$ -azo-bisisobutyronitrile and benzoyl peroxide, the homopolymerization proceeded predominantly as the grafting scarcely occurred.

The grafting was affected to a greater extent than in the case of styrene by heat treatment of raw PVA fibers.

Dry PVA fibers imbibing catalysts were also heated with vinyl acetate-methanol mixtures. The grafting proceeded slightly when fibrous structures were maintained, but proceeded considerably when fibers dissolved in monomer mixtures during the

heating. In this case the products of about 50% increased weight dissolved almost completely in acetone.

The grafting of vinyl acetate in emulsion states onto PVA fibers were also examined, but no desirable results were obtained.

The difference of grafting behaviors between vinyl acetate and styrene onto PVA fibers was similar to that onto cellulose fibers.

**Graft Polymerization of Styrene and Vinyl Acetate onto Nylon Fabric Imbibing Catalysts.** Ichiro Sakurada, Yasuyoshi Sakaguchi and Yasui Sakai. *Sen-i Gakkaishi*, 20, 613 (1964), in Japanese—Nylon fabric imbibing solution (0.1~2 g/g-fabric) of various catalysts was heated with styrene (2.0 g/g-fabric) in sealed tubes for the grafting. When potassium or ammonium persulfate were used as catalyst, the grafting generally proceeded smoothly, and the graft efficiencies of about 90 % were obtained under favorable conditions. The efficiencies were affected to a smaller extent by catalyst concentrations (0.2~2%), heating temperatures (60 and 90°C), and atmospheres of heating (air or nitrogen). In the case of hydrogen peroxide, the efficiencies were generally lower than those in the case of persulfates, and increased with decreasing catalyst concentration and heating temperature. The grafting proceeded to some extent in the case of  $\alpha$ ,  $\alpha$ -azo-bisisobutyronitrile (AIBN), but the maximum efficiencies of only about 40 % were obtained in the case of benzoyl peroxide (BPO). The grafting also proceeded smoothly when dry nylon fabric imbibing potassium persulfate (KPS) was heated with styrene-methanol mixtures.

Nylon fabric imbibing solution of catalysts was heated with vinyl acetate. The graft efficiencies were generally lower than those in the case of styrene, but persulfates gave an efficiency of about 60% under suitable conditions. The grafting proceeded only with low efficiencies in the case of hydrogen peroxide, and scarcely occurred in the case of AIBN and BPO. The grafting of vinyl acetate onto dry nylon fabric imbibing KPS was also examined, but no desirable results were obtained.

The behaviors of grafting onto nylon are generally similar to those onto cellulose and polyvinyl alcohol fibers, though the former fiber considerably differs from the latter in the chemical structure and the hydrophobic property.

**Das scheinbare sepezifische Volumen von Copolymeren in Lösung.** Hiroshi Inagaki. *Makromolekulare Chemie*, 75, 217 (1964)—The physical meaning of the apparent specific volume  $v_2^*$  of macromolecules in solution is discussed on the basis of the statistical thermodynamical theory. It is pointed out the  $v_2^*$ - value for macromolecules provides a measure for the interaction between segment and solvent molecules and is rather insensitive to changes in the molecular weight. Thus is emphasized here an important relation between the  $v_2^*$ - value and the chemical structure of solute. An application of this theory is described in connection with the chemical structure of copolymers of different monomers.

**Endgruppeneffekt des Knäuelmoleküls auf Lösungseigenschaften. (I). Polyäthylenglykol mit ionisierbaren Endgruppen.** Hiroshi Inagaki und M. Tanaka. *Makro-*

*molekulare Chemie*, 74, 145 (1964)—Um den Endgruppeneffekt von Knäuelmolekülen aufzuklären, wurde eine Modellschubstanz hergestellt. Als Ausgangsmaterial verwendeten wir Polyäthylenglykole mit verschiedenen Molekulargewichten und veresterten das Hydroxyl an jedem Ende der Kette mit Pyromellithsäure-Anhydrid. Damit besitzt das Polyäthylenglykol an jedem Ende einen dreiwertigen, ionisierbaren Rest. Durch Vergleich des Staudingerindex der wäßrigen Lösung der nicht dissoziierten Probe mit demjenigen der dissoziierten ( $-\text{COO}^- + \text{Na}^+$ ) wurde ein Expansionsfaktor der Knäueldimension  $\alpha$  ausgerechnet.

