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NEW CHINA'S PROGRESS IN THE CHEMISTRY AND CHEMICAL ENGINEERING OF HIGH POLYMERS

- COMMUNIST CHINA -

By Ch'ien Pao-kung

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NEW CHINA'S PROGRESS IN THE CHEMISTRY AND CHEMICAL ENGINEERING OF HIGH POLYMERS*

/ This is a full translation of an article by Ch'ien Pao-kung appearing in <u>K'o-hsueh T'ung-pao</u> (Scientia), No 20, 26 October 1959, pages 666 - 673./

In view of the fact that this is an era characterized by the use of materials and atomic energy of high polymers, the second half of the twentieth century has been appropriately termed a joint era of high polymers and atomic energy.

The world's gross annual production capacity of rubber, plastics and synthetic high polymer fibers as of now is placed at approximately 10 million tons, or over twice the volume of production of nonferrous This will be increased to 25-30 million tons metals. in 15-20 years. During the past thirty years, this newly developed synthetic chemistry of high polymers had achieved enormous growth and spectacular success, giving sure guidance to the creation and utilization of chemical compounds of high polymers. A modern and strict theoretical treatment of high polymers has been created, dealing with the reaction processes of their formation and dissociation, and with their structure and properties.

* This article is a resume compiled and written by Wang Pao-jen, Ho Ping-lin, Wu Hsiang-lung, Ou-yang Chun, Ch'ien Jen-yuan, Ch-ien Pao-kung and others who have contributed to the research on chemistry of high polymer during the past decade. The manuscript when completed was read by Wang Pao-jen, T'ang H'ao-ch'ing, Ch'ien Jen-yuan and others, to whom thanks are due. Because of the demand for rubber, plastics, chemical fibers and resins and other high polymer materials for socialist reconstruction in China, research work on the chemistry of high polymers expanded after Liberation under the party's leadership and support and has reached maturity in the ten years following the founding of the regime. Before Liberation this branch of science was a "bland."

The principal task of the government is to produce in quantity such high polymer materials as are being manufactured by the advanced world through China's own high polymer chemical engineering and chemical research, and on the basis of China's practical needs, resource characteristics, scientific level, and technological conditions. Much work including laboratory research and intermediate factory testing has been done during the past decade on the compounding and polymerization of individual high polymer materials and the processing and changing of properties of natural high polymer materials. Simultaneously, theoretical research on the structure of related reactions and the texture and properties of high polymers was conducted with appropriate care. According to incomplete statistics now available, about 500 research reports and treatises were compiled and written during the past decade. Two-fifths of these studies dealt with the practical phase while one-fifth was devoted to theoretical exposition.

All in all, the chemistry of high polymers has progressed from nil to notable growth in New China during the past decade; it is an accomplished fact, while an adequate contribution has been made to the training of cadres, thereby laying the foundation for further study on the chemical theory and practice of high polymerization.

I. Natural Rubber and Synthetic Rubber

Rubber is indispensable to modern industry and standards of living, and its elasticity is irreplaceable. It is principally used for the manufacture of motor vehicle and airplane tires, transmission and conveyor belting, electric cord and cable and various types of technical accessories as well as daily necessities and sanitary articles. World production of natural rubber is estimated at two million tons per annum. In two decades the production of synthetic rubber has almost overtaken that of natural rubber. The latter is applied to general use while the former is also used for specialized purposes. The prospects for developing both natural and synthetic rubber to meet natural and industrial requirements in China are bright.

<u>Natural rubber</u>. Investigations after Liberation revealed that China is richly endowed with rubber resources -- principally "san-yeh-shu" rubber /Brazil rubber/, "hsiang-chiao-ts'ao" rubber, "tu-chung" rubber /Gutta-percha/, "hsiang-chiao-t'eng" rubber /tappings from rattan/, etc. The chemical composition, molecular weight and physical and mechanical properties of these principal varieties were analyzed, examined and studied accordingly, and it was established that natural rubber produced in China (san-yeh-shu rubber) resembled that of Ceylon in chemical composition and molecular weight and that a similarity also existed between the two in technical, physical and mechanical properties. By comparison the Chinese variety is higher in primary plasticity.

In view of this characteristic, research on plasticity and plastic reduction with reference to the relationship between plasticity and molecular weight and changes in molecular weight and distribution during reduction was conducted. At the same time laboratory testing on mixed reduction was performed.

Vulcanization and aging of natural rubber was examined in relation to tire production with emphasis on the measurement of vulcanization and aging and the problem of coke combustion and vulcanization in relation to the natural rubber produced in China.

Manufacturing rubber goods directly with latex from natural rubber is an important problem confronting the modern rubber industry. In this connection, research projects on latex transformation, concentration, reduction, compounding, preparation for semi-vulcanized and vulcanized latex, macerated film latex production, "latticework" macerated film latex production, etc., were preliminarily and successfully consummated.

During the past decade, research on natural

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rubber production in China was well begun and a definite foundation was laid. Henceforth, investigation on natural rubber resources, especially its Chinese characteristics, should be made with increasing effort. Such problems as plastic and mixed reduction, vulcanization and the aging process, grafting and quality conversion of natural rubber, the utilization of natural latex and the manufacture of special rubber goods should be examined in the light of both theory and practice so that the technology of rubber production may be systematically established in China. Long-range research on the texture of caoutchouc, if conditions permit, should be made. This problem has yet to be solved by scientists.

