

~~383~~

389

Sonderdruck aus

DIE MAKROMOLEKULARE CHEMIE

Band XLIV–XLVI

1961

Seite 537–549

Crystalline Polymers of Dialkyl Ketenes

by

G. NATTA, G. MAZZANTI, G. F. PREGAGLIA, and M. BINAGHI

DR. ALFRED HÜTHIG VERLAG GMBH · HEIDELBERG

From the Istituto di Chimica Industriale del Politecnico, Milan (Italy)

Crystalline Polymers of Dialkyl Ketenes

By G. NATTA, G. MAZZANTI, G. F. PREGAGLIA, and M. BINAGHI

(Eingegangen am 5. Dezember 1960)

SUMMARY:

In the polymerization of the ketenic compounds, either the opening of the >C=C< ethylenic double bond or of the >C=O carbonyl double bond can occur.

By using cationic catalysts, such as aluminum bromide, and catalysts which generally act with an anionic mechanism, constituted by metallorganic compounds, such as triethylaluminum dimethylketene polymers which appear crystalline by means of X-ray examination have been prepared.

Two types of crystalline polymers having different chemical structures have been isolated by fractionating extraction with suitable solvents. It has been observed that one type or the other prevails according to the type of catalysts employed.

One of the crystalline polymers prepared by us, has a β -ketonic structure, and it is produced by opening of the ethylenic double bond present in the monomer. The other crystalline polymer has the structure of the polyester type, and is formed by the alternate addition of one monomeric unit formed by the opening of the ethylenic bond and of another unit formed by the opening of the carbonyl bond.

For both these polymers, the physical properties have been reported, and the degradation reactions which allows the determination of their chemical structures are described.

ZUSAMMENFASSUNG:

Bei der Polymerisation von Ketenen kann sich entweder die äthylenische Doppelbindung >C=C< oder die der Carbonylgruppe >C=O öffnen. Mit kationischen Katalysatoren wie Aluminiumbromid und anionischen Katalysatoren wie metallorganischen Verbindungen z. B. Triäthylaluminium, wurden Polymere aus Dimethylketen dargestellt, die nach den Röntgenuntersuchungen kristallin sind.

Durch fraktionierende Extraktion mit geeigneten Lösungsmitteln konnten zwei Arten der kristallinen Polymeren mit einer unterschiedlichen chemischen Struktur isoliert werden.

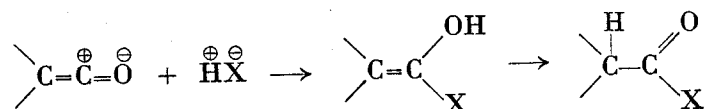
Das eine der von uns hergestellten Polymeren besitzt eine β -Keto-Struktur und bildet sich durch Öffnung der Äthylendoppelbindung des Monomeren. Das andere kristalline Polymere hat die Struktur eines Polyesters und entsteht durch eine alternierende Addition der Monomereinheiten, die einmal durch Öffnung der Äthylendoppelbindung und ein anderes Mal durch Öffnung der Carbonylbindung gebildet werden.

Für beide Polymerarten werden die physikalischen Eigenschaften angegeben. Die Abbaureaktionen, die die chemische Struktur bestimmen, werden beschrieben.

Considerations on the Polymerization of 1,2-Dienoid Monomers

From the different research works which are now performed in this Institute, we have decided to deal here with the preparation of crystalline high polymers of ketenes, since this problem seems particularly appropriate to appear in this special issue of *Makromolekulare Chemie*, dedicated to Professor STAUDINGER, who is considered both the discoverer of ketenes and the founder of macromolecular chemistry. This topic is particularly interesting because it proves that in the case of ketenes, the choice of suitable polymerization conditions can cause at will the formation of different polymers having completely different chemical structures and properties.

The substances containing two double bonds in the molecule, especially those having such bonds in an adjacent position, even if between atoms possessing the same electronegativity, show a particularly high reactivity. The ketene compounds, because of the presence of an olefinic bond joined to a carbonylic one, show an even higher reactivity and they react rapidly both with polar and non polar molecules. The non polar compounds add themselves preferably to the >C=C< double bond, the polar ones to the >C=O double bond. In practice, however, in many reactions, the products of initial addition on the carbonyl, owing to their enolic nature, are re-transformed into carbonyl compounds:



(where HX indicates a compound containing a prevailing polar bond). It is, therefore, obvious that the first products formed in the addition reaction on the carbonyl group cannot be detected in the obtained final compound.