Andererseits leiteten wir eine Gleichung für  $\alpha$  auf Grund der statistischen Theorie ab, die durch

$$\alpha^3 - \alpha = C_K \sqrt{M} + A/\sqrt{M}$$

ausgedrückt wird. Hierbei ist  $C_K$  eine nur vom Lösungsmittel und der Meßtemperatur abhängige Konstante, die sich auf den Volumeneffekt zwischen den Segmenten bezieht, während  $A$  eine rein mit der elektrolytischen Eigenschaft der Endgruppe verbundene Konstante ist. Es wurde festgestellt, daß die Meßdaten auf Grund der hier entwickelten Theorie sehr gut gedeutet werden können und daß die Wirkung des Endgruppeneffektes auf die Knäueldimension mit Zunahme des Molekulargewichtes erwartungsgemäß ziemlich schnell verschwindet. Außerdem zeigte das Experiment, daß die Einführung der Endgruppe die ungestörte Knäueldimension stark beeinflusst.

**Anwendung der Ultrazentrifugen-Methode von Archibald bei der Untersuchung verdünnter Polymerlösungen. (IV). Molekulargewichtsbestimmung von Polystyrol und Polymethylmethacrylat in Butanon.** Hiroshi Inagaki und Shuji Kawai. *Makromolekulare Chemie*, 79, 42 (1964)—Die Ultrazentrifugen-Methode von Archibald gibt dieselben Informationen über hochpolymere Lösungen wie die Lichtstreuungsmethode; sie liefert das Gewichtsmittel des Molekulargewichtes und den zweiten osmotischen Virialkoeffizienten. Diese Methode hat jedoch einen Nachteil, insbesondere bei Untersuchung der Polymeren in guten Lösungsmitteln; die Auftragung der Meßdaten nach der Theorie weist oft eine ausgeprägte, nach oben gerichtete Krümmung auf, wodurch die Extrapolation auf die Konzentration Null schwierig wird. Es wurde daher ein halbempirisches Verfahren vorgeschlagen, um diese Schwierigkeit zu vermeiden<sup>9)</sup>. Wir haben nunmehr das Verfahren durch Messungen an Lösungen von Polystyrol und Polymethylmethacrylat in guten Lösungsmitteln überprüft und die erhaltenen Molekulargewichte und zweiten Virialkoeffizienten mit den bisherigen Daten anderer Autoren verglichen.

**Second Virial Coefficient of Linear Polymer Molecules.** Michio Kurata, Masaaki Fukatsu, Hideto Sotobayashi and Hiromi Yamakawa. *Journal of Chemical Physics*, 41, 139 (1964)—A variation theory is developed for obtaining a closed expression for the second virial coefficient  $A_2$  of linear polymer molecules, which corresponds to the Fixman theory of the excluded volume effect. It is shown that the second virial coefficient of the polymer in good solvents is effectively identical with that of a nonpenetrating sphere whose radius is proportional to the root-mean-square statistical radius  $\langle S^2 \rangle^{1/2}$ . In extremely good solvents,  $A_2$  becomes a constant independent of molecular weight  $M$ . A graphical method is proposed for separate

determination of the effective bond length and the polymer-solvent interactions; the method consists of plotting  $A_2M^{1/2}$  against  $M^{1/2}$ . Applications of this method are illustrated by four examples, polystyrene in toluene, isotactic polypropylene in tetralin and in  $\alpha$ -chloronaphthalene, and nitrocellulose in acetone. The effective bond lengths obtained are in good agreement with those previously evaluated from the molecular weight dependence of intrinsic viscosity  $[\eta]$ , but the polymer-solvent interaction are not. The theoretical value of the ratio  $A_2M/[\eta]$  is about 60 in good solvents, which is approximately a half of the ordinary experimental values.

A modification of the variation theory is proposed, which corresponds to Ptit-syn's modification of the Fixman theory and leads to a more plausible value 110 for  $A_2M/[\eta]$ .

The triple contact term in the perturbation expansion series of  $A_2$  is also evaluated. It is found that the expansion of a molecular coil due to the volume effect is somewhat suppressed by intermolecular interactions in the proximity of the second molecule.

**Unperturbed Dimension and Translational Friction Constant of Branched Polymers.** Michio Kurata and Masaaki Fukatsu. *Journal of Chemical Physics*, **41**, 2934 (1964)—A theory of the conformational properties of random-flight branched molecules is developed for estimating the branching effect on the translational friction constant  $\Xi_b$  as well as on the mean-square statistical radius  $\langle S^2 \rangle_b^{2/1}$ . Calculations are made for three types of branching—star, normal (or linear) and random types, and for two types of distribution of the branch units—uniform and random types. It is found that the contraction of molecular dimensions produced by branching occurs to the highest degree in the star types of branching and to the lowest degree in the normal type of branching, and that the heterogeneity in the distance between the nearest pair of branch units generally diminishes the degree of the molecular contraction. The applicability of the Flory type equation,  $\Xi_b = \eta_0 P_b \langle S^2 \rangle_b^{2/1}$ , to the branched molecules is discussed with the intention of searching the experimental method for determination of the number of branch units involved in the various types of branched molecules. Here  $\eta_0$  is the viscosity of solvent and  $P_b$  is the proportional factor corresponding to Flory's universal constant in the linear polymers.

