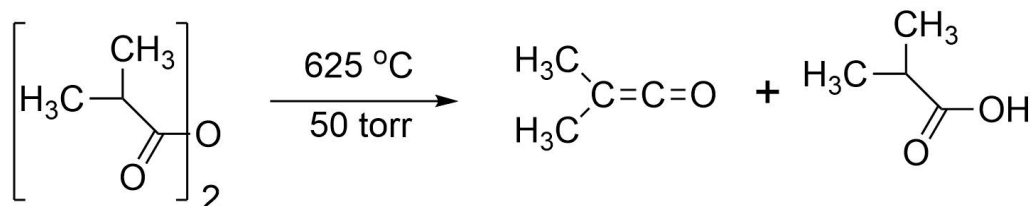


Polymerization of Dimethylketene

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A. Synthesis of Dimethylketene

1. Procedure (Note 1)

Caution! In the presence of air, dimethylketene yields highly explosive peroxides. These are dangerous also in the form of semi-invisible films on glassware. Vapors are harmful and irritating. All treatments must be carried out in an efficient hood with suitable shielding. All the parts that have come into contact with dimethylketene must be thoroughly washed with methanol soon after use and the washes should be destroyed.

Pyrolysis of the anhydride is carried out in the apparatus shown in Figures 1 and 2. The pyrolysis oven consists of a copper tube having a length of 100 cm and an inner diameter of 1.5 cm (Note 2). The copper tube is covered with a stainless steel tube. Thermocouples for temperature control are placed on the steel tube. The oven is heated with electric resistances having a power of about 2 kilowatts.

A nitrogen atmosphere is attained in the apparatus by repeated evacuation and refilling with purified nitrogen (Note 3). All stopcocks of the apparatus are closed except stopcock I. The internal pressure is regulated to 50-100 torr (absolute pressure) by a vacuum pump connected to stopcock I.

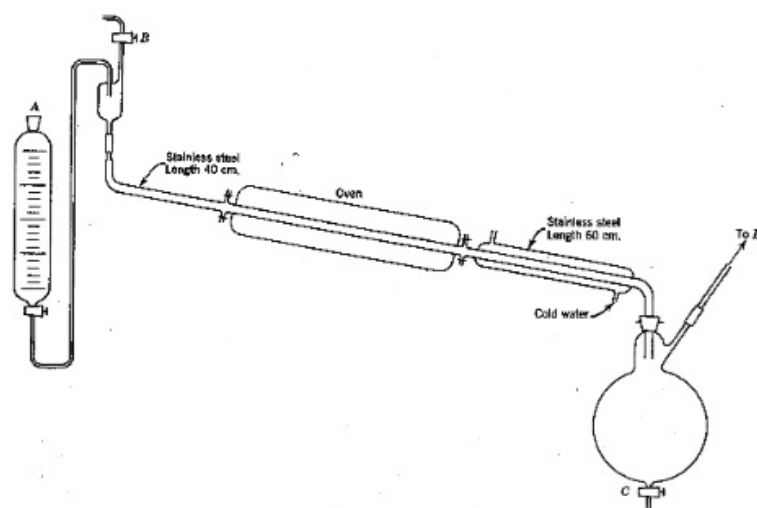


Fig. 1.