Final products, in which a keto-enolic rearrangement is not possible any more, because the structural unit is kept in the initial addition form, can be foreseen only for a polymerization.

Even if a great number of researches have been made on ketene, only low molecular weight compounds have been isolated up to now by polymerization, as shown in Table 1. Moreover, HURD³⁾, by reacting ketene with *n*-butyl- or phenylmagnesium bromide at -78°C ., succeeded in isolating a yellow, spongy solid product which, by hydrolysis, gave a viscous rubber-like substance, whose nature was not identified.

¹⁾ F. CHICK and N. T. M. WILSMORE, *J. chem. Soc. [London]* **93/94** (1908) 946.

²⁾ H. STAUDINGER, *Helv. chim. Acta* **8** (1925) 306.

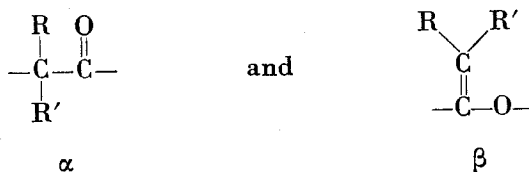
³⁾ CH. D. HURD, A. D. SWEET, and CH. L. THOMAS, *J. Amer. chem. Soc.* **55** (1933) 335.

Crystalline Polymers of Dialkyl Ketenes

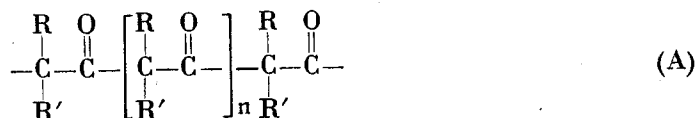
Table I. Polymerization products of ketene previously described

Polymerization Conditions	Product Obtained	Ref.
0–50 °C., without any catalyst	$\begin{array}{c} \text{CH}_3-\text{C}=\text{CH} \rightleftharpoons \text{CH}_2=\text{C}-\text{CH}_2 \\ \text{O}-\text{CO} \qquad \qquad \text{O}-\text{CO} \end{array}$	1)
70–120 °C., using pyridine as catalyst . . .	$\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \diagup \quad \diagdown \\ \text{CH} \quad \text{CH}-\text{COCH}_3 \\ \diagdown \quad \diagup \\ \text{CH}_3-\text{C} \quad \text{C}=\text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$	1)
–78 °C., in acetone solution	$(\text{C}_2\text{H}_2\text{O})_4$	2)

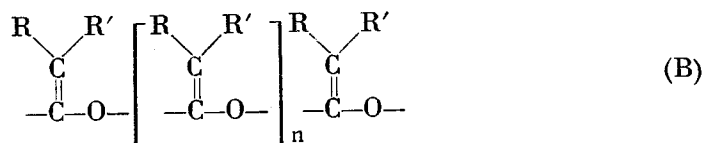
In a hypothetical linear and regular polymerization for linear polymers of any ketenic $\text{RR}'\text{C}=\text{C}=\text{O}$ compound, where R and R' may be either hydrogen atoms, or alkyl or aryl groups, two fundamental structural units are possible:



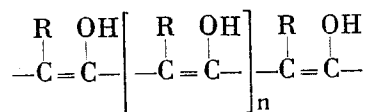
The regular head-to-tail enchainment of α -monomeric units should give origin to macromolecules having a β -ketonic structure:



By head-to-tail enchainment of the β -units, a polyacetalic structure would be formed:

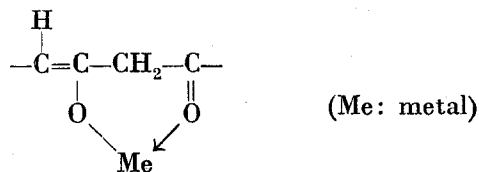


When R or R' (or both) are hydrogen atoms, the structure of the (A) type should be in equilibrium with the corresponding enolic structure:



First we made in some preliminary tests the following experiments with ketene: using FRIEDEL-CRAFTS type catalysts, such as AlCl_3 , ZnCl_2 , etc. or metallorganic compounds such as $\text{Al}(\text{C}_2\text{H}_5)_3$, LiC_4H_9 and $\text{Zn}(\text{nC}_4\text{H}_9)_2$,

whereby polymeric substances were isolated in which the metal atoms were bound in a rather stable way, with formation of chelates of the type:



This causes the deactivation of the catalyst during the polymerization of this monomer, and explains the low conversion yields, obtained by us using the above-mentioned catalysts.