**Shear Rate Dependence of Flow Birefringence of Polymer Solutions.** Ryuzo Koyama. *Journal of the Physical Society of Japan*, **19**, 1709 (1964)—The shear rate dependence of flow birefringence of polymer solutions is discussed by making use of the recent statistical theory of flexible random coiling molecule with an assumption of optical interaction between molecular segments in solvent.

The result of calculation shows that the from anisotropy of polymer molecule decreases relatively to the intrinsic anisotropy with increasing shear rate and this property explains the anomalous shear rate dependences of birefringence and extinction angle observed recently with dioxane solutions of large molecular weight polystyrene by Frisman and Tsvetkov.

The molecular connguration obtained by calculation shows a non-coincidence between the anisotropy of segments-orientation and that of molecular shape-defor-

mation in solution shear, and this confirms the anomaly of extinction angle calculated. The same calculation also shows the expansion of molecular volume by the shear, which accounts for the decrease of from anisotropy due to optical interaction in large shear rates.

**Crystallographic Study of Xylan from Wood.** Masao Horio and Rikizo Imamura. *Journal of Polymer Science, Part A, 2*, 627 (1964)—Some preparations of xylan in the form of transparent membrane or amorphous powder prepared from deciduous woods such as beech and birch show a number of Debye-Scherrer rings at the irradiation with x-ray. Of special interest from the crystallographic standpoint is the diffraction pattern of the membrane, which shows an indication of a fiber diagram with the beam parallel to the surface, and this is more obvious when the membrane is stretched to an appropriate extent by rolling. The diagram can be neatly interpreted on the basis of an end surface-centered rhombic cell whose two axes of the base plane have exactly the ratio of  $\sqrt{3}:1$ , within the limit of experimental error. It is assumed that the cell has a trigonal or hexagonal symmetry. The observed reflections are indexed on the base of orthohexagonal unit cell, whose postulated three axes are  $a=9.16$  A.,  $b=\sqrt{3}a$ ., and  $c=15.5$  A. (fiber axis). The crystalline lattice of xylan is susceptible to mechanical treatment, heat, and moisture. The crystallinity depends greatly upon the uronic acid content. The diffraction pattern becomes less distinct and the interplanar spacings are enlarged with increasing uronic acid content, until at last the pattern diffuses into a single halo.

**Dynamic Birefringence of Several High Polymers.** R. Yamada and C. Hayashi S. Onogi and M. Horio. *Journal of Polymer Science, Part C, No. 5*, 123 (1964)—The complex strain-optical coefficient, complex stress-optical coefficient, complex modulus of elasticity and the corresponding loss tangent of phase angles between the stress, strain and birefringence have been measured for several high polymers in the frequency range from 0.001 to 10 cycles/sec. Frequency and temperature dependences of the dynamic optical properties of vulcanized Hevea rubber are very similar to those of the dynamic mechanical properties. On the other hand, the dynamic optical properties of polyethylene and polypropylene show remarkable dispersions in the above frequency range. The dynamic optical behavior of these three materials are very typical and are quite different from each other. The differences have been explained by considering different frequency dependences of three kinds of deformation mechanism, namely, orientation of molecules in amorphous region, deformation of spherulites, and orientation of crystals.

**Rheological Properties of Polyethylene Melts: Effects of Temperature and Blending.** Masao Horio, Tsuguo Fujii and Shigeharu Onogi. *Journal of Physical Chemistry*, 68, 778 (1964)—Dynamic viscosity  $\eta'$ , dynamic rigidity  $G'$ , and apparent viscosity  $\eta_a$  of polyethylene blends in the molten state have been measured by means of a concentric cylinder-type rheometer which enables us to measure not only dynamic but also steady flow properties. The frequency ranges from about  $5 \times 10^{-4}$  to 1 c. p. s., and the rate of shear from about 0.004 to 4 sec.<sup>-1</sup>.  $\eta'$  and  $G'$  as functions

of frequency as well as  $\eta_a$  as a function of rate of shear for each blend of two components at different temperatures (140–200°C) can be superposed according to the usual time-temperature superposition principle, and shift factors  $a_T$  from  $\eta'$  and  $G'$  are practically the same. Master curves superposed with respect to temperature can also be superposed very well with respect to the blending ratio or to the weight-average molecular weight. For blends of two components whose molecular weights are not so different, the logarithm of the shift factor  $a_M$  bears a linear relationship to the blending ratio. On the other hand, for blends of two components differing very much in their molecular weights, the linearity holds only approximately. The theory proposed by Ninomiya for polymer blends can also be applied to  $G'$  of our systems, and the equilibrium compliance  $J_e$  and viscosity have been evaluated. The evaluated values coincide fairly well with the observed values, but  $J_e$  plotted against blending ration shows no peak. This result differs from those reported by the previous authors for blends of amorphous polymers having different molecular weights.

