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*The polymerization of cyclo-olefins, like that of olefins with an internal double bond, is sterically hindered. Within recent years it has become possible to prepare copolymers of these compounds with ethylene, with the aid of anionic coordination Ziegler catalysts. This copolymerization always results in cis-opening of the double bond. Despite the steric hindrance, cyclobutene and cyclopropene have also been homopolymerized, with opening of the double bond. — Rather surprisingly, the best catalysts for homopolymerization of cyclopentene are those which exhibit low activity in the polymerization of ethylene. Ring cleavage occurs with $\text{MoCl}_5/\text{Al}(\text{C}_2\text{H}_5)_3$ to give the *cis*-polypentenamer, whereas $\text{WCl}_6/\text{Al}(\text{C}_2\text{H}_5)_3$ gives the *trans*-polypentenamer. Both polypentenamers exhibit elastomeric properties. — Evidence from infrared spectra and oxidative degradation indicates that the monomer units in the *trans*-polypentenamer are linked head-to-tail. It is presumably the single bond adjacent to the double bond that is broken. Using X-ray methods at -50°C , it was possible to determine the crystal structure of the crystalline *trans*-polypentenamer at about 400% elongation.*

I. Introduction

In theory, cyclo-olefins should be able to polymerize, either with opening of the double bond to form polycycloalkenes, or with ring cleavage to form unsaturated linear polymers.

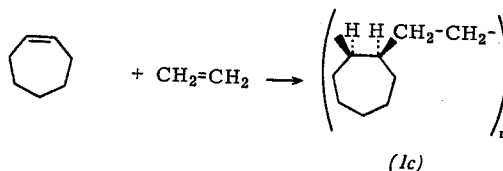
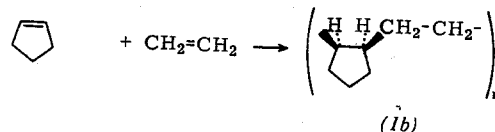
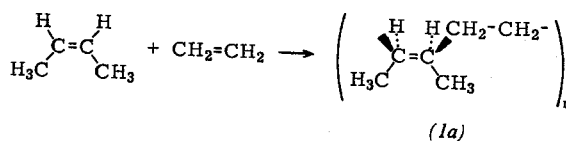
Until a few years ago, all attempts to convert cyclo-olefins into high molecular-weight homopolymers were unsuccessful. To find the reason for failure, it is necessary to consider the two possible modes of reaction.

Cyclo-olefins are related to acyclic olefins which have an internal double bond. It is well known that such olefins (e.g. 2-butene) show very little or no tendency to polymerize. One of the reasons which have long been adduced to explain this behavior is steric hindrance due to the bulk of the substituents on both carbon atoms of the double bond. In recent years we have been able to show [1-5] that steric hindrance is indeed the main reason why these olefins do not tend to polymerize *via* opening of the double bond. We have succeeded, with the aid of suitable catalysts, in obtaining high molecular-weight products by copolymerization of both aliphatic and cyclic olefins with a comonomer such as ethylene, which has only slight

steric hindrance on the carbon atoms of the double bond. Particularly suitable catalysts for this type of copolymerization are those which act by an anionic coordination mechanism, especially those prepared from vanadium salts and organoaluminum compounds.

However, even in these copolymers there is no direct linkage of monomer units derived from an olefin with an internal double bond; instead, each unit of this type alternates with one or more ethylene units. By using high molar ratios of olefins with an internal double bond to ethylene in the liquid reaction phase, we have succeeded in preparing so-called alternating copolymers, *i.e.* copolymers in which each monomer unit derived from an olefin with an internal double bond is followed by only one ethylene unit, and vice versa.

In the case of *cis*-2-butene [1,2], cyclopentene [3], and cycloheptene [4], we were able to prepare alternating copolymers in which the tertiary carbon atoms are stereoregular, with the result that these copolymers could be crystallized. The structures assigned to these alternating copolymers are shown in formulae (1a)-(1c). In all



[*] Lecture given by G. Dall'Asta at the Gordon Research Conference on Polymers, Santa Barbara, Calif. (U.S.A.) in January, 1964, and to the Macromolecular Colloquium in Freiburg/Breisgau (Germany), in March, 1964.

[1] G. Natta, G. Dall'Asta, G. Mazzanti, I. Pasquon, A. Valvassori, and A. Zambelli, *J. Amer. chem. Soc.* 83, 3343 (1961).

[2] G. Natta, G. Dall'Asta, G. Mazzanti, and F. Ciampelli, *Kolloid-Z.* 182, 50 (1962).

