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INTERNATIONAL SYNTHETIC RUBBER SYMPOSIUM

Church House, Westminster, London.

26th, 27th and 28th March, 1957

LECTURE NO. 4

# NEW SYNTHETIC ELASTOMERS



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*Reprinted from*  
*The Rubber and Plastics Age*  
*Vol. 38, No. 6, June 1957*

# New Synthetic Elastomers

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**O**UR researches on anionic polymerisation processes in the presence of metallorganic compounds and on stereospecific syntheses, particularly of isotactic polymers, have already been the object of several previous publications<sup>(1)</sup>. Recently, they were partially resumed in a lecture held in London under the auspices of The Society of Chemical Industry<sup>(2)</sup>.

In that lecture I dealt principally with the results obtained in the field of highly crystalline poly- $\alpha$ -olefines, such as isotactic polypropylene, polybutene and polystyrene, which are of interest mainly in the field of plastic materials and textile fibres. In the present lecture I shall limit myself to recalling the principal results obtained by the Milan school in the specific field of the new elastomers in these last 3 to 4 years, a period which probably will be considered revolutionary in the history of synthetic rubber.

Our researches in the field of elastomers have been carried out on two main lines:

- (1) The production of particular stereoisomers of polydiolefines having definite steric configurations;
- (2) The production of elastomers from linear olefine polymers and copolymers having very high molecular weight and improved resilience.

## New Stereoisomers of Polydiolefines

Whilst the research in my laboratory in the field of stereospecific polymerisation was chiefly concerned with the new

olefine polymers, we had already started as far back as 1953 the study of diolefine polymerisation and this in close relation to the polymerisation of ethylene with organic aluminium compounds. At the beginning of 1954, in parallel with the synthesis of isotactic and atactic poly- $\alpha$ -olefines by the use of a catalyst containing transition metals, we succeeded in polymerising diolefines into polymers having prevalingly 1-4 structure<sup>(3)</sup>.

As isoprene was not available in Europe and we had to prepare and purify it ourselves, we concentrated our researches chiefly on butadiene.

A thorough investigation of the possible mechanisms of the new polymerisa-

tion processes led to the discovery of different catalytic systems, which enabled us to obtain selectively not only diolefine polymers with substantially 1-4 enchainment or with substantially 1-2 enchainment, but also to reach a high degree of stereospecificity in the polymerisation reactions.

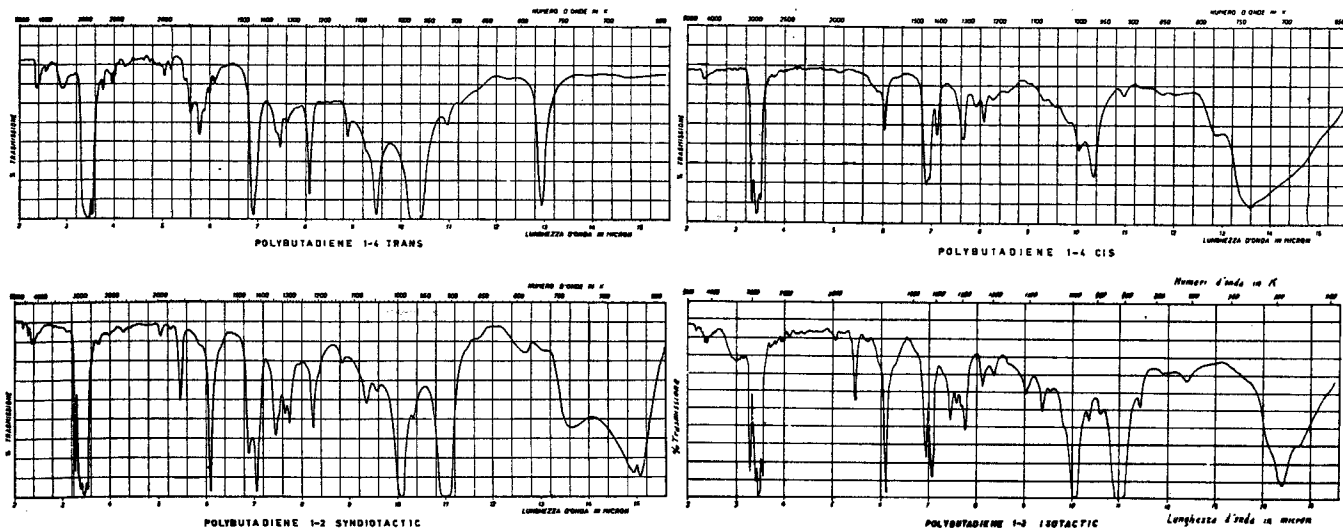
In fact, we succeeded in synthesising many different stereoisomers of linear polybutadiene with a different crystalline structure, and four of them presenting a high crystallinity (Table 1). The most interesting are:

- (1) 1-4-trans crystalline stereoisomers with more than 98 per cent purity, M.P. greater than 145°C.