Synthetic rubber. Synthetic rubber is one the important accomplishments and development landmarks in the entire field of modern high polymer chemistry. It has general, exclusive and specialized uses according to its properties. The work was begun immediately after Liberation. During this stage, the task like that for the development of synthetic materials of high polymers, was to manufacture such products as were already produced in quantity abroad. The emphasis was, therefore, placed on reaction factors necessary to the solution of industrial chemical processes particularly those from basic materials to isolated syntheses and from isolated syntheses to the production of high polymers.

Generally speaking, ethyl benzene rubber is mainly used for the production of synthetic rubber. After Liberation, stress was placed on the study of butadiene and the two processes for its synthesis, /the first being/ the synthetic catalytic derivation of butadien from alcohol, and the second the synthetic catalysis of butane-butene in petroleum distillation. As to polymerization, research was concentrated on the formula for polymerizing an improved butadiene-styrene latex with applications in modern industry with some improvement. In addition, preliminary research on the selection of oils for the making of ethyle benzene rubber for lubrication use was conducted.

Butadiene serves directly as raw material for the making of many types of synthetic rubber. "Ting-p'i" rubber, capable of resisting heat and oil, is a new line being developed in China for general and special uses, and through chemical conversion new properties may be evolved. Its development is being continued.

By means of directed polymerization, the texture of butadiene may be so regulated as to form polymerized butadiene of improved elasticity and lower molecular count; but when it is mechanically grafted to ethylene-propylene polymers of lower elasticity and higher molecular count, an adjustment may be made at will for the desired elasticity and molecular count. Its potential is bound to play an important role in the future growth of synthetic rubber for general application. This research work is being pursued in China.

By the method of directed polymerization mentioned above, isoprene may be synthetically polymerized to present a structure exactly similar to that of "synthetic natural rubber." When its unit production cost is lowered, its growth will be enormous.

Research on chlorinated latex for the manufacture of special rubber was also undertaken in China with adequate progress. However, little work was done concerning chlor-prene rubber in respect to isolated polymers and changes in the properties of chlorinated latex. New lines should henceforth be developed by exploratory testing.

Polymerized sulfonated rubber is highly oilresistant. In the past, research on A, B, and F grades of polymerized sulfonated rubber was undertaken with emphasis on their preparation in the liquid state. A mixing of this variety with diolefines could increase the latter's oil-resistance. Testing also proved that polymerized, sulfonated chlorinated rubber was superior to the butyl-nitriles type in both oil-resistance and strength.

As to special varieties, research on silicon rubber was done with definite success and preliminary work on flucrine rubber was also started in recent years.

Some gaps remain to be filled in the production of synthetic rubber. For example, abrasion-resisting butyl-carboxyl and amino-ester rubber and isobutyl rubber of low porosity as well as problems of vulcanization and aging remain to be examined.

In short, a proper foundation has been laid for the conduct of research on synthetic rubber. In the interest of consolidating the production of synthetic rubber, we should, apart from continuing to examine ethyl-benzene and chlorinated rubber for mass production, devote our study to new-type rubbers such as diolefines, "ting-p'i" and butylcarboxyl types, particularly the directionally polymerized synthetic rubber. Work on exclusive and special rubber should continue to be developed. Exploratory steps for new types should be immediately undertaken with emphasis on synthetic rubber of designated property or properties. These steps may also be taken on a long-term basis,

II. Plastic Materials and Synthetic Resin

Synthetic plastics and resins vary greatly and differ in their properties. Their applications are broad, extending to the manufacture of motor vehicles, airplanes, and machines, and to the electrical, construction and ship-building industries as well as the chemical anf foods industries, where they are used as structural, insulating, chemical engineering and decorative materials.

World production volume, of which high polymer materials account for much the greatest proportion, now exceeds 4 million tons per annum, or two times the figure of five years ago.

Sunthetic plastics and resisn may be classified according to the method of polymerization as polymeradded and polymer-condensed, in addition to a type known as ion exchange resin. Work was begun soon after Liberation but there was no important development until two or three years ago.

Polymer-added Plastic Material and Resin. Under this heading, the main variety is isolated high polymer ethylene, the symbol of the modern plastics industry.

Mainly as a result of improved methods of polymerization, high polymer ethylene in recent years has had the most rapid increase in volume of production among all plastic materials. In the wake of the development of high pressure polymerization methods came the development of intermediate and normal pressure methods. Low pressure, metallic, organic, and catalytic polymerization methods were first examined while research on the other two methods had begun. The polymerization of propylene (polymerized propylene is used for the manufacture of synthetic high polymer fibers) was brought about by the application of the catalytic polymerization method together with metallic oxides (the intermediate pressure method). Also, the radioactivity of atomic (reaction) and ultra-violet rays were utilized for the preparation of polymerized ethylene. This method for changing the properties of high polymer materials is worthy of development.

In the past, a series of studies was made of the parparation of high-use vinyl chloride by the isolated synthetic polymerization method with fairly satisfactory results. The flotation and emulsion polymerization methods were studied in somewhat greater detail. In addition, research on vinyl perchlorate and meta dichloro-ethylene was conducted. Joint polymerization of isolated materials such as vinyl perchlorate resin, meta dichloro-ethylene, and others will be given greater emphasis.