[3] G. Natta, G. Dall'Asta, G. Mazzanti, I. Pasquon, A. Valvassori, and A. Zambelli, *Makromolekulare Chem.* 54, 95 (1962).

[4] G. Natta, G. Dall'Asta, and G. Mazzanti, *Chim. e Ind.* 44, 1212 (1962).

[5] G. Dall'Asta and G. Mazzanti, *Makromolekulare Chem.* 61, 178 (1963).

three crystalline alternating copolymers, the double bonds have opened exclusively in the *cis*-direction, resulting in an *erythro*-ditactic (and in this particular case *erythro*-diisotactic) structural regularity.

Until a few years ago, *cis*-opening of double bonds during polymerizations was regarded as unlikely. Classical organic chemistry has many examples of *trans*-additions to double bonds, and this mode of reaction is also regarded as preferable on thermodynamic grounds. Surprisingly, however, all polymerizations in which the direction of the addition to the double bond has been determined in recent years on the basis of a regular steric structure of the polymer have been found to be *cis*-additions. This was first demonstrated with poly(alkenyl alkyl ethers) [6] which are prepared by cationic coordination polymerization, and subsequently for the stereospecific cationic polymerization of both *cis*- and *trans*- β -chlorovinyl ethers [7]. Investigations of Japanese workers [8,9] on the infrared spectra of crystalline polymers of deuterated propylene prepared in our Institute [10] showed that the stereospecific polymerization of propylene to isotactic polymers also proceeds exclusively by *cis*-opening of the double bond; the same is true of the polymerization of ethylene with Ziegler catalysts [11].

The apparent reasons for the *cis*-opening of the cycloolefins and of *cis*-2-butene during their copolymerization with ethylene were recently discussed in detail [5]. Our investigations have indicated that steric hindrance, which, as mentioned above, makes direct linkage of monomer units derived from cycloolefins extremely difficult and usually impossible, is of decisive importance only in cycloalkenes higher than cyclobutene. Cycloolefins with smaller rings behave differently. Following the success of American workers [12] in demonstrating that a polymer obtained by spontaneous polymerization of cyclopropene is built up of interlinked, saturated three-membered rings, we succeeded in obtaining crystalline homopolymers by stereospecific anionic coordination polymerization of cyclobutene (which does not undergo spontaneous polymerization) using vanadium catalysts [13,14]. These homopolymers have the structure of saturated polycyclobutylenes (2a); their formation has evidently been accompanied by opening of the double bond [*].

[6] G. Natta, M. Farina, M. Peraldo, P. Corradini, G. Bressan, and P. Ganis, *Rend. Accad. naz. Lincei* (8) 28, 442 (1960).

[7] G. Natta, M. Peraldo, M. Farina, and G. Bressan, *Makromolekulare Chem.* 55, 139 (1962).

[8] T. Miyazawa and Y. Ideguchi, *Polymer Letters* 1, 389 (1963).

[9] H. Tadokoro, M. Ukita, M. Kobayashi, and S. Murahashi, *Polymer Letters* 1, 405 (1963).

[10] M. Peraldo and M. Farina, *Chim. e Ind. (Milano)* 42, 1349 (1960).

[11] M. Tasumi, T. Shimanouchi, H. Tanaka, and S. Ikeda, *J. Polymer Sci. A* 2, 1607 (1964).

[12] K. B. Wiberg and W. J. Bartley, *J. Amer. chem. Soc.* 82, 6375 (1960).

[13] G. Dall'Asta, G. Mazzanti, G. Natta, and L. Porri, *Makromolekulare Chem.* 56, 224 (1962).

[14] G. Natta, G. Dall'Asta, G. Mazzanti, and G. Motroni, *Makromolekulare Chem.* 69, 163 (1963).

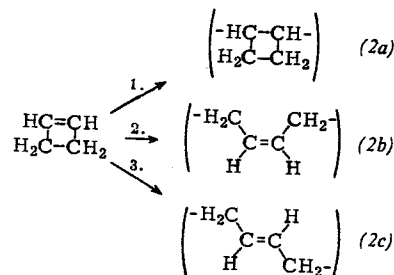
[*] According to the nomenclature adopted by the IUPAC Commission [15], polymers of this type should be referred to as poly-2-cyclobutylenamers.

The main reasons for the direct linkage of cycloolefin units during polymerization of cyclopropene and cyclobutene are probably the following:

1. In contrast to larger ring systems, both cyclopropene and cyclobutene have planar conformations. Transition to the saturated polymer (2a) enables cyclobutene to assume non planar conformations, resulting in a much larger gain in energy than in the polymerization of larger rings.

2. Steric hindrance around the doubly-bonded carbon atoms is much less in the small rings, so that effective mutual approach of the monomer molecules is appreciably easier.