Table I.—Roentgenographic data on crystalline polybutadiene—stereoisomers.

Polymer	Space group	Number of monomer per unit cell	Cell dimensions Å		Chain axis c	$\alpha$	$\beta$	$\gamma$	X-Ray density	X-Ray melting point
			a	b						
1-4 trans	(pseudohexagonal)	(1)	(4.54 Å)		4.9 Å					
1-4 cis	C2/c (monoclinic)	4	4.60	9.50	8.60	90°	109°	90°	1.02 1.01	148°C. (* )
1-2 syndiotactic	Pacm (rhombic)	4	10.98	6.60	5.14	90°	90°	90°	0.96	155°C.
1-2 isotactic	R3c (hexagonal)	18	17.3	17.3	6.50	90°	90°	120°	0.96	125°C.

(\* ) The melting temperature of pure 1-4 cis is not known. The impure polymers have melting temperatures dependent on composition and stress.



Figs. 1-4: Infra-Red Spectra of average samples of the four different Crystallisable Polybutadienes.

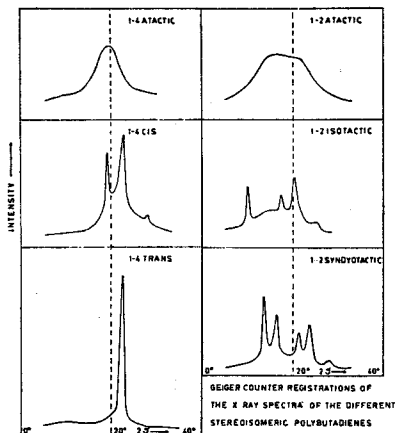


Fig. 5: Geiger Registrations of X-Ray Spectra of Different Stereo-Isomers of Polybutadiene.

- (2) 1-4-cis stereoisomers sufficiently pure to be slightly crystalline, their crystallinity strongly increasing on stretching at room temperature.
- (3) 1-4-cis-trans-amorphous or slightly crystalline copolymers.
- (4) 1-2 syndiotactic crystalline stereoisomers, M.P. greater than 155°C.
- (5) 1-2 isotactic crystalline stereoisomers, M.P. greater than 125°C.
- (6) 1-2 atactic amorphous polymers.

The infra-red spectra of average samples of the four different crystallisable polybutadienes are given in Figs. 1-4.

In Fig. 5 the Geiger registrations of the X-ray spectra of the different stereoisomers are shown. The structure of the said polymers in the crystalline state are indicated in the following figures.

A model of the structure found by us for crystalline 1-4 cis polybutadiene<sup>(6)</sup> is shown in Fig. 6.

The value found by us for the identity period (8.60 Å) is less than that one (8.75 Å) indicated by Aries in a lecture held at Atlantic City<sup>(7)</sup>. The identity period indicated by him apparently corresponds to the approximate value foreseeable for a complete planar chain.

The hypothesis that the main chain should be planar, and thence should differ in the length from the one found for poly-1-4-cis isoprene, could appear to be justified by the absence of lateral

methyl groups. Due to unsuitable methyl contacts it is most likely that the said methyl groups present steric hindrance to the planarity of the chain, this being probably only one of the reasons which cause the polyisoprene chain to deviate from planarity.

Actually, as already supposed by Bunn, there is a tendency for the C-C single bonds to stagger and therefore a staggered saturated portion of the chain cannot lie in the same plane with an adjacent double bond. Actually in the chain of crystalline 1-4-cis polybutadiene the succeeding monomeric units are contained in planes which are parallel but not coincident. The staggering is not, however, complete owing to the repulsion between two approaching hydrogens of the methylenic groups. Thence, the identity period actually found (8.6 Å) is greater than the one which could be expected from a perfect staggering of single bonds.

The structure of 1-4-cis polybutadiene and of 1-4-cis polyisoprene are compared in Fig. 7.

The crystalline polyisoprene structure proposed by us was in fact very similar to that suggested by Nyburg<sup>(8)</sup>, the only difference stressed by us being the statistical distribution of the successive layers of differently orientated chains.

