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Polyacetalic Structure**

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SUMMARY:

By polymerizing dimethylketene in ether solution in the presence of lithium derivatives such as LiC_4H_9 and LiOC_4H_9 , a new crystalline polymer has been prepared, to which an essentially polyacetalic structure can be assigned. The I.R. spectra show the characteristic bands of a carbon-carbon double bond; the results of the chain degradation by acid alcoholysis and hydrogenolysis with LiAlH_4 agree with the presence of acetalic bonds.

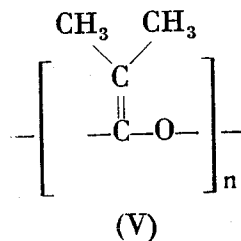
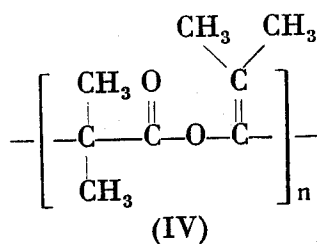
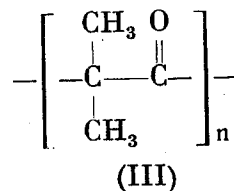
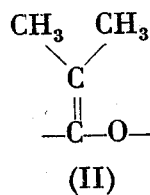
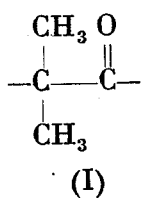
A clear likeness between the chemical reactivity of acetalic polydimethylketene and that of polyisobutyraldehyde has been found.

ZUSAMMENFASSUNG:

Durch Polymerisation von Dimethylketen in ätherischer Lösung in Gegenwart von LiC_4H_9 oder LiOC_4H_9 wurde ein neues kristallines Polymeres hergestellt, dem eine Polyacetalstruktur zugeschrieben werden muß. Die IR-Spektren zeigen die charakteristischen Banden der C=C-Doppelbindung. Die Ergebnisse des Kettenabbaus durch saure Alkoholysen und Hydrogenolyse mit LiAlH_4 bestätigen die Anwesenheit von Acetalbindungen.

Es wurde deutliche Übereinstimmung der chemischen Reaktionsfähigkeit von acetalartigem Polydimethylketen und von Polyisobutyraldehyd festgestellt.

In previous papers of ours, dealing with the polymerization of dimethyl ketene^{1,2}, we demonstrated that this monomer can react through the opening either of the >C=C< (I) or of the >C=O (II) double bond.



Polymers of Dimethylketene Having Prevailing Polyacetalic Structure

More precisely, in the presence of FRIEDEL-CRAFTS acid catalysts, a polymer with β -ketonic structure (III) is obtained, while in the presence of anionic catalysts (*i.e.* sodium-naphthalene or AlEt_3) a polyester (IV) is isolated, which is formed by the regular alternance of the two possible monomeric units.

By operating under particular polymerization conditions, we succeeded in obtaining a new crystalline polymer of dimethylketene, which is essentially of the polyacetalic type (V). Fig. 1 shows the X-ray-GEIGER registration of this crystalline polymer, compared with the diffraction shown by isotactic polyisobutyraldehyde.

