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PRECISELY CONSTRUCTED POLYMERS

by GIULIO NATTA

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Precisely Constructed Polymers

In the chainlike giant molecules made by man, the units in the chain are generally oriented at random. Now these units can be oriented in regular sequence, giving rise to polymers with useful new properties

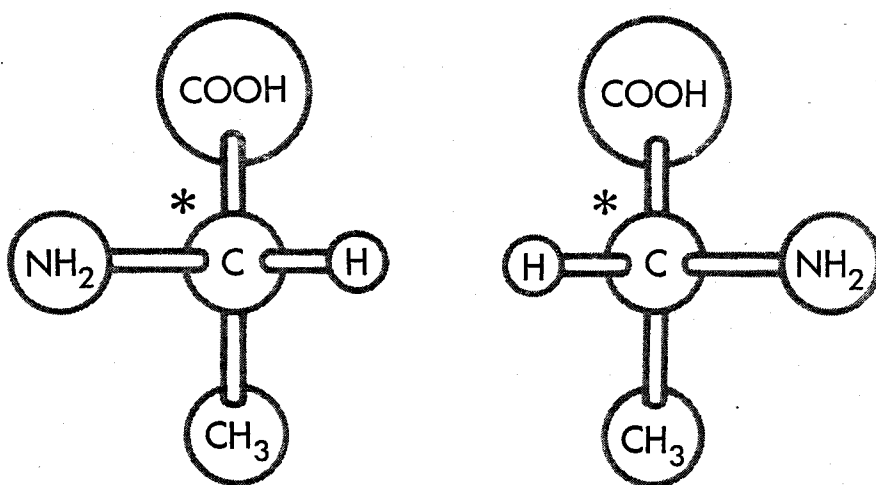
by Giulio Natta

It is often said in the chemical industry that 10 years are required to carry a new product from the test tube to tank-car production. Seven years have now passed since our laboratory in the Politecnico di Milano discovered "stereospecific" catalytic processes for creating "stereoregular" polymers from simple asymmetric hydrocarbon molecules such as those of propylene. The term "stereospecific" signifies that the catalysts are able to link the simple structural units of the polymer—the asymmetric monomers—into precisely ordered three-dimensional structures rather than into structures assembled more or less at random. The precise ordering of structure yields polymers with new and useful physical properties. The new stereoregular polypropylene polymers produced by our methods, and by similar methods successfully developed by others, have been in large-scale production in the U.S. since early this year, following the completion last year of three major plants. The polymers have been commercially available in Italy since 1957. Only last year our laboratory was successful in carrying stereospecific polymerization methods another step forward, suggesting that still-new varieties of stereoregular polymers may achieve practical importance before too many years have passed.

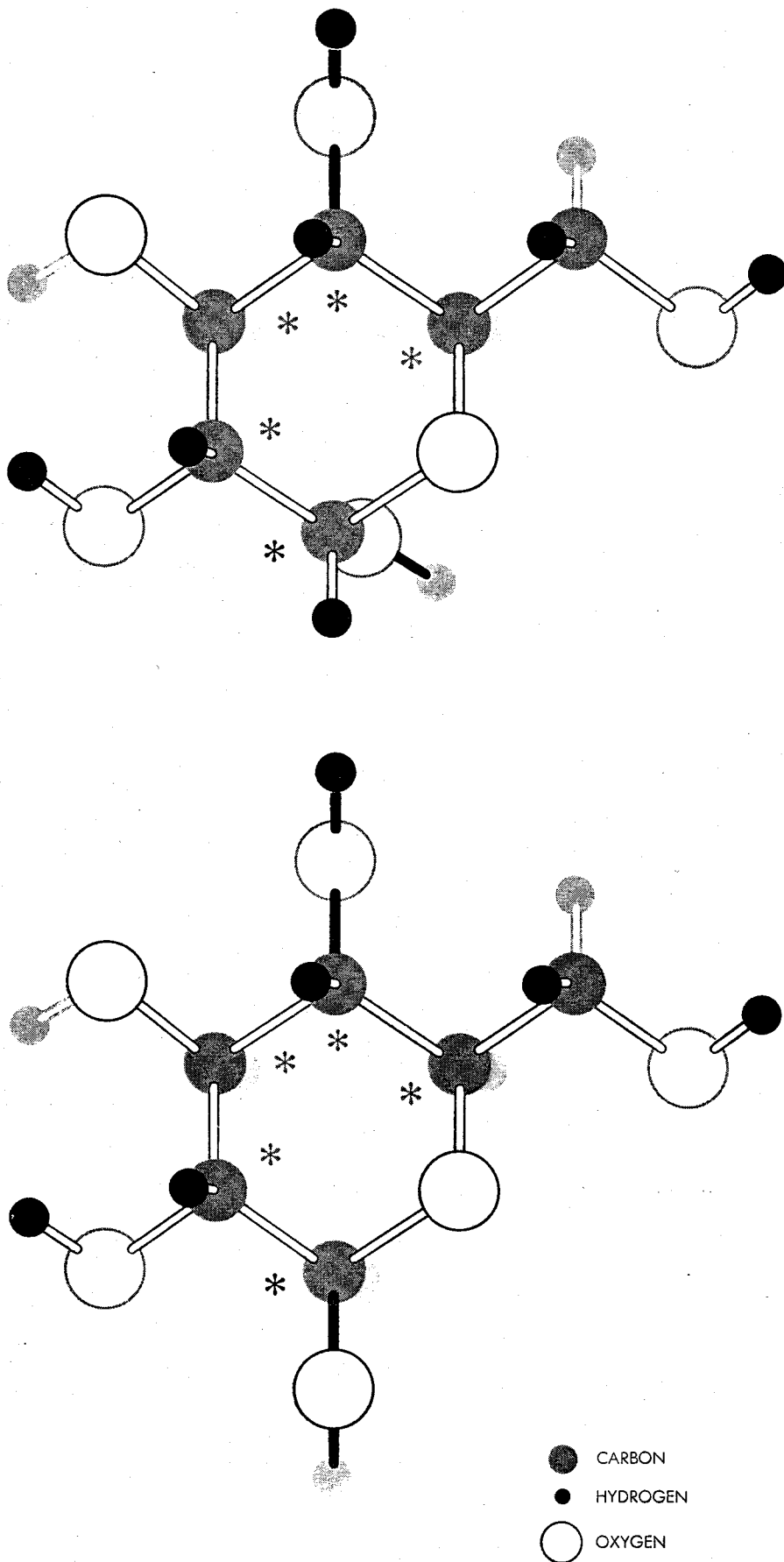
Our recent work has led to the synthesis of polymers that, when placed in solution, have the property of rotating the plane of polarization of a beam of

plane-polarized light. They are said, therefore, to be optically active. It was Louis Pasteur who discovered, about 1850, that tartaric acid comes in two isomeric forms, one able to rotate polarized light to the right, the other able to rotate it to the left. A mixture of the two forms in equal amounts is called a racemic mixture. Since Pasteur's time it has been shown that compounds with optical activity are widely used in nature

as the monomers of the polymeric constituents of living matter, for example proteins, cellulose and starch. To display optical activity an organic molecule must contain at least one asymmetric carbon atom, meaning a carbon linked to a different kind of atom (or group of atoms) through each of its four valence bonds [see illustration below]. For reasons difficult to explain (and perhaps not yet fully explained) the electron



OPTICAL ISOMERS OF ALANINE, one of the 20-odd amino acids that link up to form proteins, illustrate what is meant by an "asymmetric" carbon atom. The central carbon is asymmetric because it has attached to each of its four chemical bonds a different kind of atom or group of atoms. When in solution one configuration, called L(-)-alanine (*left*), rotates plane-polarized light to the left; its mirror image, D(+)-alanine (*right*), rotates polarized light to the right. Natural proteins are all built from L(-)-amino acids.