In order to avoid the formation of chelates of this type, we considered it convenient to study the polymerization of ketoketenic monomers. In fact, in such a case, the lack of hydrogen atoms in the main chain of the polymer "a priori" prevents the formation of the above-indicated chelating structures.

In particular, dimethylketene has been examined, the first ketoketene of the series, because its synthesis is easier, and because of the high reactivity observed by STAUDINGER and co-workers⁴⁾, for the dimerization rate with respect to the higher homologues. In fact, the dimerization rate decreases with the increase in bulkiness of the alkyl groups bound to the ethylenic carbon atom.

In the literature only few remarks concerning the preparation of high polymers of dimethylketene can be found. STAUDINGER²⁾ observed that solutions of dimethylketene rapidly polymerize if traces of $\text{N}(\text{CH}_3)_3$ are added at -80°C ., with formation of polymers, which are transformed into the monomer at temperatures ranging from 100 to 200°C .

The polymers of dimethylketene, thus obtained, do not possess a regular chemical structure. In fact, STAUDINGER found that both the (α) and (β) monomeric units, enchainned in an irregular way, were present. The results obtained with this catalyst, have been confirmed by us, by the X-ray examination which gives a diffraction spectrum corresponding to an amorphous structure. By using different types of catalysts, we succeeded in obtaining crystallizable polymers having a regular structure.

Catalytic systems having different specificity

On the basis of the results obtained by us in the field of stereoregulated polymerizations which also require a chemical regularity of the polymer, we were led to employ particular catalysts acting with an ionic mechanism.

⁴⁾ H. STAUDINGER, H. SCHNEIDER, P. SCHOTZ, and P. M. STRONG, *Helv. chim. Acta* 6 (1923) 291.

In addition we had to operate at low temperatures, in order to avoid undesired reactions, also in the case of the polymerization of dimethylketene.

Furthermore, the possibility of promoting a regular polymerization of dimethylketene, by using substances which usually give free radicals, seemed rather improbable. This is also in agreement with what indicated by E. MÜLLER⁵⁾ about the impossibility of polymerizing ketene by free radicals initiators.

The presence of a carbonyl group in the macromolecule suggested to us a similarity with the polymerization of aliphatic aldehydes, which was recently studied by some of us⁶⁾ and by other authors⁷⁾ using catalysts acting through a mechanism of an ionic type.

We have, therefore, studied the polymerization of dimethylketene in the presence of catalysts which can be grouped in two main classes:

1) acidic substances in many cases acting with a cationic mechanism having the general formula: AlX_nR_{3-n} , where X is a halide, R an alkyl or aryl radical, n is an integer ranging from 1 to 3.

2) Substances usually acting with an anionic mechanism, constituted by metallorganic compounds of very electropositive metals of small ionic diameter, such as $Al(C_2H_5)_3$, $Be(C_2H_5)_2$, LiC_2H_5 , etc.

Using catalysts belonging to both these classes, we succeeded in the polymerization of dimethylketenes. On the contrary, using metallorganic compounds which do not correspond to the above-indicated definitions and constituted by some LEWIS bases, such as trimethylantimony, polymers having structures and properties similar to the products prepared by STAUDINGER in the presence of amines were obtained. In fact, $Sb(CH_3)_3$ polymerizes dimethylketene very quickly at $-78^\circ C.$, forming a white, hornlike polymer which proved to be amorphous at X-ray examination.

In Table II are reported some results obtained in the polymerization of dimethylketene in the presence of different catalysts resulting in the formation of amorphous or crystalline polymers. We have generally observed a far lower polymerization rate in the cases in which a crystalline polymer was produced.

As far as the polymerization conditions are concerned, we have generally kept the temperature below $0^\circ C.$ in order to avoid a remarkable

⁵⁾ E. MÜLLER, *Neuere Anschauungen der Organischen Chemie*, Verlag Springer, Berlin-Göttingen-Heidelberg 1957, p. 292.

⁶⁾ G. NATTA, G. MAZZANTI, P. CORRADINI, P. CHINI, and I. W. BASSI, *Atti Accad. naz. Lincei* (8), **28** (1960) 8.

⁷⁾ J. FURUKAWA, T. SAEGUSA, H. FUJII, A. KAWASAKI, H. IMAI, and Y. FUJII, *Makromolekulare Chem.* **37** (1960) 149.

conversion of the monomer to the dimer; on the other hand, below -80°C . the polymerization rate, in particular when using catalysts which furnish crystallizable macromolecules, is very low, so that, it almost becomes negligible.