**The Theory of Crimp of Textile Fibers.** Masao Horio. *Memoirs of the Faculty of Engineering, Kyoto University*, **26**, 222 (1964)—The fundamental idea running through this paper is to correlate the crimps of textile fibers with bilateral structure which was found by the author and collaborators, and a series of results obtained by them on this line are reviewed. Section I outlines the study on the crimped rayon staple which gave rise to finding the bilateral structure. Several species of wool fibers are also endowed *a priori* with bilateral structure, which induces the fibers to crimp as shown in Section II. Section III deals with the mathematical analysis of the dynamics of crimp. The ideal form of crimp is the helical spring, which is preferred to the plane zig-zag form from the practical point of view. Section IV describes the production of bilateral fibers made up of two components by the “conjugate melt spinning” process. It is important in the processes of treating the filaments and fabrics that the component polymers in each bilateral filament should be kept inseparable. The compatibility of the several pairs of polymers is estimated by the study of epitaxy, as mentioned in Section V. It is shown in Section VI that the chemical similarity between different polymers is also an essential factor to produce strong cohesion. In Section VII, some of the practical data of crimps, such as the diameter of helix and the number of crimps per unit length are shown with several kinds of conjugate-spun fibers as a function of degree of stretching before producing coiling, the conditions of heat treatment and so forth.

**Synthesis of p-(N,N-Dialkylaminomethyl) styrene and their Polymerization.** Ryohei Oda, Shigeo Tanimoto, Hideaki Kawata and Motoaki Nomura. *Kogyo Kagaku Zasshi*, **67** 1564 (1964), in Japanese—To *p*-vinylphenylmagnesium chloride (I) in tetrahydrofuran was added N,N-diethylaminomethyl-*n*-butyl ether (II) over a period of 1 hr. After completion of the addition, the mixture was refluxed for 2.0–2.5 hr., hydrolyzed with  $\text{NH}_4\text{Cl}$  aqueous solution, and then resulting organic layer was extracted with ether. The ether solution was washed with  $\text{Na}_2\text{CO}_3$  aqueous solution, and extracted with 2% HCl aqueous solution. The aqueous solution was brought to

alkaline with  $\text{Na}_2\text{CO}_3$ , and resulting organic layer was separated and distilled in a nitrogen atmosphere, to give *p*-(N, N-diethylaminomethyl)styrene (III) (34% yield, bp 91~94°C/5mmHg).

III was polymerized in bulk with azobisisobutyronitrile. This polymer (mp 60~105°C,  $[\eta]=0.31\text{dl. g}^{-1}$  (benzene, 30±0.1°C)) is soluble in  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , benzene, petroleum ether,  $\text{CHCl}_3$ , dioxane,  $\text{CH}_3\text{COC}_2\text{H}_5$ , and insoluble in  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{COCH}_3$ , dimethylformamide, dimethylsulfoxide.

Anion-exchange resin was obtained by the copolymerization of III with divinyl benzene, and the exchange capacity of the resin per 1 g. of dry matter in contact with 0.5N HCl solution was 2.4 meq.

*p*-(N, N-Dimethylaminomethyl) styrene (IV) (28% yield, bp 117~121°C/35mmHg) was prepared in the same manner as above from I in tetrahydrofuran and N, N-dimethylaminomethylisobutyl ether (V). IV was polymerized in bulk with azobisisobutyronitrile, and the polymer ( $[\eta]=0.84\text{ dl. g}^{-1}$  (benzene, 30±0.1°C)) melted at 55~120°C.

Also, in essentially the same manner, *p*-(N, N-di-*n*-propylaminomethyl) styrene (IV) (38% yield, bp 129.5~131°C/7.5mmHg) was prepared from I in tetrahydrofuran and N, N-di-*n*-propylaminomethyl-*n*-butyl ether (VII) except that the reaction mixture was refluxed for 3.0~3.5 hr. after addition of VII to I. VI was polymerized in bulk with azobisisobutyronitrile, and the polymer ( $[\eta]=0.40\text{ dl. g}^{-1}$  (benzene, 30±0.1°C)) melted at 60~90°C.

**Synthesis of *p*-Glycidylstyrene and its Polymerization.** Shigeo Tanimoto and Ryohei Oda. *Kogyo Kagaku Zasshi*, 67, 255 (1964), in Japanese—Epichlorohydrin was added to a *p*-chlorophenylmagnesium chloride solution in tetrahydrofuran at 0~10°C in over 2 hr. The reaction mixture was stirred for 10 min., followed by hydrolysis with diluted  $\text{H}_2\text{SO}_4$ . The organic layer was then poured dropwise into  $\text{C}_2\text{H}_5\text{ONa}$  in  $\text{C}_2\text{H}_5\text{OH}$  at -5~0°C. Water and ether were added to this mixture and the organic layer was separated. This layer was distilled in vacuo and a fraction of the *p*-glycidylstyrene (b. p. 100~110°C/4.5mmHg) was collected. The yield of the *p*-glycidylstyrene, thus obtained, was about 26%.