OPTICAL ISOMERS OF GLUCOPYRANOSE, a natural sugar, each contain five asymmetric carbon atoms (*starred*). Plants make chiefly *alpha-D(+)-glucopyranose* (*top*) and *beta-D(+)-glucopyranose* (*bottom*), which differ only at one carbon (*dark star*). The former polymerizes to form starch, latter to form cellulose (*see illustrations on opposite page*).

cloud around an asymmetric atom—which need not be carbon—causes polarized light to rotate.

A compound containing one asymmetric carbon atom can exist in two isomeric forms, called enantiomers; one is the mirror image of the other, as the right hand is of the left. An optically active compound is assigned to the dextro (D) or levo (L) series according to the position of its asymmetric carbon atom (or atoms) with respect to that in certain reference compounds. This classification is independent of the way the compound in question actually rotates polarized light. If the rotation is to the right, the compound is labeled (+); if to the left, (-).

For more than a century chemists have sought methods of synthesizing one particular isomer in preference to its optical twin. Ordinary methods of synthesis produce all possible optical isomers in equal abundance. One way to obtain an excess of a particular isomer is to employ optically active starting materials. Chemists have made only negligible progress, however, in achieving an "absolute asymmetric synthesis"—one that employs unselected starting materials. The idea that irradiation of the reactants with polarized light might favor one isomeric product over another has been tested without success.

No one has been able to explain why all natural proteins should be built up from L-series amino acids. Presumably the exactly equivalent D series would do just as well. A giant molecule containing a random mixture of L and D types, however, would lack the distinctive physical properties of normal proteins. It is the ordered repetition of molecules sharing a common symmetry that endows a giant molecule with crystalline properties. By "crystalline" is meant the ability of a molecule to pack together with others in orderly array. Crystallinity endows a polymer with strength and rigidity. In contrast, a polymer lacking an ordered structure is generally amorphous.

Although two enantiomers may have almost identical physical properties, the polymers formed from them may differ greatly. A remarkable example of this is found in starch and cellulose, which are made from two D-series sugars that differ in only one isomeric detail. Starch is a chainlike polymer made from *alpha-D(+)-glucose*; cellulose is a comparable chain made from *beta-D(+)-glucose* [*see illustrations at left and on opposite page*]. The slight differences between the two sugars give rise to different types

of chain and thus to profound differences in their polymers: starch can be digested by man and animals, cellulose cannot. It is apparent, therefore, that the ability to synthesize giant molecules from optically active organic compounds—and also to decompose them—is an important characteristic of living organisms.

One would like to know if life on other planets shows the same stereoisomeric preferences as life on earth. It is generally assumed that the preference of earth life for L-amino acids and D-sugars is a simple accident, tracing back, perhaps, to an accident of catalysis when life first began. If only accident is involved, there would seem to be a good chance that life elsewhere is built around amino acids and sugars having optical activities different from those preferred on earth. If space explorers ever discover plants or animals on another planet, it will be of some importance to learn the precise steric configuration of these organisms. An extraterrestrial plant that appeared to be edible

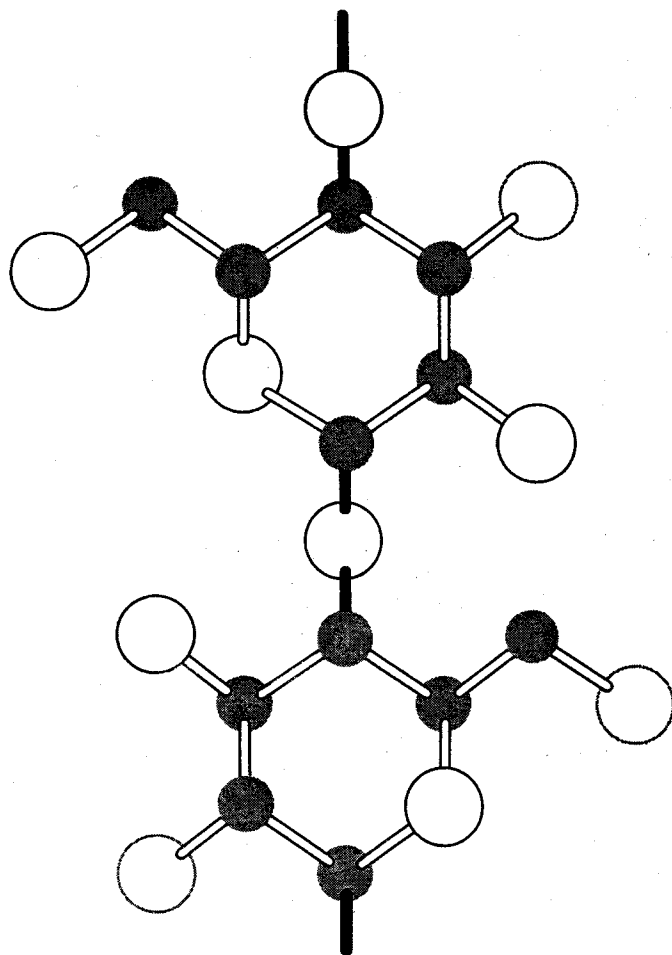
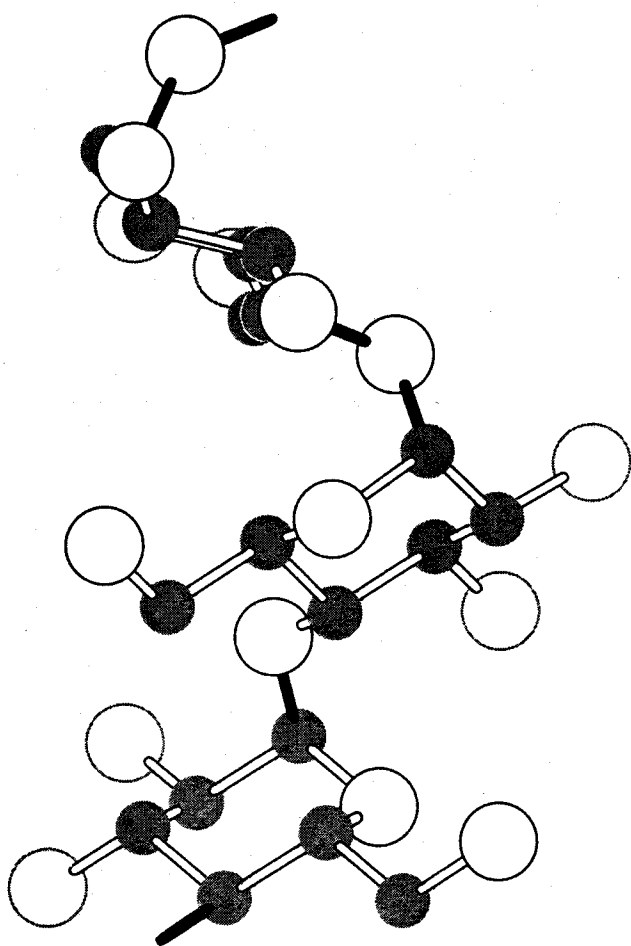
would be totally unassimilable if it contained D-amino acids and L-glucose.

