CHAPTER 7

ELASTOMERS BY COORDINATED ANIONIC MECHANISM

C. Elastomers from Cyclic Olefins

GIULIO NATTA

Istituto di Chimica Industriale del Politecnico, Milano, Italy

AND

GINO DALL'ASTA

Società Montecatini, Edison, Milano, Italy

Contents

This chapter deals with the synthesis and the properties of a new class of linear unsaturated hydrocarbon elastomers called polyalkenamers.[*] Before going into the details, we should like to review some of the more important features which render a polymer elastomeric.

1. Essentially linear structure.

2. High molecular weight which enables the macromolecules to resist extensive permanent viscous flow when oriented in parallel by stretching, thus conferring reversibility to the deformation process.

3. A flexible structure, i.e., one in which the rotation around the bonds in the polymer backbone is opposed only by low potential barriers.

[*] According to the IUPAC nomenclature (1).

4. Possibility to hinder irreversible viscous flow by chemical vulcanization or by physical phenomena having analogous effects, e.g., crystallization of macromolecules oriented under high load. The vulcanization may be facilitated by the presence of reactive chemical groups along the chains.

Considering the modest limitations thus imposed on elastomers from a chemical standpoint, it is not surprising that elastomers of greatly different chemical nature are known. However, they still appear few if the wide possibilities of modern macromolecular chemistry are considered. Especially in the field of polymers having chemical and steric regularity, a deeper study will permit us to single out many new elastomeric products. Low cost and low density have so far assured hydrocarbon polymers a preeminent position among synthetic elastomers. The polyalkenamers described here belong also to this class.

I. RELATIONSHIPS BETWEEN STRUCTURE AND ELASTOMERIC PROPERTIES IN STEREOREGULAR POLYALKENAMERS

The polymethylene chain is one of the more flexible ones. This property results above all from the absence of bulky side groups that might hinder free rotation around the bonds linking the methylene groups. In fact, linear polyethylene, when employed above its melting temperature, is an excellent elastomer (2).

Linear polyethylene, however, does not exhibit elastomeric properties at room temperature, mainly because of its great tendency to crystallize. Yet, the introduction of chemically different groups in the polymethylene chain is sufficient to decrease the melting temperature; when the number of such groups exceeds 25% and when their distribution along the chain is random, crystallization generally becomes impossible as a consequence of the chemical disorder in the chain. Since such chains, in particular when the side groups are not very bulky, substantially maintain good flexibility, polymers of this type can exhibit excellent elastomeric properties. As examples can be mentioned the ethylene-α-olefin random copolymers (3) and sulfochlorinated polyethylene (4).

When these chemically different groups are regularly introduced into the polymethylene chain so that a definite number of methylene groups is followed by a given group having a different chemical structure, a new type of order rather than disorder is established in the chains.

Therefore, these chains will still be crystallizable. Being a new and defined chemical substance, such a polymer has its own melting point which is generally different from that of polyethylene. If this melting point is sufficiently low (room temperature or below), the product may be an elastomer, provided that the other requirements mentioned above are satisfied.

Stereoregular 1,4 polybutadiene has a structure that corresponds to this concept. In fact, it contains a chemically different group, $-HC=CH-$, after every two methylene groups:

$$((-CH_2)_2-CH=CH-)_p \qquad (1)$$

In this case the unsaturated groups satisfy three requirements: (1) they modify the chemical structure giving rise to a new chemically and sterically regular substance; (2) they introduce the sites that are necessary for the vulcanization; and (3) they allow the chains to maintain a high flexibility, in that the rotation around the $-C-C=$ single bond is even more easy than around the $-C-C-$ bond.

The crystallizability of 1,4 polybutadiene obviously depends also on the degree and the type of the steric regularity of the double bonds (cis or trans). The melting temperature of the crystalline stereoregular 1,4 polybutadienes varies with the type of double bonds: cis-1,4 polybutadiene melts below room temperature ($+1°C$), hence it is an excellent elastomer (5); on the other hand, trans-1,4 polybutadiene finally melts (6) at a higher temperature ($145°C$) than polyethylene ($130°C$), therefore it does not exhibit elastomeric properties in the temperature range of the usual applications.
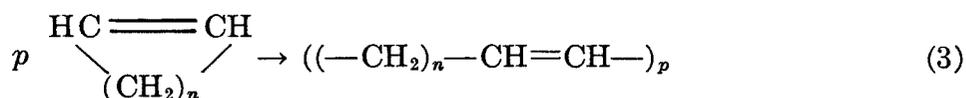
From the general point of view just described, elastomeric properties could also be expected for other stereoregular polymers containing double bonds regularly inserted between methylene sequences of a given length, but different from two. Polymers having the general structure:

$$((-CH_2)_n-CH=CH-)_p \qquad (2)$$

(where n is an integer and p the degree of polymerization) are to be called "polyalkenamers" (1). None of these polymers, except 1,4 polybutadienes (where $n = 2$), had been known until a few years ago. Only recently, mostly thanks to research initiated by Montecatini S.p.A. with the cooperation of G. Natta (7-9), a series of stereoregular polyalkenamers was obtained in which n corresponds to different values. Some of these polymers exhibit excellent elastomeric properties.

The general reaction according to which polyalkenamers were obtained is a ring opening polymerization of unsubstituted cycloolefins with reten-

tion of the double bond:

$$p \quad \begin{array}{c} HC \!\!\!=\!\!\!\!=\!\!\! CH \\ \diagdown \qquad \diagup \\ (CH_2)_n \end{array} \rightarrow ((-CH_2)_n-CH\!=\!CH-)_p \qquad (3)$$

Thus it was possible to polymerize all the cycloolefins so far examined in which $n \geq 2$, except cyclohexene, in which $n = 4$. The polyalkenamer corresponding to the latter cycloolefin, i.e., polyhexenamer, was obtained by Natta et al. (10) by alternating copolymerization of ethylene with butadiene:

$$p\,CH_2\!=\!CH_2 + p\,CH_2\!=\!CH\!-\!CH\!=\!CH_2 \rightarrow$$
$$(-CH_2\!-\!CH_2\!-\!CH_2\!-\!CH\!=\!CH\!-\!CH_2\!-\!)_p \quad (4)$$
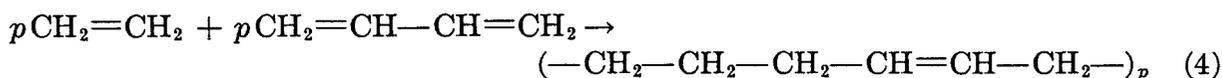
The polymerization of cycloolefins to polyalkenamers can be carried out in a stereoregular manner. It is therefore possible to prepare poly-alkenamers in which all or a predominant part of the double bonds are either *cis* or *trans*. Usually, the *trans* polyalkenamers can be obtained more easily; we shall consider them first.

Table I lists some of the most characteristic *trans* polyalkenamers, including polyacetylene and polyethylene which can be considered as the extreme members of the series. All the *trans* polyalkenamers (reported in Table I) in which the content of *trans* double bonds exceeds 70% of the total unsaturation can be made to crystallize at room temperature. However, polyalkenamers with a *trans* double bond content of 85% and, in many cases even of 95%, can be easily obtained. As already mentioned, the elastomeric properties of a polymer depend to a large extent on its melting temperature. If the latter occurs in the range between room temperature and slightly below, the polymer is usually amorphous at room temperature in the unstretched state, while it will crystallize when subjected to stretching. This is the case for natural rubber (melting temperature $+13°C$ (11)) and of *cis*-1,4 polybutadiene ($+1°C$).