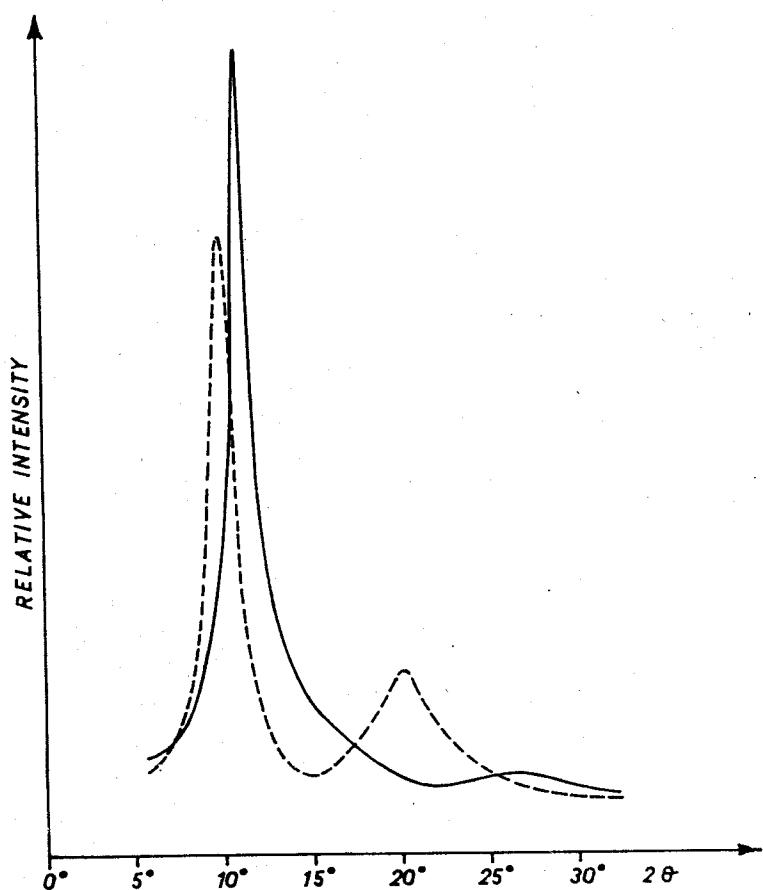


Fig. 1. X-ray-GEIGER registration ($\text{CuK } \alpha$) of polydimethylketene with polyacetalic structure (full line) and isotactic polyisobutyraldehyde (dotted line)

The spectrum of polydimethylketene shows a very strong diffraction band near the strongest band present in the spectrum of polyisobutyraldehyde. This may be justified by the great similarity of their chemical structures. We intend to examine more carefully the fiber spectrum, and to establish whether the chains of polydimethylketene, though not isotactic, possess the same spiral-shaped structure as that found for isotactic polyisobutyraldehyde.

The highest regularity of polyacetalic structure has been observed in the ether-extractable fraction (corresponding to 60–70 % of the crude polymer).

Experimental Part

In a 250 ml. flask, equipped with mechanical stirrer, 30 ml. of ether and, after cooling to $-78^{\circ}\text{C}.$, 125 mmoles of dimethylketene are introduced, in the absence of oxygen and moisture.

After adding 1 mmole of LiC_4H_9 in heptane solution, the reaction mixture is kept in motion under nitrogen atmosphere. After 7 min., the dissolved polymer is coagulated with methanol; thus 7 g. of white crude polymer, having an intrinsic viscosity $[\eta]$ in chloroform 0.21 are isolated. This polymer is completely soluble in cold benzene and CCl_4 and for the most part soluble in boiling ether and acetone, unlike the polymer having prevalingly polyester structure (IV), which is almost insoluble in these two last solvents.

The compound, which is thermally stable up to $170^{\circ}\text{C}.$, slowly softens at a little higher temperature (180 – $200^{\circ}\text{C}.$).

The I.R. spectrum of the ether-extractable fractions (Fig. 2) shows a strong band at $5.84\ \mu$, which can be assigned to the >C=C< double bonds present in the polyacetalic form (V). In fact, we have observed that also for dimethylketene-dimethylacetal, the band of the double bond falls in this position. Moreover, the U.V. spectra do not show appreciable absorption bands at about $290\ \mu\mu$; therefore we can exclude the presence of ketonic groups.

