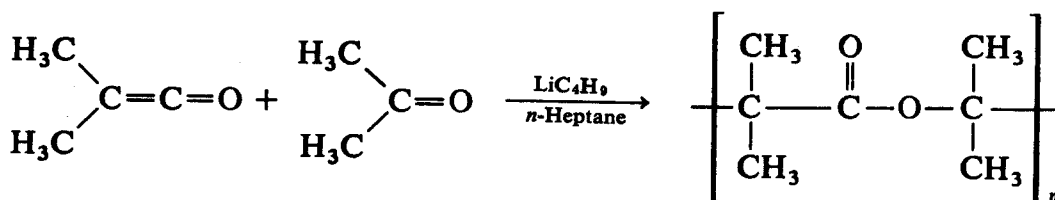


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## Alternating Copolymer of Dimethylketene with Acetone

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### I. Procedure

*Caution! In the presence of air, dimethylketene yields highly explosive peroxides. Vapors are harmful and irritating, and handling must be carried out in an efficient hood with suitable shielding. All apparatus that have come in contact with dimethylketene must be thoroughly washed with methanol soon after use.*

A 100-ml., three-necked flask is fitted with a mechanical stirrer and a tube connected to a vacuum-nitrogen line. A nitrogen atmosphere is attained in the apparatus by repeated evacuation with vacuum release (Note 1). The apparatus is kept under a slight nitrogen overpressure. The flask is charged with 30 ml. of anhydrous *n*-heptane (Note 2) and cooled externally with a Dry Ice-saturated methanol bath. Freshly distilled dimethylketene (5 ml.) (Note 3) and anhydrous acetone (5 ml.) (Note 4) are added from a pipet connected to a syringe. The stirring of the solution is started soon after and is followed by the addition of 0.6 ml. of *n*-butyllithium (Note 5). The polymerization starts almost immediately with the evolution of heat and precipitation of the copolymer. After 2 hours the reaction is terminated by adding 10 ml. of methanol

(Note 6), and the contents of the flask are transferred into a beaker containing 200 ml. of methanol. The polymer is crushed with a glass rod and allowed to stand for a few hours, then collected by filtration, washed on the filter with methanol, and dried under vacuum. The dry polymer is treated for 1 hour with 250 ml. of refluxing *n*-heptane, collected by suction, and dried again in vacuo. The residual white powdery polymer weighs 4–5 g. (55–68% yield) (Note 7).

## 2. Characterization

Dimethylketene-acetone alternating copolymer, m.p. (capillary) 162–165°C., is soluble in chloroform, boiling benzene and dioxane. Its intrinsic viscosity in phenol-tetrachloroethane (1:1) is 0.1 to 0.2. The x-ray powder diffraction pattern shows a highly crystalline structure, and the infrared absorption spectrum obtained from a film cast on a sodium chloride disk from a chloroform solution shows a characteristic band at 1724  $\text{cm}^{-1}$  (3).

## 3. Notes

1. Prepurified or lamp-grade nitrogen containing no more than 10 p.p.m. of oxygen or water should be used.
2. Reagent-grade *n*-heptane heated under reflux over sodium-potassium alloy and distilled under nitrogen, is used.
3. For synthesis, handling, storage, and purification of dimethylketene see (4).
4. Pure reagent-grade acetone, dried over anhydrous calcium sulfate and distilled under nitrogen, is used.
5. A commercial 15% solution (1.6 *M*) of *n*-butyllithium in *n*-hexane is used.
6. If the reaction mixture is still strongly yellow, the addition of methanol causes a vigorous reaction because of the presence of large amounts of unreacted dimethylketene. In this case methanol must be added very slowly from a dropping funnel. The presence of dimethylketene 1 hour after the reaction start indicates that the reactants, in particular dimethylketene, are not sufficiently pure. Dimethylketene can be further purified by distilling over trialkylaluminum.
7. The checkers also used a high vacuum apparatus and obtained a 75–80% yield of product, m.p. 167–171°C. (capillary), with an intrinsic viscosity of 0.9 to 1.2.

4. References

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