Stereospecific Polymerization of Cyclobutene

by

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SUMMARY:

The polymerization of cyclobutene in the presence of catalytic systems, prepared from transition metal compounds of the 3rd to the 8th group of the periodic table and organometallic compounds, is studied. The stereospecific polymerization to crystalline polymers having polycyclobutylene structure occurs preferably with vanadium or chromium based catalysts.

The chemical and physico-chemical structure determination and the analogies with the polymerizations of α-olefins and butadiene allow to make probable, for the two types of polycyclobutylenes, an *erythro* di-isotactic and respectively *erythro* di-syndiotactic structure.
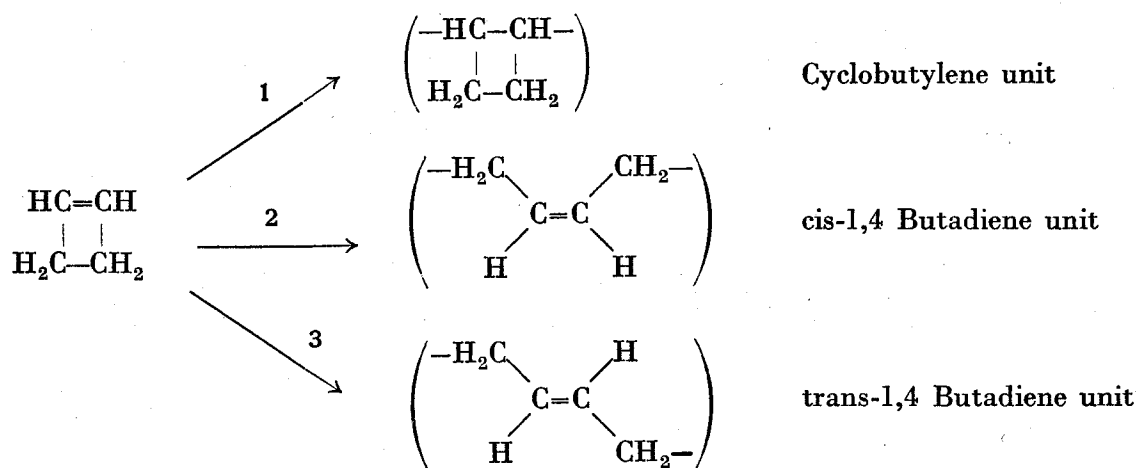
ZUSAMMENFASSUNG:

Die Polymerisation des Cyclobutens in Gegenwart von Katalysatorsystemen, die aus Übergangsmetall-Verbindungen der 3. bis 8. Gruppe des Periodensystems und metallorganischen Verbindungen hergestellt sind, wird untersucht. Die stereospezifische Polymerisation zu kristallinen Polymeren mit Polycyclobutylen-Struktur erfolgt vorzugsweise mit Katalysatoren auf Vanadium- und Chrom-Basis.

Die chemische und physikalisch-chemische Strukturermittlung und die Analogien zu den Polymerisationen der α-Olefine und des Butadiens gestatten es, für die beiden Typen von kristallinen Polycyclobutylenen *erythro*-di-isotaktische bzw. *erythro*-di-syndiotaktische Struktur wahrscheinlich zu machen.

I. *Introduction*

In a previous communication to the Editor[1] we have reported for the first time that cyclobutene can be polymerized in a stereospecific way. Suitable catalysts have been found to be some systems, prepared from transition metal salts and metalorganic compounds, belonging to the class first described by K. Ziegler[2] for the low pressure polymerization of ethylene. Depending on the particular catalytic system employed, the

cyclobutene can polymerize in three different chemical ways as illustrated in the following scheme I:

$$
\begin{pmatrix} -\text{HC}-\text{CH}- \\ \ \ \ |\ \ \ \ | \\ \text{H}_2\text{C}-\text{CH}_2 \end{pmatrix} \qquad \text{Cyclobutylene unit}
$$

$$
\text{HC}=\text{CH} \atop \text{H}_2\text{C}-\text{CH}_2
$$

1

2

3

$$
\begin{pmatrix} -\text{H}_2\text{C} \diagdown \qquad \diagup \text{CH}_2- \\ \qquad \text{C}=\text{C} \\ \diagup \qquad \diagdown \\ \text{H} \qquad\qquad \text{H} \end{pmatrix} \qquad \text{cis-1,4 Butadiene unit}
$$

$$
\begin{pmatrix} -\text{H}_2\text{C} \diagdown \qquad \diagup \text{H} \\ \qquad \text{C}=\text{C} \\ \diagup \qquad \diagdown \\ \text{H} \qquad\qquad \text{CH}_2- \end{pmatrix} \qquad \text{trans-1,4 Butadiene unit}
$$

We have also reported that reaction 1 of this scheme can distinctly yield two types of polymer, most likely formed by enchained cyclobutylene rings (polycyclobutylenamer-2 according to the nomenclature proposed by M. L. Huggins[3]), presenting marked differences in some physical properties, and in particular in the X-ray spectra.

In the present communication we describe some results of a study concerning especially two features of these polymerizations:

1. The relationship existing between the catalyst and the polymerization routes, in particular those leading to the two different polymers having polycyclobutylenamer structure.