Table II. Polymerization of dimethylketene in the presence of different catalysts

Catalyst	Solvent	Time (hrs.)	Temp. ($^{\circ}\text{C}$.)	Conversion (%)	X-ray examination	Fractionation by boiling solvent extraction				
						Ether (%)	Benzene (%)	Toluene (%)	Residue (%)	
										$[\eta]$ ($100\text{ cm}^3\text{g}^{-1}$)
$\text{Sb}(\text{CH}_3)_3$	—	1	-78	100	amorphous	20.4	46.2	18.0	15.4	—
$\text{C}_6\text{H}_5\text{MgBr}$	—	6	-78	80	crystalline	44.6	19.1	—	33.5	—
ZnCl_2	—	40	-20	traces						
$\text{BF}_3 \cdot \text{Et}_2\text{O}$	ether	20	-20	— ^{a)}	—					
$\text{AlBr}_3 \cdot \text{Et}_2\text{O}$	—	40	-30	30	crystalline	7	25	3	65	0.63 ^{b)}
$\text{AlBr}_3 + \text{C}_2\text{H}_5\text{Br}$	—	30	-30	18	crystalline	5.1	14.5	5.6	78.4	0.55 ^{b)}
AlBr_3	—	30	-30	22	crystalline	3.2	18.5	6.5	71.8	—
$\text{AlBr}_3 \cdot \text{Et}_2\text{O}$	toluene	6	-50	18	crystalline	6.7	39.0	4.3	50.0	0.75 ^{b)}
$\text{Li } n\text{-C}_4\text{H}_9$	toluene	2	-78	89	amorphous	51.6	48.4	—	—	—
$\text{Al}(\text{C}_2\text{H}_5)_3$	—	12	-25	45	crystalline	22	71.5	—	6.5	0.4 ^{c)}
$\text{Al}[\text{N}(\text{CH}_3)_2]_3$	—	2	-78	90	amorphous	53.9	37.7	—	8.4	—

a) Only dimer — b) Intrinsic viscosity in nitrobenzene at 135°C . —

c) Intrinsic viscosity of benzene extractable fraction in tetraline at 135°C .

In this first report, we shall only refer to the main results obtained from the polymerization of dimethylketene in the presence of two typical catalysts belonging to the two classes previously indicated, that is, employing aluminum tribromide and triethylaluminum.

Table III. Polymerization of dimethylketene in the presence of $\text{AlBr}_3 \cdot \text{Et}_2\text{O}$
Catalyst: 0.032 M — Solvent: Toluene

[Monomer] (Moles/l.)	Temperature ($^{\circ}\text{C}$.)	Toluene non-extractable fraction	
		%	$[\eta]^a$ ($100\text{ cm}^3\text{g}^{-1}$)
2.86	-30	33.6	0.75
1.14	-30	65	0.63
1.76	-50	46.5	0.89
2.86	-50	40.5	0.95
3.22	-50	30.35	0.97
3.58	-50	50.1	1.3

a) Intrinsic viscosity in nitrobenzene at 135°C .

The intrinsic viscosity of the polymerization products obtained with these catalysts demonstrate that they are formed by macromolecular substances (Tables II and III).

As we have recently indicated in a Communication to the Editor⁸⁾, in the polymerizations carried out either in the presence of AlBr_3 or of $\text{Al}(\text{C}_2\text{H}_5)_3$, we have obtained crude polymers which are crystalline as indicated by X-rays; and, furthermore, we have established that crystallizable macromolecules having chemically different structures are present in the two crude polymerizates.

Two types of macromolecules have been isolated by us by fractionating extraction with suitable solvents, and we have observed that one type or the other one prevails according to the type of catalyst employed.

Regular polymers of dimethylketene having a ketonic structure

The products obtained by polymerization with AlBr_3 at low temperature are white, fibrous, solid, and they have been fractionated by extractions with boiling solvents, using, successively, for example, ether, benzene, toluene.