In order to know within what limits a polymer can exhibit elastomeric properties, it is necessary to know its melting temperature. Figure 1 reports the melting temperatures of *trans* polyalkenamers vs. the length n of the methylene sequence between two subsequent double bonds. As can be noticed, the melting temperatures decrease regularly with decreasing length of the methylene sequence, from the value of normal linear polyethylene (130°C), to that of *trans* polypentenamer ($n = 3$), which has the lowest melting temperature (23°C) of the whole homologous series. Surprisingly, the curve ends with *trans* polypentenamer, in that

TABLE I

Trans Polyalkenamers and Methods for Their Preparation

Trans Polyalkenamers	Length n of the methylene sequence according to $((CH_2)_n\text{---}CH\text{=}CH\text{---})_p$	Melting temp., °C[a]	Method of preparation	Ref.
Polyacetylene	0	—[b]	Polymerization of acetylene	12
Polypropenamer*	1	—	Still unknown	—
Polybutenamer (1,4 polybutadiene)	2	145 (96)	1,4 Polymerization of butadiene or ring opening polymerization of cyclobutene	4, 5, 7
Polypentenamer	3	23	Ring opening polymerization of cyclopentene	8
Polyhexenamer	4	61 (41)	Alternating ethylene-butadiene copolymerization	10
Polyheptenamer	5	51	Ring opening polymerization of cycloheptene	9
Polyoctenamer	6	67 (62)	Ring opening polymerization of cyclooctene	9
Polydodecenamer	10	80	Ring opening polymerization of cyclododecene	9
Polyethylene	∞	130	Low pressure polymerization of ethylene	13–15

[a] Two melting temperatures refer to two different crystalline modifications.
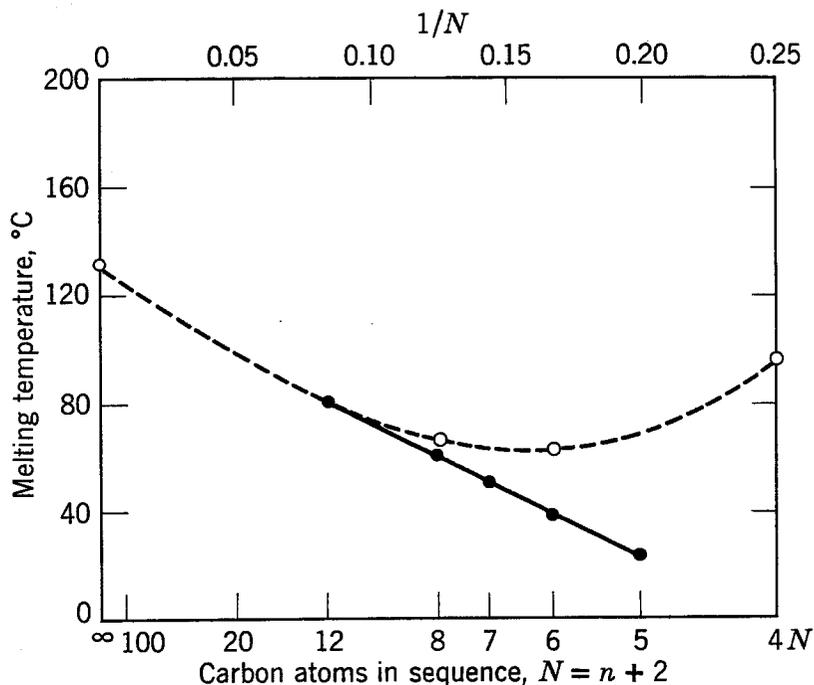[b] Decomposes before melting.

Fig. 1. Variation in melting point for the homologous series of *trans* polyalkenamers $((—CH_2)_n—CH=CH—)_p$. (N = total number of carbon atoms in the sequence ($N = n + 2$).)

the lower members of the series (*trans*-1,4 polybutadiene and *trans* polyacetylene) behave in a manner quite different from that of the other homologs. Actually, polybutadiene presents a far higher melting temperature than could be expected from this simple correlation. However, another correlation exists between *trans* polybutadiene and polyalkenamers, and we will deal with it later. With regard to *trans* polyacetylene, what causes this polymer not to melt before decomposition is probably the conjugation of the chain double bonds. It is of interest to point out a phenomenon that could not be foreseen: excluding the first members of the series (polybutadiene and polyacetytene), the lowest among the remaining members, i.e., *trans* polypentenamer, combines the highest double bond content with the lowest melting point and the best elastomeric properties at room temperature.

Although an essentially *trans* unsaturated stereoregular polymer with good elastomeric properties, i.e., *trans* poly-2-chlorobutadiene (polychloroprene), was already known in the past (16), it was a widely held opinion that primarily the unsaturated *cis*-tactic polyhydrocarbons had a chain flexibility high enough to promote good elastomeric properties. This was probably due to the fact that the best known stereoregular hydrocarbon elastomers are essentially *cis* unsaturated: *cis*-1,4 polyisoprene (natural rubber), *cis*-1,4 polybutadiene and isotactic *cis*-1,4

polypentadiene (17). In the case of *trans* polyalkenamers, and *trans* polypentenamer in particular, we can now visualize an unsaturated *trans*-tactic polymer that can compete very well as to the elastomeric properties with the best stereoregular, *cis*-tactic elastomers (Table II). From this it can be deduced that the flexibility given to the chain by a single bond adjacent to a double bond does not differ considerably in the case of a *trans* from that of a *cis* double bond.

As to the higher *trans* polyalkenamers following polypentenamer, the progressive increase in melting temperature impairs the elastomeric properties at room temperature. However, up to polyoctenamer (T_m = 67°C) the melting temperature is still low enough to allow the unstretched vulcanized product to have a predominantly amorphous structure and to give it elastomeric properties, since the vulcanization causes a further lowering of the crystallization temperature. Moreover, in these cases, said properties can be improved by a method that has already given good results for *trans*-1,4 polychloroprene (18). This polymer melts at about 80°C. Commercial products, which contain a certain amount of steric and chemical irregularities (80 or 91.5% *trans*-1,4 units) show crystalline melting temperatures of 30 and 55°C, respectively (19). The decrease in melting temperature together with a lowered ability to crystallize during stretching, improves the elastomeric properties of this polymer. Analogously, it is possible to improve some elastomeric properties of higher *trans* polyalkenamers by using products containing a certain amount of *cis*-1,4 units, which cause a decrease in the melting temperature of the polymer.

The good elastomeric properties of the *trans* polyalkenamers also derive from another structural factor that characterizes these polymers. For reasons that will be discussed in the section dealing with the polymerization mechanism of the cycloolefins, polyalkenamers do not contain any branching, unlike the polymers derived from conjugated dienes, which always contain a certain amount of 1,2 or 3,4 added monomer units (20). The elastomeric properties are worsened more by the presence of such groups than by steric irregularities (*cis*-1,4 in a *trans*-1,4 polymer or vice versa), as they hinder the free rotation around the single bonds of the chain, thus reducing its flexibility. Furthermore, the crystallizability of the chains upon stretching is reduced less if the irregularities are due to the type of double bond rather than to the presence of side groups.

