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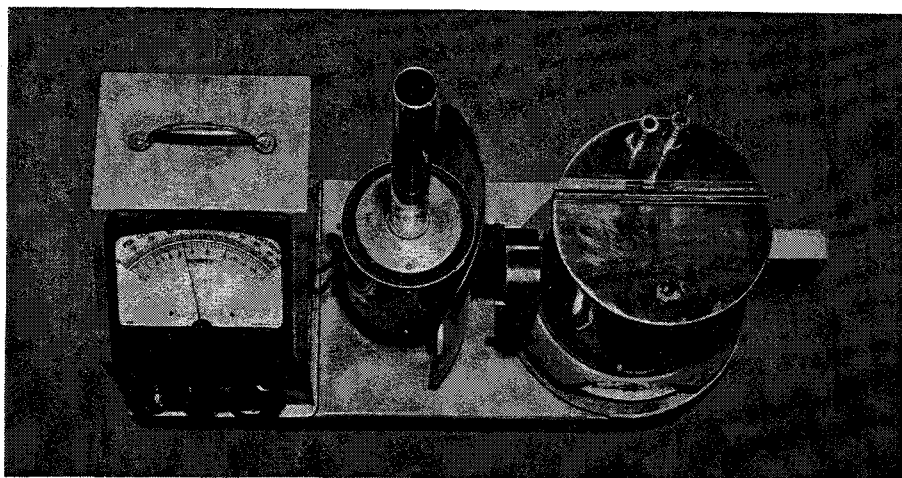
average of the squares of all these distances is taken to define the average size of the molecule.

As a specific example let us take the molecule of polystyrene in solution in benzene. A polystyrene molecule of molecular weight one million has about 20,000 C-C links, each 1.5 Angstrom units long (one Angstrom is a hundred millionth of a centimeter). From the information aforementioned, we compute that the average end-to-end distance, or diameter, of the molecule is about 300 Angstroms.

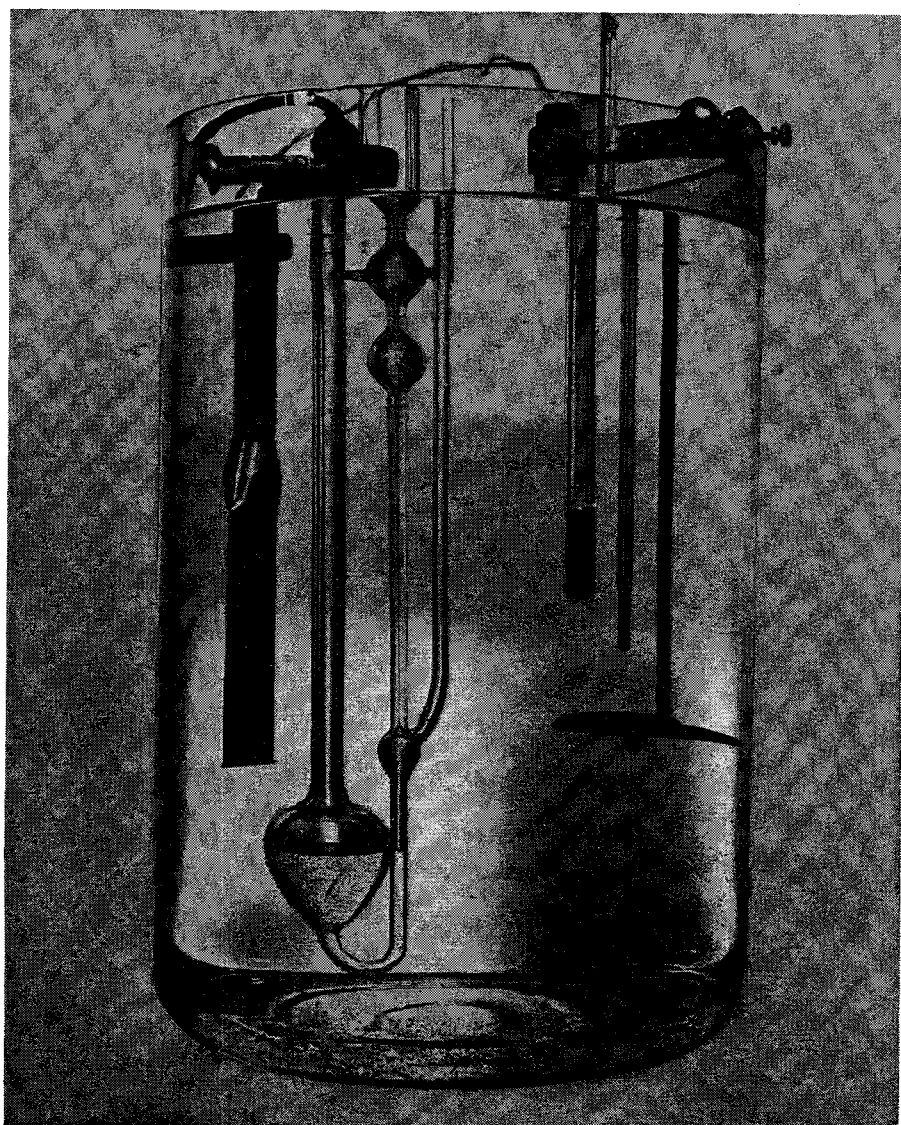
Now this size begins to be comparable with the wavelengths of visible light (which are in the neighborhood of 5,000 Angstroms). A molecule of such a size no longer acts like a single point in intercepting and reradiating light; instead, light comes from various points on the molecule, and as a result we have interference effects because of phase differences in the scattered light waves. The intensity of light-scattering now depends on the angle from which we view the beam [see diagrams on opposite page]. On the average a solution of large molecules scatters more energy forward, in the direction of the beam, than backward. What is most important, the larger the molecule, the higher the proportion of light scattered in the forward direction.