Our own efforts at asymmetric synthesis of polymers are a direct outgrowth of the work that led in 1954 to stereoregular polypropylene. It will be recalled that in 1954 polyethylene was already well known as the plastic material used in "squeeze" bottles. Ethylene (C_2H_4) is the simplest hydrocarbon containing a double chemical bond. When it polymerizes, the double bond breaks and provides two free connecting links to join with two other molecules of ethylene—one on each side—in which bonds have similarly been broken. In this fashion thousands of ethylene units can link up to form a long chain, which packs together well with other similar chains. The result is a crystalline polymer that is both strong and flexible but has a rather low melting point.

The propylene monomer (C_3H_6) is an ethylene molecule in which one hydrogen atom has been replaced by a methyl

group (CH_3). Unlike the molecule of ethylene, the propylene molecule is structurally asymmetric. Consequently if propylene is allowed to polymerize, the resulting polymer can take various steric configurations. If the polymerization is "undirected," the methyl groups will fall at random along the chain, now on one side, now on the other. Such chains do not pack well together and the result is a rubbery, amorphous polymer of relatively low strength. We called this structure "atactic," meaning without order. We found that certain catalysts would direct the polymerization so that the methyl groups would all fall on one side of the chain or would alternate regularly from side to side; in both cases the resulting polymers are crystalline. The former chains we called "isotactic"; the latter, "syndiotactic" [see illustrations on pages 6 and 9].

Isotactic polypropylene, because of its special structure, has a high melting point and yields a polymer of high crystallinity that is harder, tougher and



STARCH AND CELLULOSE (left and right) are giant molecules formed from *alpha*-D(+)-glucopyranose and *beta*-D(+)-glucopyranose respectively. In this illustration hydrogen atoms, shown

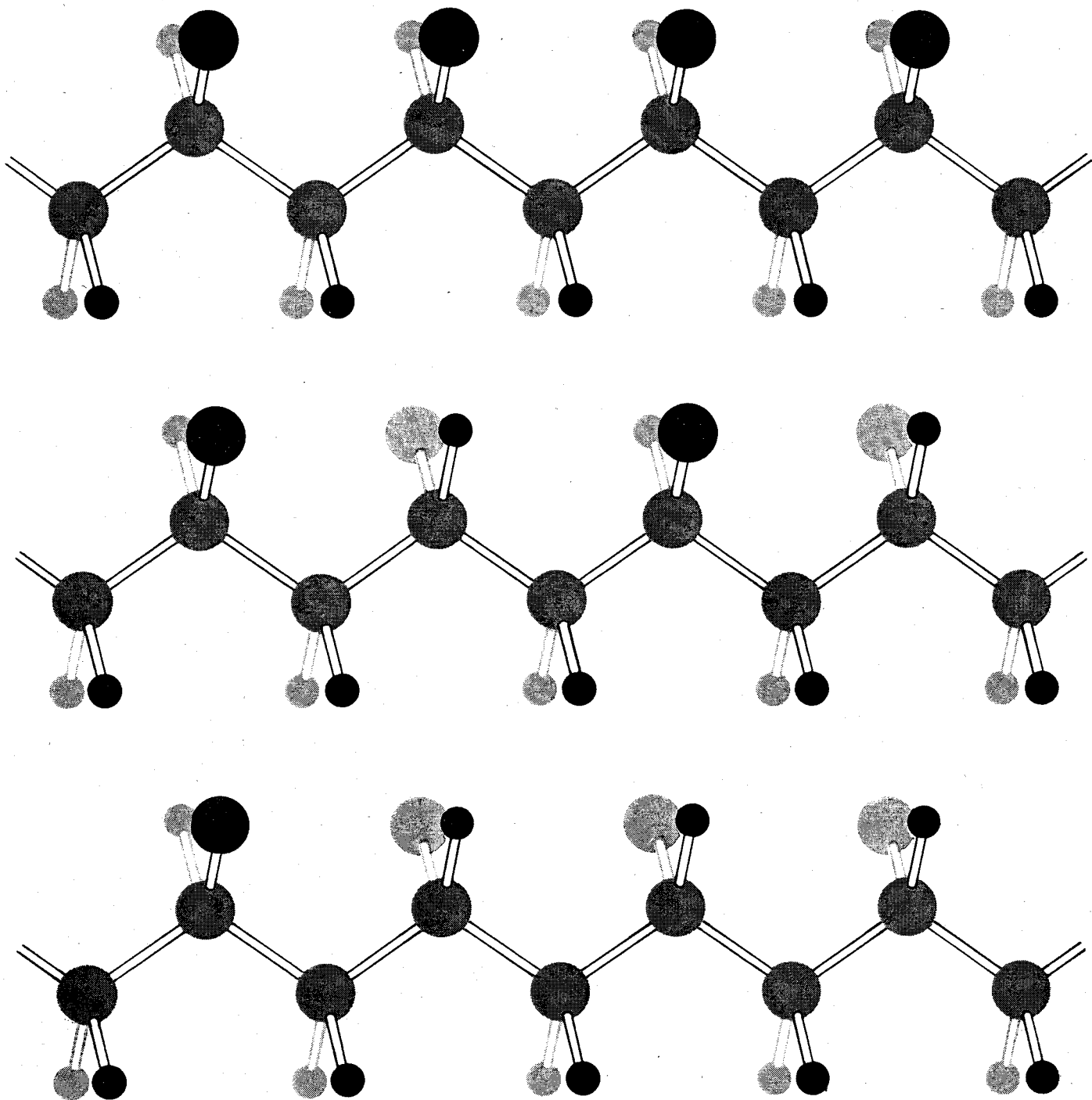
in the monomers on the opposite page, have been omitted for clarity. Although the monomers have nearly identical physical properties, the giant molecules created from each are quite different.

more heat-resistant than polyethylene. As a textile fiber it is as strong as nylon and 30 per cent lighter in weight. It can also be produced in the form of a thin transparent film, as clear as cellophane and stronger if its polymer units are oriented by stretching. Extruded into pipes or molded into complex shapes, it can

compete with metals in many applications.