Analysis of the crystal structure of *trans* polyalkenamers has revealed the existence of polymorphism. *Trans* polyalkenamers having an odd number of methylene groups between two subsequent double bonds

TABLE II

Some Elastomeric Properties of Vulcanized *Trans* and *Cis* Polypentenamers

(Vulcanization conditions: 150°C × 40 min; vulcanizing agents: sulfur + accelerators; properties determined at 23°C)

Poly-pentenamer	Mooney plasticity ML(1 + 4) at 100°C	Carbon black filler	Tensile strength, kg/cm²	Elongation at break, %	Elasticity modulus, kg/cm²			Rebound (μRE), %	Tear resistance, kg/cm
					at 200%	at 300%	at 500%		
Trans	30	Absent	140	750	11	—	20	n.d.	n.d.
	155	Absent	180	750	15	—	33	80	n.d.
	30	50 parts HAF	280	400	75	170	—	70	50
	100	50 parts HAF	315	370	110	230	—	n.d.	55
Cis	35	50 parts HAF	150	430	—	93	—	74	n.d.

usually exhibit a chain conformation with S $(2/1)m^*$ symmetry and pack into an orthorhombic crystal lattice (8,22,25) which is quite analogous to that of the usually stable modification of polyethylene. This is the main reason for the phenomenon observed in Fig. 1; i.e., the melting temperatures of *trans* polyalkenamers drop regularly with decreasing methylene sequence length n from the value for polyethylene to that for *trans* polypentenamer. The crystallographic repeat distance in these polymers always occurs after two chemical structural units.

In the case of *trans* polyalkenamers having an even number of methylene groups between two subsequent double bonds, only one chain conformation can be foreseen in the crystalline state. It is characterized by a *ti* symmetry* and contains only one structural unit in the crystalline repeat distance (9). However, these chains can pack in at least two different manners, characterized, respectively, by a monoclinic unit cell with a main spacing of 4.13 Å and by a triclinic unit cell with two main spacings of 4.48 and 3.83 Å. The first mode of packing of the even numbered *trans* polyalkenamers (modification IV) is quite analogous to that of the odd series of *trans* polyalkenamers and of the orthorhombic modification of polyethylene (9,24). This is the reason why the melting temperatures of the even numbered *trans* polyalkanemers in the monoclinic modification IV appear on the straight line in Fig. 1 that connects polyethylene with *trans* polypentenamer (lower curve).

The triclinic modification of the *trans* polyalkenamers of the even series (modification III) is characterized, especially for the lower members, by considerably higher melting temperatures. The difference between the melting points of the two crystalline modifications increases with decreasing monomer size. The mode of packing of modification III is very different from that of the odd *trans* polyalkenamers and of modification IV of the even series (9,25), but it shows analogies to that of the normally unstable triclinic modification of polyethylene (26). Very low energy minima have been calculated (27) for the triclinic modification of even numbered *trans* polyalkenamers as well as for the normally stable modification of *trans*-1,4 polybutadiene, characterized by the same chain conformation (28) but by different modes of packing (29). As expected, the entropies of fusion of both polymers are comparably low (30). For these reasons we have correlated the melting points of *trans* polyoctenamer and *trans* polyhexenamer in modification III with that of *trans*-1,4 polybutadiene (upper curve of Fig. 1). With regard to

---

* According to the nomenclature proposed by Corradini (21).

trans-1,4 polybutadiene, a melting point of 96°C was assumed in Fig. 1. This was deduced (31) by extrapolation from thermodynamic measurements. It is actually known that the normally stable modification of *trans*-1,4 polybutadiene does not melt directly, but that it undergoes an isophasic first order transition at 76°C to another modification which finally melts at 145°C, the crystal structure of which has not been completely elucidated (31–33).

Polyalkenamers having double bonds either exclusively or predominantly of the *cis* type were also obtained in our laboratories by polymerization of cycloolefins via ring opening. Although this homologous series of polymers is presently far less known than the *trans* series, some general remarks can be made. The *cis* polyalkenamers prepared so far always exhibit far lower melting temperatures than the corresponding *trans* isomers. Also in this case a phenomenon occurs which is often observed in ethylenically unsaturated hydrocarbon polymers (Table III); namely, that *trans*-tactic isomers generally exhibit melting temperatures that are at least 50°C higher than those of the corresponding *cis* isomers. This phenomenon is observed also for low molecular weight hydrocarbons, but it is enhanced in polymers. The exact melting temperatures of the *cis* polyalkenamers could not be determined yet, both because they are quite low and because of the remarkable difficulties encountered in preparing the pure *cis* isomers of polyalkenamers except in the case of polypentenamer.

With regard to the elastomeric properties of *cis* polyalkenamers (Table II) just the opposite of what is usually observed in unsaturated hydrocarbon polymers occurs: the *cis* isomer, though presenting fairly good

TABLE III

Comparison between the Melting Temperatures of Some Unsaturated *Cis* and *Trans* Hydrocarbon and Chlorinated Polymers

Unsaturated hydrocarbon polymers	Melting temperature, °C		Ref.
	Cis isomer	*Trans* isomer	
1,4 Polybutadiene	1	145	5, 6
1,4 Polyisoprene	13	74	11, 34
1,4 Poly-2,3-dimethyl-butadiene	192	272	35, 36
Isotactic 1,4 polypentadiene	44	95	17, 37
1,4 Poly-2-chloro-butadiene	70	80	38, 18
Polypentenamer	< −40	23	8

TABLE IV
Second Order Transition Temperatures of Some Elastomers

Elastomer	T_g, °C
trans-1,4 Polychloroprene	−45
Ethylene-propylene copolymer	−50
SBR	−65
Natural rubber	−70
Butyl rubber	−70
Propylene oxide rubber	−75
trans Polypentenamer	−95
cis-1,4 Polybutadiene	−115
Silicon rubber	−120
cis Polypentenamer	−140

elastic properties, exhibits much poorer mechanical properties than the *trans* isomer at room temperature. This confirms the general principle stated above, i.e., that the practically important elastomeric (especially dynamic) properties of polymers having the same basic chemical structure are better in those that have the melting point closer to room temperature. A very low melting polymer, like *cis* polypentenamer, can hardly crystallize at normal temperatures, even if subjected to elongations above 500%. However, all-*cis* polypentenamer has a second order transition temperature at about −140°C, which is exceptionally low even if compared with other low temperature elastomers (Table IV). Consequently, the range in which all-*cis* polypentenamer shows excellent elastomeric properties is that of very low temperatures (−50 to −90°C). Good elastomeric properties even at room temperature should be found in the higher members of the *cis* polyalkenamers, which, on the basis of the general rule already observed for the *trans* series, should melt at temperatures which are somewhat higher and closer to room temperature (Table IV).