Moreover, with cyclobutene we first encountered another mode of polymerization of cycloolefins [13], namely polymerization with ring cleavage, so that the monomer units in the polymer still contain the double bond. This mode of polymerization occurs preferentially in anionic coordination polymerization with catalysts based on titanium. Depending on the type of catalyst used, the products are predominantly either *cis*- (2b) or *trans*-polybutadienes (2c).



It should be pointed out in this connection that, in recent years, polymerizations accompanied by either opening of the double bond or ring cleavage have also been described for norbornene [16,17]. Its endocyclic methylene group makes this monomer a special one from both the steric and energetic points of view, and results in very high reactivity. We shall return to this case in Section IV.

Steric hindrance probably plays a much smaller part in polymerization of cyclobutene with ring cleavage than in polymerization involving opening of the double bond. For this reason, the former mode of polymerization ought to be favored. However, the opposite is in fact true. Pure polycyclobutenes can be obtained from cyclobutene, but it is impossible, even under the most favorable conditions, to convert cyclobutene into pure polybutadienes with the catalysts mentioned; this reaction is always accompanied by the formation of appreciable amounts of polycyclobutenes.

It might be supposed from the observations described above that cycloolefins higher than cyclobutene would show no significant tendency to form polymers by ring cleavage. Nevertheless, we decided to investigate the question whether higher cycloolefins, particularly cyclopentene, can homopolymerize by ring cleavage.

[15] M. L. Huggins, *J. Polymer Sci.* 8, 257 (1952).

[16] W. L. Truett, D. R. Johnson, I. M. Robinson, and B. A. Montague, *J. Amer. chem. Soc.* 82, 2337 (1960).

[17] G. Sartori, F. Ciampelli, and N. Cameli, *Chim. e Ind.* 45, 1478 (1963).

II. Attempts to Homopolymerize Cyclopentene

1. Catalysts with Anionic Coordination Reaction Mechanisms

We first carried out series of experiments in the presence of catalysts known to be suitable for the homopolymerization of ethylene and α -olefins to high molecular-weight linear polymers. To improve the expected low tendency of cyclopentene to polymerize, the experiments were carried out in the absence of solvent, and the catalyst was prepared directly in the cyclopentene itself. The results are shown in Table 1.

Table 1. Attempts to homopolymerize cyclopentene in the presence of catalysts (containing Ti, Zr, V, or Cr) with anionic coordination polymerization mechanisms (experimental conditions: 6 h at -30°C , followed by 14 h at $+20^{\circ}\text{C}$; molar ratio of cyclopentene: transition metal = 30:1; all samples undiluted).

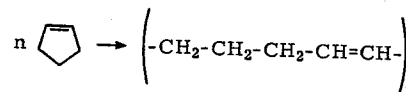
Catalyst system	Yield of polymer [%]	X-ray investigation	Chemical structure of polymer
$\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$	1	crystalline	<i>trans</i> -polypentenamer
$\text{TiBr}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$	2	crystalline	<i>trans</i> -polypentenamer
$\text{ZrCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$	1	crystalline	<i>trans</i> -polypentenamer
$\text{VCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$	1	crystalline	} alternating ethylene-cyclopentene copolymers
$\text{VOCl}_3 + \text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	3	crystalline	
$\text{V}(\text{triacac})[*] + \text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	1.5	crystalline	

[*] (triacac) = triacetylacetonate. No polymers were obtained with the catalyst systems $\text{CrBr}_3/\text{Al}(\text{C}_2\text{H}_5)_3$, $\text{Cr}(\text{triacac})/\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, and $\text{CrO}_2\text{Cl}_2/\text{Al}(\text{C}_2\text{H}_5)_3$.

The following conclusions can be drawn from the experiments:

- The behavior of cyclopentene depends largely on the transition element present in the catalyst.
- Chromium-containing catalysts do not polymerize cyclopentene.
- Vanadium-containing catalysts cannot homopolymerize cyclopentene. However, if ethylaluminum compounds are used in preparing the catalysts, the crystalline alternating cyclopentene/ethylene copolymers described above are formed. The tendency of the vanadium compounds to promote the formation of such products is evidently so strong that even the small quantities of

d) Catalysts containing a Group IV metal, e.g. titanium or zirconium, can bring about homopolymerization of cyclopentene with ring cleavage to yield (3).



