7.53), and the enantiomer, (R)-VIII (Y = CHOH), m.p. 77–79° (fd.: C, 85.94; H, 7.48) by $LiAlH_4$ reduction of (S)-XIV respectively (R)-XIV; (S)-X (Y = CH_2), m.p. 63–64° (fd.: C, 92.05; H, 8.38), by modified Clemmensen reduction of (S)-XIV; (R)-XII (Z = $C(COOEt)_2$), m.p. 165–167° (fd.: C, 61.75; H, 5.07; Cl, 17.29), from (+)-6,6'-dichloro-2,2'-bis-(bromomethyl)-biphenyl and malonic ester.

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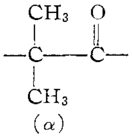
CRYSTALLINE POLYMERS OF DIMETHYLKETENE

Sir:

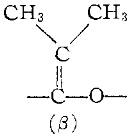
It is known that dimethylketene dimerizes readily to tetramethyl-1,3-cyclobutanedione.[1] Higher polymers were obtained by Staudinger[2] using aliphatic or aromatic amines as catalysts. These amorphous products can be considered as derived from the irregular copolymerization of the two monomeric



$$-\overset{CH_3}{\underset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-$$

(α)

and



$$-\overset{(CH_3)_2C=}{C}-O-$$

(β)

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

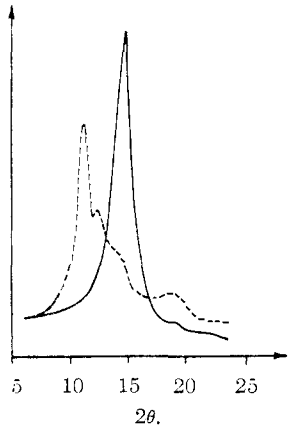


Fig. 1.—X-Ray Geiger registration (CuKα) of the two crystalline poly-dimethylketenes: ——— polymer I, --------- polymer II.

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 micromolecules 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.

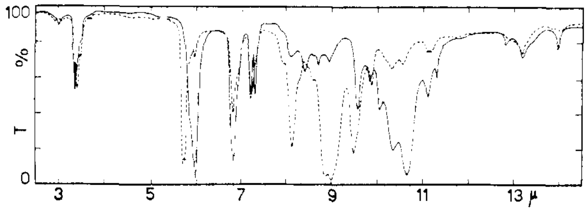


Fig. 2.—Infrared spectra of the two crystalline polydimethylketenes, mulls in Nujol and C_4Cl_6: ——— polymer I, --------- polymer II.

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 polydimethylvinyl 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.

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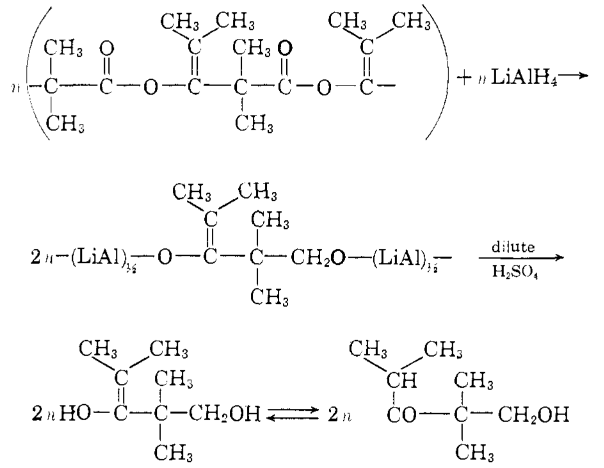
[1] H. Staudinger, H. Schneider, P. Schotz and P. M. Strong; *Helv. Chim. Acta*, **6**, 291 (1923).

