

Alternating Copolymers Having a Stereoregular Polyester Structure

G. NATTA, G. MAZZANTI, G. F. PREGAGLIA, and G. POZZI,
Istituto di Chimica Industriale del Politecnico, Milan, Italy

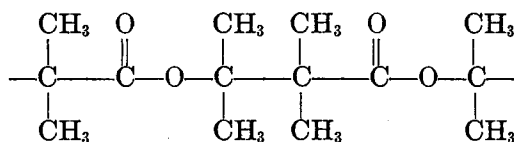
Introduction

In a previous communication¹ we briefly reported the possibility of obtaining, by operating under suitable conditions, linear polymers having a regular chemical structure, through the alternate addition of a dimethylketene molecule and of a ketone.

The monomeric unit derived from dimethylketene (I) is formed by splitting the C=C internal double bond, whereas the ketone reacts by opening of the carbonyl bond and, e.g., in the case of acetone, the monomeric unit (II) is formed.

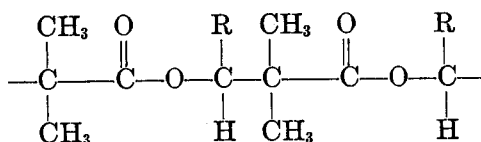


Alternate linking of the above two units takes place in such a way that the resulting polymer has a polyester structure:



The dimethylketene-acetone alternating copolymers prepared by us are highly crystalline, as revealed by x-ray examination. In this case, no stereospecificity of the polymerization process is required, since the macromolecules do not contain sites of asymmetry.

In the course of our research on the preparation of polyesters by polyaddition, we studied also the copolymerization of dimethylketene with aldehydes. As will be described in this communication, by use of particular catalytic systems, it is possible to prepare alternating copolymers with dimethylketene which still show a polyester structure:



There is an asymmetric carbon atom in the repeating unit in the macromolecules of these copolymers. In order to obtain crystallizable polymers of this type, it is necessary that the asymmetric carbon atoms show either the same steric configuration, at least for long chain portions, or that the two possible configurations follow one another in a regular way.

The preparation of alternating crystalline copolymers of dimethylketene with aldehydes represents the first example of stereospecific synthesis of polyesters.

Properties of the Polymers Obtained

Benzaldehyde or substituted aromatic aldehydes (e.g., *p*- and *o*-chlorobenzaldehyde, or anisaldehyde) or a heterocyclic aldehyde (e.g., furfural) are particularly suitable for the preparation of alternating copolymers with dimethylketene. These aldehydes do not polymerize by themselves under the same reaction conditions. In all the above indicated examples, the copolymers already show some x-ray crystallinity in the state in which they are obtained at the end of the polymerization.

The crystallinity of the crude, unfractionated dimethylketene-benzaldehyde alternating copolymer is markedly increased by annealing (at about 150°C.) or by being allowed to stand for a short time in boiling acetone. On the basis of the differences in solubility (results indicated in Table I) it is

TABLE I
Chemical Structure and Physical Properties of the
Benzaldehyde-Dimethylketene Alternating Copolymer

Repeating unit	$\begin{array}{ccc} \text{C}_6\text{H}_5 & \text{CH}_3 & \text{O} \\ & & \\ -\text{O}-\text{C} & - & \text{C} & - & \text{C} & - \\ & & \\ \text{H} & \text{CH}_3 & \end{array}$
Melting point, °C.	~290
Analytical data	
Calc. C 74.91%; H 6.87%	
Found C 74.59%; H 6.81%	
Solubility ^a	
Methanol	-
Acetone	-
Benzene	+
Chloroform	+
Nitrobenzene	+
Tetralin	±

^a (-) = insoluble; (+) = partially soluble at boiling point; (±) = swollen.

possible to separate fractions of different molecular weight and steric purity by extraction with boiling solvents. The fraction not extractable with boiling benzene is highly crystalline by x-ray examination (see Fig. 1) and melts at a very high temperature (280–290°C.). Furthermore it is

barely soluble in the organic solvents, similar in this respect to other high-melting polyesters (such as polyethylene terephthalate).