II. CATALYSTS FOR THE STEREOSPECIFIC POLYMERIZATION OF CYCLOOLEFINS

The study of the stereospecific polymerization of cycloolefins via ring opening by the authors of this article started from the investigation of the polymerization of cyclobutene (7,39–40). It was found that cyclobutene can be polymerized by four different groups of catalysts to stereoregular

polymers having four different types of structure:

$$
\begin{array}{c}
\text{H}_2\text{C——CH}_2 \qquad \text{H}_2\text{C——CH}_2 \\
\qquad\qquad \text{H} \quad \text{H} \\
\blacktriangleleft\text{C—C}\blacktriangleright\ \text{C—C}\blacktriangleleft\text{C—C}\blacktriangleright \\
\text{H} \quad \text{H} \qquad\qquad \text{H} \quad \text{H} \\
\qquad\quad \text{H}_2\text{C——CH}_2
\end{array}
$$

$$
\begin{array}{c}
\text{H} \quad \text{H} \qquad \text{H} \quad \text{H} \qquad \text{H} \quad \text{H} \\
\blacktriangleleft\text{C—C}\ \blacktriangleright\ \text{C—C}\ \blacktriangleleft\ \text{C—C}\blacktriangleright \\
\text{H}_2\text{C——CH}_2\ \text{H}_2\text{C——CH}_2\ \text{H}_2\text{C——CH}_2
\end{array}
$$

$$
\text{HC}{=}\text{CH} \quad \text{III} \qquad \text{H}_2\text{C——CH}_2 \quad \text{IV}
$$

(5)
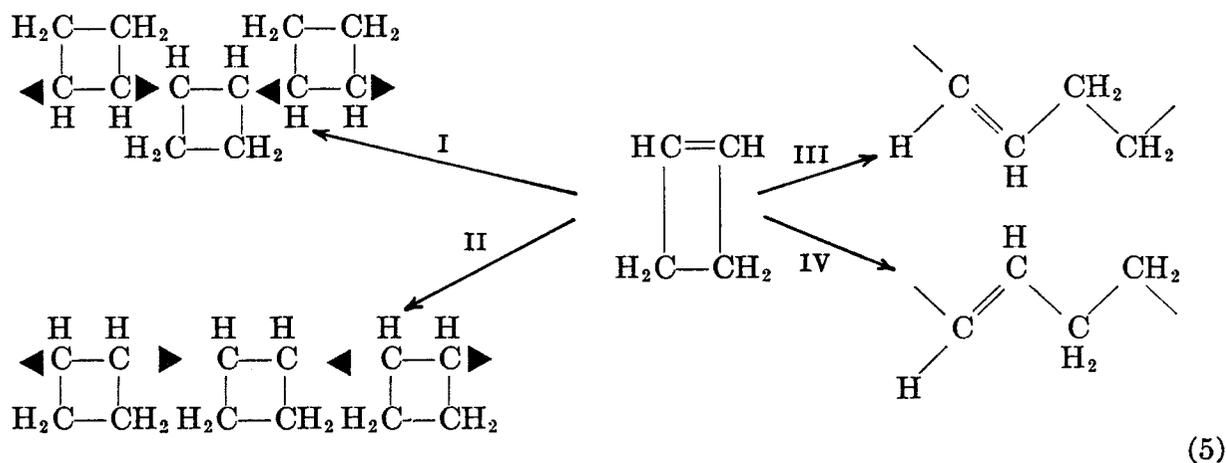
I	*erythro*-diisotactic polycyclobutene*
II	*erythro*-disyndiotactic polycyclobutene*
III	*cis* polybutenamer (corresponding to *cis*-1,4 polybutadiene)
IV	*trans* polybutenamer (corresponding to *trans*-1,4 polybutadiene)

* The assignment of the type of stereoregularity is only tentative until further experimental evidence has been obtained (38).

Table V shows some of the most significant catalyst systems, and the types of polymer they yield in the polymerization of cyclobutene. As can be seen, the type of polymerization depends first of all on the nature of the transition metal. Two classes can be distinguished among the catalysts of the system first described by Ziegler which are prepared from transition metal compounds of groups IV, V, and VI of the periodic system and organoaluminum compounds:

1. Catalysts containing chromium or vanadium, i.e., the more electronegative among these metals. These catalysts polymerize cyclobutene almost exclusively via opening of the double bond.

2. Catalysts containing titanium, molybdenum, or tungsten, i.e., the more electropositive among the metals examined. These catalysts polymerize cyclobutene primarily via ring opening to polymers having 1,4 polybutadiene structure.

(The classification of the transition metals according to their electronegativity is made following the rule that in a given period of the periodic table of elements the electronegativity increases with increasing atomic number, and in a given group with decreasing atomic weight.)

Among the catalysts made from compounds of noble metals of group

TABLE V

Catalyst Systems for the Polymerization of Cyclobutene

Catalyst system	Predominant structure of the polymer	Ref.
$CrO_2Cl_2/Al(C_2H_5)_2Cl/toluene$	Only I crystalline	39
$Cr(acetylacetonyl)_3/Al(C_2H_5)_2Cl/toluene$	Only I crystalline	39
$VCl_4/Al(C_2H_5)_3/n$-heptane	Only I crystalline	7, 39
$V(acetylacetonyl)_3/Al(C_2H_5)_2Cl/toluene$	Only II crystalline	7, 39
$V(acetylacetonyl)Cl_2/Al(C_2H_5)_2Cl/toluene$	Only I crystalline	39
$VO(OC_4H_9)_3/Al(C_2H_5)_2Cl/toluene$	Only II crystalline	39
$TiCl_4/Al(C_2H_5)_3/n$-heptane	Predom. III amorphous	7
$TiCl_4/Al(C_2H_5)_3/toluene$	Predom. IV crystalline	39
$TiCl_3xAlCl_3/Al(C_2H_5)_2Cl/toluene^a$	Predom. IV crystalline	7, 39
$MoCl_3/Al(C_2H_5)_3/toluene$	Predom. III amorphous	39
$MoCl_5/Al(C_2H_5)_3/toluene$	I + III + IV	39
$MoO_2(acetylacetonyl)_2/Al(C_2H_5)_2Cl/toluene$	III + IV	39
$WCl_6/Al(C_2H_5)_3/toluene$	I + III + IV	39
π-Allyl-Ni-bromide/C_2H_5OH	Only I crystalline	42
$RhCl_3/H_2O$	Only I crystalline	40
$RuCl_3/H_2O$	III + IV amorphous	41
$RuCl_3/C_2H_5OH$	Only IV crystalline	41

^{a} $TiCl_4$ reduced with Al and activated.

VIII and protic solvents in the absence of organometallic compounds, an analogous distinction can be made:

3. Catalysts containing the more electronegative metals, nickel and rhodium, which polymerize cyclobutene exclusively via opening of the double bond.

