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ALTERNATING COPOLYMERS OF
 DIMETHYLKETENE WITH KETONES

Sir:

High polymers in which the monomeric units are, at least in part, originated by the opening of the carbonyl bond of a ketone were not known up to now.

During our work on the polymerization of cumulative double bonds, we have found that by direct polymerization of mixtures of dimethylketene and acetone in the presence of lithium alkyls it is possible to obtain in good yields macromolecular products containing both monomers.

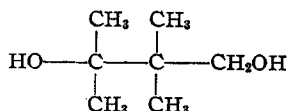
By adding, at -60° , 1.4 millimoles of butyllithium to a solution of dimethylketene (8 g.) and acetone (8 g.) in toluene (20 ml.), rapid polymerization takes place. After precipitation with methyl alcohol, 8 g. of a white solid polymer (I) is isolated. This product shows an intrinsic viscosity in chloroform at 30° of approximately 0.4, is soluble in boiling benzene and dioxane, and proves to be highly crystalline on X-ray examination. This result indicates that the polymer possesses a high regularity of structure.

The analysis of (I) demonstrates that dimethylketene and acetone are present in a molar ratio of 1:1.

Anal. Calcd. for $C_4H_6OC_3H_6O$: C, 65.60; H, 9.44. Found: C, 65.98; H, 9.55.

After reduction of the polymer, dissolved in tetrahydrofuran, with $LiAlH_4$, we have isolated in good yields (78%) a product (II) having m.p. $138-140^\circ$.

Composition analysis and molecular weight of (II) agree with the formula

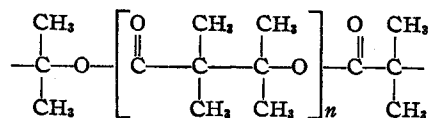


Anal. Calcd. for $C_7H_{16}O_2$: C, 63.51; H, 12.18; mol. wt., 132. Found: C, 63.51; H, 12.12; mol. wt., 138.

The structure of this glycol also has been con-

firmed by comparison with the product obtained by reduction of tetramethyl- β -propiolactone with $LiAlH_4$.

The results of the reduction of (I) indicate that it consists of an alternating copolymer of the two monomers, having the chemical structure



The presence of ester groups is also confirmed by a strong absorption band at 5.80μ .

Polymerization of mixtures containing acetone and dimethylketene in molar ratios higher than one always leads to the product described above.

Starting from mixtures in which dimethylketene prevails, some homopolymer of this monomer is present in the polymerizate.

When polymerizing mixtures of dimethylketene and acetophenone, an alternating copolymer also is produced which, however, proves to be amorphous on X-ray examination.

It is known that by treating ketenes with ketones in the presence of Friedel-Crafts catalysts, β -lactones are obtained.¹ Some β -lactones, such as β -propiolactone and β -butyrolactone, yield polyesters on heating.² We have observed, however, that under the same conditions tetramethyl- β -propiolactone loses quantitatively carbon dioxide. Even in the presence of lithium alkyls, this lactone does not yield a polyester. These results demonstrate that the alternating copolymerization of dimethylketene with acetone does not take place through successive reactions, with formation of a β -lactone as a stable intermediate product.

(1) H. J. Hagemeyer, Jr., *Ind. Eng. Chem.*, 41, 765 (1949).

(2) T. L. Cresham, J. E. Jansen and F. W. Shaver, *THIS JOURNAL*, 70, 998 (1948).

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