Figure 1

Figure 2

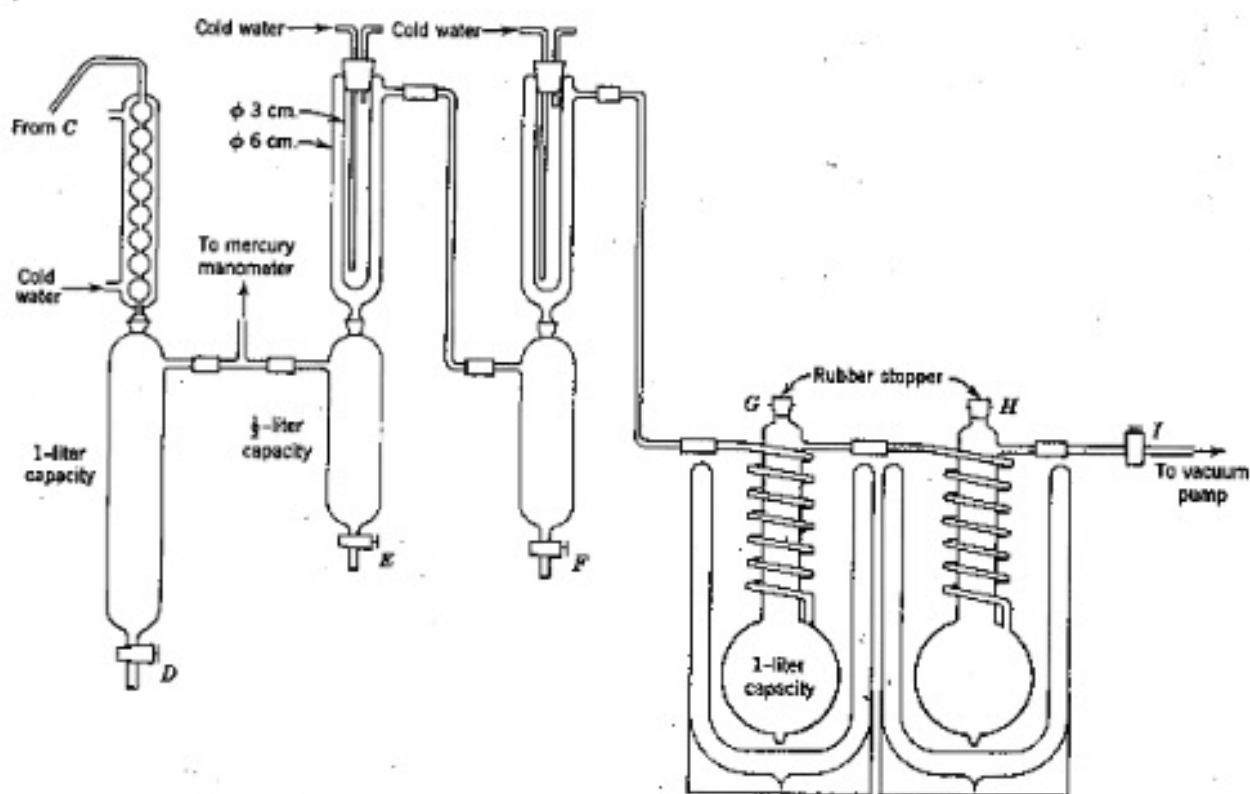


Fig. 2.

The oven is heated to 600-650°, and cold water is circulated in the coolers. Distilled isobutyric anhydride is added to the graduated dropping funnel A, and traps G and H are cooled by immersion in Dewar flasks containing liquid nitrogen or Dry Ice and methanol (Note 4).

When both temperature and internal pressure of the oven become stable, the stopcock of funnel A is regulated so that 270 g/h of isobutyric anhydride passes through the pyrolysis tube. Unreacted anhydride and isobutyric acid are collected in vessels C, D, E, and F, while dimethylketene is collected (90-100 g/h) in traps G and H.

The apparatus can operate without interruption for about 6 h; approximately 1 l of dimethylketene is obtained.

After the reaction is completed, the stopcock of funnel A and stopcock I are closed. Purified nitrogen is then introduced through stopcock B. A slight nitrogen overpressure (a few torr) is maintained in the apparatus.

Traps G and H are isolated from the remaining part of the apparatus by closing the rubber joint between F and G with a Hoffman clamp. The vacuum pump is removed from stopcock I, and a slight nitrogen overpressure is applied to traps G and H through this stopcock.

It is now possible to draw dimethylketene from traps G and H with a siphon, as shown in Figure 3. To allow complete siphoning, small wells are made at the bottom of traps G and H. Immediately after siphoning, both the siphon tubes and the traps are washed with methanol to prevent the formation of peroxides.

Dimethylketene obtained by this method is already 98-99% pure in the crude state. It is important to avoid the presence of sulfur-containing compounds during the pyrolysis.

Crude dimethylketene can be easily stored over a period of some weeks under nitrogen atmosphere at -78° in 100-250 ml graduated test tubes each fitted with a ground glass joint at the top and a side-arm stopcock (Note 5). To prevent the formation of peroxides it is necessary to add a trialkyl aluminum (e.g., triethylaluminum or triisobutyl aluminum) to dimethylketene (3-5 ml of heptane solution with 10% by weight of alkyl aluminum per 100 ml of dimethylketene, Note 6). *Caution! Trialkyl aluminum compounds are generally pyrophoric and react violently with water.* The trialkyl aluminum solution must be slowly added to dimethylketene maintained at -78° , and poured along the test tube walls to avoid violent reactions. The presence of trialkyl aluminum also allows freeing the monomer of impurities, such as isobutyric anhydride, which might modify the course of the polymerization (Note 7).