The *p*-glycidylstyrene, was then polymerized in bulk, using BPO as an initiator. The polymer was soluble in benzene, acetone, chloroform, dioxane and dimethylformamide, but insoluble in ether, petroleum ether, ethanol and water. The melting range of the polymer was 102~154°C,  $[\eta]=0.80$  (in benzene, at 30°C). This polymer could be converted to the corresponding chlorohydrin-polymer by pyridine-hydrochloride.

This polymer was then cross-linked by the reaction with ethylenediamine or with adipic acid. The resulted, crosslinked polymers were hard and insoluble in usual organic solvents and stable to acid and alkali, except  $\text{H}_2\text{SO}_4$ , for example, it was stable in conc. HCl at room temperature for 30 days and also stable in 30% NaOH at 100°C for 10 days.

**The Peroxide-induced Polymerization of Epoxides.** Akira Oku, Masaya Okano and Ryohei Oda. *Bulletin of the Chemical Society of Japan*, 35, 1216 (1964)—The peroxide-induced polymerization of epoxides has been investigated. When styrene

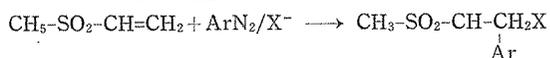
oxide was heated at ca. 140°C in the presence of di-*t*-butyl peroxide, a polyether (M.W. below 2000) was obtained in ca. 10% yield. Both its hydroxyl and carbonyl numbers, which are higher than expected values, seemed to indicate that the polyether structure should be represented in somewhat modified forms. This would arise from the hydrogen abstraction and the disproportionation of the growing alkoxy radical. In the case of phenyl glycidyl ether, a similar result was obtained. On the other hand, the reaction of styrene oxide with benzoyl peroxide at 80°C afforded a polymeric product (M.W. below 1300) having the normal polyether structure in poor yield. Based on these results, it can be concluded that the preparation of high molecular weight polyethers from epoxides by peroxide-induced polymerization is practically impossible.

**Poly(5-iminohydantoins).** Akira Oku, Masaya Okano, and Ryohei Oda. *Makromolekulare Chemie*, 78, 186 (1964).—Starting from diisocyanates and hydrogen cyanide poly(5-iminohydantoins) have been prepared by the following two methods. 1. Polyaddition between a diisocyanate and a di(carbamoyl cyanide), which corresponds to a 1:2 diisocyanate-hydrogen cyanide adduct. 2. Hydrogen cyanide-eliminating polymerization (polycondensation) of a di(carbamoyl cyanide). The former method generally gave more satisfactory results.

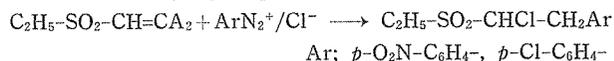
The polymers obtained by polycycloaddition of methylene bis-(4-phenylcarbamoyl cyanide) with methylene bis(4-phenyl isocyanate) and hexamethylene diisocyanate in *N*-methyl-2-pyrrolidone using pyridine catalyst showed a viscosity of  $[\eta] = 0.70$  and 1.25 (both in *N*-methyl-2-pyrrolidone at 25°C.), respectively.

## Organic Chemistry

**The Reaction of Ethyl Vinyl Sulfone with Aromatic Diazonium Chlorides.** Chikahiko Nakashima, Shigeo Tanimoto and Ryohei Oda. *Kogyo Kagaku Zasshi*, 67, 1705 (1964), in Japanese—E. Siegel and S. Peterson have recently reported that by the Meerwein reaction between methyl vinyl sulfone and some diazonium salts the arylation occurred at the  $\alpha$ -carbon atom of the vinyl group.



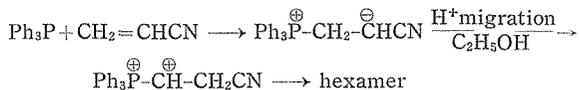
This result is quite strong and doubtful judging from the free radical nature of the Meerwein reaction. In order to elucidate this question the authors have reinvestigated these Meerwein reactions in the following cases and confirmed that the results of Siegel are quite incorrect and that the arylation occurs at the  $\beta$ -carbon atom of the vinyl group, as shown in the following equations;



The above conclusion is based on the experimental fact that the dehydrochlorinated compound of the reaction product was identical with ethyl *p*-nitrostyryl sulfone, which was authentically synthesized by the Baliah's procedure.

**The Formation of P-Ylides from Triphenylphosphine and Acrylic Acid Derivatives.** Ryohei ODA, Toshihiko Kawabata and Shigeo Tanimoto. *Tetrahedron Letters*,

No. 25, 1653 (1964)—C. C. Price has prepared acrylonitrile hexamer by treating acrylonitrile by triphenylphosphine, and suggested the reaction course as follows:



The authors have prepared the  $\beta$ ,  $\gamma$ -unsaturated acid derivatives by treating this P-ylides with benzaldehydes.