2. The structural differences existing between these two types of polycyclobutylenamers.

II. Factors Influencing the Stereospecific Polymerizations of Cyclobutene

A. Polymerization Mechanism

In the absence of particular catalytic systems, cyclobutene is a fairly stable compound, which can be distilled and stored at room temperature for a long time, unlike cyclopropene which polymerizes spontaneously already at −80 °C.[4]. The ease with which cyclobutene polymerizes in the presence of the above mentioned catalysts acting through an anionic coordinated mechanism leads to the assumption that also other types of catalysts acting through different mechanisms could induce the polymerization of that monomer. Therefore we studied the polymerization using various catalysts acting through cationic, anionic or radicalic mechanisms.

Table 1. Polymerization of cyclobutene in the presence of catalytic systems acting through different mechanisms

Run	Catalyst	Polymerization mechanism	Temperature (°C.)	Polymer conversion (%)
1	VCl_4 + $Al(C_2H_5)_3$ (molar ratio 1:2,5)	anionic co-ordinated	−20	100
2	$TiCl_4$ + $Al(C_2H_5)_3$ (molar ratio 1:2)	anionic co-ordinated	−10	100
3	$Al(C_2H_5)_3$	anionic	−20	0
4	Li $n\text{-}C_4H_9$	anionic	−20	0
5	$Al(C_2H_5)_2Cl$	*)	−20	0
6	$AlC_2H_5Cl_2$	cationic	−20	0
7	VCl_4	cationic	−20	0
8	HCl (20%)	cationic	+20	0
9	$CuCl_2$ + $Al(C_2H_5)_3$ (molar ratio 1:3)	radicalic	−20	0

*) $Al(C_2H_5)_2Cl$ can act through anionic or cationic polymerization mechanisms depending on the monomer used.

These experiments, summarized in Table 1, prove that, among the examined catalysts, only those acting through an anionic co-ordinated mechanism and therefore being able to promote the necessary co-ordination between monomer and catalytic agent, induce the polymerization of cyclobutene. The other catalysts are unable to promote this co-ordination, and therefore they do not polymerize this monomer, not even in traces.

B. Transition Metal of the Catalysts Acting through an Anionic Co-ordinated Mechanism

We have studied a great number of catalysts acting through anionic co-ordinated mechanisms in order to establish which are more active in the cyclobutene polymerization and to find relationships between the transition metal and the type of enchainments occurring in the polymers (reactions 1, 2 or 3 of scheme I).

Catalytic systems containing transition metals of the 3rd, 4th, 5th, 6th, 7th, and 8th group of the periodic table of elements have been studied, and the results are summarized in Table 2. On the basis of these results the following conclusions can be drawn:

a) the catalytic activity of the various systems depends mostly on the transition metal;

b) the highest activities are observed in the systems containing titanium, vanadium, chromium and tungsten; systems containing molybdenum show lower activity;

Table 2. Polymerization of cyclobutene in the presence of catalytic systems acting through anionic co-ordinated mechanisms and containing transition metal compounds of the 3rd, 4th, 5th, 6th, 7th, and 8th group of the periodic table of elements. (Polymerization time generally about 20 hrs.; only the runs 12, 13, 14, and 18 were quenched after 3 hrs)

Run	Catalytic system				Solvent	Temperature (°C.)	Conversion (%)	Polymer obtained		
	Transition metal compound I	Organometallic compound II	$\frac{\text{Moles II}}{\text{Moles I}}$	$\frac{\text{Moles monom.}}{\text{Moles I}}$				Cyclobutylenic	Butadienic cis-1,4	Butadienic trans-1,4
								Monomeric units cont. (%)*)		
10	YCl_3	$Al(C_2H_5)_3$	5	7	toluene	+45	0	–	–	–
11	$3\,TiCl_3 \cdot AlCl_3$	$Al(C_2H_5)_3$	3	7	n-heptane	+45	100	40	20	40
12	$TiCl_4$	$Al(C_2H_5)_3$	2	13	toluene	−10	100	5	30	65
13	$V(acac)_3$**)	$Al(C_2H_5)_2Cl$	5	20	toluene	−50	100	100	0	0
14	VCl_4	$Al(C_2H_5)_3$	2.5	20	n-heptane	−20	100	99	0	1
15	$Cr(acac)_3$**)	$Al(C_2H_5)_2Cl$	7	7	toluene	−20	100	100	0	0
16	$MoCl_3$	$Al(C_2H_5)_3$	2.5	13	toluene	+45	3	10	60	30
17	$MoCl_5$	$Al(C_2H_5)_3$	3	7	toluene	−20	5	30	30	40
18	$MoO_2(acac)_2$**)	$Al(C_2H_5)_2Cl$	5	20	toluene	−10	55	10	45	45
19	WCl_6	$Al(C_2H_5)_3$	3	7	toluene	−20	100	40	30	30
20	UF_4	$Al(C_2H_5)_3$	3	7	toluene	−20	0	–	–	–
21	UO_2Cl_2	$Al(C_2H_5)_3$	3	7	toluene	−20	0	–	–	–
22	$MnCl_2$	$Al(C_2H_5)_3$	3	7	toluene	−20	0	–	–	–
23	$FeCl_3$	$Al(C_2H_5)_3$	3	7	toluene	−20	0	–	–	–
24	$FeCl_3$	$Al(C_2H_5)(OC_2H_5)Cl$	3	7	toluene	+25	0	–	–	–
25	$CoCl_2$	$Al(C_2H_5)_2Cl$	5	180	benzene	+25	0	–	–	–