We can consult this scattering pattern, then, as a guide to the size of molecules. Polystyrene has been so studied, and it has confirmed the prediction that the size of a molecule is proportional to the square root of the number of C-C links. However, the size in each case is substantially larger than had been calculated theoretically: polystyrene of molecular weight one million has an average "diameter" (end-to-end distance) of 1,100 Angstroms instead of 300. The chief reason for the discrepancy is that in considering the possible configurations the calculation failed to take account of such factors as the impossibility of two monomers in the chain simultaneously occupying the same position in space. Naturally the molecules cannot be as compact, on the average, as such a calculation predicts.

The mathematical difficulties in dealing with these enormously complex molecules are so formidable that we are far from any fully satisfactory quantitative description of them. But all in all, the combined information from the various measurements—of viscosity, osmotic pressure and scattering of light—is beginning to give us a clear picture of their size and structure.



**PHOTOMETER** measures light scattering. Light source is a mercury arc in the cylinder in the center. The beam passes through a shutter to the dark chamber at right. This contains the scattering solution and a photocell which can be rotated by means of the graduated dial at the bottom of the chamber. The meter at the right indicates the current in the photocell.



**VISCOMETER** is essentially a capillary tube. In this photograph the capillary is the center tube in the assembly of glass at left in the large vessel. Liquid drawn up from the bottom bulb fills the two small bulbs above the capillary. It is then timed as it flows out. The rest of the apparatus in the vessel is for the purpose of maintaining constant temperature.

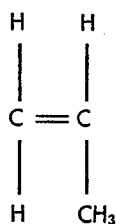
# How Giant Molecules Are Made

*New catalysts control the orientation of monomers as they are linked in chains. This greatly increases the range of properties that can be built into synthetic polymers*

by Giulio Natta

A chemist setting out to build a giant molecule is in the same position as an architect designing a building. He has a number of building blocks of certain shapes and sizes, and his task is to put them together in a structure to serve a particular purpose. The chemist works under the awkward handicap that his building blocks are invisible, because they are submicroscopically small, but on the other hand he enjoys the happy advantage that nature has provided models to guide him. By studying the giant molecules made by living organisms, chemists have learned to construct molecules like them. What makes high-polymer chemistry still more exciting just now is that almost overnight, within the last few years, there have come discoveries of new ways to put the building blocks together—discoveries which promise a great harvest of new materials that have never existed on the earth.

We can hardly begin to conceive how profoundly this new chemistry will affect man's life. Giant molecules occupy a very large place in our material economy. Tens of millions of men and women, and immense areas of the earth's surface, are devoted to production of natural high polymers, such as cellulose, rubber and wool. Now it appears that syn-



PROPYLENE is the monomer of the polymer chains depicted in formulas at right.

thetic materials of equivalent or perhaps even better properties can be made rapidly and economically from coal or petroleum. Among other things, this holds forth the prospect that we shall be able to turn much of the land now used for the production of fiber to the production of food for the world's growing population.

In this article I shall explain how the synthetic giant molecules are made. The molecules with which we are here concerned are the chainlike structures made of organic building blocks. They are formed by linking together hundreds or thousands of these units, called monomers. Let us consider the monomers first.

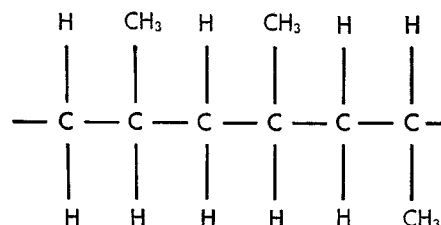
A monomer whose structure consists simply of a backbone of carbon atoms with hydrogen atoms ranged along the sides lends itself to the formation of a neat, straight chain of links hooked end to end, though it may also grow branches. Chain molecules of this type readily align themselves alongside one another and can be oriented to form fibers. The structure becomes more complex when, in place of hydrogen atoms, the monomer has side groups—for example, the methyl group ( $\text{CH}_3$ ). A chain formed of such monomers may have one of three arrangements [see diagrams at right].

(1) The side groups may occur at random on either side of the chain; this type of polymer is called "atactic," meaning lacking in order (tactic comes from the Greek word for order). (2) The groups may all lie on one side of the chain; this arrangement is called "isotactic." (3) They may alternate from one side to the other in regular order; this type is called "syndiotactic."

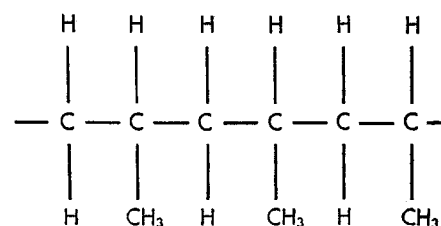
These elements of structure lead to a great variety of formations. Isotactic chains easily line up side by side and

form crystalline structures, whereas atactic chains tend to make an amorphous material. Blocks of different polymers may be joined end to end, or one polymer may be grafted onto another as a branch on the main chain [see diagram on page 89]. In each case the structure confers certain mechanical

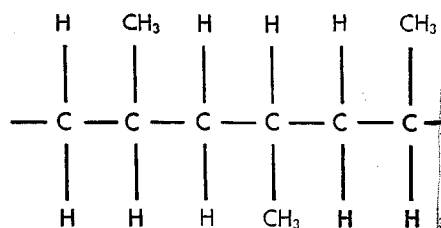
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POLYPROPYLENE can now be prepared in various forms. If the  $\text{CH}_3$  side groups (in

properties on the polymer, as Arthur V. Tobolsky explains in the following article [page 120]. For example, crystallinity gives a polymer strength and a high melting point, side-by-side alignment of the chains in bundles allows formation of a fiber, and so on.