As discussed in detail later, polymer (3) contains almost exclusively *trans*-double bonds. We shall term this polymer (which has not yet been described in the literature [*]) *trans*-polypentenamer, in accordance with the IUPAC nomenclature [15]. It is completely free from cyclopentene units resulting from opening of the double bond. The chemical and steric purity of the polymer (3) are the reasons for its crystallinity which can be observed to a small extent in the X-ray diagram of even the unstretched polymer.

e) However, polymerization of cyclopentene using the titanium or zirconium catalysts (Table 1) gives very low yields of *trans*-polypentenamer. This appeared to confirm our original supposition that the reactivity of cyclopentene would be very low compared with that of cyclobutene.

Despite the low conversion into polypentenamer with titanium or zirconium catalysts, it was observed with surprise that the reaction proceeded exclusively by ring cleavage. In view of the low ring strain in cyclopentene and the fact, mentioned above, that pure polybutadiene (2b)/(2c) is never obtained from cyclobutene under similar conditions, the polymer obtained from cyclopentene should also be expected to contain at best both possible forms of the monomer units. These observations led us to extend our investigations to other catalyst systems which, although they also act by an anionic coordination mechanism, are either inactive or nearly so in the homopolymerization of ethylene and α -olefins. The results are shown in Table 2. The catalyst systems contained metals of Groups VI, VII, and VIII of the periodic table. These experiments have, surprisingly, shown the following:

- Catalysts based on uranium, iron, manganese or cobalt are completely ineffective for polymerizing cyclopentene.
- Catalysts based on molybdenum or tungsten promote homopolymerization of cyclopentene into polymers with the polypentenamer structure, in high yield. These

Table 2. Attempts to homopolymerize cyclopentene in the presence of catalysts with anionic coordination polymerization mechanisms. Experimental conditions: 4 h at -30°C , followed by 14 h at 0°C ; molar ratio of cyclopentene: transition metal = 30:1; all samples undiluted. — No polymers were obtained with the catalyst systems $\text{UF}_4/\text{Al}(\text{C}_2\text{H}_5)_3$, $\text{UO}_2\text{Cl}_2/\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, $\text{MnCl}_2/\text{Al}(\text{C}_2\text{H}_5)_3$, $\text{FeCl}_3/\text{Al}(\text{C}_2\text{H}_5)_3$, $\text{CoCl}_2(\text{Py})_2/\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, and $\text{BaFeO}_4/\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$.

Catalyst system	Yield of polymer [%]	Infrared analysis of polymer		X-ray investigations	Chemical structure of polymer
		Cyclopentylene units [%]	Pentenamer units [%]		
$\text{MoCl}_5 + \text{Al}(\text{C}_2\text{H}_5)_3$	21	0	100	amorph.	<i>cis</i> -polypentenamer
$\text{WCl}_6 + \text{Al}(\text{C}_2\text{H}_5)_3$	39	0	100	cryst.	<i>trans</i> -polypentenamer

ethylene eliminated from $\text{Al}(\text{C}_2\text{H}_5)_3$ during the reaction with the vanadium salts are sufficient for the formation of the copolymer.

[*] Polymers formed to a very low extent by ring cleavage of cyclopentene, are mentioned in the patent literature; however, the double bonds in the polymers obtained show no stereoregularity.

polymers contain no monomer units formed by opening of the double bond. It is of interest that, in the homopolymerization of cyclobutene, these catalyst systems neither exhibit high catalytic activity nor yield polymers with a pure polybutadiene structure.

c) The polypentenamer obtained with the catalyst system prepared from WCl_6 and $Al(C_2H_5)_3$ has the same steric structure as that obtained with the titanium or zirconium catalysts described above, *i.e.* it is essentially pure *trans*-polypentenamer. The polypentenamer obtained in the presence of the catalyst prepared from

mainly owing to the absence of the absorption band 3.39μ , characteristic rather of cyclopentane structure. Quantitative determination of the double bonds gives almost exactly one double bond per pentenamer unit [*]. This interpretation of the infrared spectrum is sufficient to enable us to assign a *trans*-polypentenamer structure.

The infrared spectrum of the polymers obtained with the catalyst prepared from $MoCl_5$ and $Al(C_2H_5)_3$ is shown in Figure 2. The absorption bands at 7.12μ and $13.8-13.9 \mu$ can be ascribed to *cis*-double bonds. Onl

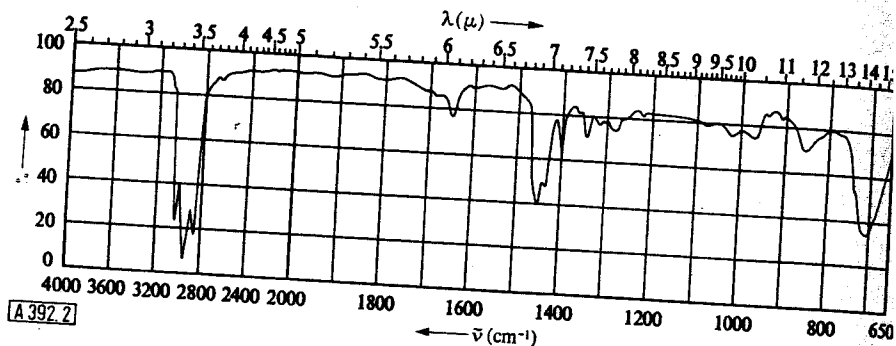


Fig. 2. Infrared spectrum of *cis*-polypentenamer (Perkin-Elmer 221 spectrophotometer; NaCl optics; film cast from benzene solution).