*) Determination by means of infrared method **) (acac) = acetylacetonate.

c) among the investigated catalysts, those containing yttrium, uranium, manganese, iron or cobalt proved to be practically inactive in the polymerization of cyclobutene;

d) under these respects, the behaviour of cyclobutene resembles much more that of ethylene and alpha-olefins rather than that of the conjugated diolefins;

e) other factors (groups bound to the transition metal, metal organic compound, solvent, temperature, etc.) exert a smaller influence on the catalytic activity, on the contrary they can in many cases determine the type of enchainment of the polymers;

f) the catalytic systems based on vanadium or chromium generally polymerize cyclobutene according to reaction 1 (scheme I), yielding polycyclobutylenamers-2;

g) the catalytic systems based on titanium, molybdenum or tungsten generally polymerize cyclobutene to polymer mixtures consisting of polybutadienes-1,4 (polybutenamers) and polycyclobutylenamers-2 (reactions 1, 2, and 3 simultaneously). The high crystallinity of these polymers suggest that they are formed by mixtures of homopolymers rather than by copolymers containing the three types of monomeric units;

h) monomeric units corresponding to 1,2-enchainments of butadiene have never been observed in these polymers, not even in traces.

C. Composition of the Catalytic Systems based on Vanadium and Chromium

As previously observed[1], some catalytic systems based on vanadium polymerize cyclobutene to two different polymers both having presumably the structure of polycyclobutylenamer-2. In particular, the catalytic system obtained from vanadium tetrachloride and tri-n-hexyl aluminum yields a polymer (type 1, m.p. $\sim 210\,°C.$) which is different, especially from a crystallographic point of view, from that (type 2, m.p. $\sim 150\,°C.$) obtained using the catalytic system prepared from vanadium triacetylacetonate and diethyl aluminum monochloride (Fig. 1). The main interplanar distances (Å) resulting from the X-ray powder spectrum of annealed samples are: Type 1 polymer, d = 5.5(s); 4.04(m); 2.97(vw); 2.28 (w); 2.12(broad). Type 2 polymer, d = 9.41(m); 5.54(s); 5.03(mw); 4.02(w); 3.19(vw); 2.96(vw); 2.29(w); 2.12(broad).

From Table 2 it also results that catalytic systems based on chromium behave like those based on vanadium as to the high specificity of the reaction mechanism.

This behaviour of the said catalysts induced us to investigate whether this type of enchainment of the monomeric units is characteristic of other catalytic systems based on vanadium or chromium, independently of the groups bound to the transition metal and to aluminum and of the polymerization conditions. Another object of these investigations was to establish how these factors influence the formation of the two different types of polycyclobutylenamer-2.
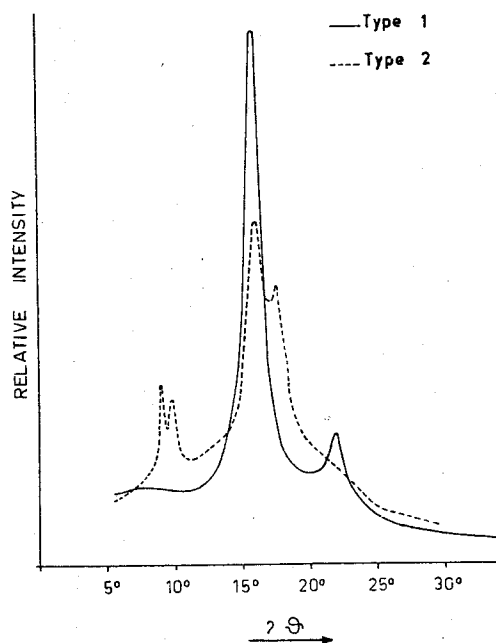

Fig. 1. Geiger-counter recorded X-ray spectrum (CuK$_\alpha$) of the two types of polycyclobutylenamers-2.

1. Soluble catalytic systems based on vanadium

The first series of experiments have been carried out employing hydrocarbon soluble catalytic systems, prepared from vanadium acetylacetonates or alkoxides and organo aluminum compounds (Table 3).

It results from these experiments that halogen must be present in the catalyst in order to obtain conversion of cyclobutene to polymers having polycyclobutylene structure. If no halogen is present, only small or no conversions are observed, and the products are constituted essentially by mixed butadiene units.

On the contrary, if halogen is present, high conversions to substantially pure crystalline polycyclobutylenes are obtained no matter if the halogen was originally bound to the vanadium or to the aluminum compound.

The valency of the vanadium in the compounds used for the catalyst preparation does not essentially affect the polymerization reaction.

A second series of experiments was carried out using hydrocarbon soluble catalytic systems prepared from acetylacetonates of vanadium and diethyl aluminum monochloride, varying the V/Al ratio, the valency of vanadium, and the polymerization temperature (Table 4).