Triphenylphosphine (40g) and benzaldehyde (16g) were mixed, and heated 120~130°C under nitrogen stream. The mixture of  $\text{CH}_2 = \text{CHCN}$  (8g) and  $\text{C}_2\text{H}_5\text{OH}$  (2.5ml) were added to the reaction mixture, and heated 140°C for 6 hrs. The volatile substance was removed by steam distillation, and the residue was distilled. Thus 5g styrylacetonitrile was obtained (Y=23%). In the same manner, the next results were obtained:

1.  $\text{CH}_2 = \text{CHCONH}_2 \longrightarrow \text{C}_6\text{H}_5\text{CH} = \text{CHCH}_2\text{CONH}_2$  (Y=10%)
2.  $\text{CH}_2 = \text{CHCO}_2\text{C}_2\text{H}_5 \longrightarrow \text{C}_6\text{H}_5\text{CH} = \text{CHCH}_2\text{CO}_2\text{C}_2\text{H}_5$  (Y=45%)
3. Diethyl maleate  $\longrightarrow \text{C}_6\text{H}_5\text{CH} = \text{C} \begin{matrix} \text{CO}_2\text{C}_2\text{H}_5 \\ \text{CH}_2\text{CO}_2\text{C}_2\text{H}_5 \end{matrix}$  (Y=16%)

And, the authors have also found that the added  $\text{C}_2\text{H}_5\text{OH}$  does not play a part in these case and the proton migration from the betaine to P-ylide occurs directly.

**Research on the Oxidation of Aromatic Primary Amines by Oxygen.** Toshihiko Kawabata, Shigeo Tanimoto and Ryohei Oda. *Kogyo Kagaku Zasshi*, 67, 1151 (1964), in Japanese—Russell and Horner have recently independently published reports the oxidation of primary aromatic amines by oxygen in DMSO and *t*-butanol in the presence of *t*-BuOK, and found that azobenzene-derivatives from substituted anilines and dibenzophenazine from  $\alpha$ - and  $\beta$ -naphthylamines are the main reaction products.

The authors have also investigated the oxidation of primary aromatic amines by oxygen at room temperature under the Russell's condition and obtained quite different results from the Horner's ones.

These are as follows:

1. *p*-Anisidine  $\longrightarrow$  *p,p'*-Dimethoxyazobenzene (Y=51%)
2. Sulfanilic acid  $\longrightarrow$  Azoxybenzene-4, 4'-disulfonic acid (Y = 76%)
3.  $\alpha$ -Naphthylamine-6-sulfonic acid  $\longrightarrow$  2-Hydroxy-*N*-(1'-naphthyl)-1, 4-naphthoquinoneimide-6,6'-disulfonic acid (Y=34%)
4. Naphthionic acid  $\longrightarrow$  1,1' -Azonaphthalene -4,4'-disulfonic acid (Y=32%)
5.  $\beta$ -Naphthylamine  $\longrightarrow$  Dibenzophenazine (Y=62%)
6.  $\beta$ -Aminoanthracene  $\longrightarrow$  Dinaphthophenazine (Y=91%)
7.  $\alpha$ -Naphthylamine  $\longrightarrow$  2-Hydroxy-*N*-(1'-naphthyl)-1,4-naphthoquinoneimide (Y=54%)

**Synthesis of *p*-Vinyibenzaldenzaldehyde Diethyl Acetal and its Polymerization.** Shigeo Tanimoto and Ryohei Oda *Kogyo Kagaku Zasshi*, 67, 506 (1964), in Japanese—Ethyl orthoformate was added slowly to *p*-chlorophenylmagnesium chloride in tetrahydrofuran at 10~15°C. The reaction mixture was heated to 100°C for 2 hr. on a water bath; during this time most of tetrahydrofuran was removed.

The residue was hydrolyzed with dilute  $\text{NH}_4\text{Cl}$  aqueous solution, and ether was

added. The organic layer was separated, and the crude product was distilled in vacuo to yield a fraction, b. p. 95~105°C/5~6mmHg.

The yield of *p*-vinylbenzaldehyde diethyl acetal was 14.5%. *p*-Vinylbenzaldehyde diethyl acetal was polymerized in bulk, the resulting polymer being soluble in C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub>, CH<sub>3</sub>COCH<sub>3</sub>, CHCl<sub>3</sub>, dioxane, petroleum ether, CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>, benzene, pyridine, and dimethylformamide, insoluble in H<sub>2</sub>O, CH<sub>3</sub>OH, C<sub>2</sub>O<sub>3</sub>H, and dimethylsulfoxide, melted at 85~155°C, and  $[\eta]=0.83$  (denzene, 30±0.1°C).