Dimethylketene must be distilled shortly before use. This operation can be suitably conducted under reduced pressure (18-20 torr) with the device shown in Figures 4 and 5.

At the beginning of the operation, test tube A which contains dimethylketene with alkyl aluminum is immersed in the Dewar flask D, while tube B is maintained at room temperature.

The stopcock of tube A is closed and that of the tube B opened; vacuum and nitrogen are repeatedly applied through the inner tube C. Finally, tube B is evacuated (18-20 torr), test tube A is removed from the Dewar flask, test tube B is cooled in the Dewar flask, and the stopcock of test tube A is opened.

To prevent bumping of the liquid dimethylketene, test tube A must be kept horizontal during the distillation. As soon as the temperature of the liquid in A has reached about -30° , dimethylketene condenses in B.

After distillation of the required amount of dimethylketene, nitrogen is introduced from tube C, the stopcocks of test tubes A and B are closed and the rubber tubing is removed. Test tube A is then immersed in a bath at -78° . Nitrogen is introduced from the stopcock of test tube B; the stopper with the inserted tube C is removed and replaced with an ordinary rubber stopper. As soon as tube C has been removed, it must be thoroughly washed with methanol to prevent formation of peroxides.

Distilled dimethylketene is used within 24 h. It must be stored at -78° until use and withdrawn under nitrogen with a pipet connected to a syringe, or with a siphon. Siphons and pipets must be thoroughly washed with methanol immediately after use to prevent formation of peroxides.

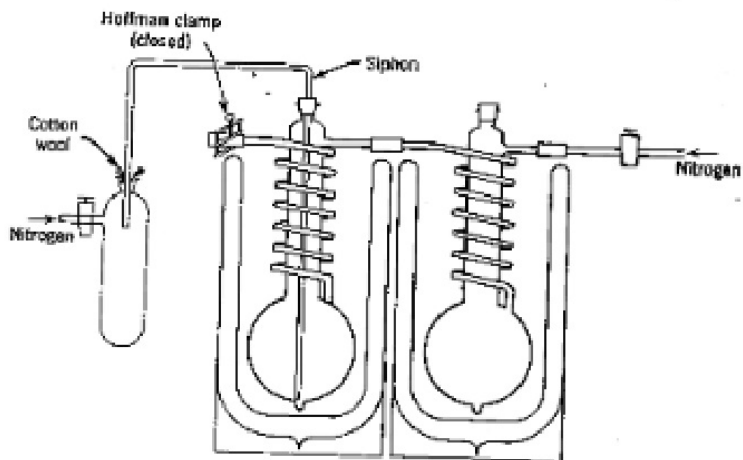


Fig. 3.

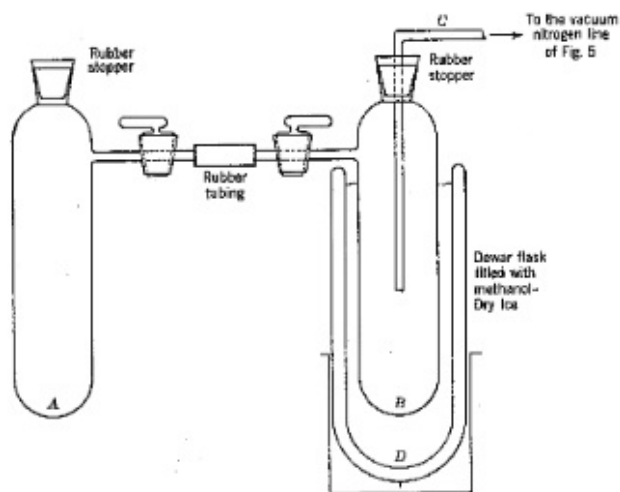


Fig. 4.

The residual distilled dimethylketene can be decomposed by dilution with 5-10 parts of toluene followed by addition of methanol, or can be stored for a longer time by addition of trialkyl aluminum in amounts similar to those reported above.