**H**ow do monomers grow into a chain; that is, how do they link themselves together? There are two ways, called condensation and addition. In the condensation process, monomers or groups of monomers, upon being heated, unite spontaneously and at random by chemically active hooks at their ends—like skaters or groups of skaters linking arms. In the addition process the polymer builds up, one monomer at a time, by a chain reaction, very much as if one person grasped a live wire and was fixed to it, a second seized the first and was himself held fast by the electricity, a third person similarly was added to the chain by seizing the second, and so on.

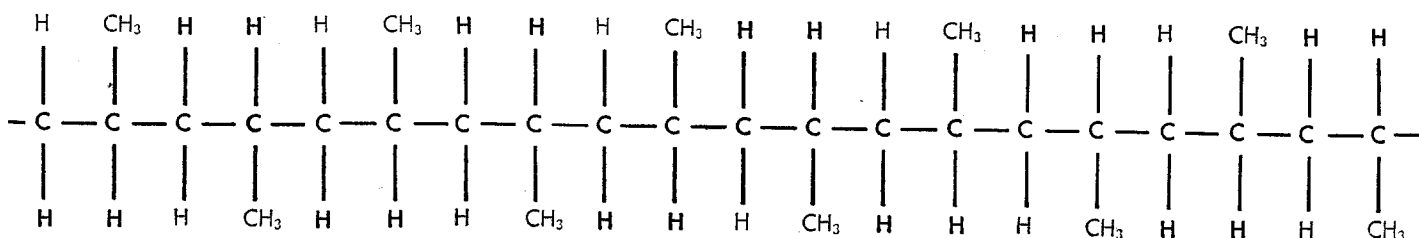
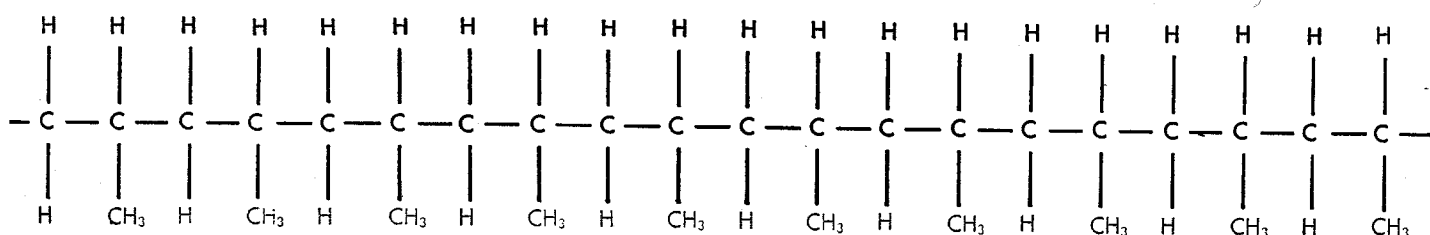
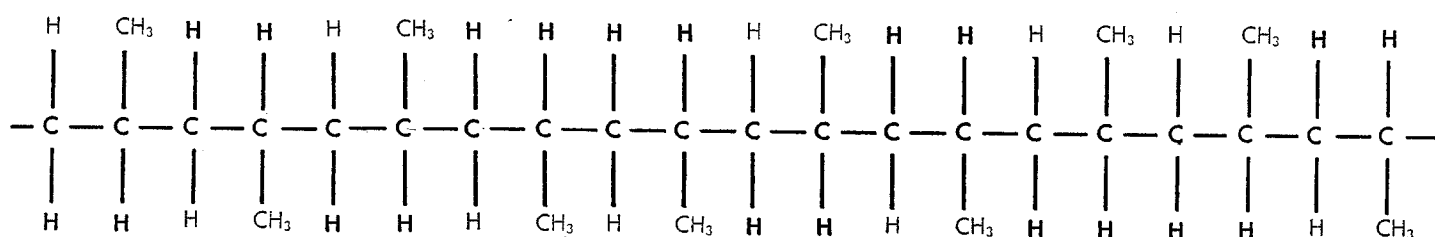
Let us follow through the condensa-

tion process. Suppose we dump a mixture of monomers into solution and heat the mixture. If the monomers are equipped with chemically active hooks, we can expect them to link up into polymers. But the product we get will be strictly accidental. Like a tile floor in which tiles of different colors are put together at random, the polymer will have no predictable pattern, because the monomers, having no preference for any particular configuration, will have linked up by chance.

If, however, we use monomers which join only in one way, we can predict what kind of chain they will form. We take, let us say, two monomers: one has a basic group, the amino group ( $\text{NH}_2$ ), at each end, the other has an acid group, carboxyl ( $\text{COOH}$ ), at each end. The two monomers will hook up end to end, the basic end of one linking up with the acid end of the other and splitting off a molecule of water in the chemical reaction [see diagrams at the bottom of pages 86 and 87]. This is the classical reaction by which, in nature, amino

acids are linked to form proteins, as Paul Doty explains in the article on page 173. It has been adapted by man to make synthetic fibers such as nylon. The monomers may have a basic group at one end and an acid at the other, or basic groups at both ends, or acids at both ends; in all cases it is the inherent chemical affinity between the end groups that causes the monomers to grow into a linear polymer.

This building plan, upon which Wallace H. Carothers of du Pont based his synthesis of nylon, is derived from the design of the natural fibers of wool and silk. They too are made by condensation of simple, regular monomers, all of the same configuration (levorotatory). Their monomers are amino acids, with an amino group at one end and a carboxyl at the other; they link up into long chains; the chains in turn are spun into strong fibers. All these lessons from the natural models have been followed by the creators of synthetic fibers. We do not know very much about how living organisms carry out their building and spinning processes,



color with adjacent hydrogen) are located at random on either side of the carbon chain, the polymer is called atactic (1). If they are

on the same side, the material is isotactic (2); if the groups are distributed from side to side in a regular way, it is syndiotactic (3).

but the chemist has his own methods.