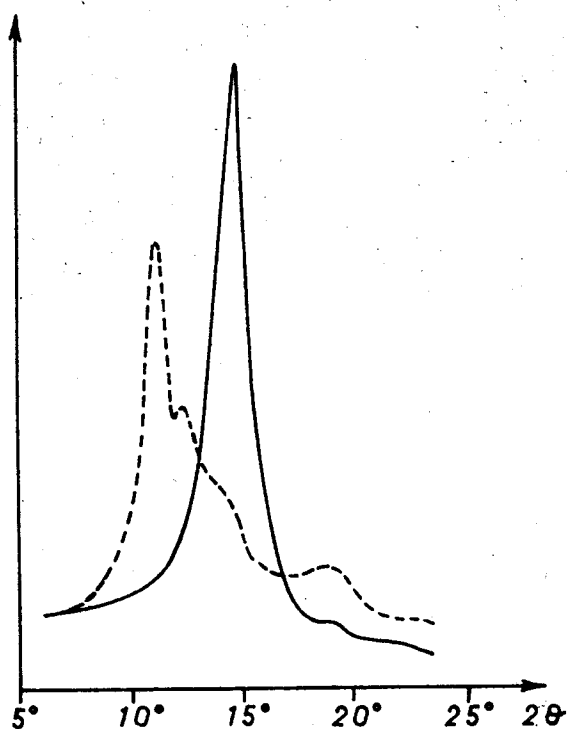


Fig. 1. X-Ray GEIGER registration (Cu K_α) of the two crystalline polydimethylketene.
 — Polymer [I]
 - - - - Polymer [II]

⁸⁾ G. NATTA, G. MAZZANTI, G. PREGAGLIA, M. BINAGHI, and M. PERALDO, J. Amer. chem. Soc. 82 (1960) 4742.

The fraction not extractable with toluene (which we shall call polymer [I]) constitutes 60–80 % of the total polymer, and is highly crystalline as indicated by X-ray examination carried out on the polymer in the powder form, as obtained after extraction (see Fig. 1).

Another crystalline modification of the same polymer [I] is obtained by melting and cooling. It proved to be highly crystalline, and possesses a different lattice structure. By extrusion and subsequent stretching, we obtained fibers which appear well oriented as shown by X-ray examination (see Fig. 2). An identity period along the chain axis of about 8.8 Å, in which are probably contained 4 monomeric units, has been calculated from the fiber spectrum.

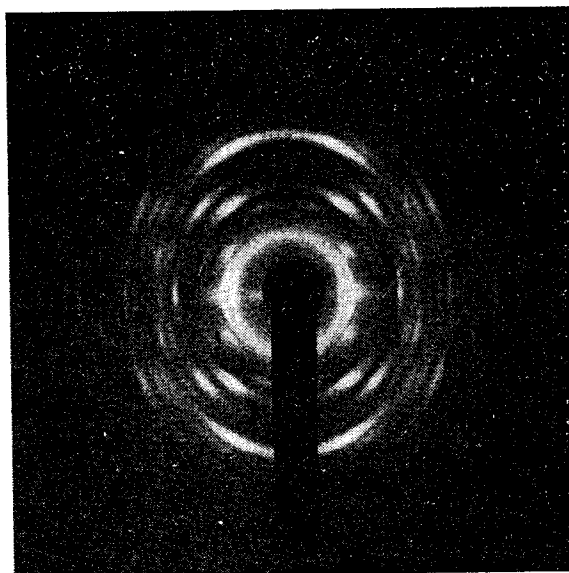


Fig. 2. X-Ray pattern of oriented fibers of the polydimethylketene [I]

The high crystallinity of polymer [I] agrees with a regular chemical structure.

Polymer [I] is soluble only in polar, high boiling solvents such as nitrobenzene, acetophenone, benzonitrile, bromobenzene, and bromoanisole and it shows melting temperatures (determined by a polarizing microscope) of about 250 °C. Polymer [I] is thermally stable up to 300 °C. and, contrary to the previously isolated polydimethylketenes²⁾, it does not depolymerize with formation of the monomer.

The molecular weight of polymer [I], the other conditions of the polymerization being equal, is higher when employing AlBr_3 etherate as catalyst. Using the same catalytic system and operating in the presence of inert solvents, the intrinsic viscosity increases with decreasing temperature and by increasing the monomer concentration (see Table III).

Crystalline Polymers of Dialkyl Ketenes

The IR spectrum shows the presence of two bands at 7.25μ , in agreement with the presence of a single type of geminal methyl groups, and a strong absorption at 5.9μ (see Fig. 3). The last could be ascribed both to carbonylic groups and to highly substituted double bonds, for instance, absorptions in this range are also present in the spectrum of ketene dialkylacetals. Therefore, the interpretation of the IR spectrum is not enough to determine the structure of polymer [I] specifically.