Emphasis was placed on studies of the isolated synthetic phase of polymerized styrene, and the dehydrogen reaction of ethyl benzene was observed with great care. The method of radioactive polymerization through the use of atomic energy and the directed polymerization method with metallic and organic materials were also explored. The radioactive and directed polymerization methods will be developed in line with broad studies on all types of isolated ethylene.

Among polymer-added ethylene materials examined during the past decade was methyl acrylate, used for the preparation of organic glass. The isolated synthetic method was also improved. The effect of a slight amount of oxygen on the acceleration of isolated polymerization and the effect of an excessive amount of oxygen on the retardation of polymerization of methyl acrylate and other esters was observed to affect the speed of polymerization, and when compounding of acrylic acid or stannic ester of methyl-acrylic acid was explored, the polymer was observed to have acquired new properties.

Vinyl acetate, ethylene alcohol, acetal and other materials of high polymer may be used for the manufacture of plastics material, paint, adhesive and fibers, on which a series of research projects had been conducted in the past, Polymerized ethylene alcohol and condensed butyl aldehyde used for the production of adhesive and polymerized ethylene alcohol and condensed methyl alcohol employed for the preparation of synthetic fibers were more carefully studied.

Also, plastic materials containing fluorine and possessing high temperature and corrosion resistance, N-vinyl used as substitute for plasma, polymerized vinylite pyridine used as an ion-exchange agent, and polymerized methyl alcohol with possibility for potential development were examined.

In the field of ethylene research, there are gaps to be filled. Some principal forms of derived and homologous products mentioned above including vinylite ether and isobutene employed for ionic polymerization remain to be studied.

It is evident from the description given above that the principal varieties of polymer-added ethylene were largely, if not completely, examined during the last few years and that a definite foundation has been In view of the fact that most varieties of isolated laid. ethylene were involved in the production scheme of heavy, organic synthetic and petroleum industries and that many of then were concurrently regarded as raw materials for the preparation of synthetic rubber and fibers, the development of all these products should be given joint consideration. Because of their wide industrial application, emphasis should be placed on the growth of polymerized ethylene and vinyl chloride. At the same time, future research work should be directed toward the creation of new properties, new polymerization and property conversion methods and, more particularly, the development of high polymer ethylene materials with greater heat resistance.

<u>Condensed</u>, <u>Polymerized Plastic Materials</u> and <u>Resins</u>. Resins and plastic materials that were obtained by the method of condensation and polymerization, ranging from older aldehyde phenate plastics to more recent reinforced plastic materials, were generally examined during past few years.

Aldehyde phenate resins used for the preparation of plastic materials, paint and adhesives are not produced in comparatively large quantities in

China. As a result of a few years' effort, it has been possible to breaden the scope of production from simple electrical appliances and daily necessities to acidresisting aldehyde phenate plastics containers, colloids, etc., for chemical industrial application, friction-resistant brake-lining and adhesives for motor vehicles, silent gears and axles for machinery, aldehyde phenate paint and plyboard for industrial use, We should continue to solve these problems etc. and to increase the number of varieties in order to broaden their scope of application. It is imperative that resin or rubber be polymerized by the grafting method so as to create high-temperature-resistant and corrosion-resistant plastic materials of high strength as a partial substitute for nonferrous metals.

The prospect for the development of furfural resin and plastic materials is considered good in view of the fact that furfural may be made available in China from her bounteous agricultural production. The problem of processing furfural was resolved with great effort only recently. The preparation of furfural synthetic resin was related to the problem of catalysis, the solution of which facilitated the improvement of techniques in the processing of plastic materials. Again, there was the development in recent years of furfural-acetone resin. In solid form, its mechanical properties and its chemical stability surpassed aldehyde phenate plastic. materials in quality. It is worthy of development in China.

It was a general practice to treat ureaformaldehyde resin by the low temperature method but when the high temperature method was adopted, production procedure was simplified. Highly heated urea-formaldehyde foam plastics with very low specific gravity was found in a trial experiment to have prevented urea-formaldehyde emission plastics material through evaporation. Urea-formaldehyde plastics material would henceforth be tested with solid fuel. Little research was done on paraformaldehyde which is similar in type to urea-formaldehyde resin. With satisfactory procurement of raw suited to the development of plastics goods in China with extensive applications in light and heavy industry, it would be possible to manufacture low-priced high-quality daily necessities.

During past two years, studies on how to reinforce plastics material with unsaturated and cyclic oxygen resin were undertaken. Reinforced plastics now play a very important role in the growth of the plastics industry. Their strength already approaches that of hard steel-aluminum alloy, They are low in specific gravity, corrosion-resistant, elastic, good for insulation, capable of being processed into articles of odd shapes and suited to the production of automobile radiators, shiphulls, machinery, oil tanks, piping. These plastics should be regarded in China as a etc. key-point for development. Our main problem lies in the acquisition of resources for the manufacture of reinforced plastic materials (fiber-glass and other fibers of high tensile strength) and resin In addition there is the problem of compounds. adhesion. Cyclic oxygen resin, which is an adhesiv agent, should therefore be developed.