Depending upon the catalyst and the conditions adopted, this fraction may vary from 30 to 80% of the total polymer produced. Hitherto, we have not had sufficient data concerning the molecular weight of these polymers. However, it can be observed that the ether- and benzene-extractable fractions of the dimethylketene-benzaldehyde copolymer show intrinsic viscosities in chloroform ranging from 0.1 to 0.6, and it is possible that the insoluble fractions show higher $[\eta]$ and therefore higher molecular weights.

As may be seen from Table II in the case of alternating copolymers with furfural, *p*-chlorobenzaldehyde, *o*-chlorobenzaldehyde, or *p*-methoxybenzaldehyde, it is also possible to isolate fractions with different degrees of steric order (as may be deduced on the basis of their different degrees of crystallinity) through fractionation by extraction with boiling solvents.

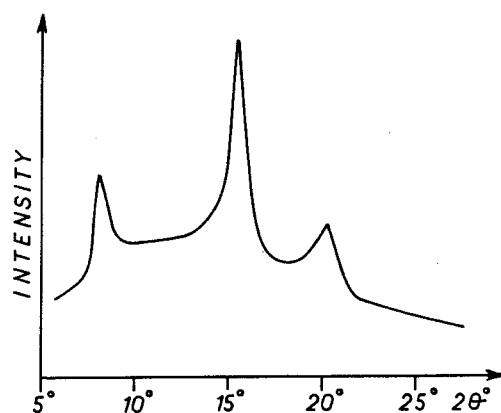


Fig. 1. X-ray diffraction spectrum ($\text{Cu } K\alpha$) of dimethylketene-benzaldehyde alternating copolymer.

The polyester structure of the copolymers prepared by us is proved by the elementary analysis, which corresponds to a unit molar ratio between the two monomers present in the copolymer. The infrared absorption spectrum shows only one band at 5.75μ in the region of the carbonyl groups; this absorption can be attributed to ester groups. A further demonstration of the regularity of the chemical structure of the polyesters is given by the structure of products obtained by breaking the linear chain by reduction with LiAlH_4 in ether solution. For instance, by treating benzaldehyde-dimethylketene polyester under these conditions, we have isolated in very high yields a crystalline compound to which, on the basis of elementary analysis and molecular weight determination, one can ascribe the structure:

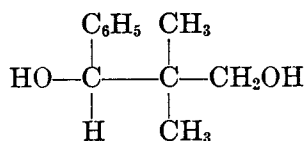
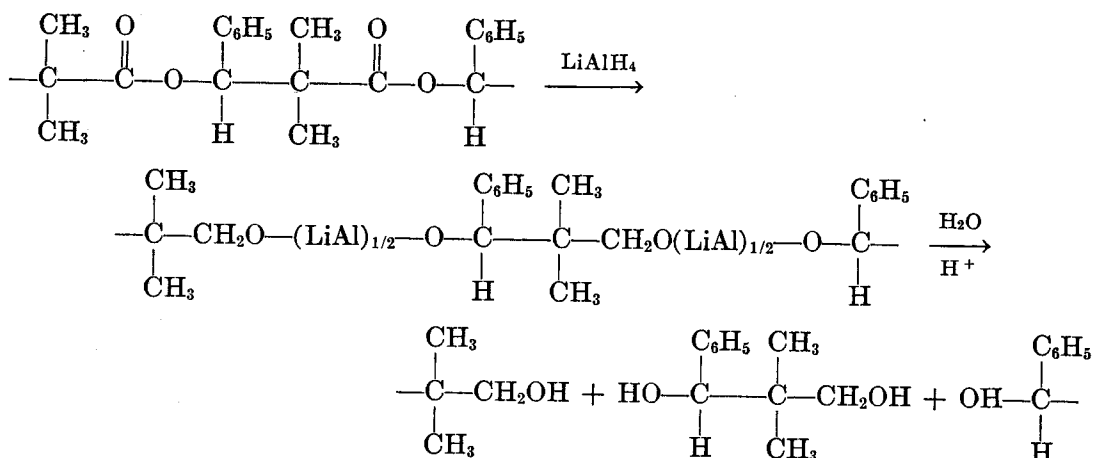