The construction of polymers by the condensation method is rather slow and tends to come to an almost complete stop before the molecules have attained a truly giant size, because as the chains grow they become less mobile and less numerous and therefore less likely to encounter free building blocks in the solution. Fortunately products such as nylon have acquired their valuable properties when they reach a molecular weight of 10,000 to 20,000. But to build molecules with molecular weights in the hundreds of thousands or millions by condensation is very difficult.

The addition method, on the other hand, can produce giant molecules of almost unlimited size. Starting from an active center (an activated monomer which serves as a kind of seed), it adds one monomer at a time and rapidly builds a chain which in theory can go on growing indefinitely as long as the supply of building blocks holds out. The process is comparatively simple but difficult to control. As I mentioned, the monomers here employed do not start with built-in chemical hooks, as condensing monomers do: instead the hooks have to be generated. Each monomer,

upon joining the chain, thereby acquires a hook to seize another. There are various ways of generating such a hook, or bond; each requires a catalyst.

One method employs free radicals as the catalyst. (Actually they differ from true catalysts in that they are consumed in the polymerization reaction.) A free radical is a compound with an unpaired electron—usually a fragment of a larger molecule which has been split by heating. The unpaired electron makes the radical very reactive: it readily hooks itself to another molecule by its odd electron. Suppose it encounters a monomer. In an organic monomer the carbon and hydrogen atoms are held together by covalent bonds, meaning that the bond consists of a pair of electrons shared between a pair of atoms. The conventional symbol C-C represents two carbon atoms linked by an electron pair. Frequently the carbon atoms are joined by a double bond (C=C)—that is, two pairs of electrons. Now when a free radical encounters a double bond, it may pair with one of the electrons in the extra bond, leaving the other member of the pair without a partner. Thus the monomer itself becomes a radical: it now has an unpaired electron at one end [see diagrams at top of pages 86 and 87]. It

promptly reacts with a second monomer; the newly released electron at the end of the second seizes a third monomer; the third grasps a fourth, and so the chain grows. It can grow to giant size and might increase without limit but for the fact that the reactive end of the chain is not restricted to reacting with monomers: it may combine with other molecules in the solution, or two chains may join head on (*i.e.*, at their free-radical ends), thus closing the growing points of both.

Among the polymers that can be made by the free-radical method are polyethylene [see article on page 139], polystyrene and polyvinyl chloride. Some of these giant molecules are perfectly linear, like a long snake; some are branched, like a tree. Branches develop when free radicals start side growths at points along the chain. This is particularly likely to happen when a polymer is produced at high temperature. For example, polyethylene made by the high-pressure process (at pressures above 1,000 atmospheres and temperatures above 212 degrees Fahrenheit) is highly branched: it may have several long branches and hundreds of small ones. The branches interfere with packing of the chains in crystalline (*i.e.*, regular) arrangements, and as a result polyethylene synthesized by this method has a comparatively low crystallinity—30 to 60 per cent. With low crystallinity go low strength and a low melting point.

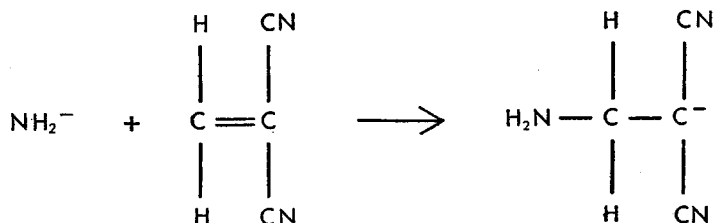
Free radicals are one type of catalyst that can grow polymers by addition; another method involves the use of ions as catalysts. The latter is a very recent development, and to my mind it portends a revolution in the synthesis of giant molecules, opening up large new horizons.

Under certain circumstances the electrons of a double bond between the carbon atoms in a monomer can be so displaced that one of the carbon atoms in effect has a positive charge while the other end of the molecule is negative. The carbon atoms are "polarized," so to speak. If we now neutralize the positively charged carbon atom by causing it to react with a negative ion, the other end of the monomer becomes negatively charged, because of its unneutralized negative carbon atom. It will then act as a negative ion and attach itself to the positively charged end of a second "polarized" monomer [see diagram at the left]. This again leaves a negative charge at the growing end of the molecule. Thus, by a chain reaction like the or

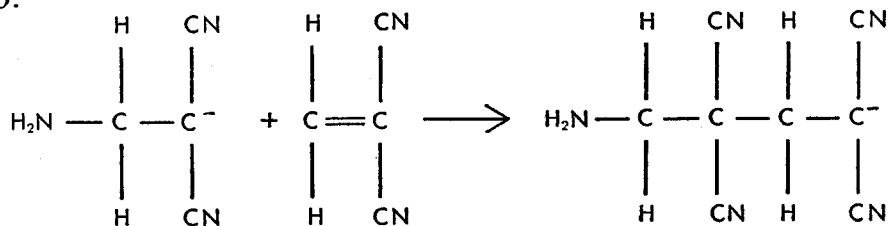
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IONIC ADDITION is illustrated by example. Sodium amide splits into ions (1). A negative  $\text{NH}_2^-$  ion combines with the positive end of a vinylidene nitrile monomer (2). The negative end of this monomer then combines with the positive end of a second (3), and so on.