Also, hydroxyl-carboxylic acidic resin used for the manufacture of synthetic paint may be extracted from a phenate compound found in Chinese paint for the manufacture of corrosion-resistant paint and woodoil plastic material. In the past, research on this problem was especially conducted to ascertain the composition of Chinese paint and the structure of its phenol content. The paint industry is considered an important branch of the high polymer industry. How to utilize Chinese raw materials and resin compounds for the manufacture of high-quality paint now looms as an important problem for research.

Finally, the study of silicon materials of high polymer should be dealt with. Main work in recent years was confined to the examination of isolated compounds involving the improvement of the traditional method of preparing polymerized silica paraffins in isolated form, the isolated aspect of chemical properties, the production of silicon oil, silicon resin, silicon paint, silicon rubber and other materials of high polymer. Apart from the silica types of high polymer mentioned above, exploratory work was done on silicon-silicon type, silicon-carbon-silicon-oxygen compounds of high polymer, etc.

Because of their wide application in the Chinese national economy and because of the availability of raw materials, adequate foundation has already been laid for the further study of the condensed, polymerized resins and plastics mentioned above. For these studies, the stress will be placed on reinforced and foam plastics, silicon materials of high polymer, new lines of condensed, polymerized production and their development and creation.

Ion-exchange resin. Ion-exchange resin, the "tool-less equipment," is known for its broad applications in the chemical industry and other related departments, employed as it is for the purification of water, dissociation of metals and rare elements, dissociation and purification of antibiotics and other valuable chemical products.

It is a poly-added or poly-condensed product. Being an acid or alkali radical of high polymer, it is classifiable either as a positive or negative ion.

The earliest study in our research on ion-exchange resin was associated with sulfonated coal used industrially for the purification of water. Subsequent research was related to studies on sulfonyl aldehyde phenate resin and sulfonyl stryrene phosphate resin -- two effective acid-type exchange resins. Also, stryrene phosphate resin -- a medium acid-type exchange resin -was experimentally manufactured. A weak acid-type positive ion-exchange resin was developed along with the extraction of streptomyoin (an antibiotic), vegetable alkaloid and other bicchemical products. Many lines of high-quality products were produced, and an insoluble type of exchange resin was developed.

In connection with negative ion-exchange resin, research on amino salts -- a strong alkali-type exchange resin of high quality -- was undertaken. In addition, a series of weak alkali-type exchange resins was compounded. These negative exchange resins were used to purify water, to eliminate slight quantities of carbon dioxide, to extract uranium, and to dissociate natural products.

Apart from the uses just mentioned, ion-exchange resin is extensively used for chemical analysis, Positive-ion-negative-ion resin, by virtue of its reassociation property, is utilized to purify seawater,

The demand for ion-exchange resin is bound to rise as industries are developed in China, In the past, a sound foundation was laid to facilitate the development of new types of ion resin such as highly selective, heat-resistant, radioactive ion-exchange agents, ionexchange film, paper or liquid resin, electron-exchange resin, optically active resin, etc. Theories on the electrolytic properties of high polymers are worthy of

research.

III. Artificial Fibers and Synthetic Fibers

Chemical fibers are being broadly developed as textiles, cords, thin films, fish-nets and substitutes for wool, silk and hides.

Chemical fibers consist of two main varieties: artificial fiber and synthetic fiber. The volume of world production already exceeds 3 million tons per annum, or one-third of the production volume of natural fibers (cotton, wool and silk). Artificial fibers and synthetic fibers are currently produced in a ratio of 9 to 1 but the development of the latter variety is proceeding at an accelerated pace.

Provided as she is with the requisite resource and performance factors, China will witness a rapid development in the production of artificial and synthetic fibers.

Artificial fibers. Artificial fiber or viscose is artificial silk developed from natural fibers by the adhesive method. Fibers from coniferous woods are traditionally regarded by the world as raw materials for the production of viscose. As the resource situation in China is different, it is necessary to consider the utilization of fibers other than wood fibers.

After careful study and intermediate testing, it was found possible to substitute bagasse for coniferous wood fibers as raw material for the manufacture of viscose. During the past two years, experiments have been performed on a large scale to determine whether grass fibers such as reeds, wheat stalks, rice straw, bamboo, kaoliang, and cotton stalks, etc., could be used for the production of artificial fibers or viscose. Altogether, over 20 varieties of plants were tested.

Adequate methods and conditions were established for the dissociation and refinement of grass fibers, Vheir viscosity, polymerization, energy of reaction, ultra-molecule structure, chemical composition, etc., were examined with varying degrees of intensity. Research on the simplification of viscose processing and preparatory steps for the production of reinforced artificial silk undertaken with preliminary success.

In addition to research on grass fibers, the derivatives of ester and ether and changes in the propert-

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ies of other natural fibers were examined, too.

The natural cause for fiber chemistry in China seemed to lie in the utilization of her unlimited grass fiber resources. Achievements in the modern chemistry of high polymers will be utilized to improve the quality of artificial fiber and to change the properties of natural fibers as well as to examine to the structure and energy of reaction fo fiber in general.

Sunthetic fibers. Synthetic fibers known for their fine quality have developed greatly during the past two decades. They may be classified under the two categories of polymer-added and polymer-condensed fibers according to the method of polymerization, the latter variety being the more important. They were examined in China recently with varying degrees of intensity.