TABLE II
Chemical Structure and Physical Properties of Some Dimethylketene-Aldehyde Alternating Copolymers

Comonomer	Repeating unit	Analytical data		Solubility ^a			Melting point, of the benzene insoluble fraction °C.	
		Element	Calc., %	Found, %	Acetone	Ether		Chloroform
<i>p</i> -Chlorobenzaldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ \text{---C---} \\ \\ \text{CH}_3 \end{array} \text{---} \begin{array}{c} \text{C}_6\text{H}_4\text{Cl} \\ \\ \text{C---O---} \\ \\ \text{CH}_3 \end{array} \text{---}$	Cl	16.85	17.1	—	—	+	260
<i>m</i> -Methoxybenzaldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ \text{---C---} \\ \\ \text{CH}_3 \end{array} \text{---} \begin{array}{c} \text{C}_6\text{H}_4(\text{OCH}_3) \\ \\ \text{C---O---} \\ \\ \text{CH}_3 \end{array} \text{---}$	C H	69.9 6.8	69.7 6.95	—	—	+	240
<i>m</i> -Nitrobenzaldehyde	$\begin{array}{c} \text{O} \\ \parallel \\ \text{---C---} \\ \\ \text{CH}_3 \end{array} \text{---} \begin{array}{c} \text{C}_6\text{H}_4(\text{NO}_2) \\ \\ \text{C---O---} \\ \\ \text{CH}_3 \end{array} \text{---}$	N	6.33	6.23	+	—	+++	240
Furfural	$\begin{array}{c} \text{O} \\ \parallel \\ \text{---C---} \\ \\ \text{CH}_3 \end{array} \text{---} \begin{array}{c} \text{C}_4\text{H}_3\text{O} \\ \\ \text{C---O---} \\ \\ \text{CH}_3 \end{array} \text{---}$	C H	65.06 6.1	65.21 6.3	++	—	+	180

^a (+) = partially soluble at boiling point; (++) = soluble at the boiling point; (+++) = soluble at room temperature; (—) = insoluble.

The formation of this glycol may be explained through the following reactions:



Synthesis of Alternating Copolymers

As we have previously indicated, crude dimethylketene-aldehyde alternating copolymers, free of homopolymers, can be obtained in good yield if aldehydes used are ones which do not yield homopolymers in the presence of the same catalysts. In this case, by operating under suitable conditions, it is possible to avoid the formation of nonalternating copolymers. Some catalysts acting through an anionic mechanism proved to be suitable for promoting the stereospecific alternating copolymerization of dimethylketene and of benzaldehyde. In particular, the best stereospecific catalysts consist of lithium alkyls or of lithium alcoholates. As may be seen from Table III in the copolymerization of dimethylketene and benzaldehyde in the presence of these catalysts, even with very small amounts of catalyst and at low temperature, very high reaction rates are observed. In a few minutes, conversion yields of monomers higher than 50% and very high yields referred to the amount of catalyst employed (more than 400 g. of copolymer/g. of lithium alkyl) are obtained.

TABLE III
Copolymerization of Benzaldehyde (BZA) and Dimethylketene (DMK) in the Presence of Toluene as Polymerization Medium

BZA, mmoles	DMK, mmoles	Toluene, ml.	Catalyst	Catalyst, mmoles	Time, min.	Temp., °C.	Yield, %
51	47	83	LiC ₄ H ₉	0.5	12	-12	68.5
51	47	83	LiC ₄ H ₉	0.5	12	-50	74
70	63	40	LiOC ₄ H ₉	1.5	5	-40	77
44	39	66.5	NaC ₁₀ H ₇	0.25	10	-30	86
61	57	40	NaOC ₂ H ₅	0.09	30	-78	100

It is interesting to point out that, in order to form alternating copolymers with the aid of the above-mentioned catalysts, it is not necessary to

operate with a great excess of benzaldehyde. Alternating copolymers, free of dimethylketene homopolymers are usually obtained also when the two monomers were used in equimolecular amounts, or with only a slight excess of aldehyde.