$MoCl_5$ and $Al(C_2H_5)_3$, on the other hand, has essentially a *cis*-polypentenamer structure. This polymer, too, has hitherto not been described in the literature. The next Section shows how the structures of the two polypentenamers were elucidated.

2. Chemical and Steric Structure of the Polypentenamers

The infrared spectra of the various polypentenamers enabled us to draw important conclusions regarding their chemical structures. It was first shown that the various polymers obtained in the presence of catalysts containing titanium, zirconium, or tungsten have practically identical infrared spectra (Fig. 1). These all show an intense absorption band at 10.35μ , characteristic of *trans*-double bonds; *cis* double bonds are present to an extent of only 2-3%. Absorption bands due to other

a small percentage of *trans* double bonds are present; other types of double bond are essentially absent. These spectra are also completely free from bands characteristic of cyclic structures. Quantitative determination again shows exactly one double bond per pentenamer unit [**]. Interpretation of the spectrum enables us to assign a *cis*-polypentenamer structure.

In order to define the chemical structure of the polymers precisely it is necessary to specify whether the monomer units are linked in a head-to-tail or a head-to-head-tail-to-tail arrangement. The polymers expected in the two cases differ in the number of methylene groups between the pairs of double bonds. In head-to-tail polymers, each consecutive pair of double bonds must be separated by three methylene groups. In head-to-head-tail-to-tail polymers, on the other hand, two

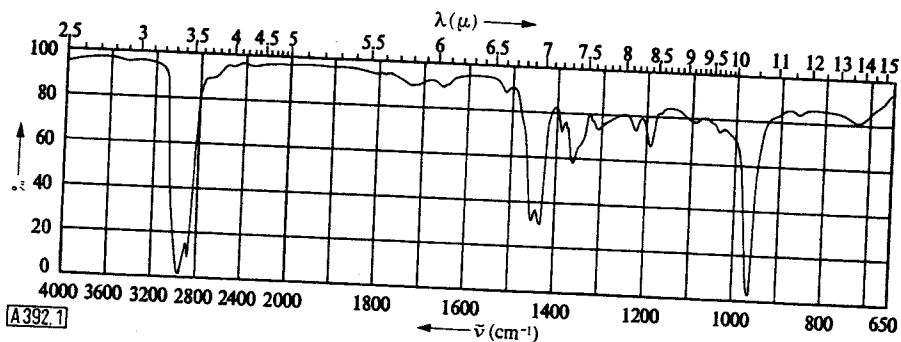


Fig. 1. Infrared spectrum of *trans*-polypentenamer (Perkin-Elmer 221 spectrophotometer; NaCl optics; film cast from benzene solution).

types of double bonds (*e.g.* vinyl, vinylidene, conjugated or other cumulative double bonds) are absent. Cyclic structures can be excluded owing to the absence of certain characteristic bands between 8 and 8.5μ , but

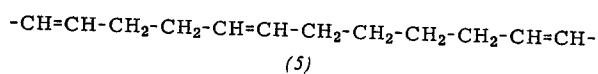
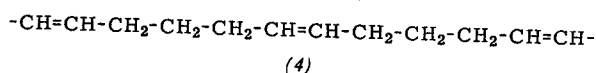
[*] The quantitative determination of the *trans*-double bonds was based on the following absorption coefficient: $K(10.35 \mu) = 10 \times 10^4$ [mole-cm²/g] [18].

[**] Quantitative determination of the *cis*-double bonds was based on the following absorption coefficient: $K(7.12 \mu) = 0.83 \times 10^4$ [mole-cm²/g] [18].

[18] D. Morero, A. Santambrogio, L. Porri, and F. Ciampelli, *Chim. e Ind.* 41, 758 (1959).

structures are possible, according to the position in which the cyclopentene ring has been opened. If the single bond adjacent to the double bond is broken, the number of methylene groups between consecutive double bonds should be alternately six and none. If the ring opens at the single bond remote from the double bond, we should find alternately two and four methylene groups between two consecutive double bonds.