If ethylene is doubly substituted so that one hydrogen atom on each carbon is replaced with a different group of atoms, yielding a molecule with the type formula $\text{CHR}:\text{CHR}'$, stereospecific polymerization gives rise, as shown in the il-

lustration on the opposite page, to three ordered configurations: threo-di-isotactic (R and R' on the same side of the chain), erythro-di-isotactic (R and R' on opposite sides) and di-syndiotactic (R and R' alternating regularly from one side to the other). Polymers of each of these configurations, made in our laboratory,



ORDERED AND DISORDERED POLYMERS can be produced when so-called vinylic ($\text{CH}_2:\text{CHR}$) monomeric units link up in head-to-tail succession. "R" (colored ball) may represent any group of atoms; thus if R is CH_3 , the vinyl monomer is propylene and the polymer is polypropylene. The main chain of carbon atoms has

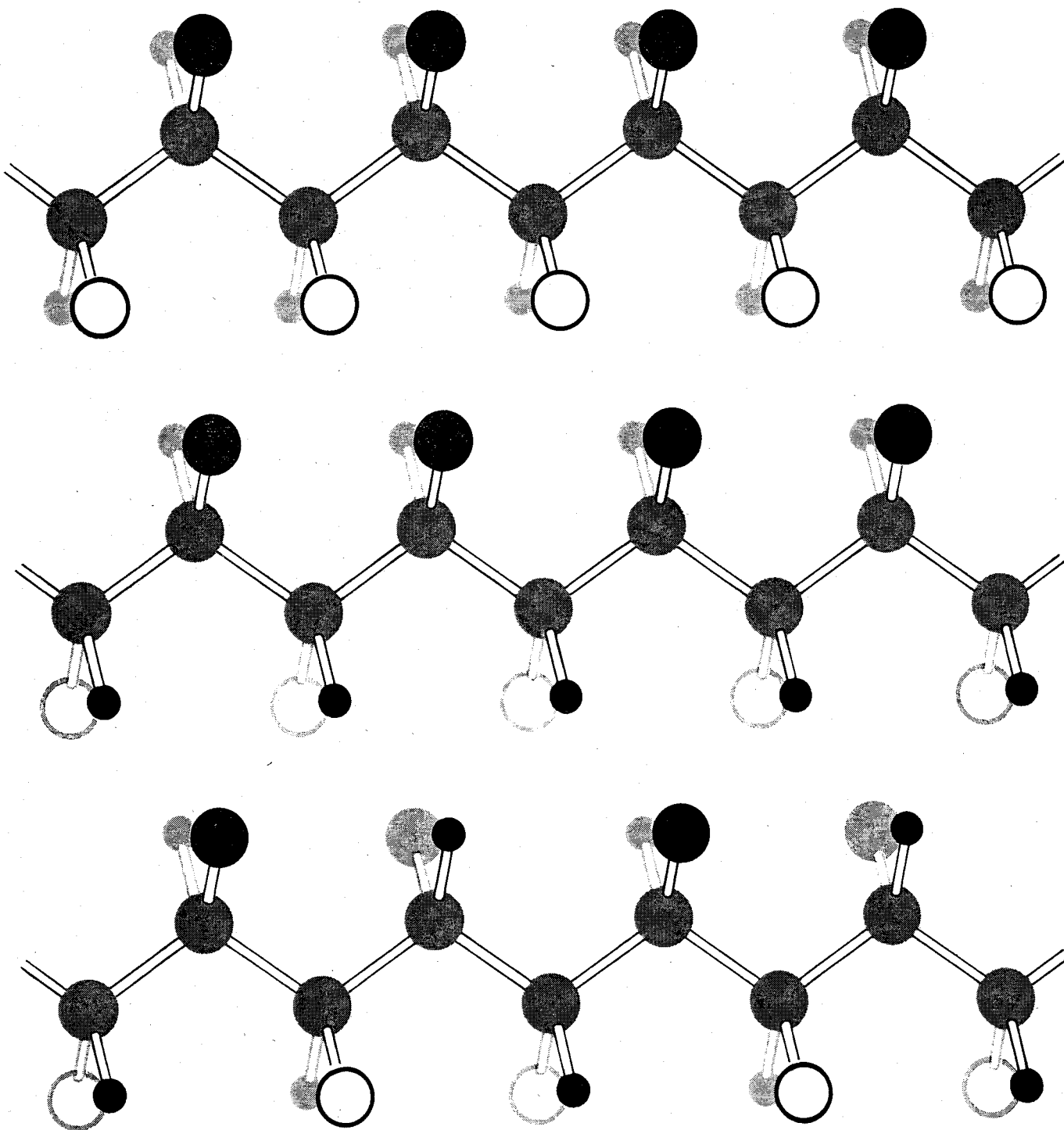
been drawn as if flattened in a plane. (*Three-dimensional views appear on page 9.*) When R groups are all on one side of the chain (*top*), the polymer is called "isotactic." When R groups alternate from side to side (*middle*), the polymer is "syndiotactic." When R groups are disposed at random (*bottom*), the polymer is "atactic."

show a number of interesting properties. Their commercial value remains to be determined.

These various stereoregular polymers represented a small but definite step toward asymmetric synthesis in that each giant molecule is formed by long sequences of monomeric units having the

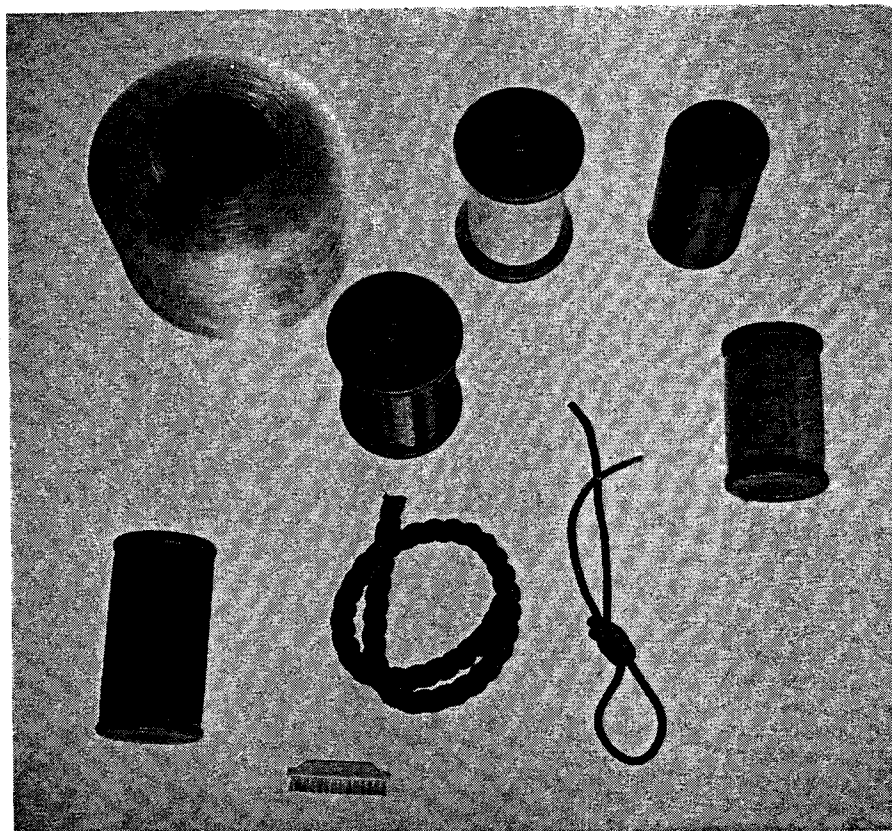
same steric configuration. However, the giant molecules forming a crude vinyl isotactic polymer, such as isotactic polypropylene, do not display optical activity, primarily because inner compensations cancel out whatever slight optical activity might arise. It is true that in such polymers each carbon attached to a