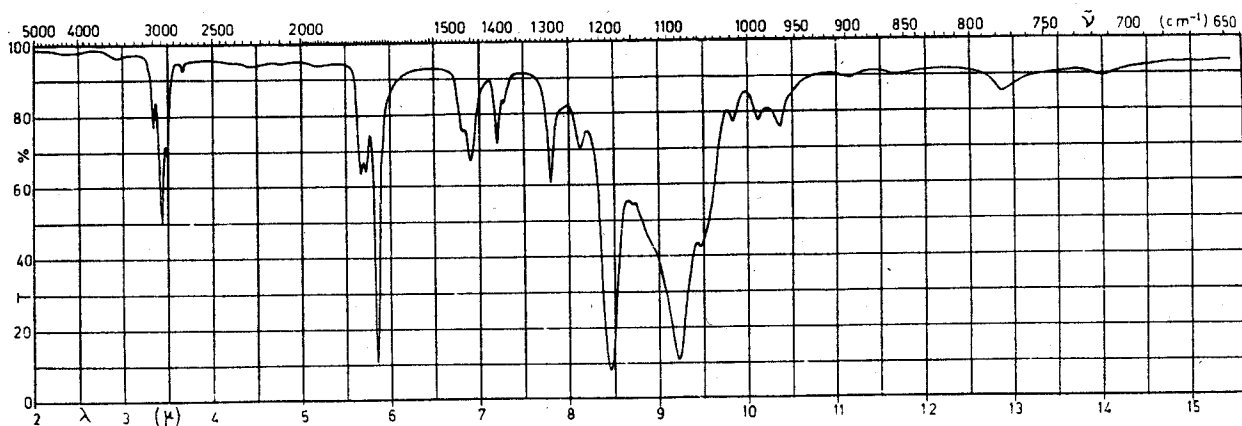


Fig. 2. Infrared spectrum of the polydimethylketene having prevalingly polyacetalic structure (nujol mull)

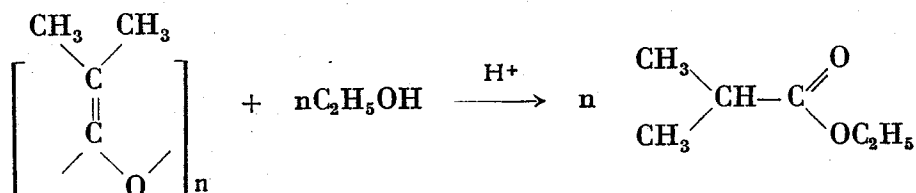
It was also observed in the I.R. spectrum of the ether extractable fraction, the presence of a band at $5.66\ \mu$ for solid samples obtained from chloroformic solution (at $5.68\ \mu$ for samples in chloroformic solution), whose intensity varies depending on both the polymerization conditions and the catalyst employed.

This absorption is attributable to carbonyl groups belonging to the IV-type monomeric units, that is to carbonyl groups of vinyl-ester type, isolated in the polyacetalic chains. In all the ether extracts examined, sequences of these units, though in very small quanti-

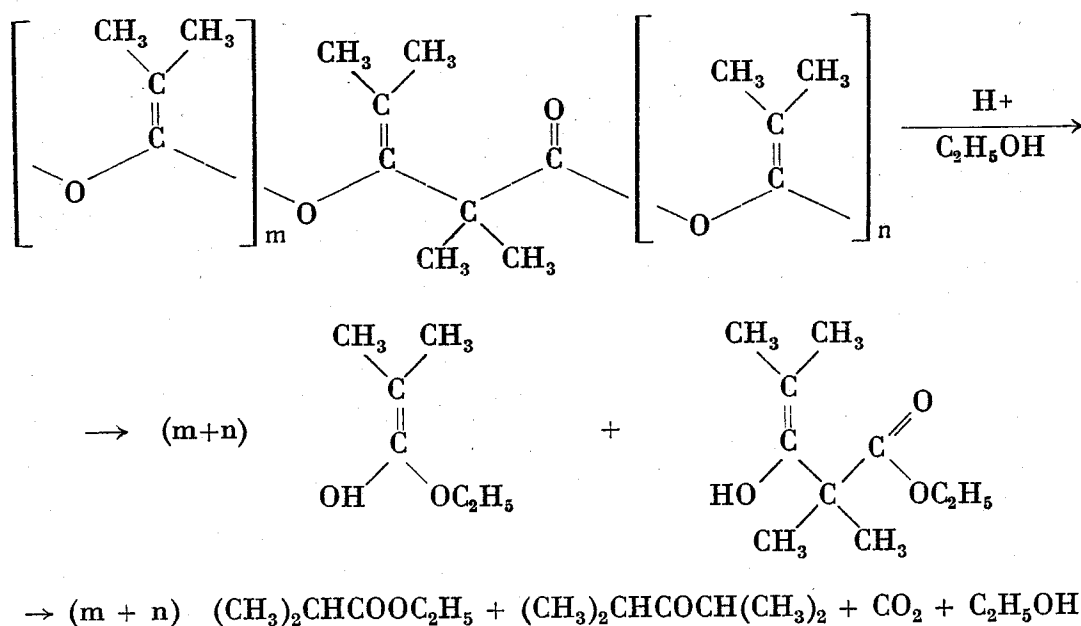
Polymers of Dimethylketene Having Prevalingly Polyacetalic Structure

ties, were also observed; these sequences constitute small chain segments having the polyester structure (IV) (absorption bands at $5.73\ \mu$, $8.13\ \mu$, $9.47\ \mu$, and $9.48\ \mu$; the band at $5.73\ \mu$ moves to $5.75\ \mu$ in chloroformic solution).