Since the infrared spectrum excludes the presence of conjugated double bonds, we rejected the possibility of an alternating series of six and no methylene groups, which would correspond to a polymer with pairs of conjugated double bonds. The remaining two cases, *viz.* head-to-tail and head-to-head-tail-to-tail linkages, are shown in formulae (4) and (5), respectively.



In order to decide between these two possibilities, the *trans*-polypentenamer was ozonized in carbon tetrachloride and subjected to oxidative degradation with hydrogen peroxide. The sole degradation product from the first polypentenamer (4) should be glutaric acid, while the second polymer (5) should give equimolar amounts of succinic and adipic acids. The *trans*-polypentenamer yielded glutaric and succinic acids in a molar ratio of about 4:1, but no adipic acid [*].

In interpreting this result, it must be borne in mind that the oxidative degradation method used generally yields not only the expected acid, but also considerable quantities of the acid having one less carbon atom, as demonstrated by Ziegler et al. [19]. Degradation of the acid to the next lower homologue occurs during the treatment with hydrogen peroxide, probably by oxidation of an α -carbon atom followed by decarboxylation.

In view of this and of the fact that no adipic acid was found, it may be concluded that the polymer in question is head-to-tail *trans*-polypentenamer. Although our investigations on the *cis*-polypentenamer are not complete, we have good reason to believe that this polymer is also built up of units linked in a head-to-tail arrangement. The head-to-tail linkage was confirmed for the *trans*-polypentenamer by X-ray analysis. This polymer exhibits the behavior typical of many elastomers, particularly natural rubber: it is practically amorphous or only slightly crystalline in the unstretched state at room temperature, but on cooling or stretching it crystallizes to a considerable extent. A filament stretched to 400% elongation and cooled to about -50°C gives the spectrum of a highly oriented fiber with a large number of reflections (Fig. 3). According to this spectrum, the *trans*-polypentenamer has an orthorhombic unit cell with the following constants: $a = 7.28 \text{ \AA}$; $b = 4.97 \text{ \AA}$; c (fiber axis) $= 11.9 \text{ \AA}$.

[*] The acids were determined by thin-layer chromatography.

[19] K. Ziegler, W. Hechelhammer, H. D. Wagner, and H. Wilms, Liebig's Ann. Chem. 567, 99 (1950).

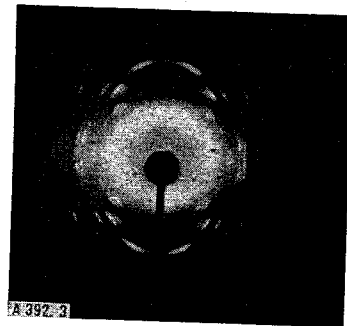


Fig. 3. X-ray fiber spectrum of the head-to-tail *trans*-polypentenamer (elongated by about 400%; temperature $\approx -50^\circ\text{C}$).

The model suggested by us for the macromolecule in the crystal lattice is shown in Figure 4. This model is characterized by a series of internal rotation angles of 120° and 240° about the single bonds adjacent to the double bond, and of 180° about all the other bonds.

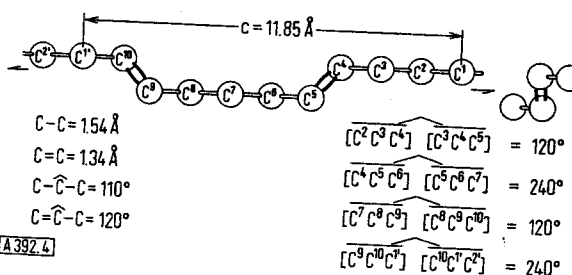


Fig. 4. Model of the crystalline *trans*-polypentenamer in side and front elevations (internal rotation angles which are not given separately are 180°).

The recurring unit contains two monomer units; the symmetry element relating them is a twofold screw axis. The identity period of 11.85 \AA calculated for this model agrees very closely with the experimental value.

Further interpretation of the fiber spectrum is possible on the basis of the unit cell described above; the most likely space group is either C_{2v}^9 or the centrosymmetric D_{2h}^{16} . The structural factors for these models agree closely with the experimental values.

III. Properties of Polyentenamers with a Head-to-Tail Structure

The polyentenamers with regular *cis*- or *trans*-double bond structures described above are soluble in aromatic, alicyclic, and chlorinated hydrocarbons, but insoluble in alcohols, aliphatic ketones, and aliphatic ethers. The intrinsic viscosity [*] may lie between about 0.3 and 10, and was found to be between 2 and 8 for most polymers investigated.