2. Notes

1. This preparation is essentially the one reported earlier.³
2. A much shorter pyrolysis tube (45 cm) can be used; however, it results in a slightly decreased yield, i.e., 64% instead of 74-82%.
3. The nitrogen should not contain < 10 ppm of oxygen or water.
4. For traps G and H, liquid nitrogen cooling is preferred.
5. To seal test tubes, rubber stoppers are preferred to ground glass.
6. Care must be taken to adhere to this concentration of trialkyl aluminum. Excess trialkyl aluminum causes vigorous reaction and polymerization during distillation.
7. Dimethylketene obtained by methods other than the pyrolysis of isobutyric anhydride generally contains greater amounts of impurities which impair polymerization. They can be removed, however, by repeated distillation of dimethylketene over trialkyl aluminum by the same methods and with the same amounts of aluminum alkyl mentioned above.

In general, two or three distillations are sufficient in the case of dimethylketene obtained by pyrolysis of dimethylmalonic anhydride and of 2,2,4,4-tetramethyl-1,3-cyclobutanedione. The dimethylketene obtained from α -bromoisobutyryl bromide, according to the method reported in **Organic Syntheses**,⁴ is not recommended for polymerization because complete elimination of ethyl acetate solvent is very difficult.

3. Methods of Preparation

Dimethylketene has been prepared by treatment of α -bromoisobutyryl bromide with zinc^{4,5} and by pyrolyses of isobutyrylphthalimide,⁶ dimethylmalonic anhydride at 180°,⁷ α -carbomethoxy- α , β -dimethyl- β -butyrolactone,⁸ the dimer of dimethylketene, 2,2,4,4-tetramethyl-1,3-cyclobutanedione,⁹ isobutyric acid and anhydride at about 700°,³ and 3-diazobutanone at 180°.¹⁰

B. Polymerization of Dimethylketene

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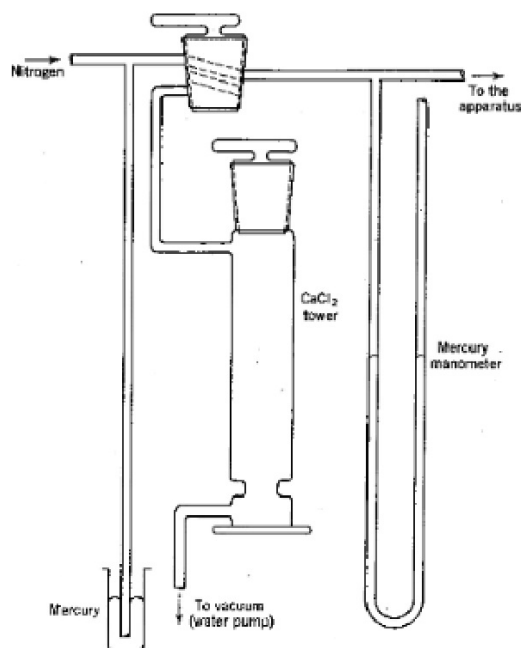
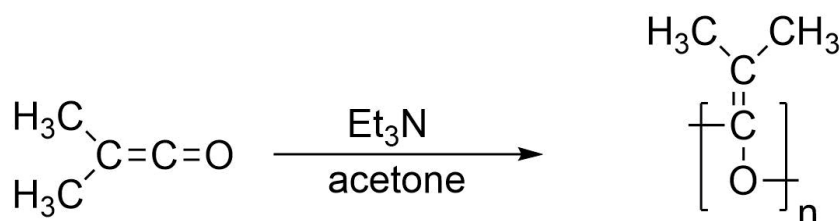


Fig. 5.

1. Procedure 1. Acetalic Polymer: Caution!

Park A. Synthesis for warning

A 100 ml, four-necked flask is fitted with a mechanical stirrer, a low temperature thermometer and a tube connected to a vacuum/nitrogen line, constructed as shown in Figure 4.

A nitrogen atmosphere is attained in the apparatus by repeated evacuation with vacuum release to purified nitrogen (Note 1). The apparatus is kept under a slight nitrogen overpressure. The flask is charged with 200 ml of anhydrous acetone (Note 2) and cooled externally with a Dry Ice-methanol bath so that the inner temperature is lowered to about -70° . Freshly distilled dimethylketene (20 ml, Note 3) is added from a pipet connected to a syringe. Stirring of the solution is started soon after, then 0.4 ml of triethylamine (Note 4) is added. The solution becomes cloudy almost immediately with a decrease of the yellow color. After 30 min the polymerization is stopped by addition of 50 ml of methanol (Note 5), and the contents of the flask are transferred to a beaker with the aid of 500 ml of methanol. The suspension is allowed to settle for several hours. The upper clear liquid is siphoned, and the very finely divided residual suspension is centrifuged (Note 6). The sticky solid that separates is suspended in 100 ml of methanol and recentrifuged. This procedure is repeated three times. Finally the solid is dried under vacuum at room temperature (Note 7). After drying, 11-12 g of a finely divided white polymer is obtained (69-81% yield).