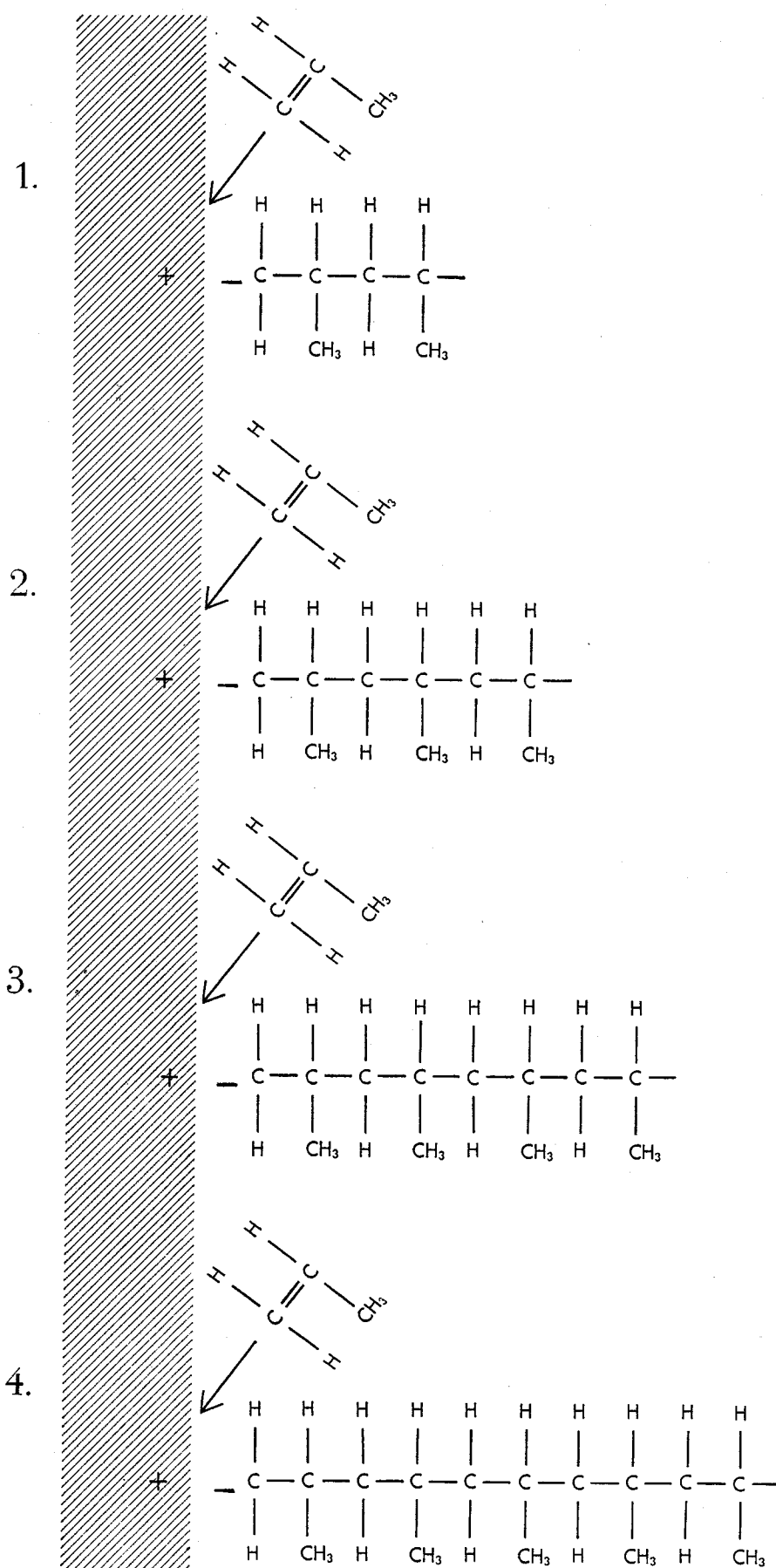
catalyzed by free radicals, the molecule grows to a high polymer. This version of the ionic process uses negative ions (anions) as the catalysts. The process also works in reverse: if positive ions (cations) react with the negatively charged end of a polarized monomer, it will grow from the positively charged end.

The cationic method has produced some very interesting high polymers: for instance, butyl rubber, the synthetic rubber used for tire inner tubes. But the anionic catalysts, a more recent development, have proved far more powerful. They yield huge, made-to-order molecules with extraordinary properties.

Experiments with anionic catalysts had been carried on for a number of years. Before World War II Russian chemists, by a process using sodium as the catalyst, had produced a synthetic rubber from butadiene, but the rubber was of rather poor quality. In the U. S. the polymer chemist Avery Morton had obtained very large polymers of butadiene and styrene with an ionic process. And Michael Szwarc had generated tremendous chains of polystyrene which he called "living molecules," because even after they had stopped growing, they would start growing again if more styrene was supplied later.

Only in the last four years, however, have the great possibilities of ionic catalysis begun to take shape. In 1953 Karl Ziegler in Germany, and less than a year later the du Pont Company in the U. S., patented new ionic processes for making polyethylene. These processes made it possible to synthesize polyethylene at atmospheric pressure and temperatures as low as 90 degrees F., instead of the very high pressures and temperatures previously required. For the first time the molecule could be polymerized in a regular, unbranched form, producing a strong, crystalline material with high resistance to heat.

Early in 1954 our group in the Institute of Industrial Chemistry of the Polytechnic Institute of Milan, using certain special catalysts, succeeded in polymerizing more complex monomers of the vinyl family (of which ethylene is a member). We were able to generate chains of very great length, running to molecular weights in the millions (up to 10 million in one case), and to produce at will either isotactic or syndiotactic or atactic forms of the chains. In other words, we found that it was possible, by a



**NEW IONIC CATALYST** is a solid material (*colored band*) containing complex positive ions. It grows ordered polymers, in which new units add themselves at the inside end of the growing chain. Shown here are four stages in the growth of isotactic polypropylene.