As to polymer-added products, the prospect for the growth of polymerized propylene fiber seems to be bright because its cost of production is as low as that of cotton fiber and also because it is comparable to synthetic fiber in quality. The problem is being studied in China with particular reference to the improvement of the directed polymerization method,

Polymerized propylene fiber (orlon), agingresistant and similar to wool in quality, is being tested. A special solvent (dimethylamine) was heeded for drawing fiber. To avoid using this solvent, two measures were considered: polymerization could be performed in salt solution and acrylonitrile and vinyl chloride could be polymerized on an isolated basis. The experiment was conducted with preliminary success but further research is necessary.

The compounding of polymerized ethylene alcohol and methyl alcohol fiber /wei-ni-lun/ with polymerized vinyl chloride by the addition of carbide is being tested. The properties of these two types of fibers, especially those of polymerized vinyl chloride, remain to be examined. Therefore, improvements should be sought in the method of polymerization and fiber drawing.

Regarding condensed, polymerized products, nylon fibers play a dominant role among synthetic fibers. In recent years, much research work has been done in China to perfect the compounding of nylon fibers 6,9,11,66, 96, 1010, etc.

The source of isolated elements and the method of compounding were emphasized. The method of polymerizing amino fiber was improved. From castor oil were extracted polymerized amines 9 and 11 for the compounding of amino pelargonic acid, and from furfural was drawn polymerized amine 66 for the compounding of butane dicarboxylic acid and hexylamine. While basic materials -- castor oil and furfural -- may readily be obtained from China's agricultural resources, their synthesis is nonetheless complicated, and simplification is expected.

The condensation of polymerized products, especially the reaction from hexylamine, was examined with care. An improved surface condensation method for the preparation of polymerized amine 66 was considered. The synthesis of polymerized ester fiber was given preliminary study. The mechanism of this polymerized ester reaction was studied in relation to the general structure of polymerized ester reactions.

In the case of condensed, polymerized products, there are gaps to be filled. Among recently developed synthetic high polymer fibers may be listed polymerized amino-ester, polymerized resin carbonate, anhydride, etc. Fiber-drawing is especially important in the study of synthetic fibers. The development of this technique, involving high polymer physics, is only at the initial stage.

All in all, the study of synthetic fibers has begun in China. The development of fibers and the clarification of conditions under which the study of a particular variety may become dominant, as is the case with the other types of synthetic high polymer products, can only be the result of intensive research. Our examination of synthetic fibers reveals that the weak link seems to be the problem of surface condensation and fiber drawing; this problem should be examined from both the theoretical and the practical standpoints. The exploratory work for the discovery of new types of synthetic fibers should be conducted on the basis of what has already been accomplished.

IV. Reaction Mechanism and Dynamics

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The mechanism of a reaction of high polymer formation and dissociation is a dominant scientific problem in the study of high polymer chemistry. It concerns procedures of preparation, processing, property conversion and operation, which must be examined from both the theoretical and the practical standpoints. Research on these problems has been conducted throughout

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the world. While work in China has begun only recently, the Chinese contribution to the solution of some theoretical problems, especially the problem of the mechanism of condensation reactions and some aspects of dynamics, is obvious.

Reaction of polymer addition. This reaction may be considered as a high polymer reaction to the polymerization of isolated vinyl, and has been proved to be a chain-reaction. In analyzing the dynamic aspect of this reaction, Bodenstein's hypothesis of stability was often taken for granted. Its validity was questioned because the hypothesis did not stand the test of strict mathematical analysis. When the spontaneous reaction to polymer addition was examined through dynamic analysis, the reasonableness of his hypothesis was proved. It is here perfectly applicable.

In practice, emulsion polymerization is a method widely adopted for the preparation of synthetic rubbwr and plastics. Whether reaction to polymerization occurs at the absorption layer of the smulsion or within the emulsion itself during the process remains debatable since the evidence permits both interpretations. Careful examination of the procedure for emulsion polymerization of styrene showed that the speed of polymerization was determined by activity at the surface area of the emulsion, suggesting that Medvedev's contention that reaction to emulsion polymerization occurred at the absorption layer was more likely to be the case.

Reaction of condensation. This is another important reaction in the preparation of chemical compounds of high polymer. It was generally believed that the condensation-dissociation equilibrium that occurred during reaction would affect the distribution of the molecular weights of condensed products. But when a typical case of condensation reaction was analyzed from the standpoint of dynamics, the results demonstrated that, granting that dissociation reaction was present, it was still possible for the molecular weight of the condensed products to be distributed according to Flory's law.

But in the course of condensation reaction, especially toward the close of amino-compound polymerization, adhesiveness seemed to increase in the substance. Under this circumstance, smaller molecules were more likely to expand and dissociate while larger molecules were provided with more numerous dissociation bonds. These two types of molecules were likely to undergo chain exchange reaction, causing medium-size molecules to be formed and their molecular weight to be concentrated in such a manner as to contradict Flory's theory of distribution. This phenomenon was clearly visible in the processing of hexylamine compounds.

The reaction of polymerized ester is typical of condensation reactions. The process rate of its reaction has, however, elicited much discussion. On the basis of practical results and dynamic inference, it was felt that the reaction to simple ester activity seemed to agree with the catalytic process of hydrogen ion. The theory expounded by scholars that the binary acid molecule was a catalytic agent in itself and that reaction to polymerized ester was but a reaction to double molecular activity was not entirely borne out by the At the same time, the hypothesis that the energy facts. of reaction was not connected with isolated chain activity -- a basic hypothesis for the analysis of condensation dynamics -- was verified.