side group is asymmetric, but the asymmetry is very slight because it is due almost solely to difference in length and in configuration of the two portions of chain linked to two of its bonds. As we shall see, appreciable optical activity will occur in a polymer only when the asymmetry arises from strong nonuni-

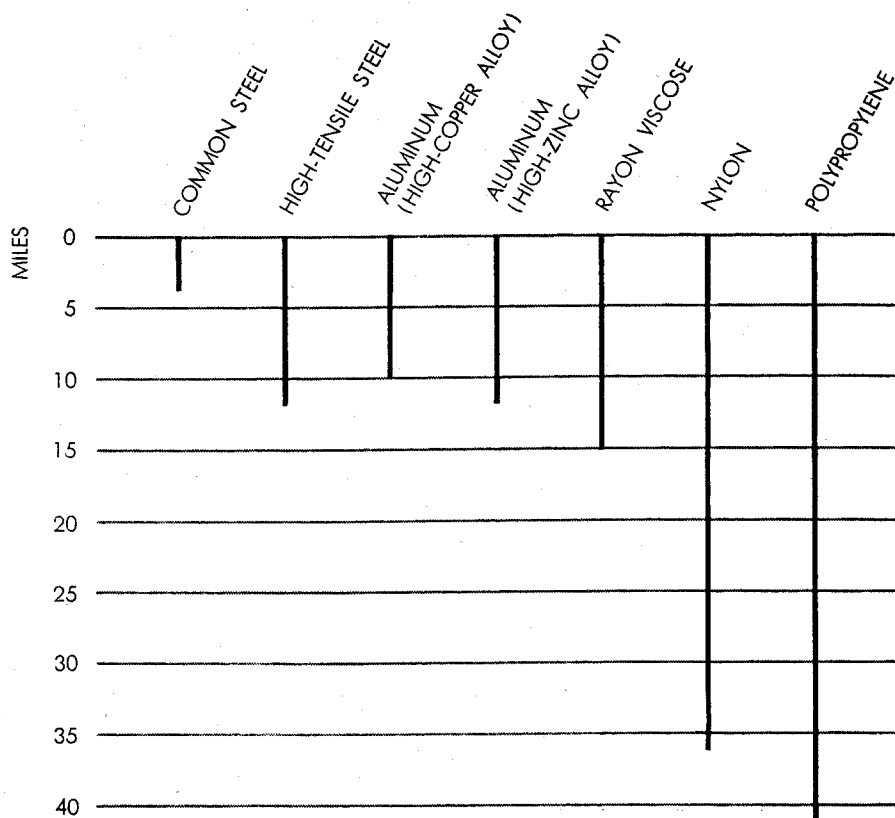


MORE INTRICATE STEREO-ORDERING can arise when the vinyl monomer contains a different R group on each carbon, yielding a molecule of the form $\text{CHR}:\text{CHR}'$. New spatial arrangements are possible because the first carbon carries a hydrogen atom plus an R group, instead of two hydrogens, which are indistinguishable.

When R and R' are on the same side of the plane defined by the carbon chain (*top*), the polymer is threo-di-isotactic. When all the R groups are on one side and all the R' groups on the other side (*middle*), the polymer is erythro-di-isotactic. When R and R' alternate from side to side (*bottom*), the polymer is di-syndiotactic.



POLYPROPYLENE MONOFILAMENTS can be fabricated into a variety of forms. The strength of the polymer derives from its stereoregularity and high crystallinity. "Crystallinity" means that long-chain molecules of the polymer lie side by side in orderly fashion.



SELF-SUPPORTING LENGTHS OF VARIOUS FILAMENTS reflect, in a single value, a material's weight as well as its strength. The value is independent of diameter. Aluminum, although weaker than steel, can support as many miles of its own length. Polypropylene is almost as strong as nylon and 30 per cent lighter, hence its superiority by this measure.

formities of atomic configuration in the immediate vicinity of each of many carbon atoms.

So far we have not mentioned a common and important type of isomerism that is due simply to variations in three-dimensional structure and which is therefore called geometric isomerism. Geometric isomers arise in organic compounds that contain a double bond between two carbon atoms. When connected by a double bond, two carbon atoms are no longer free to rotate around a common axis, as they are when they are joined by a single bond. As a result it is possible to create isomers of different spatial geometry, depending on whether or not distinctive substituents attached to the two carbons are locked on the same side of the molecule, giving rise to the "cis" isomer, or on opposite sides, yielding the "trans" isomer.

In nature two well-known polymers, identical in chemical composition, are distinguished by their *cis* and *trans* geometric isomerism. *Cis*-1,4-polyisoprene is natural rubber, whereas *trans*-1,4-polyisoprene is gutta-percha [see top illustration on page 10]. The properties of the two substances are very different. Rubber, when vulcanized, is strong and elastic. Gutta-percha, vulcanized, becomes hard and tough rather than strong. It is often used as a covering for golf balls.

Early efforts to synthesize natural rubber failed because the monomer, isoprene (C_5H_8), would not link up in the required stereoregular form. In 1954, with new principles of stereospecific polymerization, a true synthetic rubber was synthesized in the U.S. and a true gutta-percha was created in our Milan laboratories. The polyisoprene synthetic rubber is now being produced commercially by at least two U.S. firms.

Our laboratory was the first to show that an excellent synthetic rubber is also produced by *cis*-1,4-polybutadiene. Cheaper than isoprene, butadiene (C_4H_6) has a single hydrogen atom where isoprene has a methyl group. Butadiene was commercially manufactured on a large scale in the U.S. during World War II as the principal ingredient in butadiene synthetic rubbers, which have been made in large volume ever since. The new stereoregular polymers of butadiene show elastic and dynamic properties quite similar to those of natural rubber and are far superior to those of the old butadiene synthetics, which have a nonuniform chemical composition and a disordered three-dimensional structure.