The melting point of the *trans*-polyentenamer, $+23^\circ\text{C}$, was determined by dilatometry; that of the *cis*-polyentenamer, though probably much less than 0°C , is still undetermined. In this connection, it should be recalled that the melting point of pure *trans*-polybutadiene is $+145^\circ\text{C}$, and that of pure *cis*-polybutadiene is $+2^\circ\text{C}$. Hence, as regards their melting points, it can be seen that an analogy exists between the polyentenamers

[*] The intrinsic viscosity is ten times the Staudinger viscosity z [l/g].

and polybutadienes. Chemically, the former differ from the latter in possessing an additional methylene group per monomer unit. This additional methylene group produces considerable changes in the symmetry of the macromolecule and evidently causes *inter alia*, an appreciable depression of the melting point of the two polypentenamers. The very different melting points involve considerable differences in certain physical characteristics, especially the elastomeric properties.

It is well known that *cis*-polybutadiene possesses good elastomeric properties, whereas the *trans*-isomer is a thermoplastic material, mainly owing to its very high melting point, and exhibits no elastomeric properties at room temperature, even after vulcanization. The appreciable depression of the first-order transition temperature observed on passing from the polybutadienes to the polypentenamers brings both the *trans*- and the *cis*-polypentenamer into the elastomer field. In fact, *trans*-polypentenamer possesses excellent elastomeric properties.

Preliminary analysis indicates that these properties are due both to the large number of sequences of methylene groups, which confer high flexibility on the chains, and to the fact that the melting point is close to room temperature, like that of natural rubber.

The *trans*-polypentenamer can be readily vulcanized with all the systems commonly used for unsaturated elastomers. For example, we have vulcanized *trans*-polypentenamer using recipes based on either sulfur and accelerators or sulfur donors and accelerators.

The mechanical properties of these rubbers are excellent both with and without reinforcing fillers, *e.g.* carbon black. The stress-strain curve (Fig. 5) shows that the pure gum vulcanizate (curve I) gives the strong upward curvature characteristic of rubbers (*e.g.* natural rubber) which crystallize on stretching. Vulcanizates prepared in the presence of reinforcing fillers (curve II) show excellent mechanical and dynamic properties.

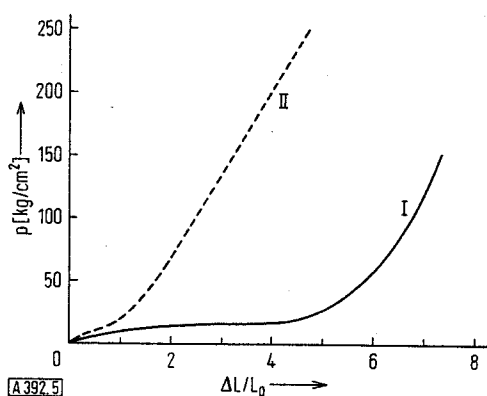


Fig. 5. Stress-strain diagram for unreinforced vulcanizates (curve I) and for rubber vulcanizates reinforced with HAF black (curve II).

Ordinate: Stress [kg/cm²].

Abscissa: Relative change in length.

The resilience [*] is shown in Figure 6 as a function of temperature. The temperature at which the rebound reaches a minimum is evidently very low. In this respect, the behavior of *trans*-polypentenamer resembles that of

[*] The resilience is defined by the relative rebound height (cosine value) of a pendulum after impact on the sample (measure of the conversion of kinetic energy into heat on impact.)

cis-1,4-polybutadiene, and differs from that of natural rubber.

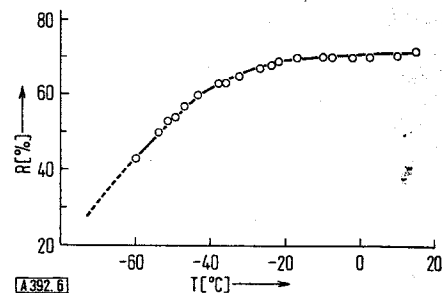


Fig. 6. Temperature-dependence of the rebound (R) of pure rubber vulcanizates.

(Micropendulum from Pirelli, S.p.A., Milan (Italy); height of fall = 0.125 mm).

IV. Observations Concerning the Mechanism of Homopolymerization of Cyclopentene with Catalyst Systems Based on Molybdenum or Tungsten

The peculiar behavior of cyclopentene in the presence of catalysts prepared from molybdenum or tungsten salts and organoaluminum compounds induced us to investigate the mechanism of these catalysts in greater detail.

The polymerization mechanism is probably of the anionic coordination type. Evidence for this is provided by the observation that the individual components from which the catalyst is prepared and which normally exhibit a cationic or classical anionic mechanism, cause practically no polymerization of cyclopentene when used alone. The same is true of other Friedel-Crafts catalysts and a catalyst which acts by a free-radical mechanism (Table 3).