In the case of the other stereoisomeric crystalline polybutadienes no steric factor hinders the staggering of single bonds, and in fact, the staggering is found to be perfect (Fig. 8). In Fig 9 models of the structures found by us for isotactic and syndiotactic polybutadienes, are shown. Isotactic polybutadiene shows a helicoidal chain configuration<sup>(9)</sup>, with threefold symmetry similar to that of poly-alpha-butene<sup>(10)</sup>. The relating projection normal to the chain axis is shown in Fig. 10. The electron density maxima show a statistical distribution of up

Table II.—Rebound (\*) of some cured polybutadienes (substantially amorphous after curing)

	Rebound at	
	20°C. %	90°C. %
1-4 trans ...	75-80	90-93
1-4 prevailing cis ...	88-90	92-95
1-2 ...	45-55	90-92

(\*) ASTM D 1054-49T

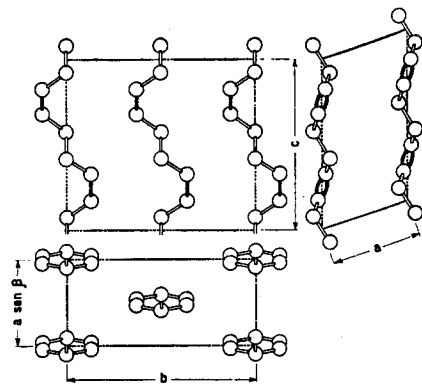


Fig. 6: Model of Structure for Crystalline 1-4-cis Polybutadiene.

and down molecules in the same lattice site (Fig. 11).

Syndiotactic polybutadiene has a chain along which enantiomorphous units alternate<sup>(11)</sup>, Fig. 12.

The pure high-melting-point crystalline stereoisomers are not elastomers at room temperature, unless their crystallinity is considerably reduced.

1-4 (cis or trans) products have, in the amorphous state, excellent resilience.

1-2 amorphous polymers have lower resilience than 1-4 amorphous polymers because of lesser flexibility of the saturated main chain, which does not contain the more freely rotating single bonds adjacent to double bonds (Table 2).

It is interesting to note that the resilience of 1-2 atactic polybutadiene, which increases rapidly as the temperature goes up, is much higher than that of atactic poly-alpha-butene also at room temperature; 1-2 polymers, because of their vinyl side groups, are very reactive and this can favour their use even outside the field of elastomers.

Among 1-4 enchainned butadiene polymers, those which possess a trans structure (% of trans double bonds > 98% of total) are highly crystalline<sup>(12)</sup> and have a very high melting point (140-148°). They can be used for the production of hard rubber characterised by a high modulus only if the crystallinity is reduced. If suitably cured, they have good resilience values, even at room temperature.

CONFORMATION OF CARBON-CARBON BONDS ADJACENT TO DOUBLE BONDS IN CRYSTALLINE POLYBUTADIENE ISOMERS.

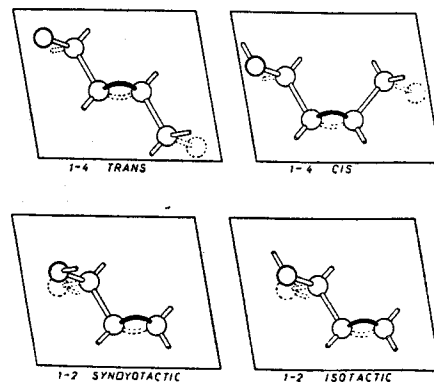


Fig. 8: Staggering of Single Bonds in Stereoisomeric Crystalline Polybutadienes.

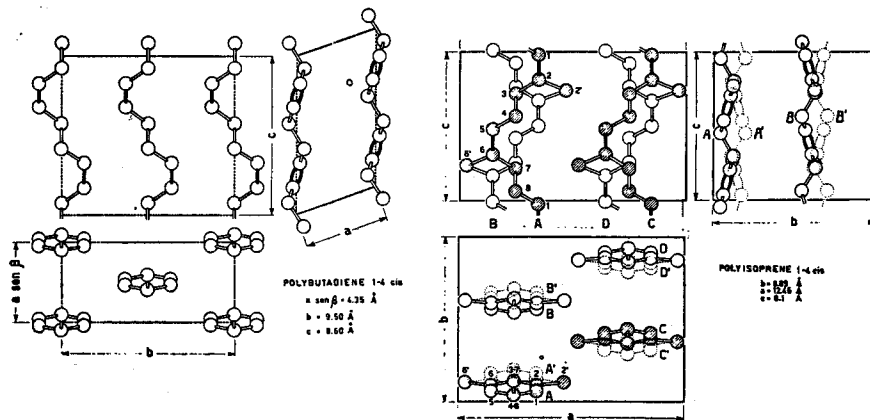


Fig. 7: Comparison of Structure of 1-4-cis Polybutadiene and 1-4-cis Polyisoprene.