With all the conditions equal, when sodium-naphthalene or sodium alkyls are used instead of alkyls or lithium alcoholates, dimethylketene-benzaldehyde alternating copolymers having a regular chemical structure are obtained. They are, however, totally extractable with benzene and slightly crystalline or completely amorphous by x-ray examination. The lower stereospecificity of the anionic catalysts containing sodium may be attributed to the fact that the ionic radius of sodium is larger than that of lithium. The small radius and the consequently greater coordinating power of lithium can compel more strictly the steric configuration of the monomeric units in the coordination step which immediately precedes the polymerization.

TABLE IV
Copolymerization of Dimethylketene and Some Aldehydes in the Presence of Toluene as Polymerization Medium

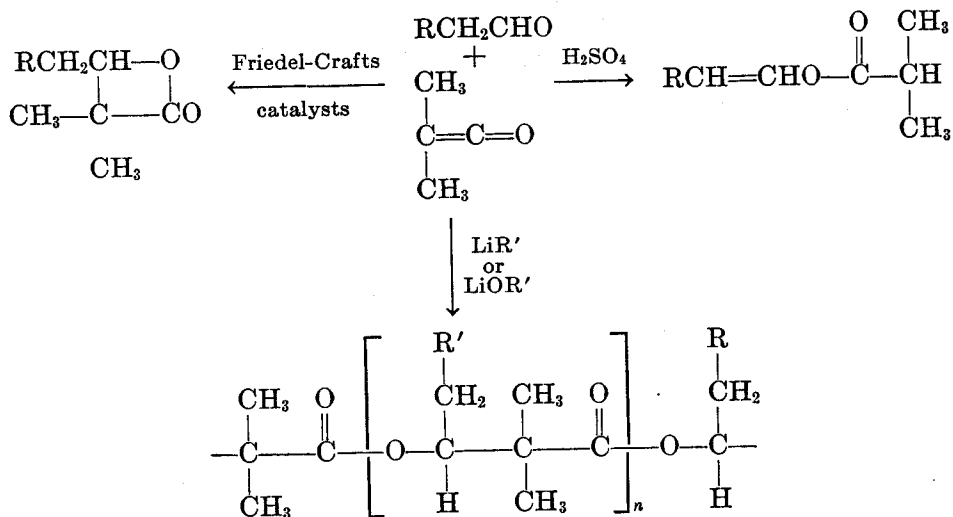
Aldehyde	Aldehyde, mmoles	DMK, mmoles	Toluene, ml.	Butyl-Li, mmoles	Time, min.	Temp., °C.	Yield, %
<i>o</i> -Chlorobenzaldehyde	69	46	40	1.3	180	-50	40
<i>p</i> -Chlorobenzaldehyde	46	50	50	0.65	150	-35	100
<i>p</i> -Methoxybenzaldehyde	56	51	50	1.06	60	-78	29
<i>m</i> -nitrobenzaldehyde	40	40	70	0.7	180	-30	29
Furfural	153	51	25	0.7	420	-78	12

Table IV shows some data on the copolymerization of dimethylketene with furfural, *o*-chlorobenzaldehyde, *p*-chlorobenzaldehyde, *p*-methoxybenzaldehyde, and *m*-nitrobenzaldehyde in the presence of alkyls or lithium alcoholates. As may be seen, in these cases, the overall copolymerization rate is lower than that of the copolymerization with benzaldehyde.

Mechanism of the Alternating Copolymerizations

It has long been known that ketenes and carbonyl compounds can react in an equimolecular ratio. Staudinger described for the first time the formation of β -lactone by condensation of diphenylketene with quinone.²

As indicated below an aldehyde may react in the presence of particular catalysts to yield a β -lactone or an enolacetate; if there are no active hydrogen atoms in the position α to the aldehyde group (e.g., in benzaldehyde), obviously only compounds of the first type can be obtained.