4. Catalysts containing the more electropositive ruthenium which polymerize cyclobutene exclusively via ring opening.

The behavior of the higher cycloolefin homologs toward the catalysts mentioned above also shows many analogies with what has just been described for cyclobutene; the catalysts containing the more electronegative transition metals tend to polymerize higher cycloolefins via opening of the double bond while those containing the more electropositive ones tend to do it via ring opening (8). As our present interest is especially focused on the methods that lead to elastomeric products, we shall disregard those catalysts which polymerize cycloolefins via opening of the double bond, since they yield polymers that do not show interesting

TABLE VI
Efficiency of Various Catalyst Systems in the Polymerization of Cyclopentene
(Polymerization conditions: 4 hr at $-30°C$; molar ratio of transition metal to
$Al(C_2H_5)_3$ and $Al(C_2H_5)_2Cl$ = 1:2.5 and 1:5, respectively; molar ratio of
monomer to transition metal = 500:1; polymerization in the absence
of diluent except for the run with $RuCl_3$ which was carried out
in ethanol at 20°C)

Catalyst system	Polymer yield, %	Polymer structure	Intrinsic visc. in toluene at 30°C, dl/g	Internal double bonds	
				Cis, %	Trans, %
$TiCl_4/Al(C_2H_5)_3$	<1	Polypentenamer	n.d.	<5	>95
$ZrCl_4/Al(C_2H_5)_3$	<1	Polypentenamer	n.d.	7	93
$CrO_2Cl_2/Al(C_2H_5)_3$	0	—	—	—	—
$MoCl_5/Al(C_2H_5)_3$	27	Polypentenamer	1.6	99	1
$WCl_6/Al(C_2H_5)_3$	30	Polypentenamer	3.3	15	85
$WCl_6/Al(C_2H_5)_2Cl$	53	Polypentenamer	2.6	12	88
$UO_2Cl_2/Al(C_2H_5)_2Cl$	0	—	—	—	—
$RuCl_3/C_2H_5OH$	0	—	—	—	—

elastomeric properties, and we shall only consider the catalysts of classes
2 and 4, i.e., those that cause formation of polyalkenamers. The results
obtained with such catalysts in the polymerization of cyclopentene are
summarized in Table VI.

Cyclopentene shows a higher selectivity with regard to catalysts than
cyclobutene. In fact, catalysts based on halides of group VIII metals
(ruthenium) in protic solvents do not polymerize cyclopentene. The
organometal type catalysts containing transition metals of group IV
(titanium, zirconium) and group VI (molybdenum, tungsten) polymerize
cyclopentene to polypentenamer, i.e., exclusively via ring opening (8).
But, while the former exhibit a very modest catalytic activity, the latter
allow us to obtain high yields of polypentenamer. With regard to
stereospecificity, the titanium- or zirconium-containing catalysts yield
almost exclusively trans-tactic polypentenamers; those based on molyb-
denum pentachloride yield all-cis polypentenamer. Oxygen containing
compounds, especially peroxides, hydroperoxides, and alcohols were
reported to act as cocatalysts enhancing the activity of the catalysts pre-
pared from tungsten halides and organoaluminum compounds (43,44).

Among the catalysts prepared from Group VIB metal salts and organo-
aluminum compounds only the tungsten and molybdenum catalysts
induce the polymerization of cyclopentene to polypentenamer. This is

surprising in view of both the high reactivity of these catalysts and a du Pont patent (45) stating that cyclopentene and cyclohexene can be polymerized, though in very low yields and with less stereospecificity, via ring opening with activated chromium or molybdenum oxide supported on aluminum oxide as the catalyst. The latter seems to be the first recognized case of a ring opening polymerization of a low-strained cycloolefin described in the literature. More recently Ziegler-Natta catalysts containing niobium or tantalum pentachloride as the transition metal salt were also reported to be active in the ring opening polymerization of cycloolefins, but their activity seems to be limited to cyclopentene (46). The polypentenamer thus obtained is built up from 60–65% *trans* and 30% *cis* units. Due to this low stereoregularity, the elastomeric properties of this polymer are poor at room temperature. The best catalysts for the preparation of *trans* polypentenamer presently known with respect to both catalytic activity and the elastomeric properties of the polymer are those based on WCl_6. The ability of the niobium and tantalum catalysts to polymerize cyclopentene via ring opening, unlike analogous vanadium catalysts which exclusively polymerize cycloolefins via opening of the double bond, is in line with the above reported rule that the tendency toward ring opening polymerization increases with increasing electropositivity of the transition metal.

The polymerization of cycloolefins higher than cyclopentene to stereoregular polyalkenamers (Table VII) appears even more selective with regard to the catalyst system (9). Contrary to what is observed with cyclopentene, the catalysts based on transition metals of the group IV appear ineffective and those based on molybdenum exhibit little activity. The catalysts based on tungsten halides, however, are very active and stereospecific in the polymerization of this group of cycloolefins. In general, tungsten catalysts yield all-*trans* polyalkenamers from higher cyclolefins. Also the $MoCl_5/Al(C_2H_5)_3$ system, which in the case of cyclopentene yields pure *cis* polypentenamer, polymerizes higher cycloolefins essentially to *trans* polyalkenamers. Cyclohexene behaves very differently in that it never yields high polymers, not even in traces, with any of these catalysts (Table VII).

III. MECHANISM OF THE RING OPENING POLYMERIZATION OF CYCLOOLEFINS

In order to establish the mechanism of polymerization of cycloolefins to polyalkenamers, a series of runs were carried out with representative examples of various classes of catalysts. The $CuCl_2/Al(C_2H_5)_3$ catalyst system, which gives rise to the formation of a great number of free

TABLE VII

Polymerization of Higher Cycloolefins in the Presence of Catalysts Based on Metals of Goups IV and VI

(Polymerization conditions: 5 hr at −30°C, then 20 hr at +20°C; molar ratio of transition metal to $Al(C_2H_5)_3$ and $Al(C_2H_5)_2Cl$ = 1:2.5 and 1:5, respectively; molar ratio of monomer to transition metal = 500:1; polymerization in the absence of diluent)

| Cycloolefins | Catalyst system | Con-version, % | $[\eta]$ dl/g[a] | Polymer structure | Internal double bonds | | X-ray exam. |
					Cis, %	Trans, %	
Cyclohexene	$MoCl_5/Al(C_2H_5)_3$	0	—	—	—	—	—
Cyclohexene	$WCl_6/Al(C_2H_5)_2Cl$	0	—	—	—	—	—
Cycloheptene	$TiCl_4/Al(C_2H_5)_3$	0	—	—	—	—	—
Cycloheptene	$MoCl_5/Al(C_2H_5)_3$	5	n.d.	Polyheptenamer	7	93	Crystalline
Cycloheptene	$WCl_6/Al(C_2H_5)_2Cl$	18	1.1	Polyheptenamer	9	91	Crystalline
cis- Cyclooctene	$WCl_6/Al(C_2H_5)_3$	23	2.4	Polyoctenamer	15	85	Crystalline
Cis/trans(1:2) Cyclododecene	$WCl_6/Al(C_2H_5)_2Cl$	34	2.2	Polydodecenamer	6	94	Crystalline

[a] Intrinsic viscosity in toluene at 30°C.

radicals, does not polymerize either cyclobutene or cyclopentene. Similarly, the organometallic compounds alone (e.g., $Al(C_2H_5)_3$, $Al(C_2H_5)_2Cl$, $Li\text{-}n\text{-}C_4H_9$) do not polymerize these monomers. The same is the case for some typical cationic catalysts, such as $AlCl_3$, $TiCl_4$, and CrO_2Cl_2. Among such catalysts, only WCl_6 can polymerize cyclopentene, though in extremely low yield (a few percent conversion after some weeks of contact) to low molecular weight, essentially atactic polyalkenamers. This means that the situation is similar to that observed in the case of α-olefins. Thus, for example, propylene can be polymerized, though in low yield, by titanium halides ($TiCl_2$ (47) or $TiCl_3 \cdot xAlCl_3$ (48)) to polymers of low stereoregularity. However, for both propylene and cycloolefins, only the presence of an organometallic compound, such as an aluminum alkyl, in addition to the transition metal, makes it possible to obtain a high polymerization rate and a high stereospecificity.