[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:



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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EVIDENCE FOR INVOLVEMENT OF A METHIONINE RESIDUE IN THE ENZYMATIC ACTION OF PHOSPHOGLUCOMUTASE AND CHYMOTRYPSIN

Sir:

In studies to clarify the role of histidine in phosphoglucomutase action it was found[1] that loss of enzyme activity on photoöxidation could be explained on the basis of the model shown in equation 1. Here the various enzyme species are indicated by subscripts which identify intact amino acid residues. Thus, E_{XY} refers to original enzyme with X and Y unchanged, E_X refers to enzyme in which X is intact but Y has been oxidized, etc. E_X has an activity equal to about 8% of the original activity, while E_Y and E are inactive in the present assay systems.[1] Since Y has been identified as histidine, it was clearly of interest to identify X which is apparently even more important to enzyme activity.

$$\begin{tikzcd} E_{XY} \arrow[r, "k_X"] \arrow[d, "k_Y"'] & E_Y \arrow[d, "k_Y"] \\ E_X \arrow[r, "k_X"] & E \end{tikzcd} \qquad (1)$$

To allow such an identification, the rate constants for oxidation of the susceptible residues of the protein were obtained for comparison with the value of 0.38 min.$^{-1}$ attributed to X by both rate and "all-or-none" assays. Aliquots of the enzyme were removed at various time intervals during photoöxidation, hydrolyzed and assayed on the automatic amino acid analyzer of Spackmann, Stein and Moore.[2] Since acid hydrolysis is known to destroy tryptophan and was found to cause regeneration of methionine from methionine sulfoxide, these residues were determined after barium hydroxide hydrolysis of the photoöxidized protein. Other residues were determined after acid hydrolysis except for cysteine which was determined by the *p*-chloromercuribenzoate reaction.

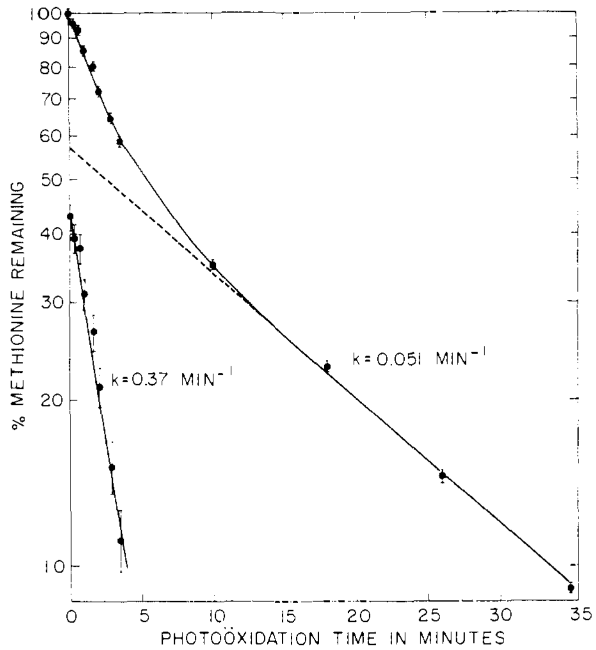

Fig. 1.—Loss of methionine on photoöxidation of phosphoglucomutase.

The fraction of methionine remaining as a function of photoöxidation time is shown in Fig. 1. This biphasic curve can be analyzed as described previously[3] giving oxidation constants of 0.37 min.$^{-1}$ for the accessible methionines and 0.051 min.$^{-1}$ for the inaccessible residues. The constants obtained for other amino acids were cysteine, 0.07 min.$^{-1}$, tryptophan, about 0.01 min.$^{-1}$, and tyrosine, about 0.01 min.$^{-1}$. No other residues were detectably affected. X can therefore be identified as an accessible methionine residue. Since photoöxidation of this residue produces enzyme which is inert in the "all-or-none" assay, methionine oxidation decreases enzyme activity by a factor of more than 200. It is of interest in this regard that Gundlach, Stein and Moore have found that carboxymethylation of methionine also reduces ribonuclease activity.[4]

Since a similarity in the bond-breaking or "catalytic" residues at the active sites of phosphoglucomutase and chymotrypsin had been indicated in previous work,[3] it was of interest to per-

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(1) W. J. Ray, Jr., J. J. Ruscica and D. E. Koshland, Jr., THIS JOURNAL, **82**, 4739 (1960).

(2) D. H. Spackmann, W. H. Stein and S. Moore, *Anal. Chem.*, **30**, 1190 (1958).

(3) D. E. Koshland, Jr., W. J. Ray, Jr., and M. J. Erwin, *Federation Proc.*, **17**, 1145 (1958).

(4) H. G. Gundlach, W. H. Stein and S. Moore, *J. Biol. Chem.*, **234**, 1754 (1959).