Table 3. Polymerization of cyclobutene in the presence of soluble catalytic systems prepared from acetylacetonates and alkoxides of vanadium and organo aluminum compounds. (Polymerization time: 20 hours; solvent: toluene)

Run	Catalytic systems				Temperature (°C.)	Conversion (%)	Polymer obtained			
	Transition metal compound I	Organometallic compound II	$\frac{\text{Moles II}}{\text{Moles I}}$	$\frac{\text{Moles monom.}}{\text{Moles I}}$			Monomeric units contained*)			
							Cyclobutylenic		Butadienic	
							Type	(%)	cis-1,4 (%)	trans-1,4 (%)
26	V(acac)$_3$**)	Al(C$_2$H$_5$)$_2$Cl	5	27	−20	100	2	100	0	0
27	V(acac)$_3$	Al(C$_2$H$_5$)$_3$	10	14	−10	1	—	0	~20	~80
28	V(acac)$_3$	Al(C$_2$H$_5$)$_3$	6	14	+20	1.5	mixed butadienic units			
29	VO(acac)Cl$_2$	Al(C$_2$H$_5$)$_3$	2.5	7	−20	90	1	90	traces	10
30	VO(OC$_4$H$_9$)$_3$	Al(C$_2$H$_5$)$_2$Cl	5	7	−20	100	2	90	0	10
31	VO(OC$_4$H$_9$)$_3$	Al(C$_2$H$_5$)$_3$	2.5	7	−20	15	mixed butadienic units			

*) Determination by means of infrared method.   **) (acac) = acetylacetonate.

Table 4. Polymerization of cyclobutene in the presence of soluble vanadium acetylacetonates/diethyl aluminum monochloride catalytic systems. (Polymerization time: 20 hours; solvent: toluene)

Run	Catalytic systems				Temperature (°C.)	Conversion (%)	Polymer obtained			
	Transition metal compound I	Organometallic compound II	$\frac{\text{Moles II}}{\text{Moles I}}$	$\frac{\text{Moles monom.}}{\text{Moles I}}$			Monomeric units contained*)			
							Cyclobutylenic		Butadienic	
							Type	(%)	cis-1,4 (%)	trans-1,4 (%)
32	V(acac)$_3$**)	Al(C$_2$H$_5$)$_2$Cl	5	27	−20	100	2	100	0	0
33	V(acac)$_3$	Al(C$_2$H$_5$)$_2$Cl	50	270	−20	35	2	100	0	0
34	V(acac)$_3$	Al(C$_2$H$_5$)$_2$Cl	5	20	−50	100	2	100	0	0
35	VO(acac)$_2$	Al(C$_2$H$_5$)$_2$Cl	5	7	−20	70	2	95	0	5

*) Determination by means of infrared method.   **) (acac) = acetylacetonate.

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Under all conditions, substantially pure high crystalline polycyclo-butylenes type 2 (as previously denominated) were obtained. The variation of the temperature does not affect either the conversion or the specificity of the reaction. On the contrary, the use of high V/Al ratios (keeping constant the monomer/Al ratio) markedly reduces the catalytic activity, but has no effect on the specificity. Catalysts obtained starting from acetylacetonate of trivalent vanadium generally exhibits higher specificity and higher activity than those obtained from tetravalent or pentavalent vanadium.

Assessed that all examined soluble catalytic systems which originally contained halogen only in the organo aluminum compound ($Al(C_2H_5)_2Cl$) yield exclusively type 2 polycyclobutylenes, we have studied how the simultaneous presence of chlorine atoms in the transition metal and in the organo aluminum compound affects the stereospecificity of the polymerization. We have therefore examined a series of catalytic systems prepared from diethyl aluminum monochloride and vanadyl compounds containing an increasing number of chlorine atoms (Table 5). One observes that, when the number of chlorine atoms bound to the vanadyl compound exceeds that of those bound to the aluminum compound, a shift occurs from type 2 to type 1 polycyclobutylenes.

Table 5. Polymerization of cyclobutene in the presence of vanadium catalysts: dependence of polymerization mechanism on halogen content of vanadium compound. (Polymerization time: 20 hours; solvent: toluene; temperature: $-20\,^{\circ}C$.; monomer/vanadium molar ratio: 7; Al/V molar ratio 5; Al-compound: $Al(C_2H_5)_2Cl$)

Run	Transition metal compound in catal. system	Conversion (%)	Polymer obtained			
			Monomeric units contained [*]			
			Cyclobutylenic		Butadienic	
			Type	(%)	cis-1,4 (%)	trans-1,4 (%)
36	$VO(acac)_2$ [**]	70	2	95	0	5
37	$VO(acac)_2Cl$	83	2	100	0	0
38	$VO(acac)Cl_2$	80	1	100	0	0
39	$VOCl_3$	95	1	100	0	0

[*] Determination by means of infrared method; [**] (acac) = acetylacetonate.

Though the presence of halogen strongly influences the polymerization mechanism, as shown in Tables 3 and 5, we do not know if the effect just discussed is really connected with the relative number of halogen atoms present in the two components of the catalytic system. In fact, such

change of the type of stereospecificity could also be ascribed to a lower degree of homogeneity of the catalytic systems: those composed by VO(acetylacetonate)$_3$ or VO(acetylacetonate)$_2$Cl and Al(C$_2$H$_5$)$_2$Cl are almost certainly homogeneous, while the homogeneity of those containing VO(acetylacetonate)Cl$_2$ or VOCl$_3$ and Al(C$_2$H$_5$)$_2$Cl is not sure.