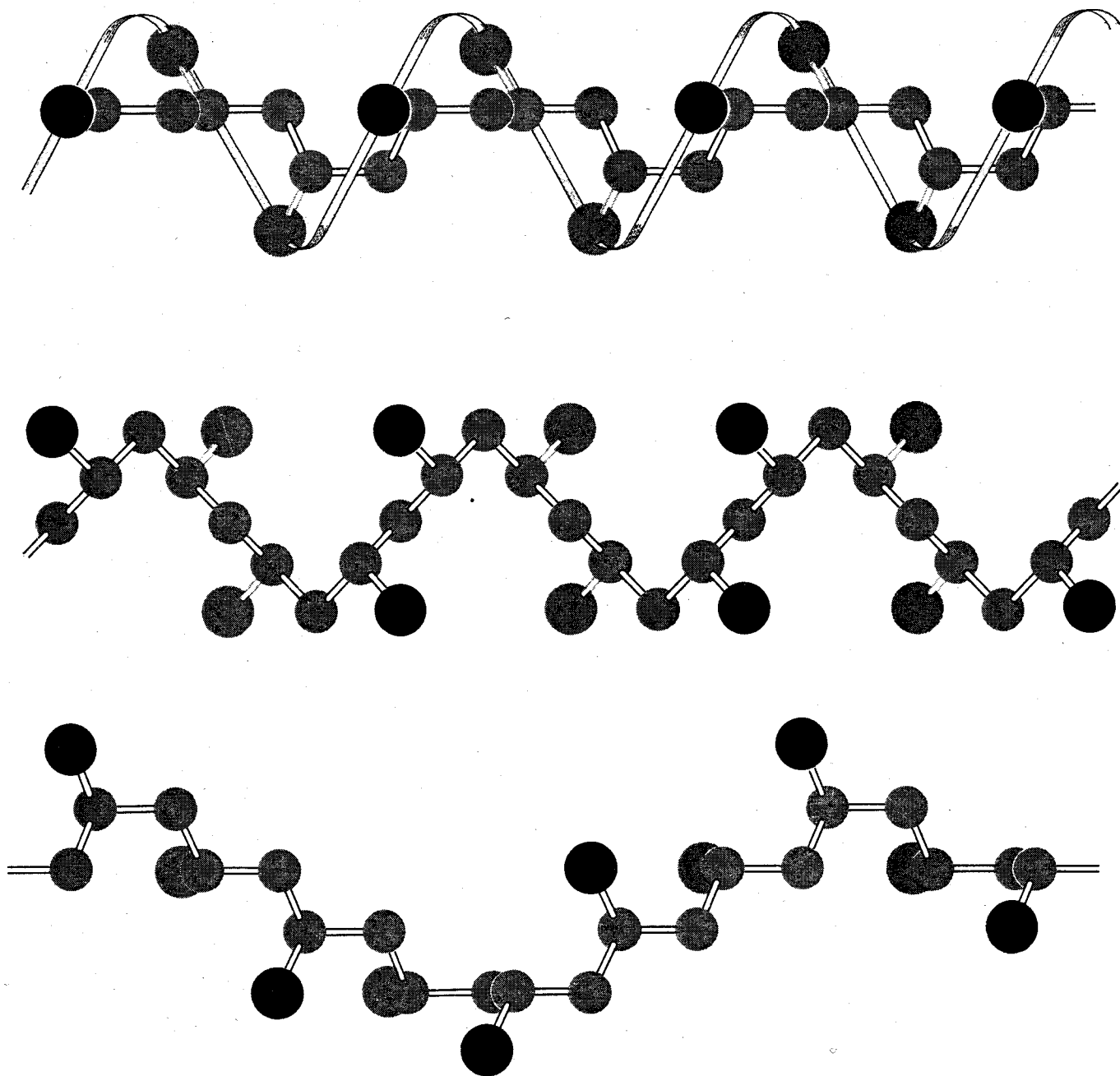
We have been able to produce synthetic rubbers containing more than 98 per cent of *cis*-1,4-polybutadiene, which even exceeds the steric purity of 97 to 98 per cent of *cis* units found in natural rubber. Automobile tires made from these high-purity polybutadienes compare very favorably with tires of natural rubber in durability, riding qualities and low heat build-up when operating at high speeds.

Out of this work with butadiene and

related diolefins (molecules with two sets of double bonds) have come polymers demonstrating optical as well as geometric isomerism. Our approach to achieving optical isomerism has been to create polymers from derivatives of diolefins, such as butadiene, in which at least one hydrogen atom in each molecule has been replaced with more complex atomic substituents. When monomers of this sort are polymerized in a stereospecific way, the repetition of

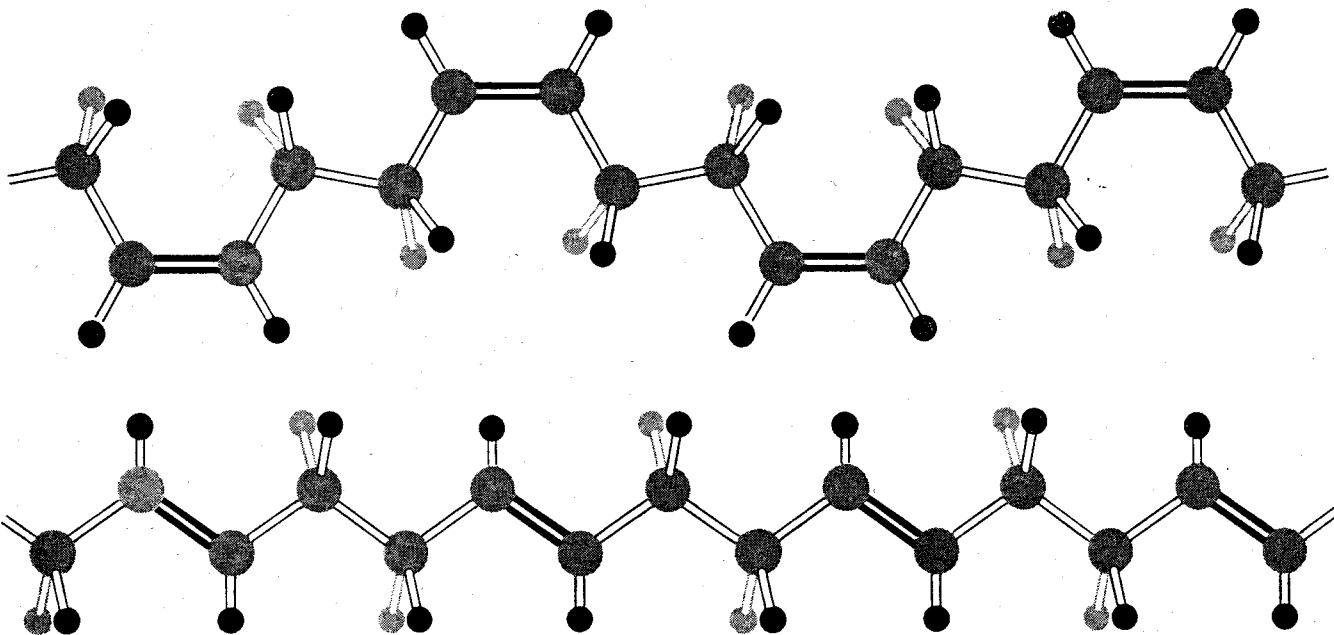
complex configurations produces strong local asymmetries in a large fraction of the carbon atoms. Each single giant molecule, if it could be extracted from the polymer and examined alone, should show optical activity. As normally produced, however, the polymer mix will contain equal numbers of isomeric molecules of opposite optical activity.