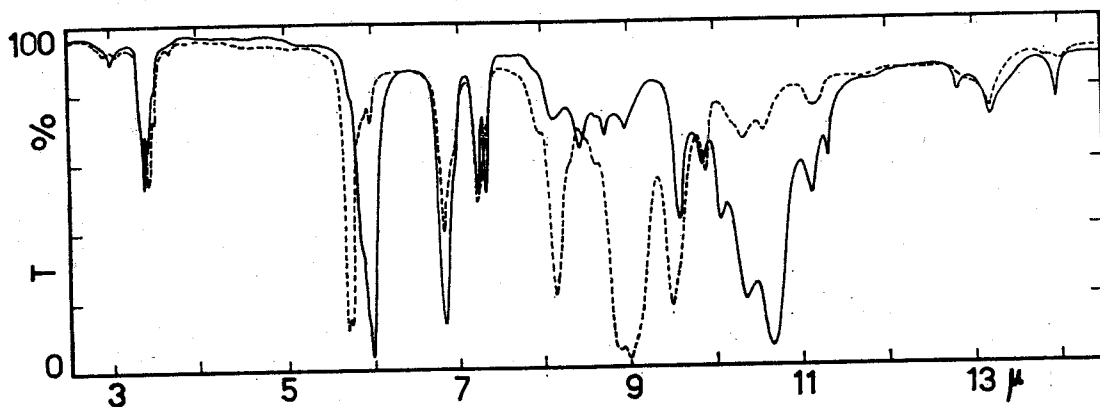


Fig. 3. Infrared spectra of the two crystalline polydimethylketene mulls in Nujol and C_4Cl_6

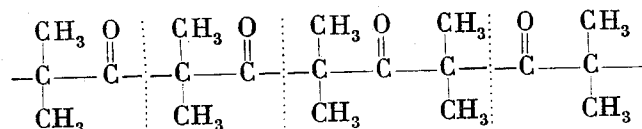
— Polymer [I]
 - - - - Polymer [II]

The examination of the UV spectrum, carried out on a laminar sample, showed a remarkable absorption in the range of carbonyls at $295 m\mu$.

However, we were able to demonstrate by a chemical way, that the macromolecules of polymer [I] possess the β -ketonic structure, which we have indicated as (A). In fact, after a long treatment at high temperatures ($200-260^\circ C.$) with ethyl alcohol and small amounts of sodium ethylate, we have isolated ethyl isobutyrate and diisopropylketone, besides a small amount of unreacted polymer.

The formation of diisopropylketone is particularly significant since the ethyl isobutyrate could also be formed by acetalic structures.

Taking into account what is known on the alcoholysis of β -diketones, one has to assume that alkaline alcoholysis causes the breakdown of the chain containing carbonyl bonds, corresponding to the indicated positions:



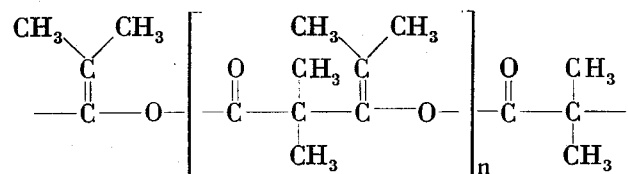
Dimethylketene polymer having a polyester structure

The dimethylketene polymer obtained in the presence of $\text{Al}(\text{C}_2\text{H}_5)_3$ was isolated by precipitation with methanol in the form of a white powder. By fractionation with the same series of solvents, however, we have obtained a large fraction (which we shall call polymer [II]) insoluble in acetone, but extractable with boiling benzene; generally constituting 50–70 % of the total polymer. The final melting temperature is difficult to determine by the polarizing microscope. It appears to lie between 160 and 170 °C.

The X-ray diffraction spectrum of polymer [II] registered on a powder sample as obtained after the extraction (Fig. 1) exhibits a crystalline structure which is different from that of polymer [I]. A great difference in the chemical structure is also shown from the analysis of the IR (see Fig. 3) and the UV spectra.

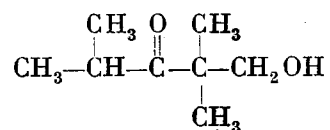
In fact, the two bands at 5.71 and 5.76 μ (only one at 5.74 μ in solution) prove the presence of ester groups, whereas, the absence of carbonyl groups is proved by the lack of absorption in the 2,900 Å range.

The chemical properties of polymer [II] allowed us to establish, that it possesses the following structure of the polyester type:



In fact, by ozonolysis of polymer [II] at -10°C ., we have obtained good yields of acetone (more than 50 %).