**Cyclopropanes-(XVII). The Absolute Configurations of *Trans*-1,2- Cyclopropanedicarboxylic Acid and *Trans*-2-Phenylcyclopropanecarboxylic Acid** Yuzo Inouye, Toshio Sugita and H. M. Walborsky. *Tetrahedron*, **20**, 1695 (1964)—The absolute configuration of (–)-*trans*-1,2-cyclopropanedicarboxylic acid was established as 1*R*:2*R* by a direct chemical correlation with known (–)-(1*R*:2*R*)-*trans*-1,2-dimethylcyclopropane. Ozonolysis of (+)-*trans*-2-phenylcyclopropanecarboxylic acid yielded (+)-*trans*-1,2-cyclopropanedicarboxylic acid which shows that (+)-*trans*-2-phenylcyclopropanecarboxylic has the 1*S*:2*S* configuration. The significance of these results to the Wittig reaction involving optically active styrene oxide and phosphoacetates will be discussed.

**Blätteralkohol. (XII). Gaschromatogramm der bei der Blätteralkohol-reaktion erhaltenen Alkohole.** Minoru Ohno und Akikazu Hatanaka. *Agricultural and Biological Chemistry*, **28**, 908 (1964)—Um die geometrischen Isomeren des *n*-Hexen-1-ols als Ausgangsmaterial in der Blätteralkohol-reaktion in reiner Form zu isolieren und dann um die Struktur der bei dieser Reaktion gewonnenen Alkohole nachzuweisen, wurde Gaschromatographie ausgeführt.

**Blätteralkohol. (XIII). Herstellung des 2-Butyl-octylalkohols bei der Blätteralkohol-reaktion.** Akikazu Hatanaka und Minoru Ohno. *Agricultural and Biological Chemistry*, **28**, 910 (1964)—In der letzten Arbeit dieser Forschungsreihe wurde mitgeteilt, daß bei der Blätteralkohol-reaktion eine 2-Propyl-5-äthylbenzylalkohol unerwartungsmäßig erhalten wird. In dieser Mitteilung handelt es sich um die Tatsache, daß 2-Butyl-octylalkohol aus *n*-Hexylalkohol, der als Nebenprodukt in der Blätteralkohol-reaktion entsteht, abgeleitet werden kann.

**The Synthesis of Methylacetylene by the Pyrolysis of Propylene. The Effect of Pyrolysis Conditions on Product Yields.** Yasumasa Sakakibara. *Bulletin of the Chemical Society of Japan*, **37**, 1262 (1964)—Propylene has been pyrolyzed in a flow system over a wide range of conditions (temperature, 800~1400°C; contact time, 4.4×10<sup>-4</sup>~2.3 sec.; pressure, 40~160mmHg) to find suitable conditions for producing methylacetylene (and allene) and for obtaining data concerning the distribution of pyrolysis products. Under proper conditions, the pyrolysis occurred without any appreciable production of tarry and carbonaceous materials. High temperatures (1200~1300°C), short contact times (millisecond order; conversions below 30%), and low pressures (below 100mmHg) were found to be required for the good production of methylacetylene-allene. A methylacetylene-allene yield of 38 mol. per 100 mol. of propylene pyrolyzed was realized at 1200°C, 50mmHg pressure (partial

pressure of propylene, 40 mmHg), and 24 % conversion (contact time, 1.7 msec.). The other gaseous products were found to be methane, ethylene, hydrogen, acetylene, 1-butene and butadiene, in decreasing order.

**The Synthesis of Methylacetylene by the Pyrolysis of Propylene. (II). The Mechanism of the Pyrolysis.** Yasumasa Sakakibara. *Bulletin of the Chemical Society of Japan*, **37**, 1268 (1964)—A study has been made of the mechanism of the pyrolysis of propylene at high temperatures (800~1400°C). Of the gaseous products, hydrogen, methane, ethylene, allene, and 1-butene, obtained in the yields of 25, 43, 40, 27, and 9 mol. per 100 mol. of propylene pyrolyzed (3 % conversion) respectively, have been found to be the primary products, while methylacetylene, acetylene, and butadiene, obtained in the yields of 9, 4, and 2 mol. respectively, have been found to be the secondary products. In view of the results of the pyrolysis of allene itself, even at a low conversion of 3%, allene appears to undergo considerable secondary reactions, such as isomerization to methylacetylene, addition to propylene and allyl radicals, and decomposition, for example, to acetylene and methane via methylacetylene. On the basis of the observed results, free-radical mechanisms have been proposed for the primary reactions and main secondary reactions. The mechanism for the primary decomposition reaction is a chain process in which the chain is initiated by the reaction  $C_3H_6 \rightarrow C_3H_5 \cdot$  (allyl radical) + H, and is, via the chain-propagating step, terminated by two types of reactions,  $C_3H_5 \cdot + H \rightarrow C_3H_6$  and  $C_3H_5 \cdot + CH_3 \cdot \rightarrow 1-C_4H_8$ . The formation of allene-methylacetylene has been satisfactorily explained by considering secondary reactions.