Our goal, therefore, was to find conditions that would favor the polymeriza-



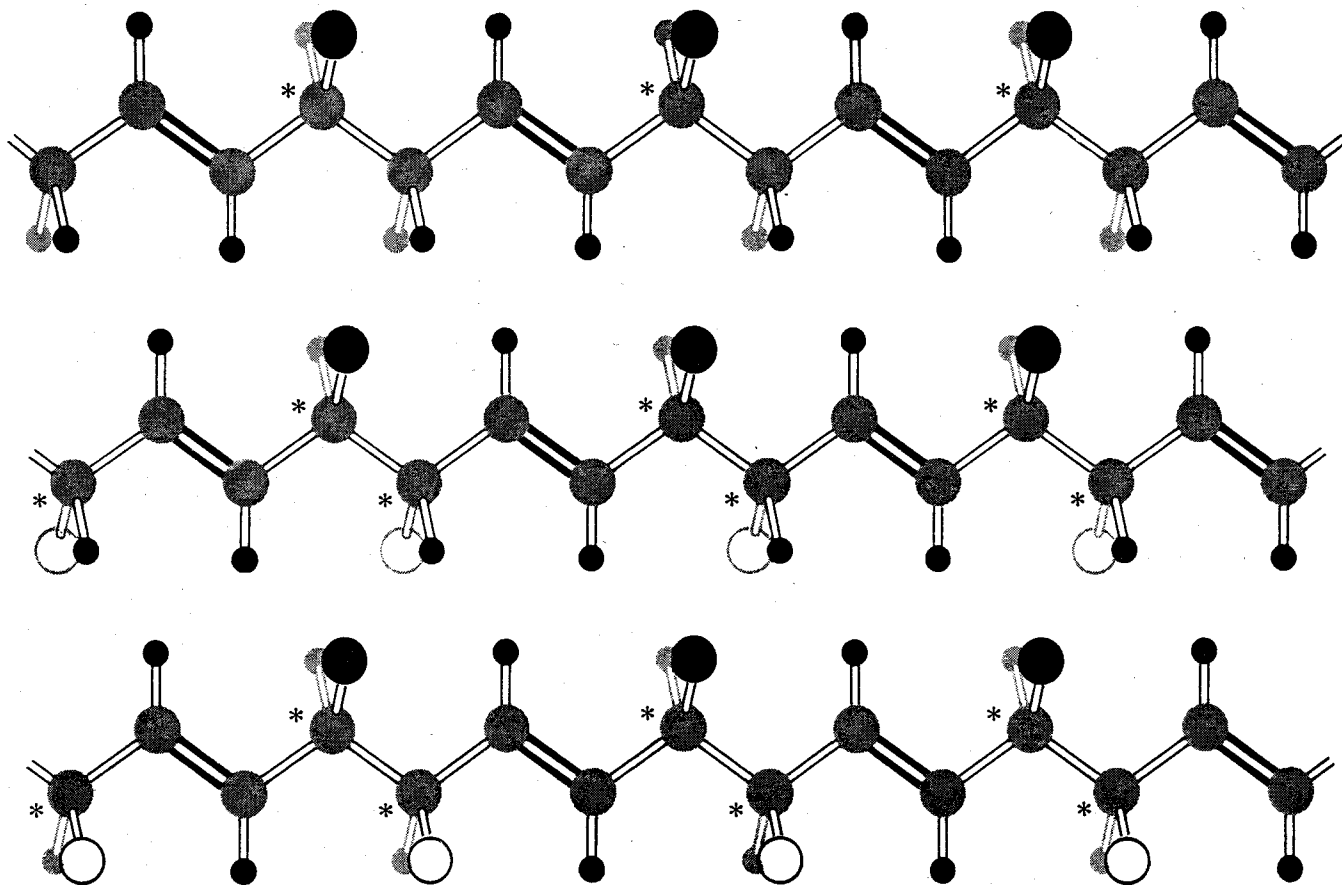
THREE-DIMENSIONAL VIEWS OF POLYPROPYLENE correspond to the simplified views on page 6, except here hydrogen atoms are omitted. Colored balls represent methyl groups (CH_3). In

isotactic polypropylene (*top*) the CH_3 groups define a helix (*gray ribbon*). In syndiotactic polypropylene (*middle*) structure is also regular. Atactic polypropylene (*bottom*) is nonregular in form.



RUBBER AND GUTTA-PERCHA (*top and bottom*) are geometric isomers built up from units of the same monomer, isoprene (C_5H_8). Rubber is *cis*-1,4-polyisoprene. The "*cis*" means that a methyl group (*color*) and a neighboring hydrogen (*black*) are on the same side of each pair of carbon atoms joined by a double bond. The "1,4" means that the four-carbon chain of the monomer is

linked into the polymer through its first and fourth carbons. Gutta-percha is *trans*-1,4-polyisoprene, indicating that methyl groups and adjacent hydrogens lie across from each other. If the methyl groups in rubber are replaced by hydrogen atoms, the resulting polymer is *cis*-1,4-polybutadiene, a new and commercially promising synthetic with properties very similar to those of *cis*-1,4-polyisoprene.



OPTICALLY ACTIVE POLYMERS can be created from butadiene monomers containing substituents (*color*) for hydrogen either on the first carbon atom or on the first and fourth in the four-carbon chain of the monomer. The polymer of singly substituted butadiene

(*top*) is of the *trans*-1,4-isotactic type. Polymers of doubly substituted butadiene can show erythro-di-isotactic succession (*middle*) or three-di-isotactic succession (*bottom*). The asymmetric carbons are starred; each polymer can exist in the form of its mirror image.

tion of only one of the two optically active forms. The first successful asymmetric synthesis of this kind was achieved last year at the Politecnico di Milano with esters of sorbic acid.