Table 3. Attempts to polymerize cyclopentene in the presence of various catalyst systems with different polymerization mechanisms.

Catalyst	Solvent	Polymerization mechanism	Yield of polymer [*]
TiCl ₄	none	cationic	0
CrO ₂ Cl ₂	toluene	cationic	0
CrO ₂ Cl ₂	n-heptane	cationic	0
WCl ₆	none	cationic	slight; oil
Al(C ₂ H ₅) ₂ Cl	none	anionic	0
Al(C ₂ H ₅) ₃	none	anionic	0
CuCl ₂ + Al(C ₂ H ₅) ₃	none	free-radical	0

[*] After a reaction time of 24 h.

Another important point is to check whether any analogy exists between the mechanism of these polymerizations and that of the polymerization of aliphatic olefins (such as ethylene) in the presence of the same catalysts. For this reason, the experiments listed in Table 4 were carried out. It was found that the molybdenum and tungsten catalysts homopolymerize cyclopentene rapidly, but homopolymerize ethylene much more slowly. On the other hand, attempts to copolymerize cyclopentene with ethylene yielded no copolymers, but only homopolymers of cyclopentene, as if no ethylene had been present.

Table 4. Attempts to homopolymerize cyclopentene or ethylene and to copolymerize cyclopentene with ethylene.

Catalyst system	Monomers [a]		Conversion [moles of monomer/ moles of catalyst]	Structure of polymer
	Cyclopentene	Ethylene		
MoCl ₅ + Al(C ₆ H ₁₃) ₃	—	+	1	polyethylene
WCl ₆ + Al(C ₂ H ₅) ₂ Cl	—	+	10	polyethylene
MoCl ₅ + Al(C ₆ H ₁₃) ₃	+	—	20	<i>cis</i> -poly-pent-enamer
MoCl ₅ + Al(C ₆ H ₁₃) ₃	+	+	20	<i>cis</i> -poly-pent-enamer [b]
WCl ₆ + Al(C ₂ H ₅) ₂ Cl	+	+	30	<i>trans</i> -poly-pent-enamer [b]

[a] A minus sign indicates the absence, plus sign the presence of the monomer in question.

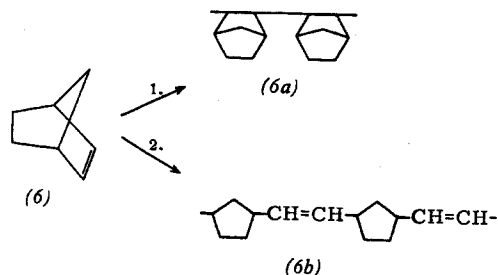
[b] The absence of ethylene units in the polypentenamer obtained from copolymerization of cyclopentene with ethylene was demonstrated using ethylene labelled with ¹⁴C.

The most likely explanation for this is that the coordination of cyclopentene to the catalytically active centers is greatly favored, *i.e.* the cyclopentene immediately occupies all active centers, so that the ethylene is unable to participate in the reaction.

As regards the position at which the cyclo-olefin ring opens during the polymerization, two possibilities arise in theory: cleavage of a single bond adjacent to the double bond, or cleavage of a single bond remote from the double bond. It is not easy to solve this problem by direct methods since, in a head-to-tail polymer, the structure of the macromolecule must be the same, irrespective of the position at which the ring opens. However, various considerations have led us to adopt the view that the cyclopentene ring opens at a single bond next to the double bond. The following two points support this view.

1. In the polymerization of norbornene (6), in the presence of catalysts acting by an anionic coordination mechanism [16], the unsaturated five-membered ring is cleaved exclusively at the single bond adjacent to the double bond. The position of cleavage in this molecule is known with certainty from the structure of

the polymer (6b). However, this ring cleavage of norbornene is due to special circumstances, since the polymer which would be formed by cleavage of the unsaturated five-membered ring at a bond not adjacent to the double bond would still contain a ring unsaturation (in the six-membered ring).



2. The double bond of cyclopentene is a *cis*-double bond. Ring cleavage at a single bond remote from the double bond would therefore be expected to yield exclusively, or at least predominantly, *cis*-polypentenamer, since this type of double bond is already present. Cleavage of a single bond next to the double bond, on the other hand, should have very little or no effect on the steric structure of the double bond in the polypentenamer, since the formation of *trans*-polypentenamer would require only isomerization of an electron pair. In this type of reaction the catalyst would probably determine the steric structure of the double bond in the growing chain. This consideration agrees with the experimental findings.

It is not easy at present to formulate a detailed reaction mechanism which explains all the observations reported above, including some others which will be reported later; however, it is hoped that this will be possible when more detailed information is available.

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