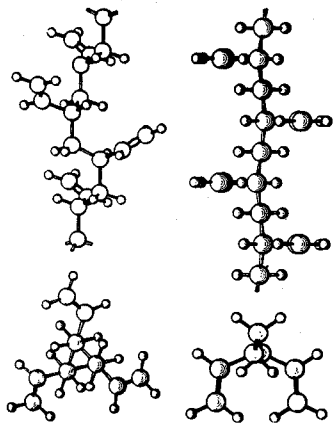
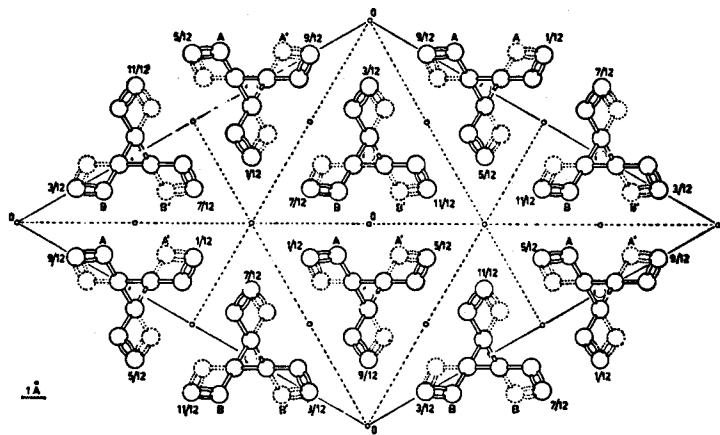


Fig. 9. Model of Structures for Isotactic and Syndiotactic Polybutadienes.



POLYBUTADIENE 1-2 ISOTACTIC

Fig. 10. Projection Normal to Chain Axis of Isotactic 1-2 Polybutadienes.

The presence of small quantities of 1-4-cis monomeric units in the chiefly 1-4 trans enchainment polymer lowers its crystallinity considerably and also its melting point, and 1-4 polymers, rich in the trans form, which melt at lower temperatures (even below 100°) are easily obtainable.

The resilience of 1-4-cis polybutadiene is very near to that of 1-4-cis polyisoprene. The mechanical and particularly the elastic properties of 1-4-cis polybutadiene depend obviously on its steric purity, and in fact impure not crystallis-

able polymers have an elongation-stress diagram which differs considerably from typical diagrams of rubbers bound to crystallise under stretching.

The preparation, with high yield, of the pure linear 1-4 cis stereoisomer, free of cross-links, and with a molecular-weight exceeding 200,000, present more difficulties than the preparation of the other stereoisomers, although recently great progress has been made.

Fig. 13 shows a comparison between two X-ray spectra of relaxed and stretched samples of polybutadiene, cured with standard recipe containing ZnO as activator. They show the crystallisation under stretching of the 1-4-cis isomer. Fig. 14 reproduces the spectra of a 1-4-cis polybutadiene cured in the absence of ZnO activator.

The properties of the polymers with 1-4 enchainment containing both the cis and trans forms, depend on the way the monomeric units, having different steric configurations, are distributed along the chains. The properties of a polymer constituted by macromolecules having a random distribution around a certain average value of cis and trans double bonds differ considerably from those of polymers having the same average stereoisomeric composition, but constituted by mixtures of macromolecules widely different from each other in the steric composition.

The possibility therefore clearly emerges of obtaining a large number of

different products with different properties, and I believe that further extensive research will be necessary for a thorough study of the properties of the new stereoisomeric polydiolefines.

The stereoisomeric purity is not the only factor which determines the properties of a polymer. The way the impurities are distributed is of enormous

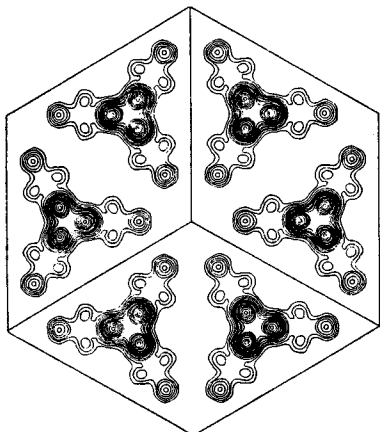
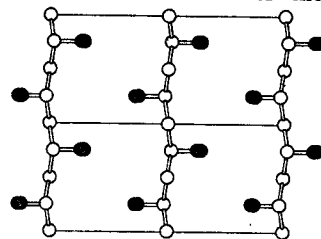


Fig. 11: Statistical Distribution of Up and Down Molecules in Same Lattice Site (Isotactic Poly-alpha-butene).



POLYBUTADIENE 1-2 SYNDIOTACTIC

Fig. 12: Alternating Enantiomorphic Units along Syndiotactic Polybutadiene Chain.



Fig. 13: X-Ray Spectra of Relaxed and Stretched Polybutadiene Cured with Standard Recipe Containing Zinc Oxide.