Furthermore, the reduction with LiAlH_4 at room temperature, allowed us to obtain the 2,2,4-trimethyl-1-pentanol-3-one in good yields (80 %):

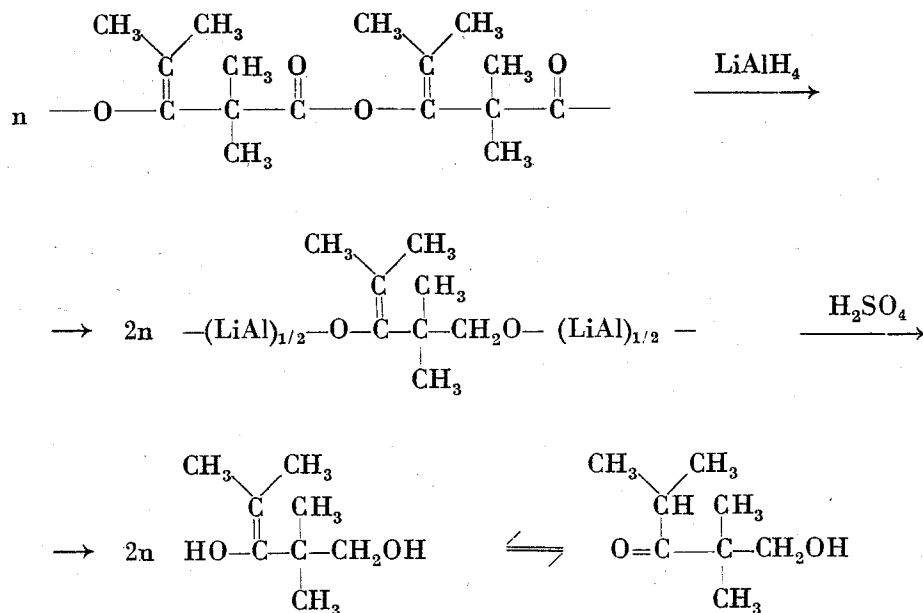


Analyses: Calc. for $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{COO-C}_3\text{H}_{15}\text{O}$: C 53.25, H 5.33, N 8.28; m.w. 338
Found: C 53.15, H 5.19, N 8.26; m.w. 333

It is known that in a reaction with lithium aluminum hydride the formation of a primary alcoholic group can occur only by reduction of a carboxylic group, while a carbonyl group can be formed by rearrangement of a salt of the enolic form of a ketone.

Therefore, we can assume that the formation of the indicated keto-alcohol occurs according to the following scheme:

Crystalline Polymers of Dialkyl Ketenes



Dimethylketene polymer having a mixed structure

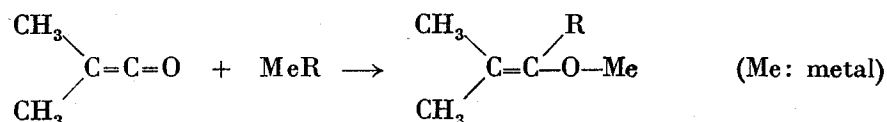
It is interesting to point out, that the fractions soluble in acetone and ether of the two polymers obtained with AlBr_3 and $\text{Al}(\text{C}_2\text{H}_5)_3$ do not show crystallinity by X-rays; which can be ascribed mainly to the irregularities in the chemical structure of the chains, rather than to the very low average molecular weight.

On the contrary, both the fractions insoluble in acetone and ether, but soluble in benzene and toluene of the polymer obtained with AlBr_3 , and the benzene not extractable fraction of the polymer obtained with $\text{Al}(\text{C}_2\text{H}_5)_3$ furnish X-ray diffraction spectra and IR absorption spectra, from which it is possible to deduce the presence of both the crystalline structures of the polymers [I] and [II]. Researches are now under way in order to establish whether long regular sequences having different structures (respectively of the [I] and [II] type) are present in the same macromolecule.

Conclusions

By choosing specific operating conditions and catalysts, we succeeded in preparing two types of regular linear high polymers, having different crystalline structures, corresponding to different chemical structures. Polymers having a polyketonic structure have been obtained using cationic catalysts, whereas metallorganic catalysts generally acting with an anionic mechanism yield polymers having a polyester structure.