The inefficiency of other catalyst systems and the analogy with the behavior of α-olefins suggest that the polymerization of cycloolefins via ring opening also takes place by a coordinated anionic mechanism. It can also be concluded that tungsten, among all transition metals, presents the highest tendency to coordinate with cycloolefins; this enables it to polymerize these monomers even by itself in the absence of an organometallic compound.

The polymerization of cycloolefins to polyalkenamers differs from a thermodynamic point of view from the usual polymerization of vinyl monomers. In the polymerization of the vinyl monomers, the transformation of a double bond in the monomer into two single bonds in the polymer chain is thermodynamically favored by a high exothermicity (about 20 kcal/mole). In the ring opening polymerization, the bonds contained in the monomer are exactly the same as those appearing in the corresponding segment of the resulting polymer chain, both with respect to number and type. No enthalpy factor resulting from bond transformation is to be considered, therefore. Thus, the thermodynamic factor that mainly favors the ring opening polymerization is the release of the ring strain energy. This energy greatly varies with the ring size of the cycloolefin (Table VIII). In cyclopropene (49,50) and cyclobutene (51) it is even higher than the heat of reaction of a normal vinyl polymerization, which explains the great tendency of these monomers to polymerize in the presence of a great number of catalysts. By contrast, in cyclopentene (52), cycloheptene (54), and cis cyclooctene (54) the ring strain energy is rather low. This may explain why only a few catalysts are able to polymerize them to polyalkenamers. The low heat

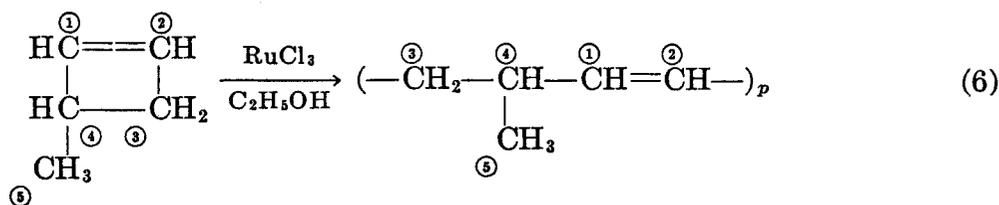TABLE VIII
Ring Strain in Several *Cis* Cycloolefins

Cycloolefin	Ring strain expressed as $\Delta H°_f(g)$ exp. $- \Delta H°_f(g)$ calc. kcal/mole[a]	Ref.
Cyclopropene	~54.5	49, 50
Cyclobutene	>26.1	51
Cyclpentene	4.9	52
Cyclohexene	0.8	53
Cycloheptene	~5	54
Cis cyclooctene	~6	54

[a] The calculated value refers to a corresponding open chain.

of reaction involved in their polymerization also accounts for the rapidly reached polymerization-depolymerization equilibrium. In addition to the ring strain, an enthalpy factor also seems to favor the ring opening polymerization of cycloolefins. In cyclohexene the ring strain is extremely low (53) since the conformation of a six-membered ring is nearly equivalent to that of the corresponding open chain. This explains why cyclohexene shows no tendency to polymerize via ring opening not even with formation of low molecular weight polymers.

Polymerization via ring opening has been generally observed only in unsubstituted cycloolefins and not in alkyl substituted ones. The alkyl substituted cyclopentenes could not be polymerized via ring opening with the catalysts described above, independent of the position of the substituent, whereas 3-methyl- as well as 3-phenylcyclooctene have recently been reported (55) to polymerize, although in significantly lower yield than cyclooctene, via ring opening in the presence of the above tungsten-based Ziegler-Natta catalysts. This decrease in reactivity is also caused by thermodynamic factors (56). It has been observed in ring opening polymerizations of cyclic ethers, too. Thus, while for instance tetrahydrofuran can be easily polymerized via ring opening (57), its alkyl substituted derivatives are not polymerizable (58–61). In the case of a four-membered ring, the stabilizing effect of the alkyl substituent is insufficient from an energetic point of view to balance the high ring strain. Thus, 3-methylcyclobutene can be converted by all the catalysts reported above to polymers having polypentadiene structure, though at a far lower rate than in the case of cyclo-

butene (41):

$$\underset{\underset{\underset{\overset{|④ ③}{\underset{CH_3}{⑤}}}{HC\rule{0.8cm}{0.4pt}CH_2}}{\overset{①\qquad②}{HC\rule{0.05cm}{0pt}=\rule{0.05cm}{0pt}CH}}} \xrightarrow[C_2H_5OH]{RuCl_3} \underset{\underset{CH_3}{⑤}}{(-\overset{③}{CH_2}-\overset{④}{CH}-\overset{①}{CH}=\overset{②}{CH}-)_p} \qquad (6)$$

This reaction can be stereospecific with regard to the double bond. For instance, the system $RuCl_3/C_2H_5OH$ yields a polypentadiene having exclusively *trans* double bonds. However, the reaction is not stereospecific with respect to carbon atom 4, not even with the catalysts prepared from Ti alkoxides and organoaluminum compounds or from $VCl_3 + Al(C_2H_5)_3$, which polymerize pentadiene to polymers that exhibit stereoregularity both with respect to the double bonds and the tertiary carbon atoms. This demonstrates how much the mechanism of the ring opening polymerization of cycloolefins differs from that of the conventional polymerization of conjugated dienes, although in many cases the reaction products are the same.

A modest energy gain in the polymerization of cycloolefins via ring opening may result also from the transformation of the *cis* double bond, which characterizes most cycloolefins, into a *trans* double bond in the polymer chain. This is probably the reason why the higher members of the cycloolefin series have a greater tendency to form all-*trans* polyalkenamers than *cis* isomers. Cycloolefins up to the seven-membered ring are known only in the *cis* form. From cyclooctene onward the *trans* isomer is also known. Relative stability of the *trans* isomer increases with increasing ring size. In cyclododecene at equilibrium, the *trans-cis* ratio is 2:1. If such a mixture is used in a polymerization, both isomers polymerize to the same *trans* polydodecenamer, but the more energetic *cis* isomer seems to polymerize more rapidly than the *trans* isomer.