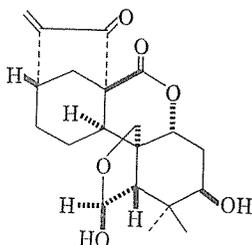
**The Synthesis of Methacrylic Esters by Carboxylation Reaction of Methylacetylene. (1). Methyl Methacrylate: Reaction Conditions and Products.** Yasumasa Sakakibara. *Bulletin of the Chemical Society of Japan*, **37**, 1601 (1964)—The synthesis of methyl methacrylate (MMA) by the carboxylation reaction of methylacetylene has been investigated.

Stoichiometric process: The carboxylation reaction was carried out under atmospheric pressure by premixing a 25~50 vol.% of acetylene in methylacetylene and under pressure (heating to 80°C). The total yields of MMA and MAA (methacrylic acid) were 45 % (based on the methylacetylene consumed) under atmospheric pressure and 49 % (66% (based on the nickel carbonyl used)) under pressure. Small amounts of methyl *trans*-crotonate, methyl isobutyrate, acetone, etc., were obtained as by-products, together with considerable amounts of high-boiling materials (not investigated).

Catalytic process: The reaction proceeded comparatively smoothly at 170~180°C and under about a 10 atm. partial pressure of carbon monoxide when triphenylphosphine nickel bromide complexes and nickel carbonyl-concentrated hydrochloric acid were used as catalysts. A triphenylphosphine nickel bromide catalyst,  $(Ph_3P)_2NiBr_2$ , gave the best total yield, 47%. It was found that, without the addition of acid, nickel carbonyl exhibits a catalytic action in the presence of water at 170~180°C. The total yield of MMA and MAA by this method was 46%. Fortunately, scarcely any acetone or methyl ether were formed. In view of this series of experimental results, it may be supposed that the poor total yield of MMA and

MAA is chiefly due to the loss of methylacetylene by polymerization.

**The Constitution and Stereochemistry of Enmein.** T. Kubota, T. Matsuura, T. Tsutsui, S. Uyeo, M. Takahashi, H. Irie, A. Numata, T. Fujita, T. Okamoto, M. Natsume, Y. Kawazoe, K. Sudo, T. Ikeda, M. Tomoeda, S. Kanatomo, T. Kosuge and K. Adachi. *Tetrahedron Letters*, No. 20, 1243 (1964)—Enmein, a diterpene bitter principle isolated from *Isodon trichocarpus* KUDO, has been shown, on the basis on chemical evidence and with the result of X-ray analysis by Iitaka and Natsume (*Tetrahedron Letters*, No. 20, 1257 (1964)), to have the structure, stereochemistry and absolute configuration depicted in the following formula.



### Biochemistry

**Isolation of  $\gamma$ -L-Glutamyl-S-allylmercapto-L-cysteine and S-Allylmercapto-L-cysteine from Garlic.** Michiyasu Sugii, Tomoji Suzuki, Shigeharu Nagasawa and Keisuke Kawashima *Chemical and Pharmaceutical Bulletin*, 12, 1114 (1964)—During the course of studies on the sulfur-containing amino compounds in garlic, new sulfur-containing amino acid and peptide have been isolated in the crystalline state from garlic bulbs by chromatography on ion exchange resins.

Based upon the elementary analysis, optical rotation, infrared spectrum and nitroprusside-cyanide reaction, these compounds have been shown to be S-allylmercapto-L-cysteine and  $\gamma$ -L-glutamyl-S-allylmercapto-L-cysteine.

**New Sulfur-containing Amino Acid in Cabbage: Isolation and Identification of L-Homomethionine (L-5-Methylthionorvaline)** Michiyasu Sugii, Yasunobu Suketa and Tomoji Suzuki: *Chemical and Pharmaceutical Bulletin*, 12, (9), 1115 (1964)—Using tracer technique for the detection of sulfur-containing amino acids in cabbage, the authors were aware of a presence of unknown methionine-like amino acid, and the structure of amino acid was examined by the colorimetric reactions and the nuclear magnetic resonance spectrum. From these results, the amino acid isolated was considered to be L-homomethionine (L-5-methylthionorvaline). Such a presumption was finally proved by comparing the R<sub>f</sub> values and nuclear magnetic resonance spectrum with those of the authentic sample of DL-homomethionine.

### Correction

The title of the note published in Vol. 42, No. 5, p. 422 is to be replaced by "Nucleon Polarization Effect of  $\mu$ -Mesonic Hydrogen Atom," and the name of its first author is to be omitted.

Hideki Yukawa and Shigeru Matsuo