The crude polymer, obtained in the presence of LiC_4H_9 , absorbs bromine rapidly in CCl_4 solution. By acid alcoholysis (H_2SO_4 as catalyst) good yields of ethyl isobutyrate are isolated, together with small quantities of di-iso-propylketone. Treating the polymer having polyester structure (IV) under the same experimental conditions, no degradation of the starting product occurs. The presence of ethyl isobutyrate proves the polyacetalic structure, according to the scheme:



The small quantities of di-iso-propylketone are probably due to the presence of some monomeric units of the type I in the chain. The units yield a ketoester which, in the acid hydrolysis loses CO_2 according to the following scheme:



By acid alcoholysis of the ether-soluble fraction of polydimethylketene, di-iso-propylketone is isolated in a lower quantity than in the crude polymer. In any case, if the alcoholysis reaction is incomplete, the residual polymer shows a strong absorption band at $5.75\ \mu$, as revealed by I.R.

analysis, while the band at 5.84μ disappears almost completely. This indicates the higher stability of the chain segments formed by regular alternance of the I and II monomeric units.

By means of LiAlH_4 reduction in ether solution at room temperature, good yields of isobutyric aldehyde are isolated after hydrolysis, whereas 1-hydroxy-2,2,4-trimethyl-3-pentanone is isolated from polyester IV.

The adoption of suitable conditions in the polymerization of dimethylketene is very important in order to obtain a product mainly with acetalic structure; in particular, the type of solvent, the temperature, the quantity and type of catalyst used play an important role.

Even if all hydrocarbons are good solvents and permit obtaining polymers in which structure (V) prevails, we have obtained better results when using oxygenated compounds of basic nature, such as ethyl ether, as solvent during the polymerization. In fact, by operating in the presence of these solvents, it is possible to isolate polymers with a highly regular polyacetalic structure.

Beside the alkyl lithium compounds, we have employed other lithium organic derivatives, reported in Table 1, which, as catalysts, proved equally specific.

Table 1. Yields of polymer having polyacetalic structure in the polymerization of dimethylketene at -78°C .

Catalyst	$\frac{\text{Monomer moles}}{\text{Catalyst moles}}$	Solvent (ml.)	Time (min.)	Yield (%)
$\text{C}_4\text{H}_9\text{Li}$	260	Toluene 50	15	47
$\text{C}_4\text{H}_9\text{OLi}$	40	Toluene 25	30	91
$\text{C}_4\text{H}_9\text{Li}$	115	THF ^{b)} 20	12	86
$\text{C}_4\text{H}_9\text{Li}$	230	Ether 25	300	52
$\text{NptLi}^{\text{a)}$	140	Toluene 20	3	93
$\text{C}_2\text{H}_5\text{ONa}$	35	Toluene 25	10	100

^{a)} NptLi = Lithium naphthalenide complex.

^{b)} THF = Tetrahydrofuran.

It is interesting to note the likeness existing between the chemical properties of the polymers of dimethylketene (V) and isobutyraldehyde, in agreement with the fact that polyaldehyde can be considered as the hydrogenation product of the polyketene obtained by us. In particular, the relative chemical instability of the two products obtained under the

same polymerization conditions is evident. However, polydimethylketene with acetalic structure shows, in comparison with polyisobutyraldehyde, a greater thermal stability, probably due to the absence of hydroxy end groups.

1) G. NATTA, G. MAZZANTI, G. F. PREGAGLIA, and M. BINAGHI, J. Amer. chem. Soc. **82** (1960) 4742.

2) G. NATTA, G. MAZZANTI, G. F. PREGAGLIA, and M. BINAGHI, Makromolekulare Chem. **44-46** (1961) 537.