2. Characterization

High molecular weight polydimethylketene with acetalic structure is partially soluble in several organic solvents (e.g., benzene, chloroform, cyclohexanone). It is completely soluble in boiling diphenyl ether. In a sealed capillary tube it does not decompose below 290° . Between 290 and 310° it melts with gas release.

The polymer has little stability in air and degrades slowly to a light yellow viscous liquid.

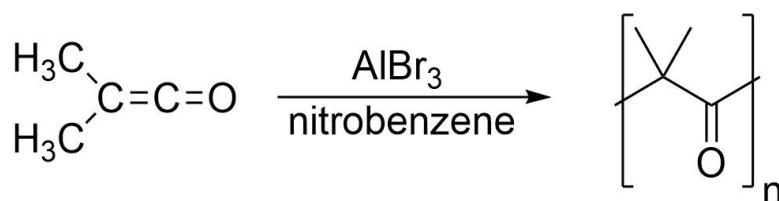
The powder x-ray diffraction pattern shows a highly crystalline structure. The infrared absorption spectrum is obtained from a Nujol mull. It shows a characteristic absorption band at 5.85μ .¹¹

3. Notes

1. Prepurified nitrogen containing < 10 ppm of oxygen or water is used.
2. Reagent grade acetone, dried over anhydrous calcium sulfate and distilled under nitrogen, is used.
3. See part A.
4. Reagent grade triethylamine, dried over anhydrous calcium sulfate and distilled under nitrogen, is used.
5. 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 30 min after the start of the reaction indicates that the products used, and in particular dimethylketene, are not sufficiently pure. Dimethylketene can be further purified by redistilling it over a trialkyl aluminum compound.
6. Because the solid is very finely divided, it is very difficult to separate it by filtration.
7. This operation is preferably carried out by applying vacuum directly to the vessel in which the polymer has been centrifuged. This prevents losses on transferring the sticky solid.

1. Procedure 2. Vinyl Polymer.

Part A Synthesis warning: Caution!



A 100 ml four-necked flask is equipped with a 10 ml dropping funnel with pressure-equalizing tube, mechanical stirrer, and tubing connected to a vacuum-nitrogen line, constructed as shown in Figure 4. A nitrogen atmosphere is attained in the apparatus by repeated evacuation with vacuum release to purified nitrogen (Note 1). The apparatus is maintained under a slight nitrogen overpressure. Anhydrous carbon tetrachloride (20 ml), 13 ml of anhydrous nitrobenzene (Note 2), and 20 ml of freshly distilled dimethylketene (Note 3) are introduced into the flask. Nitrobenzene (7 ml) and 3 ml of a nitrobenzene solution of AlBr_3 (Note 4) are introduced to the dropping funnel. The flask is cooled externally with a bath at -30° and stirring is started. The contents of the dropping funnel are dropped into the flask over a period of about 15 min and stirring is continued for a further 75 min.

The reaction is stopped by the addition of 20 ml of methanol (Note 5) and the contents of the flask are transferred to a beaker containing 250 ml of methanol. Concentrated hydrochloric acid (5 ml) is added and the colored polymer lumps are crushed with the aid of a stirrer. The polymer is allowed to stand for a few hours, then it is filtered, washed with methanol, and resuspended in 250 ml of methanol containing 50 ml of concentrated hydrochloric acid. This procedure is repeated until the polymer is perfectly white; it is filtered and dried under vacuum at room temperature; yd 9-10 g of fiber-forming white polymer (56-63%).