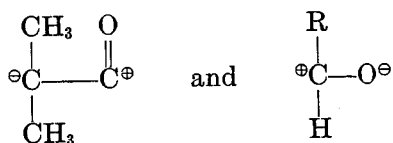
As it is known that some β -lactones yield linear macromolecules by splitting of the four-membered ring, we thought it interesting to check whether β -lactones formed by condensation of dimethylketene and an aldehyde may act as an intermediate compound in the formation of the alternating copolymer.

In the presence of the catalysts and under the conditions adopted by us for preparing alternating copolymers, we have experimentally found that the β -lactone obtained from benzaldehyde and dimethylketene does not yield even small amounts of high molecular weight linear polyester.

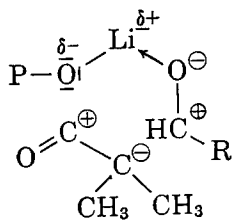
When studying a possible mechanism of alternating copolymerization, it is useful to bear in mind the equivalence observed by us between the catalytic activities of lithium alkyl and of lithium alcoholate.

Since a lithium alcoholate is always obtained in the reaction of a carbonyl group with a Li-carbon bond, it is possible to suppose that, in the chain propagation phase, the Li alcoholate is the actual polymerization catalyst.

The presence in the chain of the repeating unit, formed by the regular linking of the two monomeric units polarized in the sense indicated in the following scheme:



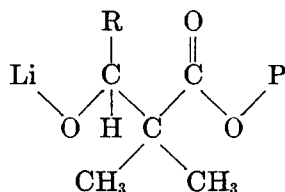
may be explained by a simultaneous coordination of two monomer molecules to the lithium alcoholate. The chain propagation, therefore, should take place through the formation of a complex of the type:



where P denotes the polymeric chain.

In the above-mentioned complex, the aldehyde is coordinated on the lithium atom by polarization of the carbonyl bond, whereas the dimethylketene molecule shows a distribution of charges that is analogous to that foreseeable for other of its reactions (for instance in the formation of β -lactone) and is also in agreement with its low electric moment.

The formation of a new lithium-oxygen bond with the aldehyde restores the catalyst already existing at the moment of the coordination:



This hypothesis of mechanism explains the formation of the alternating copolymer under experimental conditions in which dimethylketene by itself should form a homopolymer. In fact, whereas on one hand the carbonyl group of the ketenic compound is analogous to that of an acid compound, the C=O bond of the aldehyde shows a higher electron-donor power and therefore is coordinated on the lithium atom of the alcoholate more easily. The higher basic character of the ketonic group may justify, in an analogous way, the alternating copolymerization of dimethylketene with acetone.

Experimental

Dimethylketene was obtained by the method described by H. Staudinger,³ that is, by pyrolysis of dimethylmalonic anhydride; before polymerization, the monomer was distilled at low temperature in the presence of trialkylaluminum.

Aldehydes used as comonomers were pure grade products, and were distilled and kept under nitrogen atmosphere in order to remove the traces of acids and peroxides present.

Toluene used as solvent was also distilled on trialkylaluminum in order to remove oxygen and moisture present.

The experimental procedure consists in the introduction in the reaction flask of a solution of dimethylketene and of aldehyde in suitable ratios under nitrogen atmosphere.

Then the catalyst, either solid or in solution, is rapidly added. The reaction is usually fast and occurs with evolution of heat. The color of dimethylketene disappears, and the viscosity of the solution increases considerably.

The polymer is coagulated and finally washed repeatedly with methanol in order to eliminate the aldehyde still present.

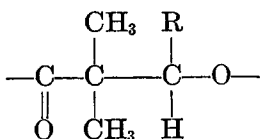
References

1. Natta, G., G. Mazzanti, G. F. Pregaglia, and M. Binaghi, *J. Am. Chem. Soc.*, **82**, 5511 (1960).

2. Staudinger, H., and N. Kon, *Liebigs Ann. Chem.*, **384**, 51 (1911).
3. Staudinger, H., *Helv. Chim. Acta*, **8**, 306 (1925).