Like in other cases which occur in the field of catalysis, a substance acts in a catalytic way under specific conditions which are near to those in which it can decompose or react in a stoichiometric way. That is why, when operating at low temperature, we could also employ, as catalysts, some metallorganic compounds which, at room temperature, react adding themselves to the ketenic system according to a reaction of the following type:



The results obtained by us demonstrate that, in the presence of some catalytic systems, dimethylketene behaves, in the polymerizations, as an olefin containing an internal double bond.

The selective polymerization of dimethylketene on the ethylenic double bond permits, for the first time, the formation of linear polymers, in which, ketonic groups are arranged in regular sequences along the main chain.

However, up to now, it has been possible to effect a corresponding polymerization involving only the carbonyl group, with formation of polyacetalic structures.

By using catalysts, able to add themselves to the carbonyl bond, a structure of the polyester type is formed. In this case, to each monomeric unit derived from the opening of the ethylenic double bond is bound a monomeric unit originated by the opening of the carbonyl double bond. Probably, when using this type of catalyst, two monomer molecules simultaneously, coordinate themselves to the catalyst itself at the very moment of polymerization.

The study of the crystalline structure of the two different dimethylketene polymers, which is now in progress in this Institute, will be the subject of other papers.

Experimental part concerned with the polymerization

Monomer

Dimethylketene has been prepared by pyrolysis of dimethylmalonic anhydride, as described by STAUDINGER²⁾, collecting the monomer at the temperature of -78°C .

The purity of the monomer strongly influences the results of the polymerization. Traces of oxygen in the collection vessel of dimethylketene, besides forming explosive peroxide, slow down and sometimes stop the polymerization; also, small amounts of sulphur inhibits the polymerization.

Crystalline Polymers of Dialkyl Ketenes

A purification system which has given good results consists in the addition of small amounts of $\text{Al}(\text{C}_2\text{H}_5)_3$ to the monomer which is cooled to -80°C ., and the subsequent distillation of dimethylketene under an inert atmosphere and at reduced pressure. Under these conditions, the catalytic effect of alkyl aluminum for the polymerization is almost null.

As an example we report here the description of two polymerization runs with AlBr_3 and with $\text{Al}(\text{C}_2\text{H}_5)_3$, respectively.

Polymerization with AlBr_3

In a test tube of 100 ml. equipped with a side tap, and maintained at -78°C ., 15 ml. of dimethylketene are distilled under an atmosphere of nitrogen and at reduced pressure. 15 ml. of toluene, previously cooled, and 1 ml. of a 10% solution of AlBr_3 in heptane are added. By raising the temperature to -50°C ., the viscosity of the reaction mixture increases very slowly and its colour turns lighter.

After 20 hrs., the reaction mixture appears almost solidified, but by distillation at reduced pressure, 8 ml. of a very concentrated solution of dimethylketene in toluene are collected. Methanol is slowly added to the residue in order to eliminate the residual ketene, and then the polymer is coagulated with an excess of alcohol. In order to remove all traces of the catalyst, it is washed repeatedly, first in the cold and later in the warm, with solutions of HCl.

Lastly 3.1 g. of polymer are obtained and then fractionated by extraction with solvents, keeping the sample at the boiling temperature of the employed solvent.

Thus the following fractions have been obtained:

acetone extract	6.20%
ether extract	0.60%
benzene extract	7.80%
toluene extract	3.80%
residue	81.60%

Polymerization with $\text{Al}(\text{C}_2\text{H}_5)_3$

To 20 ml. of dimethylketene distilled at reduced pressure, $1 \cdot 10^{-3}$ moles of $\text{Al}(\text{C}_2\text{H}_5)_3$ in a 10% heptanic solution are added under an atmosphere of nitrogen and at -80°C .. By keeping the reaction flask at this temperature, the viscosity does not increase. After 3 hrs., the monomer is distilled again into another reaction flask, maintained at -25°C ., and 1 ml. of a 10% solution of $\text{Al}(\text{C}_2\text{H}_5)_3$ is added.

The viscosity of the product increases rapidly and after 6–7 hrs. the mixture is solidified. After 12 hrs., the unreacted monomer is distilled at reduced pressure, and then an excess of methyl alcohol is added. It is washed with an aqueous solution of HCl. After filtering and drying, 8.4 g. of white, granulous polymer are isolated. By warm extraction with ether a fraction corresponding to 22% is isolated, whereas, in the subsequent extraction with boiling benzene, a fraction corresponding to 71.3% is extracted.

The detailed description of the degradation reactions which allowed the determination of the structure of the two types of polymers, the results of which have been reported in this text, will be made in another paper which will be published in an Italian Journal.