The ease by which the *cis* double bond of the cycloolefin is transformed into a *trans* double bond in the polymer is one of the phenomena suggesting that the site of the opening of the cycloolefin is one of the single bonds adjacent to the double bond. It has been ascertained that the catalysts that polymerize olefins via ring opening do not isomerize the double bond of the monomer. Therefore it seems very unlikely that the site of ring opening is a single bond far from the double bond; because if that were the case the monomer unit in the polymer should contain *cis* internal double bonds just as the monomer itself. By contrast, ring opening at a bond adjacent to the double bond gives rise to a

monomeric unit with a terminal double bond, which when inserted in the polymer chain, can easily assume either *cis* or *trans* configuration, depending on the properties of the active center and on the thermodynamics of the reaction.
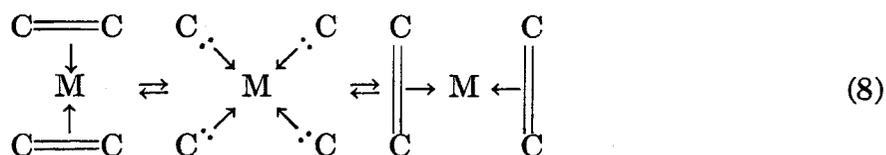
The site at which the cycloalkene rings open is still a matter of discussion. Three possibilities can be visualized: (a) at the single bond in alpha position with respect to the double bond, (b) at the one in beta position, and (c) at the double bond itself. The schemes of classical organic chemistry are in favor of (b). It is actually known that cyclobutene may be transformed at high temperature to butadiene via opening of the single bond in beta position (62). However, in that case the reaction is thermal and proceeds through a radical mechanism, in contrast with the present polymerizations which are ionic and involve a coordination mechanism. The ease by which the *cis* double bond of the cycloolefins is transformed into a *trans* double bond in the polymer along with the established lack of isomerization of the double bond in any cycloolefin polymerization with the above catalysts favors hypotheses (a) and (c) over (b). If the single bond in beta position opened, the polymer should preferably contain *cis* internal double bonds just as the monomer. By contrast, ring opening at the bond adjacent to the double bond gives rise to a monomeric unit with a terminal double bond, which, when inserted into the polymer chain, can easily assume either *cis* or *trans* configuration, depending on the active center and on the thermodynamics of the reaction.

Other strong evidence against (b) is the structure of the polymers obtained in the ring opening polymerizations of norbornene (63), of bicyclo[4,2,0]oct-7-ene (64), and of bicyclo[3,2,0]hexa-2,6-diene (64). In these monomers the single bond in beta position is a part of a further ring, which is retained in the polymer, as illustrated for norbornene:

$$\text{(structure)} \longrightarrow \text{—CH=CH—} \text{—CH=CH—} \tag{7}$$
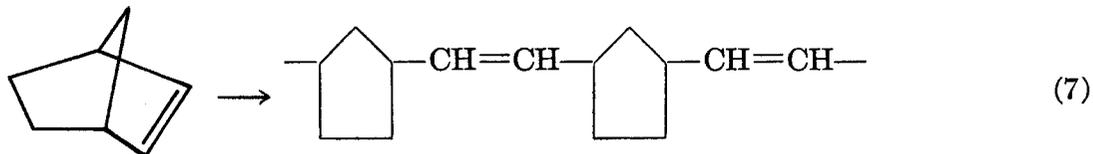
The choice between hypotheses (a) and (c) is harder to make at present. In our earlier publications we favored (a) over (c) mainly on the basis of the vinyl endgroups that characterize especially the lower molecular weight polymers of unsubstituted cycloolefins and the vinylidene endgroups exhibited by the ring opening polymers of 3-methylcylobutene (40). More recently, evidence in favor of hypothesis (c) has been furnished by the so-called olefin metathesis, a dismutation reaction of

alpha-olefins as well as of internal olefins by the action of a $WCl_6/$ $AlEtCl_2/C_2H_5OH$ catalyst (65,66). As an example, metathesis of 2-pentene produces essentially a 1:2:1 mixture of 2-butene, 2-pentene, and 3-hexene. This reaction can be interpreted on the basis of an eight electron transposition:

$$
\begin{array}{ccc}
C\!\!=\!\!C & C \quad C & C \quad\quad C \\
\downarrow & \searrow \nearrow & \| \quad\quad \| \\
M & \rightleftarrows \quad M \quad \rightleftarrows & \rightarrow M \leftarrow \\
\uparrow & \nearrow \searrow & \| \quad\quad \| \\
C\!\!=\!\!C & C \quad C & C \quad\quad C
\end{array}
\qquad (8)
$$

It can be traced back to an early observation made in our laboratory that propylene is partially dismutated to ethylene and 2-butene during its polymerization in the presence of supported molybdenum catalysts, yielding ethylene-propylene copolymers (67), as well as to the Phillips propylene dismutation process, which yields equimolecular amounts of ethylene and butenes (68,69). This reaction has been extended to cycloolefins. A Phillips patent (70) reports the synthesis of 1,6-heptadiene from cyclopentene and ethylene and of 1,7-nonadiene from cyclohexene and propylene.

An eight electron transposition (metathesis) has recently been proposed (71) also for the ring opening polymerization of cycloolefins with tungsten halide catalysts on the basis of the formation of a ring structure (macrocycle) containing the polyalkenamer thus obtained. This result appears in contrast with the above reported experimental evidence for the presence of vinyl endgroups in such polymers. Experimental work is now in progress in various laboratories in order to establish whether the cycloolefin polymerization proceeds through pathway (a) or (c).

The fact that cycloolefins open at only one definite site accounts for the perfect linearity of the polyalkenamers obtained with organometallic catalysts acting through a typically anionic coordinate mechanism. Analysis of the structure of high molecular weight polyalkenamers has actually demonstrated the absence of monomeric units of the type resulting from 1,2 polymerization of conjugated dienes (8). Saturated monomer units stemming from the opening of the double bond are equally absent. Their presence would have implied a "copolymerization" of monomeric units derived from the same cycloolefin via ring cleavage and via opening of the double bond. However, even if such a reaction is possible in principle, it must be ruled out on the basis of experimental evidence. In fact, when attempting to copolymerize cyclopentene with ethylene in the presence of a typical ring opening catalyst at low tempera-

ture, only polypentenamer completely free of monomeric units derived from ethylene is obtained.

References

1. Report on Nomenclature in the Field of Makromolecules, IUPAC, *J. Polymer Sci.*, **8**, 257 (1952).
2. A. Ciferri, C. A. Hoewe, and P. Flory, *J. Amer. Chem. Soc.*, **83**, 1015 (1961).
3. See this book, chapter by G. Natta, A. Valvassori, and G. Sartori on "Propylene-Ethylene Rubbers," p. 679.
4. See this book, chapter by H. S. Makowski on "Chlorination, Grafting and Related Techniques," p. 905.
5. G. Natta and P. Corradini, *Nuovo Cimento*, **15**, *Nuovo Cimento Suppl.*, **1**, 111 (1960).
6. G. Natta and P. Corradini, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, **19**, 229 (1955); G. Natta, L. Porri, P. Corradini, and D. Morero, *Chim. Ind (Milan)*, **40**, 362 (1958).
7. G. Dall'Asta, G. Mazzanti, G. Natta, and L. Porri, *Makromol. Chemie*, **56**, 224 (1962).
8. G. Natta, G. Dall'Asta, and G. Mazzanti, *Angew. Chem.*, **76**, 765 (1964); *Angew. Chem. Internat. Edit.*, **3**, 723 (1964).
9. G. Natta, G. Dall'Asta, I. W. Bassi, and G. Carella, *Makromol. Chemie*, **91**, 87 (1966).
10. G. Natta, A. Zambelli, I. Pasquon, and F. Ciampelli, *Makromol. Chemie*, **79**, 161 (1964).
11. W. Cooper, *J. Polymer Sci.*, **A1**, 159 (1963).
12. G. Natta, G. Mazzanti, and P. Corradini, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, **25**, 3 (1958).
13. K. Ziegler, E. Holzkamp, H. Breil, and H. Martin, *Angew. Chem.*, **67**, 541 (1955).
14. Phillips Petroleum Co., Belg. Pat. 530,617 (1953).
15. Standard Oil Company of Indiana, U.S. Pat. 2,658,059 (1951).
16. See this book, chapter by C. A. Hargreaves on "Neoprene," p. 227.
17. G. Natta, L. Porri, G. Stoppa, G. Allegra, and F. Ciampelli, *Polymer Letters*, **1**, 67 (1963).
18. I. Maynard and W. E. Mochel, *J. Polymer Sci.*, **13**, 235; 251 (1954).
19. R. Nagao, *Polymer*, **9**, 517 (1968).
20. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N.Y., 1953, p. 238–246.
21. P. Corradini, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, **28**, 1 (1960).
22. G. Natta and I. W. Bassi, *Atti Accad. Nazl. Lincei, Rend., Classe Sci., Fis., Mat., Nat.*, **38**, 315 (1965); *J. Polymer Sci. Part C*, **16**, part **5**, 2551 (1967).
23. G. Natta and I. W. Bassi, *European Polymer J.*, **3**, 31 (1967).
24. G. Natta and I. W. Bassi, *European Polymer J.*, **3**, 43 (1967); G. Natta, I. W. Bassi, and G. Fagherazzi, *ibid.*, **3**, 339 (1967).
25. G. Fagherazzi and I. W. Bassi, *European Polymer J.*, **4**, 151 (1968).
26. A. Turner-Jones, *J. Polymer Sci.*, **62**, 53 (1962).
27. Private communication of P. Corradini.