However, opportunity arises to state that in other systems containing halogen atoms in both the components of the catalyst the change of the stereospecificity easily occurs (e.g. using different solvents or V/Al ratios).

2. Heterogeneous catalytic systems based on vanadium halides

When using vanadium chlorides combined with trialkyl aluminum, only one type of polymerization reaction occurs: all polymers having cyclobutylene structure are of type 1, independently of the valency of the vanadium compound used, of the alkyl groups bound to the organo aluminum compound, of the solvent, and of the temperature (Table 6). However, the most heterogeneous one among these systems (VCl$_3$ + Al(C$_2$H$_5$)$_3$) exhibits only very low activity and, when increasing it by raising the temperature, considerable amounts of polymers having polybutadiene structure are formed together with those having polycyclobutylene structure. This fact is consistent with the observation that, when the polymerization mechanism 1 (scheme I) is not favoured by the catalyst (see also Table 3), the reaction more easily turns over to routes 2 or 3.

We can conclude that in all cases in which the halogen was originally contained only in the organo aluminum compound, the polycyclobutylenes obtained are exclusively type 2, whereas in all cases in which the halogen was originally bound only to the vanadium compound, they are exclusively type 1. Later on we shall try to correlate these observations with the type of stereoregularity involved in these polymerizations.

3. Catalytic systems based on chromium

The results of the cyclobutene polymerization in the presence of chromium based catalysts (Table 7) are, under many aspects, analogous to those obtained in the presence of those based on vanadium. Also in this case polycyclobutylenes are formed only if the catalyst contains halogen atoms, otherwise the conversion is comparably low, and the polymers are made up by butadiene units.

The most heterogeneous systems (runs 47 and 48) show very low activity. However, reducing the heterogeneity by complexation of the chro-

Table 6. Polymerization of cyclobutene in the presence of heterogeneous catalytic systems prepared from vanadium halides and trialkyl aluminum. (Polymerization time generally: 20 hours; however, run 40 and 45 were quenched after 3 hours and run 41 after 40 hours)

Run	Catalytic systems				Solvent	Temperature (°C.)	Conversion (%)	Polymer obtained			
	Transition metal compound I	Organometallic compound II	$\dfrac{\text{Moles II}}{\text{Moles I}}$	$\dfrac{\text{Moles monom.}}{\text{Moles I}}$				Monomeric units contained *)			
								Cyclobutylenic		Butadienic	
								Type	(%)	cis-1,4 (%)	trans-1,4 (%)
40	VCl_3	$Al(C_2H_5)_3$	2.5	20	n-heptane	−10	0	—	—	—	—
41	VCl_3	$Al(C_2H_5)_3$	2.5	14	n-heptane	+45	19	1	80	0	20
42	VCl_4	$Al(C_2H_5)_3$	2.5	7	n-heptane	−20	100	1	99	0	1
43	VCl_4	$Al(n-C_6H_{13})_3$	2.5	20	n-heptane	−50	100	1	97	0	3
44	VCl_4	$Al(n-C_6H_{13})_3$	2.5	14	n-heptane	+20	100	1	95	0	5
45	VCl_4	$Al(C_2H_5)_3$	2.5	14	toluene	−20	77	1	99	0	1
46	$VOCl_3$	$Al(C_2H_5)_3$	3	7	toluene	−20	90	1	90	0	10

*) Determination by means of infrared method.

Table 7. Polymerization of cyclobutene in the presence of catalytic systems based on chromium. (Polymerization time: 20 hours; monomer/Cr ratio: 7; solvent: toluene; temperature: −20 °C., in run 48 +45 °C.)

Run	Catalytic system			Con-ver-sion (%)	Polymer obtained			
	Transition metal compound I	Organo-metallic compound II	$\dfrac{\text{Moles II}}{\text{Moles I}}$		Monomeric units contained[a]			
					Cyclobutylenic Type	(%)	Butadienic	
							cis-1,4 (%)	trans-1,4 (%)
47	$CrBr_3$	$Al(C_2H_5)_3$	3	0	—	—	—	—
48	$CrCl_3$	$Al(C_2H_5)_2Cl$	3.5	1	1 (impure)	95	0	5
49	$CrCl_3 \cdot 3\,PYR$ [b]	$Al(C_2H_5)_3$	3	75	1	80	0	20
50[c]	CrO_2Cl_2	$Al(C_2H_5)_2Cl$	5	100	1	100	0	traces
51	CrO_3	$Al(C_2H_5)_2Cl$	7	0	—	—	—	—
52	$Cr(acac)_3$ [d]	$Al(C_2H_5)_3$	2.5	37	—	0	30	70
53	$Cr(acac)_3$	$Al(C_2H_5)_2Cl$	7	100	1	100	0	traces

[a] Determination by means of infrared method
[c] catalyst preparation at −78 °C.

[b] PYR = pyridinate
[d] (acac) = acetylacetonate

mium trihalides with pyridine, the activity of the resulting catalytic system rises greatly (run 49).