Synopsis

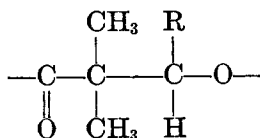
In the presence of catalysts acting through an anionic mechanism (alkyls or alcoholates of lithium), it was possible to obtain alternating crystalline copolymers of dimethylketene with some aromatic and heterocyclic aldehydes (having the general formula RCHO) consisting of macromolecules in which the repeating unit corresponds to the formula:



Owing to the presence of an asymmetric carbon atom in the repeating unit of the products obtained, this copolymerization represents the first example of stereospecific synthesis of polyesters. The chemical structures of the copolymers obtained have been demonstrated by chemical and infrared analyses and by the identification of the products obtained by hydrogenolysis with LiAlH_4 . The preparation of alternating copolymers of dimethylketene with various aldehydes and the properties of the products are described. Furthermore a possible reaction mechanism according to which the two monomers are simultaneously coordinated to a molecule of the catalyst is proposed.

Résumé

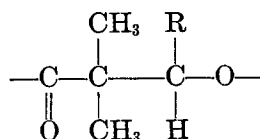
En travaillant en présence de catalyseurs à mécanisme anionique (alkyllithium ou alcoolates de lithium) on a pu obtenir des copolymères cristallins dans lesquels les unités monomériques que de di méthylcétène alterne avec celles des aldéhydes aromatiques et hétérocycliques (de formule générale RCHO), consistant en macromolécules dans lesquelles il y a répétition de l'unité structurale suivante:



Cette copolymérisation représente le premier exemple d'une synthèse stéréospécifique de polyesters due à la présence d'un carbone asymétrique dans l'unité mentionnée ci-dessus. On a démontré les structures chimiques des copolymères obtenus par des analyses chimiques et infrarouges et par l'identification des produits obtenus par hydrogénéolyse au LiAlH_4 . On a décrit la préparation et les propriétés des copolymères alternats de diméthylcétène avec différents aldéhydes. Ensuite on a proposé un mécanisme de réaction possible selon lequel les deux monomères sont liés simultanément à une molécule du catalyseur.

Zusammenfassung

Mit anionisch wirkenden Katalysatoren (Lithiumalkyle oder -alkoholate) war es möglich alternierende, kristalline Copolymere von Dimethylketen mit einigen aromatischen und heterocyclischen Aldehyden (mit der allgemeinen Formel RCHO) zu erhalten, die aus Makromolekülen mit der Grundeinheit



bestehen. Infolge der Gegenwart eines asymmetrischen Kohlenstoffatoms in der Grundeinheit der erhaltenen Produkte, stellt diese Copolymerisation das erste Beispiel einer stereospezifischen Synthese von Polyestern dar. Der chemische Aufbau der erhaltenen Copolymeren wurde durch chemische und I.R.-Analyse und durch Identifizierung der mit LiAlH_4 erhaltenen Hydrogenolyseprodukte aufgeklärt. Die Darstellung alternierender Copolymerer von Dimethylketen mit verschiedenen Aldehyden und die Eigenschaften der Produkte werden beschrieben. Weiters wird ein Reaktionsmechanismus vorgeschlagen, nach welchem die beiden Monomeren gleichzeitig Koordination mit einer Katalysatormolekel eingehen.

Discussion

R. N. Lewis (*Olin Mathieson Chemical Corporation, New Haven, Conn.*): Is it possible to obtain similar polymers from β -lactones, or to obtain stereospecific polymers from optically active β -lactones, e.g., β -phenyl- α,α -dimethylpropiolactone?

G. Natta: Under reaction conditions similar to those adopted by us using β -lactones as monomers (i.e., β -phenyl- α,α -dimethylpropiolactone), we have obtained no polymer yields or else very low ones (less than 1%). We cannot exclude that, duly modifying the polymerization technique, it is possible to obtain polyester compounds of the type described by us, by employing β -lactones as starting products.

W. J. Wasserman (*American-Marietta Company, Seattle, Wash.*): How, did you say the glycol was obtained?

G. Natta: By reaction of the polymer with an ethereal solution of lithium aluminum hydride.