28. G. Natta, P. Corradini, L. Porri, and D. Morero, *Chim. Ind. (Milan)*, **40**, 362 (1958).

29. S. Iwayanagi, H. Nakane, and I. Sakurai, Paper presented at the Intern. Sympos. on Macromol. Chem., Tokyo 1966, preprint 2-4-11.

30. N. Calderon and M. C. Morris, *J. Polymer Sci. A-2*, **5**, 1283 (1967).

31. G. Moraglio, G. Polizzotti, and F. Danusso, *European Polymer J.*, **1**, 183 (1965).

32. G. Natta, M. Pegoraro, P. Cremonesi, and A. Pavan, *Chim. Ind. (Milan)*, **47**, 716; 722 (1965).

33. G. Natta and G. Allegra, Paper presented at the Intern. Sympos. on Macromol. Chem., Tokyo 1966.

34. L. Mandelkern, *Chem. Rev.*, **56**, 903 (1956).

35. T. F. Yen, *J. Polymer Sci.*, **35**, 533 (1959).

36. T. F. Yen, *J. Polymer Sci.*, **38**, 272 (1959); J. F. Brown Jr. and D. M. White, *J. Amer. Chem. Soc.*, **82**, 5671 (1960).

37. G. Natta, L. Porri, P. Corradini, G. Zanini, and F. Ciampelli, *J. Polymer Sci.*, **51**, 463 (1961).

38. C. A. Aufdermarsh, Jr. and R. Pariser, *J. Polymer Sci.*, **A2**, 4727 (1964).

39. G. Natta, G. Dall'Asta, G. Mazzanti, and G. Motroni, *Makromol. Chemie*, **69**, 163 (1963).

40. G. Natta, G. Dall'Asta, and G. Motroni, *J. Polymer Sci. B*, **2**, 349 (1964).

41. G. Natta, G. Dall'Asta, and L. Porri, *Makromol. Chemie*, **81**, 253 (1965).

42. L. Porri, G. Natta, and M. C. Gallazzi, *Chim. Ind. (Milan)*, **46**, 428 (1964).

43. G. Dall'Asta and G. Carella (to Montecatini Edison), Ital. Pat. 778,370 (1965).

44. G. Dall'Asta and R. Manetti, *European Polymer J.*, **4**, 145 (1968).

45. H. Soura Eleuterio (to E. I. du Pont de Nemours), U.S. Pat. 3,074,918 (1957).

46. C. A. Uranek and W. J. Trepka (to Phillips), U.S. Pat. Appl. filed 1966, Serial No. 589,855.

47. C. J. K. Benning, W. R. Wszolek, and F. X. Werber, Abstracts of Papers, Meeting Polymer Div. Am. Chem. Soc. Washington D.C., March 1962, Vol. 3, 138; Polymer Preprint, **1**, 122; 138 (1965).

48. J. Boor, Jr. and E. A. Youngman, *J. Polymer Sci. B*, **2**, 265 (1964).

49. J. W. Knowlton and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **A43**, 113 (1949).

50. K. B. Wiberg, W. J. Bartley, and F. P. Lossing, *J. Am. Chem. Soc.*, **84**, 3980 (1962).

51. S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.*, **71**, 261 (1952).

52. F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, *Selected Values of Physics and Thermodynamics of Hydrocarbons and Related Compounds*, Carnegie Press, Pittsburgh, 1953.

53. H. A. Skinner, *J. Chem. Soc.*, **1962**, 4396.

54. J. D. Cox, *Tetrahedron*, **19**, 1175 (1963).

55. N. Calderon, E. A. Ofstead, and W. A. Judy, *J. Polymer Sci. A-1*, **5**, 2209 (1967).

56. F. S. Dainton, T. R. E. Devlin, and P. A. Small, *Trans. Faraday Soc.*, **51**, 1710 (1955).

57. H. Meerwein, Ger. Pat. 741,478 (1939).

58. H. Meerwein, *Angew. Chem.*, **59**, 168 (1957); K. Hamann, *Angew. Chem.*, **63**, 231 (1951).

59. P. A. Small, *Trans. Faraday Soc.*, **51**, 1717 (1955).

60. C. L. Hamermesh and E. V. Hanry, *J. Org. Chem.*, **26**, 4748 (1962).

61. S. C. Temin, *J. Polymer Sci.*, **62**, S91 (1962).

62. E. Vogel, *Angew. Chem.*, **72**, 21 (1960).
63. W. L. Truett, D. R. Johnson, I. M. Robinson, and B. H. Montague, *J. Amer. Chem. Soc.*, **82**, 2337 (1960).
64. G. Dall'Asta and G. Motroni, *J. Polymer Sci. A-1*, **6**, 2405 (1968).
65. N. Calderon, H. Y. Chen, and K. W. Scott, *Tetrahedron Letters*, **1967**, 3327.
66. N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Amer. Chem. Soc.*, **90**, 4133 (1968).
67. Private communication of G. Mazzanti.
68. R. L. Banks and G. C. Bailey, *Ind. Eng. Chem., Prod. Res. Dev.*, **3**, 170 (1964).
69. C. P. C. Bradshaw, E. J. Howman, and L. Turner, *J. Catalysis*, **7**, 269 (1967).
70. G. C. Ray and D. L. Crain (to Phillips), French Pat. 1,511,381 (U.S. Prior. 1966).
71. K. W. Scott, N. Calderon, E. A. Ofstead, W. A. Judy, and J. P. Ward, 155th Meeting A. C. S., San Francisco, 1968, preprint 54.
72. N. Calderon, Proc. 11th Intern. Conf. Coord. Chem., Haifa 1968, preprint p. 38.

To Robert McKay Thomas

Inspirer, Inquirer, Inventor

———THE EDITORS

POLYMER CHEMISTRY OF SYNTHETIC ELASTOMERS

Part II