2. Characterization

Polydimethylketene having a ketonic structure is soluble in hot nitrobenzene, acetophenone, anisole, and cyclohexanone. Its intrinsic viscosity in nitrobenzene at 135° is 0.8-0.9; its melting point in a capillary tube is $195\text{-}205^\circ$. The polymer may be pressed into film between aluminum foil at $200\text{-}220^\circ$. The powder x-ray diffraction pattern shows a highly crystalline structure.¹² The infrared absorption spectrum is obtained from a Nujol mull. It shows a characteristic band at 5.99μ .¹³

3. Notes

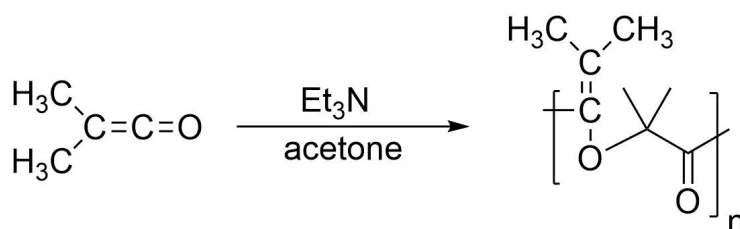
1. Prepurified nitrogen containing < 10 ppm of oxygen or water is used.
2. Reagent grade carbon tetrachloride that was dried over anhydrous calcium sulfate and distilled under nitrogen is used. Reagent grade nitrobenzene is dried over calcium chloride, distilled under reduced pressure, and maintained under a nitrogen atmosphere.
3. See part A.
4. A solution containing 350 g of AlBr_3 per liter of solvent is used. It is prepared from anhydrous nitrobenzene (Note 2) and reagent grade anhydrous aluminum bromide distilled under nitrogen.
5. See Note 5 of previous procedure.

4. Methods of Preparation

Polydiphenylketene with a polyketonic structure has also been obtained by polymerization with PbCl_4 as catalyst.¹⁴

1. Procedure 3. Ester Polymer

Part A. Synthesis warning: *Caution!*



A 250 ml, four-necked flask is equipped with a mechanical stirrer, a reflux condenser, and a 50 ml dropping funnel with pressure equalizing tube. The top of the reflux condenser is connected to a vacuum-nitrogen line constructed as shown in Figure 4. A nitrogen atmosphere is attained in the apparatus by repeated evacuation with vacuum release to purified nitrogen (Note 1). The system is maintained under nitrogen overpressure.

Anhydrous ether (120 ml, Note 2) and 1 ml of a 0.1M solution of sodium naphthalene in tetrahydrofuran (Note 3) are introduced into the flask at room temperature. Anhydrous ether (30 ml) and 20 ml of dimethylketene (Note 4) are introduced into the dropping funnel. Stirring is immediately started and the dimethylketene solution is added at the rate of about 5 ml/min. A few minutes after the addition starts, the mixture begins to cloud and the solvent begins to reflux. Occasional external cooling with a cold water bath may be necessary to moderate the boiling rate. After dimethylketene has been added, stirring is continued for 2 h, then the reaction is stopped by the addition of 20 ml of methanol (Note 5). The contents of the flask are transferred to a beaker with the aid of 50 ml of methanol. The polymer is repeatedly washed with methanol, filtered, and dried under vacuum at room temperature. A finely divided white polymer is obtained (14-15 g; 87-94% yd).

2. Characterization

Polydimethylketene having a polyester structure is soluble in different hot solvents, such as toluene, tetralin, anisole, cyclohexanone. Its intrinsic viscosity in tetralin at 135° is 0.3-0.4. Its melting point in a capillary tube is 195-220°. The polymer may be pressed into a film between aluminum foil at 150-170°. The powder x-ray diffraction pattern shows a highly crystalline structure. The infrared absorption spectrum is obtained from a film cast on NaCl disk from chloroform solution. It shows a characteristic absorption band at 5.75 μ .¹⁵

3. Notes

1. Prepurified nitrogen containing < 10 ppm of oxygen or water is used.
2. Reagent ether is refluxed over lithium aluminum hydride for 10 h and then distilled twice under nitrogen.
3. The sodium naphthalene solution is prepared from tetrahydrofuran distilled twice over lithium aluminum hydride under a nitrogen atmosphere. The amounts of clean sodium and reagent grade naphthalene necessary to obtain a 0.1 M solution are added and the mixture is left at room temperature until the sodium completely dissolves.
4. See part A.
5. See Note 5 in first polymer procedure.

4. Methods of Preparation

Polymethylphenylketene and polydiphenylketene having a polyester structure have also been obtained by polymerization with anionic catalysts.^{14,16,17}

5. References

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