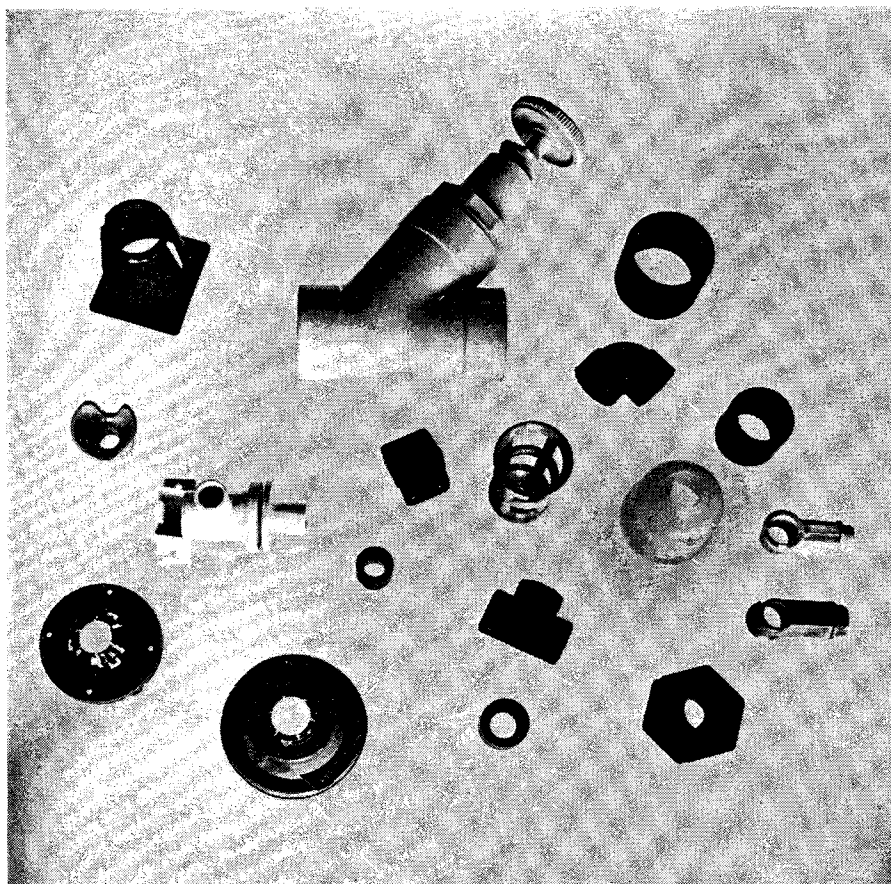
Sorbic acid itself can be regarded as a butadiene molecule that has been lengthened by a methyl (CH_3) group at one end and by a carboxyl (COOH) group at the other. Stereospecific polymerization of certain sorbic acid esters yields crystalline polymers having a "polytactic" structure: each monomer has three different sites of stereoisomerism—one of geometric type and two of optical type—which repeat regularly throughout the polymer.

In polymerizations carried out with a catalyst (butyllithium) that does not have in itself centers of optical asymmetry, there is nothing to establish at the outset a preference for one steric configuration over another. The result is a polymeric substance in which half the molecules have one configuration and half have another. Both molecules, however, are of the erythro-di-isotactic type [see bottom illustration on opposite page].

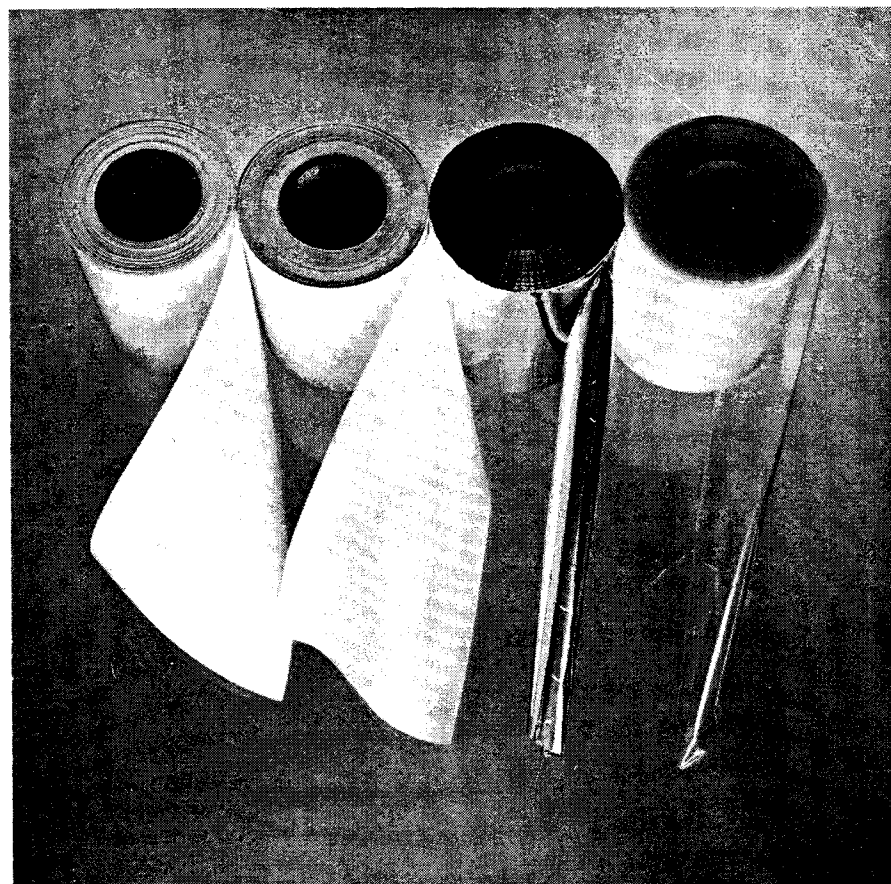
When a catalyst (isoamyllithium) that has a center of optical asymmetry was selected, the resulting molecules were preponderantly of one optical configuration. This was the first asymmetric synthesis of a giant molecule starting from a monomer that was not itself optically active. It is true, however, that the optically active macromolecules contain an optically active end group derived from the catalyst, which is partially consumed during the polymerization.

Subsequently we achieved asymmetric synthesis without consumption of pre-existing optically active reagents. The catalyst for this polymerization was a so-called organometallic compound that was bound to an optically active organic base. Although the base does not take part in the chemical reaction, it provides the steric guidance for the synthesis. (The catalyst is of ionic nature, meaning that the giant molecule grows outward from the catalyst like a growing hair. Oriented monomeric units are fed in at the base of the "hair" with the formation of an ionic bond that joins the end of the hair to the catalyst.)

This is not yet an "absolute" asymmetric synthesis inasmuch as some optical activity is required in the catalyst. The synthesis may suggest, nevertheless, a simplified model of the way nature carries out at least some stereospecific syntheses of optical isomers.



ARTICLES OF MOLDED POLYPROPYLENE yield tough parts and fittings coming into industrial use. In addition to strength the polymer has good heat and chemical resistance.



POLYPROPYLENE FILM resembles polyethylene but is stronger. The articles shown on this page and on page 3 are fabricated from polypropylene made by Montecatini of Italy.

The Author

GIULIO NATTA is director of the Institute of Industrial Chemistry at the Politecnico di Milano. Born at Imperia on the Italian Riviera in 1903, Natta studied chemical engineering at the Politecnico di Milano, where he received a degree in 1924. From 1926 to 1933 he taught at the University of Pavia, and from 1933 to 1939 he was professor of physical chemistry at the University of Rome. He joined the Institute of Industrial

Chemistry in 1939. A fellow of Italy's famous Society of Lynxes (to which Galileo belonged), Natta was the first chemist to synthesize wood alcohol. His development of a method for converting alcohol to butadiene became the basis of the Italian synthetic-rubber industry. Natta was the author of "How Giant Molecules Are Made," which appeared in the September 1957 issue of SCIENTIFIC AMERICAN.