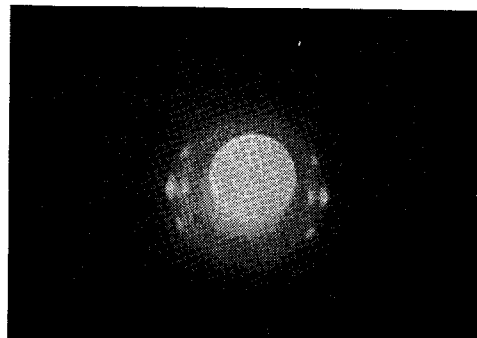


Fig. 14: Spectra of 1,4-cis-Polybutadiene Cured in Absence of Zinc Oxide.

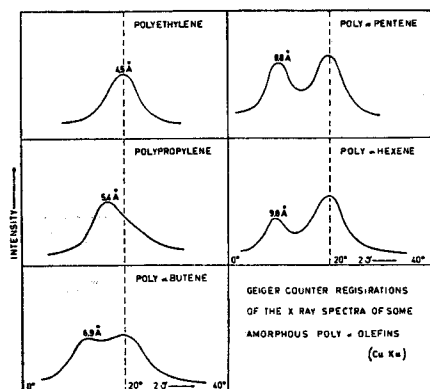


Fig. 15: X-Ray Spectra of some Amorphous Linear Poly-Alpha-Olefines.

importance. A limited percentage of sterically different and random distributed units should be in theory sufficient to destroy the X-ray crystallinity of a 1-4 stereoisomer of a diolefin, whilst products of every composition are crystalline when the sterically different units are distributed in blocks.

One cannot therefore relate properties with stereoisomeric composition unless, besides this, the way in which the stereoisomeric units are distributed is known. This is the principal reason for our so cautiously describing the properties of the new products and in particular the mechanical properties which especially depend on the way in which the stereoisomeric units are distributed in the individual chains.

#### Alpha-Olefin Polymers

One may estimate the costs of the different olefines (propylene, ethylene, butylene) to range between 1/3-1/5 of that of butadiene, whilst the cost of the pure commercial isoprene is expected to be higher than that of butadiene. We are therefore of the opinion that due to the low cost of the raw materials the new olefinic rubbers are worthy of considerable attention.

Already during our researches on alpha-olefine polymerisation with the new anionic processes at the beginning of 1954, we found that stereospecificity and activity of the catalyst are two independent properties and that it is possible by using certain types of catalysts, to obtain crystalline polymers (isotactic), whilst with other types, amorphous polymers (atactic) are obtained<sup>(13)</sup>.

We had also found that said atactic polymers greatly differ from alpha-olefine polymers obtained by conventional processes (which act by means of cationic or radical mechanism). Further researches enable us to obtain very high molecular - weight polymers (over 100.000) with linear structure, practically without branchings, and with a random distribution of d and l monomer units<sup>(14)</sup>.

Most of the chains are of the following type :

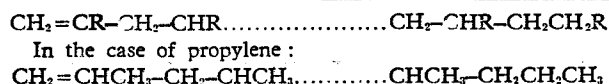


Table III.—Rebound (\*) of some copolymers, having a high olefine content.

	Rebound at	
	20°C. %	90°C. %
Ethylene-propylene (35-65% C <sub>3</sub> H <sub>6</sub> ) ...	55-65	65-80
Ethylene-propylene-isoprene (< 10% C <sub>5</sub> H <sub>8</sub> ) ...	50-65	65-80
Propylene-isoprene (< 10% C <sub>5</sub> H <sub>8</sub> ) ...	18-20	55-65
Butyirubber ...	16-20	55-60

(\*) ASTM D 1054-49 T

This implies that they contain vinylidene terminal groups and n-propyl, n-butyl, etc., terminal groups according to the monomer taken into consideration. The presence of long branches cannot be made apparent by conventional methods.

Poly-alpha-olefines known beforehand, obtained by cationic polymerisation, have completely different structures, with vinyl and isopropyl terminal groups, branchings and irregularities of different types.

The atactic polymers with linear structure produced by us have properties of unvulcanised elastomers when the molecular-weight is sufficiently high. In the Fig. 15 the X-ray spectra of some amorphous linear poly-alpha-olefines are shown and they can be related with the linearity of the main chain. Indeed, the amorphous maximum is shifted to low angles as a function of the bulkiness of the side groups, and therefore of the distance between the main chains.

Before our findings only two types of aliphatic olefines having highly linear structure and high molecular-weight were known: polymethylene and polyisobutylene.

The first is not an elastomer, at least at room temperature, it being a high-melting crystalline polymer. The second can give elastomers but has the drawback of low resilience at room temperature.