The structure of hydrogen ion reaction was demonstrated by studies on the dynamics of three-directional polymerized ester reaction. The gel activity of threedirectional condensation reaction was again demonstrated in practice as well as in theory.

In the case of lactams, the mechanism of reaction was complicated because lactams are a cyclo-isolation. The mechanism of its reaction is being examined throughout the world. Chinese scholars felt that in the opencycle condensation mechanism were included such processes as polymer-adding activity, increasing condensation, and the chain-exchange equilibrium reaction. It was believed that the double-ion structure resulted from polymeradding activity and that the distribution of molecular weight was influenced by chain-exchange.

Also, the dynamic aspect of the condensation reaction of dimethyldihydroxy-silico-paraffin was examined. It was proved that a definite ratio was maintained between an isolation and a double polymer and that the latter was polymerized on the one hand while it was converted into an isolation on the other.

<u>Radioactive interchange</u>. Statistical theory on radioactive interchange has developed with the advancement of radioactive interchange of high polymers. Charlesby's erroneous theory of solubility was corrected by Chinese scholars who demonstrated the solubility of radioactive interchange products of high polymer such as ethylene, etc.

The mechanism of the light sensitivity exchange reaction brought about by the effect of ultra-violet rays on ethylene had never been examined before. After some preliminary research, it was felt that there was a linear relationship between the rate of interchange in the light sensitivity exchange reaction and the logarithm of the time factor. This was probably due to the selffilter photo effect of photochemical products. A new path was opened for the selection of a photo-stabilizing agent of high polymer.

China's research on the mechanism and dynamics of high polymer during the past 3-5 years has been summarized above. Though this research was not heavy, the results were satisfactory. We should henceforth concentrate on newly discovered important reactions of high polymer chemicals of such as directional polymerization, static radioactivity, surface condensation, mechanical polymer grafting, radioactive interchange, aging process, etc. In theory and in practice, this research should be of a systematic, penetrating and exploratory nature so that the mechanism of reactions may be clarified and the scope of their applications widened. Thus, a method for the preparation of new-type high polymers may also be created.

V. The Structure and Properties of High Polymers

Because of their superior and varied physicalmechanical properties, materials of high polymer gain in an important manner significant increase in the scope of their applicability depends largely on the structure of chemical compounds of high polymer. Therefore, studies on their structure and properties and the relationship between them have become the central theme in the examination of chemical compounds of high polymer. These studies have both theoretical and practical value and importance. This research work has begun in China, and some contribution has been made to studies on end edge range of high polymers, their solubility, molecular weight, etc.

Structure of High Polymers. High polymers are characterized by long chain action. The short-range and long-range structure of the chain and the structural behavior at the time of collection should be examined. Regarding short-range structure, the interior-

exterior double-bond and interior double-bond structure of ethylene polymer and rubber molecules exercise an important influence on the properties of a polymer. In connection with the polymerization of butadiene, benzoyl oxide was utilized to measure differences in the speed of its reaction on the interior-exterior double-bond, and infrared rays were employed to measure the ratio between the interior double-bond and the reversed structure. Here, polymerized ethylene compounds played an important role in directioned polymerization. With the aid of infrared rays, the content of double-bonds in various types of vinyl from polymerized vinylite chains was examined to observe changes in double-bonds during interchange.

Regarding long-range structure, the fundamental problem lay in the determination of the geometric structure of linear high polymer chains. In calculating the edge range ["mo-tuan chu-li"] of a high polymer, scholars in China advanced a hypothesis on the inner rotation of carbon-carbon chains to derive a general formula for equi-square end edge range and to establish the relation between equisquare radius and equi-square end edge range. It was also possible to compute the value of high polymer isoprene at equi-square end edge range under high temperature. But this remained to be proved by further testing. As to laboratory evaluation of inner rotation ["ts'an-shu"], it was not necessary to depend on the coupling method for computing the degree of polymerization and the nature of the solvent.

As to structural orde, r research began with the problem of ascertaining the degree of crystallization in partly crystallized polymers. Thus, thin films of polymerized vinylite were measured with the aid of infrared rays to ascertain the extent of its crystallization. A working curve indicative of the relation between polymerized vinylite concentration and the degree of crystallization was also obtained. Infrared bias rays were utilized to examine the direction of distribution in crystallization area during the pulling period of vinylite polymerization. Also devices to measure expansion were used to check the crystallization rate of natural rubber. It was observed that under varying crystallization temperatures and heating circumstances, there were varying formulas to describe the formation of crystals

and their development.

Soluble Properties of High Polymers. The form of a polymer in solution is a major factor in the determination of its solubility. The effect of its form on the viscosity of the solution is first indicated by the development of side molecular chains. This side chain development was demonstrated during research through the viscosity behavior of flexible high polymer chains in solution. For example, the dependence of viscosity on the concentration in solution of polymerized ethyle benzene rubber heated from 50° to 5° was clearly evidence of the side chain development of high polymers. This was in contrast with the visible absence of such action in the case of flotation-polymerized vinyl chloride.