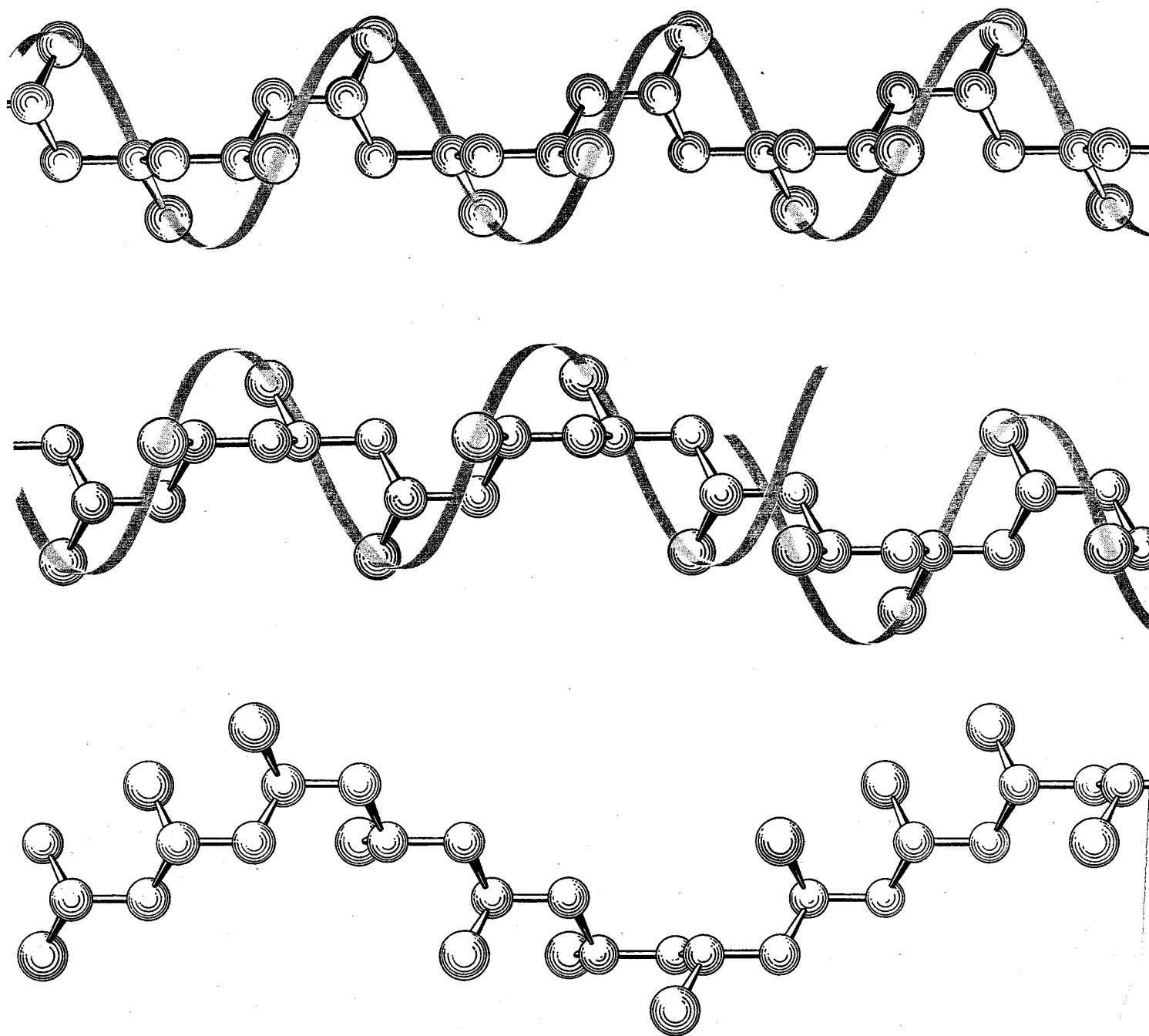
proper choice of catalysts, to control the growth of chains according to predetermined specifications.

Among the monomers we have polymerized in this way are styrene and propylene, both hydrocarbons derived from petroleum. The polypropylenes we have made illustrate the versatility of the method. We can synthesize them in three forms: isotactic, atactic or "block isotactic," that is, a chain consisting of blocks, one having all the side groups

aligned on one side, the other on the opposite side [see diagrams below]. The isotactic polypropylene is a highly crystalline substance with a high melting point (346 degrees F.); it makes very strong fibers, like those of natural silk or nylon. The atactic product, in contrast, is amorphous and has the elastic properties of rubber. The block versions of polypropylene have the intermediate characteristics of a plastic, with more or less rigidity or elasticity.

The possibility of obtaining such a

wide array of different products from the same raw material naturally aroused great interest. Furthermore, the new controlled processes created properties not attainable before: for example, polystyrene, which had been known only as a glassy material with a low softening point (under 200 degrees F.), now could be prepared as a strong, crystalline plastic with a melting point near 460 degrees. The new-found power of the anionic catalysts stimulated great activity in polymer research, both in Europe



DEGREES OF ORDER in polypropylene molecules can be varied. Isotactic molecule (top) has CH<sub>3</sub> side groups (the balls through