The new amorphous poly-alpha-olefines have the advantage of behaving like elastomers whose chains at temperatures far from the transition temperature have more flexibility than those of polyisobutylene, the reason is that the steric hindrances to the rotation around the C-C single bonds in the main chain, owing to the presence of only one side group bound to a tertiary carbon atom, are smaller than those observed when two side groups are bound to a quaternary carbon atom in the chain.

The comparison between the elastic properties of rubber obtained from poly-alpha-olefines indicates that resilience at room temperature increases with an increase in the length of the side chains in the alpha-olefine macromolecule. This is in relation also with the variation of the transition temperature, which decreases as the length of the linear side groups increases (from C<sub>1</sub> to C<sub>4</sub>).

Alpha-olefine copolymers show, in general, lower transition temperatures than the homopolymers, and higher resilience as well.

Ethylene-propylene copolymers, and in particular those very rich in ethylene,

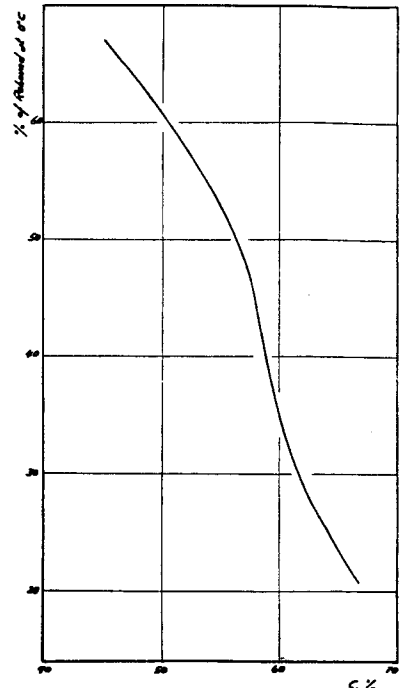


Fig. 16: Elastic Properties of Ethylene-Propylene Copolymers. Best Values at Lower Propylene Percentages.

show very high resilience value although they are saturated macromolecules (Table III).

- The causes are to be found in :
- (1) Increase in chain flexibility because of reduced steric hindrance to rotation around the -CH<sub>2</sub>-CH<sub>2</sub>-bond, compared with the -CH<sub>2</sub>-CHR-bond.
  - (2) Lower second order transition temperature of the copolymer, compared with amorphous polypropylene.
  - (3) Hindered crystallisation of the unstretched polyethylene chain due to the random distribution of propylene units in the chain.

The best values of the elastic properties are obtained with the lower propylene percentages (Fig. 16), which are sufficient to prevent the crystallisation of polyethylene in the unstretched state. Theoretically very small propylene percentages should be sufficient for this purpose as long as they are randomly distributed and not concentrated in some of the macromolecules or in certain parts of each of them. At the beginning we have met some difficulties in obtaining homogeneous copolymers free of homopolymers or of mixtures of copolymers of very different composition and also in obtaining high molecular-weight poly-

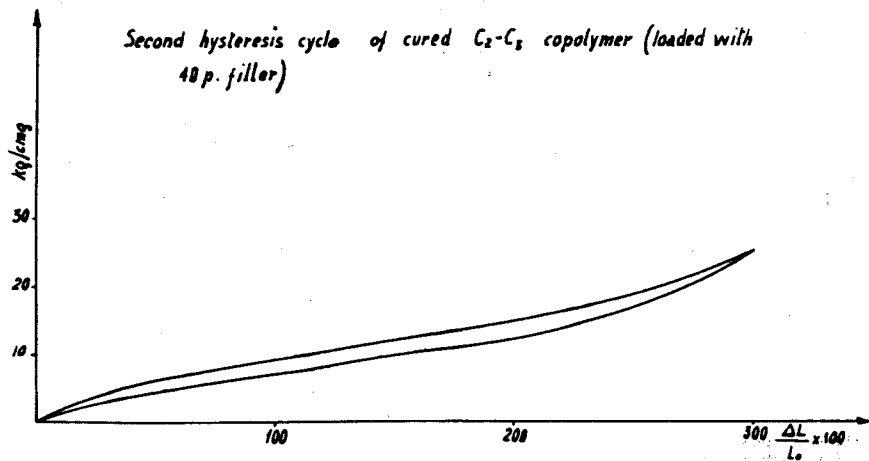


Fig. 17: Second Hysteresis Cycle of Cured  $C_2-C_3$  Copolymer (Loaded with 40 parts Filler).

mers. It is to be emphasised that the properties of the crude polymers are very different, according to the way they have been prepared, and to their being more or less heterogeneous.