In contrast to the behaviour of chlorine in the vanadium based catalysts, in the catalysts based on chromium, it is of no importance for the polymerization mechanism if the halogen was originally bound to the transition metal or to the aluminum compound. Indeed, whenever formed, polycyclobutylenes are of type 1. This feature presents a certain analogy to the behaviour of chromium based catalysts in the stereospecific polymerization of butadiene[5]. Such catalysts show the tendency to promote the formation of isotactic polybutadiene-1,2.

III. Structure of the Polycyclobutylenes

In analogy with the results obtained in the copolymerization of higher cycloolefins (cyclopentene, cycloheptene) with ethylene in the presence of catalysts acting through anionic co-ordinated mechanisms[6] we can assume that the stereospecific homopolymerization of cyclobutene exclusively occurs with cis opening of the double bond. Moreover, let us assume that the two types of crystalline polycyclobutylenes obtained have the same chemical structure and that they differ only in the configuration of their tertiary carbon atoms of the main chains (see the

examination of the two types of polymer hereinafter). Then we must conclude that one of the two polymers is *erythro* di-isotactic and the other *erythro* disyndiotactic [*)].

erythro   diisotactic

erythro   disyndiotactic
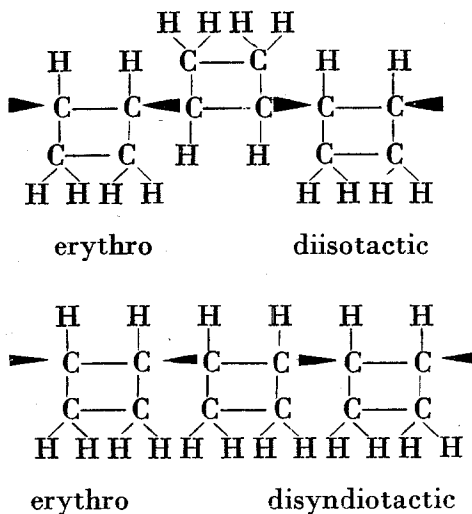
A definitive assignment of the steric structure to the two types of polymers under examination can be made only when it will be possible to determine their X-ray structures. However, we must attribute the difference between type 1 and type 2 polycyclobutylenes to differences in the steric structures, since we succeeded in demonstrating with sufficient evidence, as it will be described hereinafter, the identical chemical structure of the two types of polymers. Considering the nature of the catalysts giving rise to the formation of the two types of polymers and the analogies with the polymerization of α-olefins we are since now inclined to attribute an *erythro* di-isotactic structure to the polycyclobutylenamer-2 of type 1 and an *erythro* di-syndiotactic one to that of type 2.

Among these analogies, which suggest these attributions, the most important ones are:

1. the formation of isotactic polypropylene is highly favoured by the presence of heterogeneous catalysts, analogously to what occurs for the type 1 polycyclobutylene;

2. the formation of syndiotactic polypropylene is favoured by soluble or highly dispersed catalysts, in particular by those based on vanadium [10]; analogously polycyclobutylene type 2 is preferably formed under such conditions;

[*)] We prefer the terms *threo* and *erythro* [7, 8], in order to describe the relative steric structure of two adjacent main chain carbon atoms belonging to the same ring, to those of *trans* and *cis*, recently proposed [9], because the latter would require an own terminology for any type of enchained rings constituting a polymer chain and would not allow to distinguish between saturated and unsaturated polymers.

3. low transition metal/organometallic compound molar ratios favour the formation of syndiotactic polypropylene and of type 2 polycyclobutylene;

4. the polymerization of butadiene to isotactic polymer occurs almost exclusively in the presence of certain chromium based catalysts; analogously, said catalysts exclusively promote the formation of type 1 polycyclobutylenes with very high stereospecificity.

The analogies just pointed out show how the comprehension of the various mechanisms of olefinic polymerization of cyclobutene can be useful in order to better understand the more general mechanism of stereospecific polymerization of the α-olefins, owing to the high stereoregularity and to the high polymerization rate generally presented by this monomer in the isotactic as well as in the syndiotactic polymerization routes.

A. *Physico-chemical Examinations*

Since it had not yet been possible to obtain oriented fibres from the polymers having polycyclobutylene structure, we had to limit our X-ray measurements to establish whether the two types of polymers are two sterically different forms or else whether they represent two crystalline modifications of the same polymer.

On this purpose we subjected the two types of polymers to several cycles of melting and re-crystallization (even under pressure). After such treatments the crystalline structure of the starting polymer always re-appears, without any possibility to transform one of the two forms into the other. This demonstrates that they are not two modifications of the same polymer, but two chemically or configurationally different forms.
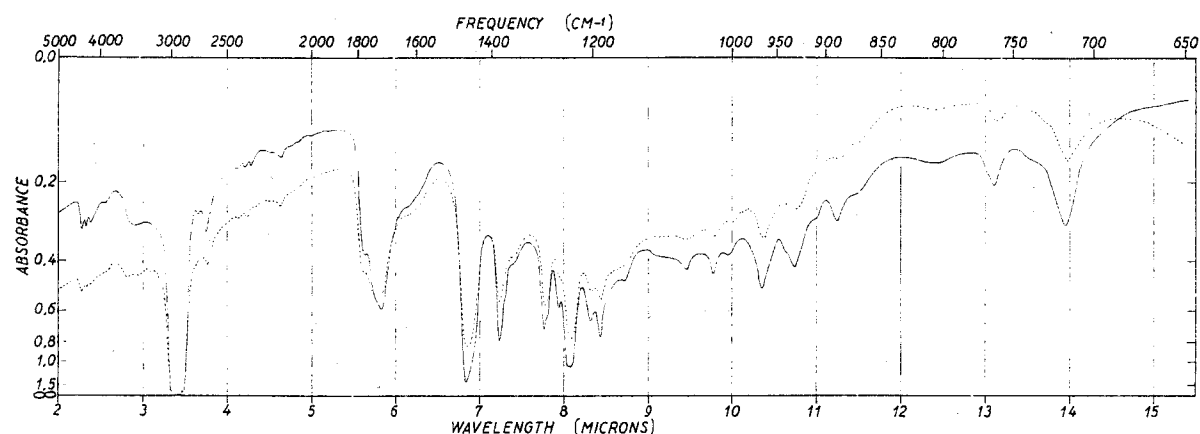