Non-Newton flow was shown in solution in which high polymers were adequately polymerized, thus contributing to the understanding of the flexibility of high polymer chains. During research, the possibility of reversion to Newton flow under low shearing speed should be considered. The viscosity value of ethyl benzene rubber in toluene solution under low temperature was determined with certainty. The osmosis of hish polymer solution concentration and its dependent nature were generally shown in "wei-li" form, the second "weili" coefficient depending on the molecular weight and the influence of diffusion. Regarding the influence of solution diffusion on coefficient, a preliminary conclusion was reached by the methyl acrylate mixed grading method and the duplicate grading method. The quantitative measurement of this dependent relationship of the molecular weight of the second "wei-li" coefficient remains to be done.

<u>Molecular Weight and Its Distribution</u>. The molecular weight of chemical compounds of high polymer depends partly on their physical-mechanical properties and partly on the process of polymerization and the nature of the solution in which these chemical compounds of high polymer are formed. Their molecular weight is not uniform. Because of the problem of molecular weight distribution, only a statistical average can be given.

Basic methods for the measurement of molecular weight of high polymers such as terminal chemical analysis by mathematical average, elevation of boiling point, reduction of freezing point, osmosis, re-average radiation, average viscosity, etc., have been improved upon from time to time since the manufacture of the necessary apparatus was begun in China. In this respect, the technique has already been mastered and is being extended to other fields of research. As to the super-speed centrifugal and precipitation methods, preliminary work has been started.

Although the absolute value of molecular weight cannot be measured by the viscosity method, the simplicity of this method renders it easy to obtain the relative value of the molecular weight. In recent years this method has been widely used. Formulas have been given for the viscosity and molecular weight of methyl acrylate, methyl acrylate palmitate, 50° and 5° polymerized sthyle benzene rubber, "ting-p'i" rubber, hexylamine, etc. Also, the molecular weight of natural rubber and nitrocellulose have been investigated.

During the past few years, much has been achieved in improving the technique of measuring molecular weight. Examples include improvement in the terminal analysis of amides, the development of osmosis meter glass melting and crystallization, the improvement of radiation refraction tanks, and the designing of semimicro viscose dilution meters and viscosity gauges equipped with lightproof, anti-oxidation and overfiltration devices.

Regarding the distribution of molecular weight, ethyl benzene rubber, natural rubber, vinyl chloride, polymerized amides, etc., were studied and measured by grading methods. By studying the mechanism of reactions during polymerization, changes in molecular weight distribution have been observed.

<u>Physical and Mechanical Properties</u>. The applications of chemical compounds of high polymer are determined by their physical-mechanical properties -- e. g., the elasticity of rubber, the plasticity of plastics, the strength and insulating power of machinery, the textile and tensile strength of fibers, etc. Some work has been done in China.

The thermo-mechanical behavior of high polymer materials should first be examined in the light of their usefulness under a wide range of temperature. This rule was applied to tests for increasing the plasticity of organic glass and also in connection with the problem of radiation and light sensitivity interchange of ethylene. This work may yet be extended.

The viscosity-elasticity of high polymer materials

is of primary importance among their mechanical properties. The viscosity-elasticity of natural rubber was given a preliminary examination, and its flow characteristics were established to be non-Newton in type. The crystalizing cause for the conversion of viscous flow into plastic flow was also observed, on the basis of which the relationship between viscosity itself and the molecular weight was established.

Also, increase in the plasticity of ethyl benzene rubber through thermal oxidation was investigated. The relationships between solubility and the vulcanization time of natural rubber and the solubility of "ting-p^{*}i" rubber after treatment with amino-salts were studied, too.

The dielectric property of natural rubber, the transparency of organic glass, the double refraction property of fibers, etc., were also examined.

Research done in China during recent years in connection with the structure and properties of high polymers has been mentioned above. The work was mainly concerned with high polymer physics. Regarding this branch of science, we must start from the beginning. Only through the development of this science can we acquire deep understanding of the structure and properties of high polymers and the relationship between them.

VI. Future Prospects

High polymer chemical research was begun after Liberation. During the past decade, and especially the last three years, much work has been done. Measured by its scope and speed of growth, this accomplishment was undoubtedly important. It was, after all, an initial stage mainly devoted to the study and mastery of modern high polymer chemistry in order to establish a high polymer industry in China. Thus the foundation was laid for the future development of high polymer chemistry in China. It is a stage through which the development and establishment of modern science in any country must pass.

To relate these developments with the circumstances prevailing in China and to develop China's potentialities in the whole area of high polymer chemistry, future research works, as in other branches of science, should follow party's line for the conduct of scientific research in the service of socialist reconstruction. This development is to come through close collaboration between theory and practice and the adoption of the policy of "walking on two legs."

In a nutshell, the basic task of high polymer chemistry is the solution of problems concerning the synthesis of high polymer materials and their processing and application,* At this initial stage in the development of the high polymer chemical industry, the synthesis, processing and application of "well-known" high polymer materials should be studied, mastered, and developed while the "unknown" high polymer materials should be explored, opened up and developed. With this in view, important scientific problems should be examined in relation to national needs and production practices. The concrete problems that are worthy of research have already been discussed.