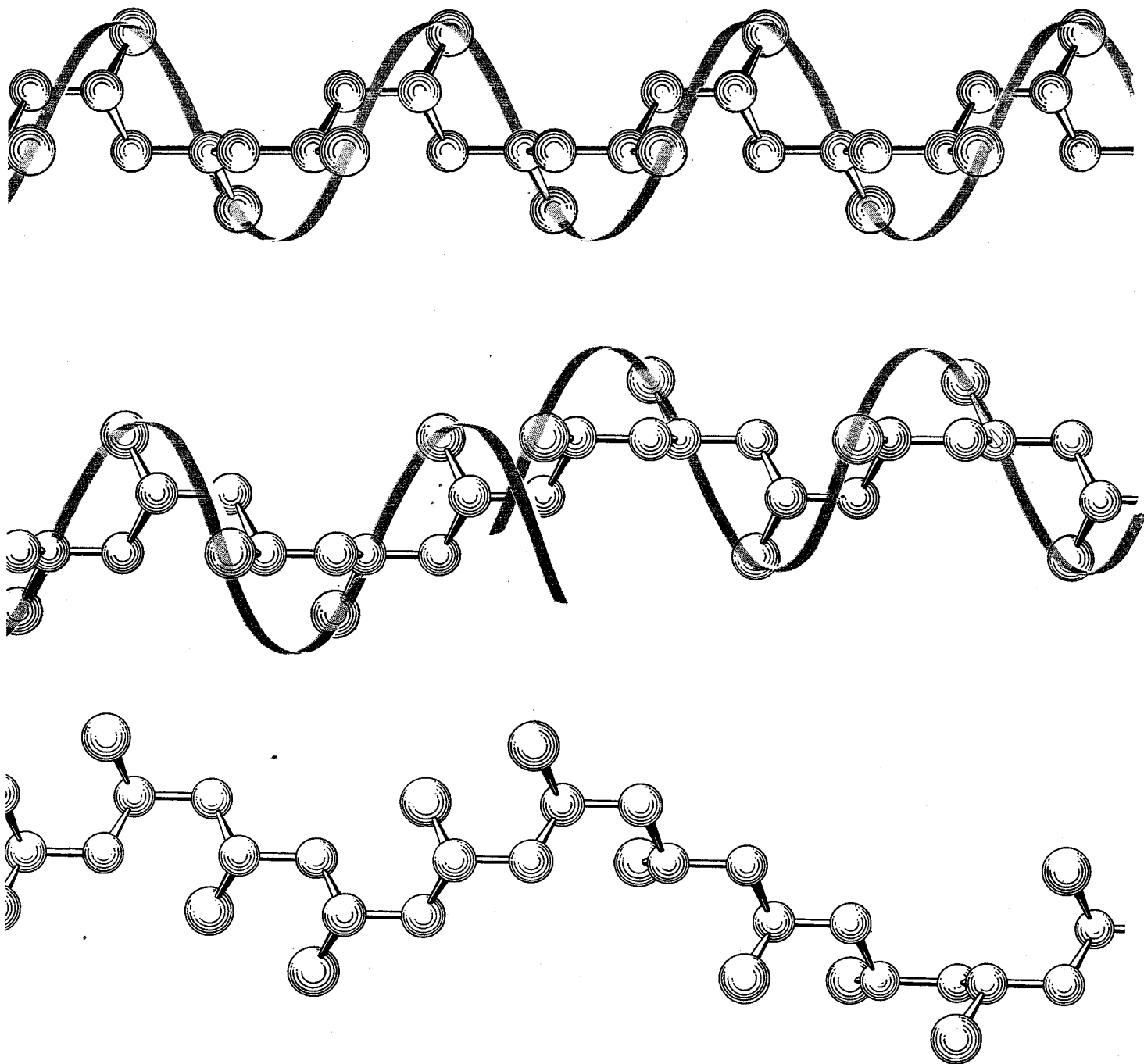
which the imaginary colored ribbon passes) in a regular helical sequence around the central chain. It forms crystalline fibers. The

and in the U. S. New polymers were made from various monomers. In our own laboratory we synthesized all of the regular polymers, and some amorphous ones, that can be made from butadiene; some of the products are rubber-like, others not. At about the same time the B. F. Goodrich Company and the Firestone Tire and Rubber Company both announced that they had synthesized, from isoprene, a rubber identical to natural rubber—a problem on which chemists throughout the world had

worked in vain for more than half a century.

What are the magical new catalysts that have shown such remarkable powers? Most of them are complexes consisting of several substances: for instance, the chloride of a metal with an unfilled electron shell (*e.g.*, titanium) and an “organometallic” compound (*e.g.*, aluminum linked to an alkyl group). Groups of ions of these substances serve as the active centers from which giant

molecules grow. The character of the growing molecule is controlled by the nature of the generating complex and by temperature. When the catalytic complex is firmly fixed on solid crystals with a layer structure and the reaction proceeds at low temperature, it generates a perfectly regular, isotactic molecule of tremendous length. When the generating complex is less firmly rooted in the crystals, or when the process is carried out at high temperatures, the chain changes its pattern of growth from time

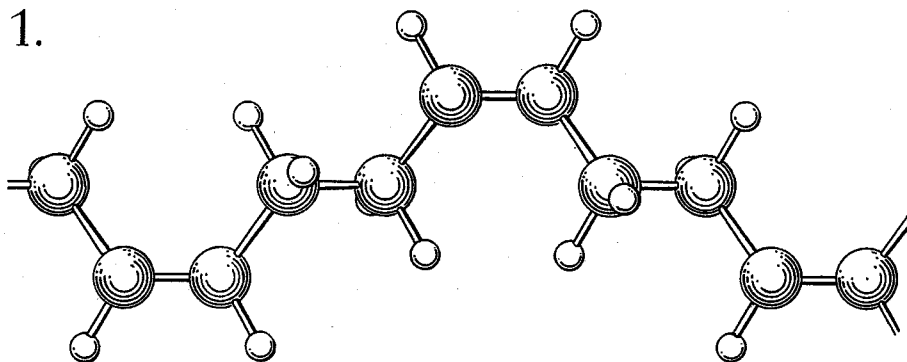


middle diagram shows a section of a block polymer with three isotactic parts. It forms a less crystalline, leathery material. A random

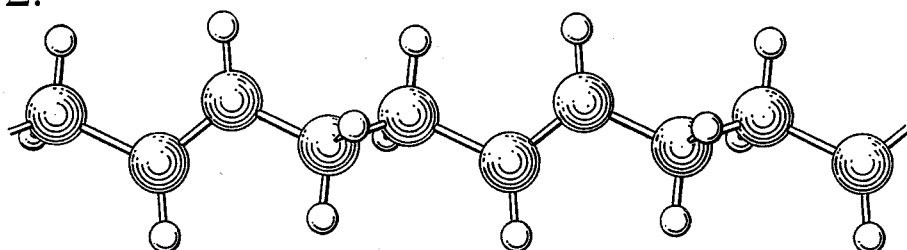
molecule (*bottom*) forms an amorphous, rubbery substance. The balls in the backbone represent, alternately, CH<sub>2</sub> and CH groups.