Fig. 2. Polycyclobutylene Type 1. (—): Crystalline in Nujol, 30 °C.; (---): Partially melted in Nujol, 200 °C.

These results have been confirmed also by the I. R. absorption spectra. Moreover, the spectra of the two types of polymer differ somewhat also in the molten state (Fig. 2 and 3).
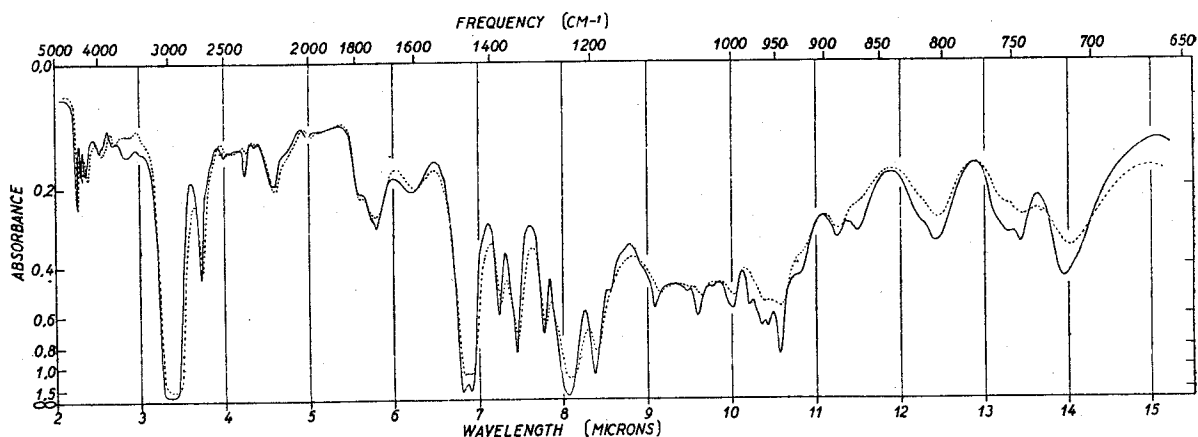

Fig. 3. Polycyclobutylene Type 2. (—): Crystalline, 30 °C.; (---): Melted, 150 °C.

The most characteristic differences concern the presence of one band at 8,43 μ in the polycyclobutylene of type 2 and two at 8,33 and 8,45 μ in the polycyclobutylene of type 1. Moreover, the I.R. examination allows to state that both types of polymer essentially consist of polycyclic hydrocarbons (bands at 3,78 μ and at 8,12 μ and lack of bands characteristic of other structures). However, a band attributable to methyl groups (7,28 μ) is present (more intense in the polymer of type 2 having a rather low molecular weight), but it is caused very likely by end groups most probably deriving from the catalyst.

The N.M.R. spectrum of type 2 polycyclobutylene (in hexachlorobutadiene) exhibits two intense bands at about 210 cps. from the reference one of benzene and at about 29 cps. from the previous one. The intensity ratio between these two bands is 2:1; since the former can surely be attributed to CH_2 groups in ring, and the latter to CH groups in ring, the only possibly valid structure is that proposed by us. Other bands are absent, especially those attributable to open-chain structures, except a third weak band attributable to the already mentioned methyl end groups.

B. *Chemical Structure*

The elementary analysis of the two types of polymers is in agreement with the chemical structure proposed:

$(C_4H_6)_n$ (54,05)$_n$ \..lcd. C 88.8 H 11.2

Type 1 Found C 87.2 H 11.2

Type 2 Found C 87.6 H 11.1

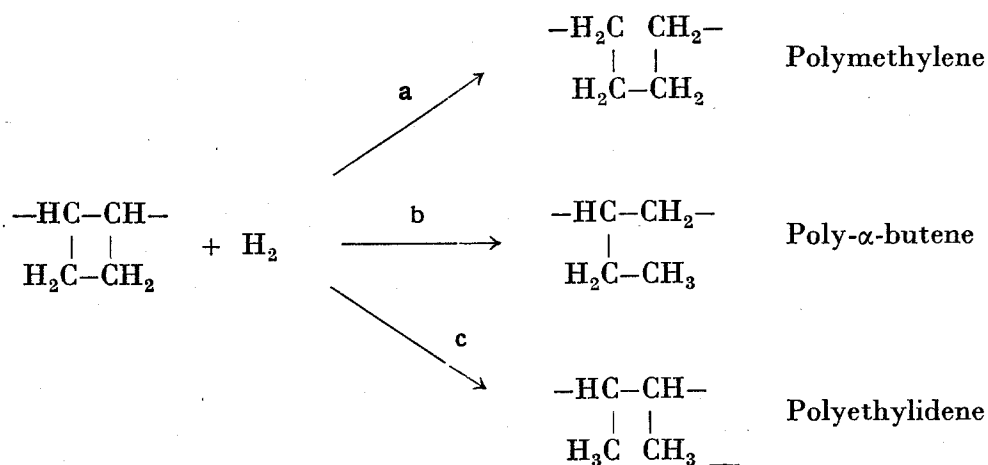We have also tried a chemical characterization of the two polymers by subjecting them to a catalytic hydrogenolysis (20 hrs., 170 °C., RANEY-Nickel, 180 at H_2, in cyclohexane). Both types of polycyclobutylenes have given practically the same reaction products, thus indicating the same chemical structure. The following reaction products have been obtained, e.g. for the type 2 polycyclobutylenes:

A solid fraction (30 % of the starting polymer), insoluble in diethyl ether, essentially consisting of the starting product, but with reduced degree of crystallinity.

An oily fraction (50 % of the starting polymer), soluble in diethyl ether and consisting, as revealed by I.R. analysis, of a copolymer formed by methylene sequences (band at 13,9 μ) and by ethylidenic groups (band at 7.28 μ) in almost equal amounts.

The appearance of these two groups, together with the absence of branchings higher than methyl, indicates that the hydrogenolysis of the polymer, which could have taken the three following routes:

$$
\begin{array}{ccc}
 & & \begin{matrix} -H_2C & CH_2- \\ | & | \\ H_2C & -CH_2 \end{matrix} \quad \text{Polymethylene} \\[2em]
\begin{matrix} -HC-CH- \\ | \quad | \\ H_2C-CH_2 \end{matrix} + H_2 \xrightarrow{\;\;b\;\;} & \begin{matrix} -HC-CH_2- \\ | \\ H_2C-CH_3 \end{matrix} \quad \text{Poly-}\alpha\text{-butene} \\[2em]
 & & \begin{matrix} -HC-CH- \\ | \quad | \\ H_3C \quad CH_3 \end{matrix} \quad \text{Polyethylidene}
\end{array}
$$

(routes a, b, c as shown)

Actually only mechanisms (a) and (c) occurred. This does not prove completely the structure proposed by us, but it is in agreement with it.

Milder hydrogenolysis conditions (150 °C) are more specific; in fact, only ethylidenic units are formed according to mechanism (c). However the rate is low, so that after 40 hrs. only 10 % of the polymer is converted.

IV. Conclusions

The polymerization of cyclobutene has been proved to occur through anionic co-ordinated mechanisms. Active catalysts are those prepared by reaction of titanium, molybden, tungsten, vanadium, and chromium

compounds with organometallic compounds. Catalytic systems based on the first three transition metals generally promote the formation of polymer mixtures containing cyclobutylenic, butadienic cis-1,4, and trans-1,4 units. In the presence of vanadium or chromium based catalysts, on the contrary, nearly always crystalline polymers having polycyclobutylene structure are formed.

The presence of halogen in the latter catalytic systems has proved to be necessary in order to obtain these polymers. Moreover, it is important which of the two components of the catalytic system the halogen was originally bound to. This feature is determining for the type of stereospecificity (isotactic or syndiotactic) which regulate the course of the polymerization.

Heterogeneous catalysts having high chlorine content in the transition metal compound and no halogen in the organometallic compound promote exclusively formation of type 1 polycyclobutylene, whereas soluble catalysts containing halogen only in the organoaluminum compound induce polymerization exclusively to type 2 polycyclobutylenes.

The two types of crystalline polycyclobutylenes differ in the steric structure. Considering the nature of the catalysts used and the analogies with the polymerizations of α-olefins and butadiene, it was possible to propose the attribution of an *erythro* di-isotactic structure to type 1 and of an *erythro* di-syndiotactic to type 2 polycyclobutylene.

V. *Experimental*

Typical polymerization procedure

The polymerization is carried out in a three-necked reaction vessel, fitted with machanical stirrer, nitrogen inlet, and dropping funnel with cooling jacket. The apparatus is swept with dry nitrogen, and 40 ml. of pure solvent and 1 mM of transition metal compound are introduced. The vessel is cooled to polymerization temperature and the organometallic compound is added slowly with stirring. A solution of 1 ml. (14 mM) of cyclobutene in 10 ml. of the same solvent, cooled to about the polymerization temperature, are added slowly (5 min.) from the funnel into the stirred catalytic mixture. The reaction mixture is maintained during 20 hrs. under stirring at the polymerization temperature.

The reaction mixture is then introduced into 250 ml of methanol containing 1 ml. of conc. HCl and a little quantity of phenyl-β-naphthyl amine. The precipitated polymer is rinsed with methanol and dried at reduced pressure.

Procedure for higher polymerization temperatures

The runs requiring polymerization temperatures above +10 °C. are carried out in a Carius tube, sealed, after the introduction of all the components at −78 °C., and rocked in a thermostatic bath.

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