To provide for the establishment and develop-(1)ment of high polymer industry in China against a scientific and technological background, we have already progressed at key points in the preparation of major types of high polymer materials that are being produced in quantity in the world, such as natural rubber, butyl synthetic rubber, ethylene and vinyl plastics and resins, reinforced plastics and ion-exchange resins, grass fibers, and butyl-amides synthetic fibers. This research should be conducted with greater intensity so that a systematic, penetrating and overall research structure may be erected on the foundation that has been laid. It is important that we should master and improve the chemical industrial procedure for the preparation of isolated synthetics and high polymer materials. Their quality should also be controlled and elevated and new lines should be developed at the same time with the development of new methods and uses.

(2) The processing and application of materials of high polymer employs a range of scientific techniques. Here lies the weakest link of research work in China. The development of the Chinese high polymer industry will be hindered unless this problem is resolved immediately.

* Reference: V. Akarrin, "Basic Problems of High Polymer Chemistry" (appearing March 1959 in a report before the Eighth Congress of "Man-che-lifu" Chemical Association, translation appearing in "Kao-fen-tzu T'ung-hsin" (High Polymer News), Vol. 3, No 4, 1959, page 175. Regarding the vulcanization of rubber, the processing and molding of plastics and the drawing and stretching of chemical fibers, these techniques should be improved and broadened on the existing foundation by comprehensively absorbine modern methods and by conducting scientific research including research on processing equipment.

Concerning testing and inspection of the technical properties of high polymer materials, national standards should be set up in China without delay. To meet the requirements for the creation of new-type high polymer materials, the problem of testing and inspecting small-model trial samples for processing should be studied and solved as soon as possible,

In a vast territory like China covering tropical and frigid belts, it is especially important that the problem of aging in which the structure and properties of high polymer materials are altered under the sustained influence of heat, oxygen, light, radiation, mechanical force and chemical and pharmaceutical agents, should be examined with a view to prolonging the life of high polymer materials and leading to the creation of aging-resistant high polymer materials.

(3) To meet the demands of modern industry and "peak" techniques, new-model high polymer materials should be created with the object of increasing their heat stability without sacrificing their working flexibility under the desired temperatures, their mechanical properties, or their aging-resistant qualities. To fulfill this goal, we should start with isolated and high polymer chemical compounds by adopting new methods of polymerization, property conversion and processing. It is now known that some cyclochain high polymers (benzene, alkyl anilines, etc.) and hetero-cyclic compounds of high polymer (ester carbonate, anhydride, high polymer fluorine, high polymer silicon, etc.) have softening temperatures and disintegration temperatures. It is possible under varying conditions to increase the heat stability of isolated or high polymer chemical compounds by adopting directioned polymerization, polymer grafting, radiation interchange, and pulling and stretching methods. The scope of application of high polymer materials may be widened by close examination of the behavior of high polymer chemical compounds under high temperature of through examination of thermo-chemical or thermomechanical behavior when heat and oxygen coexist, Also, the problem of processing and molding heat-resistant

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high polymer materials is even more worthy of examina-

tion, for otherwise these materials would have no applications. Radioactive stability increases with the improvement of the quality of high polymer materials -a development so important in relation to the peaceful use of atomic energy. This would lead to the application of atomic energy to high polymer chemical activity as in radioactive polymerization, grafting and conversion of properties. Further development should be brought about in China so that the two eras of high polymers and atomic energy may truly be united.

(4) To create high polymer materials of specified behavior is one of the basic tasks and objectives for the development of high polymer chemistry, This should begin with entirely new isolated substances. In this connection, the study of high polymer components will be most productive. Among the known facts are the high temperatureresistance of high polymers containing fluorine and the temperature-flexible silica oxide chain high polymer. From the latter chemical compound is evolved a high temperature-resistant silicon-oxygen-metallic chain high polymer. The high temperature-resistance characteristics of high polymers containing phosphorus, boron and nitrogen have been clarified gradually. Other element which predominate in high polymer chains should be explored on a large scale. The development of studies of the elements in high polymer should be linked with the study of inorganic high polymers. The structure and behavior of the high polymer elements themselves present a new problem.

It is entirely possible to create synthetic high polymers by adding vinyl, which is capable of polymeradding, or "kung-neng-t'uan," which is capable of condensation, to organic materials possessing special characteristics (such as dyestuffs, drugs, luminous substances, catalytic agents, stabilizing agents, etc.). The prospect for developing a synthetic high polymer having semiconductive qualities is very promising. This is an entirely new problem.

(5) In the basic tasks and the directions for development given above are included problems of theory such as the reaction mechanism in the formation and dissociation of a high polymer, the structure and behavior of high polymers and the relationship between them, etc. These studies are related to polymerization, condensation, interchange and dissociation reaction mechanisms as well as the study of dynamics. Thus, improvement of old methods and discovery of new reactions are substantially assured. The statistical theory of high polymers, the thermodynamic properties in solution and the hydrodynamic behavior of high polymers, the thermodynamic qualities of cohesive high plymers and the mechanical and dielectric properties of molecular structure -- all these need to be examined and formulated. This work is of special significance to the understanding of high polymers that are regular in structure and biologically active.

Any advancement in theoretical research is bound to accelerate the development of high polymer chemistry. At the same time, neighboring or peripheral sciences such as high polymer physics, high polymer physical chemistry, high polymer radioactive chemistry and high polymer biochemistry will respond to the general development of high polymer science.

In short, the future development of high polymer chemistry in China has unlimited promise.

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