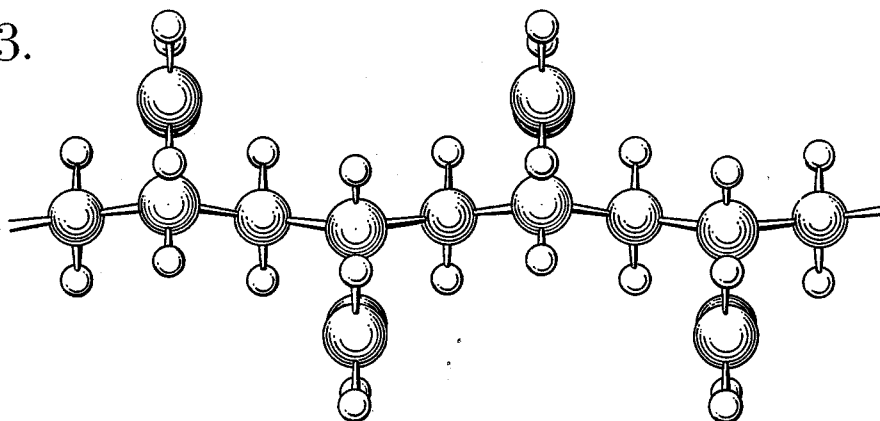
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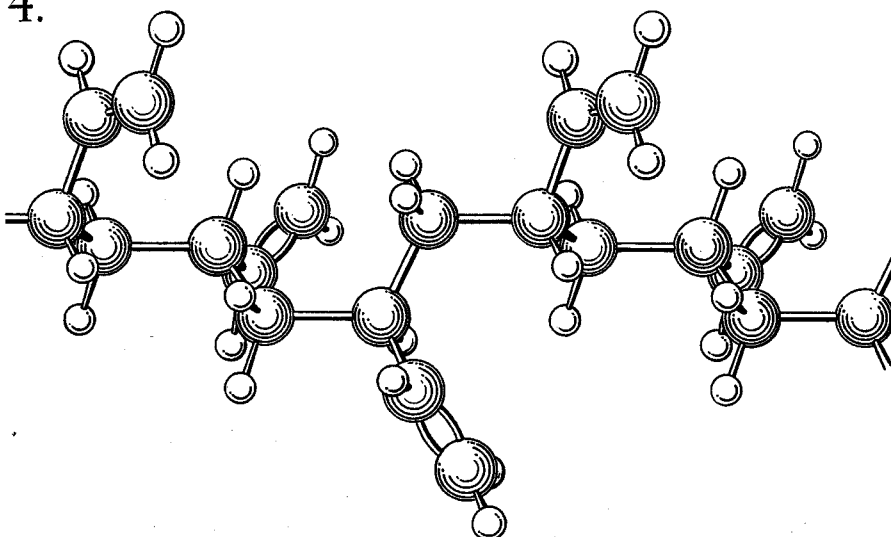
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**POLYBUTADIENE** has recently been prepared in all four possible stereoisomeric forms by Natta and his colleagues in Milan. In these diagrams the large balls represent carbon atoms; the small balls, hydrogen atoms. Form 1 is a rubbery substance; form 2 is fibrous.

to time and we get a molecule of the block type. When the catalysts are embedded in an amorphous support, we get atactic, or irregular, molecules.

The giant molecules themselves do not suggest life, but the catalytic complexes that generate them do. We should speak not of "living molecules," as Szwarc did, but of "living complexes." A molecule growing from the catalytic complex on the surface of a crystal is like a hair growing from its root: that is, the monomers are added at the root. The long molecule is very thin and very delicate—far more easily torn loose than an actual hair. Even eddies produced by stirring the liquid will tear the molecule from its generating complex, as a windstorm can tear a slender plant stem from its roots. But the generating complex, like a root, does not die; it retains the ability to send forth new shoots. It is, however, subject to a number of mortal dangers: certain poisons will kill its ability to generate molecules, freezing or lack of nourishment will render it inactive, and so on.

No one will be misled into supposing that these complexes bear any basic resemblance to a living organism. Nevertheless the analogies between the way they build giant molecules and the way an organism does are striking, and very hopeful for the future of polymer chemistry. A living creature builds its high polymers, precisely tailored according to a set design, by means of catalysts (enzymes). We are now in a position to hope that, with man-made catalysts, we shall be able to produce predesigned giant molecules in the same controlled and orderly way.

In some respects we can improve on nature. As I have mentioned, we shall probably be able to create many new molecules which do not exist in living matter. They can be made from simple, inexpensive materials. And we can manufacture giant molecules more rapidly than an organism usually does. For example, a single active center in a catalyst can generate more than 10,000 polypropylene molecules of molecular weight 200,000 in 20 hours—polymerizing monomers at the rate of 250,000 per hour!

Although it is less than four years since the new methods for controlled synthesis of macromolecules were discovered, already many new synthetic substances—potential fibers, rubbers and plastics—have been made. Thousands of chemists are now devoting themselves to this new field of research, and unlimited possibilities have been opened to their imagination.