These difficulties have been overcome by using suitable catalytic systems<sup>(15)</sup>, by means of which the ratio between the growth rates of the chains of each monomer remains constant with time and is not sensibly modified by the nature of the last monomer unit linked with the growing chain. This last condition must be fulfilled if random distribution is desired and the formation of blocks is to be avoided.

Uncured atactic polyolefines and amorphous olefine copolymers, also with molecular-weight of the order of hundreds of thousands still have considerable creep properties under prolonged stress.

The problem of avoiding creep has been solved by us in different ways.

- (a) By chemical vulcanisation processes which lead to formation of bridges between the chains, and some of which are known to be used for other elastomers;
- (b) By processes which we consider as physical vulcanisation processes in which the forces opposing creep depend on the binding energy in crystalline microelements.

Many chemical methods have been used successfully by us, and we would like to mention only the most practical ones:

- (1) Random copolymerisation with small quantities of diolefines and other monomers with reactive groups with the purpose of obtaining products vulcanisable like butyl rubber;
- (2) Introduction into the macromolecules of acid groups (e.g.  $SO_3H$ ,  $SO_3Cl$ ,  $COOH$ , etc.), or basic groups capable of ensuring the formation of polyvalent acids or bases respectively;
- (3) Other methods based on the great reactivity of the tertiary carbon atom, causing cross-links between the chains.

In Figs. 17 and 18 are shown some characteristics of rubber obtained with ethylene-propylene copolymers. The polymers have stress-elongation curves characterised by very low initial elastic moduli and by very high tensile strength and reversible elongation, without reinforcing fillers, a behaviour very much like that of the polymers which crystallise under stretch. This is probably due to portions of chains having regular structure and being constituted of methylene sequences.

Rebound properties are somewhat inferior to those of natural rubber and 1-4 cis polybutadiene, but are quite good, in fact, better than for GR-S rubber.

We think that ethylene-propylene copolymers will prove to be of great practical interest.

In respect of what we consider physical vulcanisation processes, we have observed elastomeric properties, like vulcanised products, in some ethylene copolymers and also in linear alpha-olefine homopolymers, when these are built up by stereoblocks with very small crystallinity. In the case of poly-alpha-olefines, stereoblock macromolecules are characterised by the fact that they contain ordered chain portions with ordered structures which are of short length, compared with the total length of the macromolecules<sup>(16)</sup>.

A plausible model of a stereoblock macromolecule may be given for instance by a chain built up of portions of variable lengths, each of these portions being constituted of monomeric units with the same steric configuration, alternating with portions in which the monomeric units have opposed configurations.

We observe elastomeric properties when short portions of isotactic chains, still sufficiently long to crystallise, alternate with large portions which are not crystallisable (Fig. 19).

These stereoblock polymers have a melting point which is notably lower than that of pure isotactic polymers. For example, in the case of polypropylene, polymers having 15-25 per cent crystallinity melt completely at 110-120°, but, notwithstanding the fact that they contain microcrystals, they maintain elas-

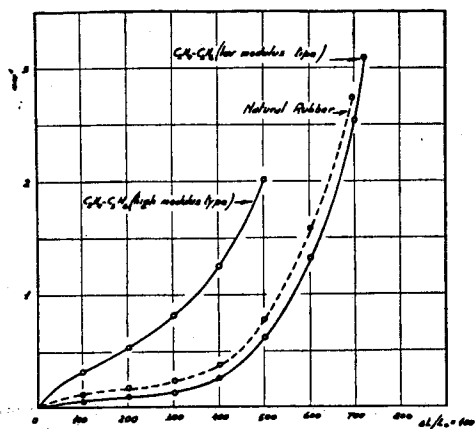


Fig. 18: Stress-Strain Curves for Ethylene-Propylene Copolymers.

tomeric properties even below room temperatures.

Elastomeric properties are evident in products which have been re-stretched (e.g. a yarn or a sheet pre-stretched in one direction up to a temporary elongation of about 700 per cent).

The stress-elongation graphs (Fig. 20) of these stereoblock polymers are characterised by initial elastic moduli which are not very high, by elastic elongations of about 100-200 per cent (increasing with molecular weight and decreasing with crystallinity), and by very high tensile strength. In the case of very high molecular-weight polymers creep is very limited.

An interesting characteristic of the stereoblock polymers is that, contrary to the chemically vulcanised elastomers, they can be melted and re-shaped at temperatures above the melting point, because the material keeps unchanged its thermoplastic properties as well as the property of orientating itself and of crystallising by stretch.

