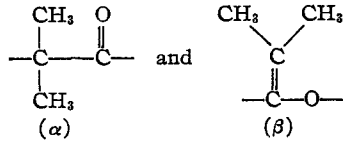
[Reprinted from the Journal of the American Chemical Society, 82, 4742 (1960).]

CRYSTALLINE POLYMERS OF DIMETHYLKETENE

Sir:

It is known that dimethylketene dimerizes readily to tetramethyl-1,3-cyclobutanedione.[1] Higher polymers were obtained by Staudinger[2] using aliphatic or aromatic amines as catalysts. These amorphous products can be considered as derived from the irregular copolymerization of the two monomeric



units formed, respectively, by the opening of the ethylenic or of the carbonyl double bond.

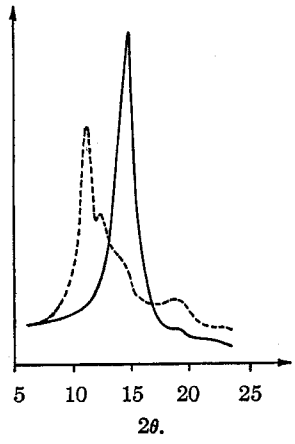


Fig. 1.—X-Ray Geiger registration (CuKα) of the two crystalline poly-dimethylketenes: ——— polymer I, -------- polymer II.

Using ionic catalysts, we have prepared two new types of crystalline dimethylketene polymers of regular chemical structure. Dimethylketene in toluene solution was polymerized at −60° in the presence of aluminum tribromide (moles monomer/moles catalyst approximately 1500); the fraction, which was not extractable with boiling toluene, had an intrinsic viscosity of 0.7 in nitrobenzene at 135°; m.p. 250–255° (determined with a polarizing microscope).

The high crystallinity (see Fig. 1) of this fraction (polymer I) indicates that it is made up of macromolecules having a regular structure. The strong absorption in the infrared spectrum (Fig. 2) near 5.9 μ indicates the presence of carbonyl groups, a conclusion which is confirmed by the ultraviolet spectrum. The two bands around 7.25 μ are in accord with the presence of one type only of gem methyl groups.

From the chemical properties of polymer I we conclude that it consists of macromolecules formed by the regular head-to-tail enchainment of monomeric units of type (α). In fact, polymer I behaves chemically like a β-diketone; treatment of I suspended in tetrahydrofuran with excess ethyl alcohol and a small quantity of sodium ethoxide, for a long time (100 hours) at 200–260°, yielded ethyl isobutyrate and di-isopropyl ketone in addition to the unchanged polymer.

The structure assigned to polymer I has been confirmed by the results of reduction of the carbonyl groups with $LiAlH_4$. Treatment of I suspended in tetrahydrofuran with $LiAlH_4$ gave a white, amorphous polymer (90% yield) which was insoluble in ether and acetone, but soluble in acetic acid and ethyl alcohol. The infrared spectrum shows that only traces of carbonyl groups remain, whereas there is strong absorption at 3.02 μ which is attributable to associated hydroxyl groups. This reduction product, therefore, is an atactic polymer of dimethylvinyl alcohol.

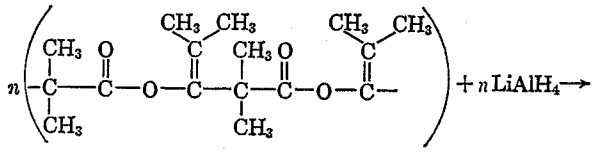
Polymerization of dimethylketene under the conditions previously mentioned with triethylaluminum as the catalyst, gave a polymerizate, 70% of which can be extracted with boiling benzene, but not with boiling acetone. This fraction (polymer II) has an intrinsic viscosity of 0.4 (in tetralin at 135°) and a regular structure as indicated by its high crystallinity (see Fig. 1).

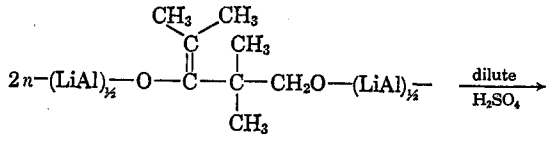
The two bands at 5.71 and 5.75μ (only the 5.75μ band occurs in solution) indicate the presence of ester groups. That only traces of carbonyl groups are present is demonstrated by the weak absorption bands at 295 mμ in the ultraviolet.

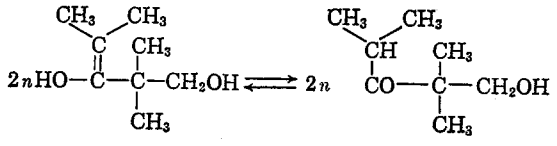
(1) H. Staudinger, H. Schneider, P. Schotz and P. M. Strong; *Helv. Chim. Acta*, **6**, 291 (1923).

(2) H. Staudinger, *ibid.*, **8**, 306 (1925).

When polymer II dissolved in tetrahydrofuran was treated with $LiAlH_4$, we obtained 2,2,4-trimethyl-1-pentanol-3-one (80% yield). This result agrees with a structure of the polyester type:







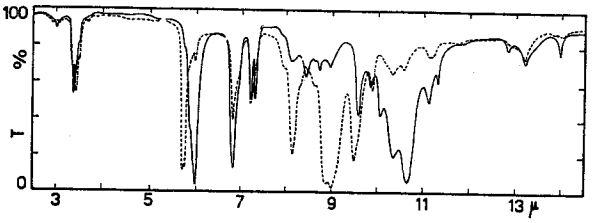


Fig. 2.—Infrared spectra of the two crystalline polydimethylketenes, mulls in Nujol and C_4Cl_6: ——— polymer I, -------- polymer II.

Furthermore, ozonolysis of II gave a good yield of acetone. The chemical behavior of polymer II enables us to conclude that it consists of macromolecules derived from the regular, alternate polymerization of the two monomeric units (α) and (β).

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