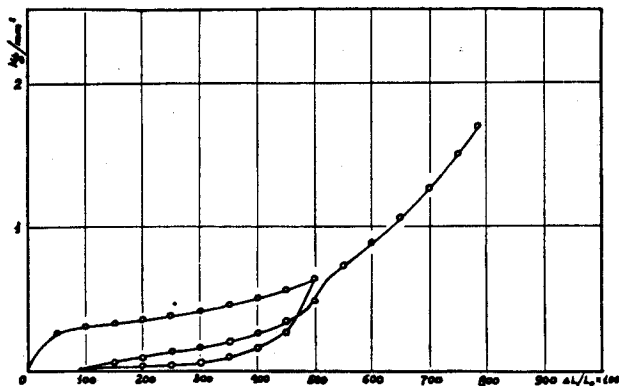
The resistance that the crystallised macromolecule sections oppose to viscous creep may be compared to a thermolabile reversible vulcanisation.

#### Conclusions

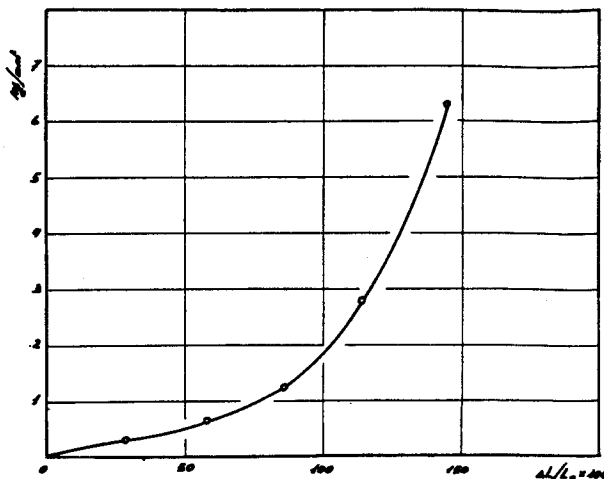
From the points briefly set out above we can conclude that the new polymerisation processes have allowed us to obtain new classes of very high molecular-weight, and substantially linear, macromolecules, and to isolate, in the case of diolefines and alpha-olefines, new crystalline and amorphous stereoisomers.

Not only is the field of plastic materials interested in this evolution of macromolecular chemistry, but we can foresee wide repercussions and important developments also in the field of synthetic rubber.

Although recent literature has pointed out that the American industry is strongly interested in synthetic polyisoprene obtained from costly isoprene, I would venture to say that no less interest should be devoted to rubbers from special butadiene stereoisomers and particularly to rubbers obtained from the very much cheaper alpha-olefine copolymers.



Left—Fig. 19: Elastomeric Properties of Stereoblock Macromolecule when short portions of Isotactic Chains alternate with Non-Crystallisable large portions.



Right—Fig. 20: Stress-Strain Curves of Pre-Stretched Stereoblock Polymers.

Although their low temperature resilience is not so high as that of natural rubber or of 1-4-cis polybutadiene, ethylene-propylene copolymers have sufficiently good resilience values and high mechanical strength. Their chemical and ageing resistance is far superior to those of the known synthetic unsaturated rubbers.

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#### DISCUSSION

**Dr. W. Cooper — Dunlop Research Centre :**

Q.—I wonder whether Professor Natta could comment on the conditions where the 1, 2 structure groups in polybutadiene do not act as olefines to cause the polymerisation to form branched molecules.

A.—We use a catalyst which cannot polymerise alpha olefines. Of course, if you employ a catalyst which can also polymerise alpha olefines you can obtain a branched polymer, but if you employ a catalyst which cannot polymerise alpha olefines it is possible to obtain linear 1, 2 polymers.

**Dr. G. Kraus—Phillips Petroleum :**

Q.—Do you disclose in which way the

low modulus and high modulus ethylene/propylene copolymers differ? What gives you high modulus in the one instance and low modulus rubber in the other?

A.—We use different curing conditions.

**Dr. G. Kraus :**

Q.—Is this in each case chemical vulcanisation?

A.—Yes.

**L. R. Mernagh — Firestone (Great Britain) :**

Q.—What is the maximum 1:4 cis content of any polybutadiene polymer produced to date?

A.—It is difficult to say because we had no 100 per cent 1:4 cis polybutadiene available to determine exactly the I.R. absorption coefficients. One can estimate between 80 to 90 per cent, but the analytical methods must be controlled.

One sample of polybutadiene rich in 1:4 cis units is shown in Fig. 2.

**Dr. W. Cooper :**

Q.—In the case of polybutadiene polymerisation, do you find it possible to go to very high conversions? Can you continue to polymerise until all the butadiene has been polymerised without any sacrifice in physical properties of the polymer.

A.—That depends on a number of factors, like concentration, etc. It is very variable: it depends on catalyst and operating conditions. In dilute solutions it is possible to obtain very high conversion, but generally it seems preferable to stop the polymerisation at about 50 per cent conversion.