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Homopolymerization of Maleic Anhydride

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NOTE

Homopolymerization of Maleic Anhydride

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It is well known that molecular oxygen inhibits the homopolymerization of vinyl-type monomers [1]. During several attempts in this laboratory to homopolymerize vinyl acetate in benzene, no polymer was formed over a period of one week, even though the initiator was varied as to type and concentration.

However, vinyl acetate polymerized rapidly in benzene when the following sweeping technique was applied to remove molecular oxygen from the reaction mixture. The monomer and the initiator were dissolved in the appropriate solvent in the reaction vessel. Dry nitrogen which was freed from oxygen traces by passing through Fieser solution and calcium chloride consecutively, was bubbled into the reaction mixture for about 5 min. Approximately 10 g of Dry Ice was then introduced into the reaction vessel via a side arm, and allowed to dissolve in the reaction mixture. The apparatus was then evacuated to a pressure of 10-15 Torr. A Dry Ice-acetone-cooled trap was inserted between the apparatus and the vacuum line to avoid any loss of solvent and monomer. The vacuum inside the apparatus was replaced by oxygen-free nitrogen. This sweeping process was carried out twice before the reaction was started. The reaction was protected against moisture and molecular oxygen by keeping a positive flow of pure nitrogen throughout the whole reaction time.

When this sweeping technique was applied to solutions of maleic anhydride in benzene and the reaction was allowed to proceed at 75

TABLE 1

Maleic anhydride (g)	Benzene (ml)	Benzoyl peroxide (g)	Reaction time (hr)	Reaction temperature (°C)	Yield (g)	Yield (%)	$\overline{M_n}$ (VPO)
10	150	0.15	24	75	0.735	7.35	710
10	150	0.2	47	80	1.285	12.85	625
10	150	0.15	24	75	0.936	9.36	680

or 80°C with benzoyl peroxide initiator, a product was obtained which was characterized as poly(maleic anhydride). Data for these reactions are shown in Table 1.

The polymer, which is a creamy white powder, precipitated out of benzene as it was formed. It was filtered and washed with hot benzene until all traces of the monomer were removed. The polymer dissolves in acetone, acetonitrile, and dilute alkaline solutions, giving canary yellow solutions.

The number-average molecular weight was determined by vapor pressure osmometry and ranged between 625 and 710. The infrared spectrum of the maleic anhydride monomer is shown in Fig. 1 and that of the polymer in Fig. 2. Strong carbonyl peaks at 1859 and 1780 cm^{-1}, characteristic of the anhydride, appeared in both spectra. The main difference is that the peaks were much broader in the polymer spectrum. The same broadening is also noticed in the finger print area of the spectrum. Broadening of the peaks is characteristic of polymeric materials. Based on the molecular weight data and the infrared spectra, it was concluded that the product is poly(maleic anhydride).

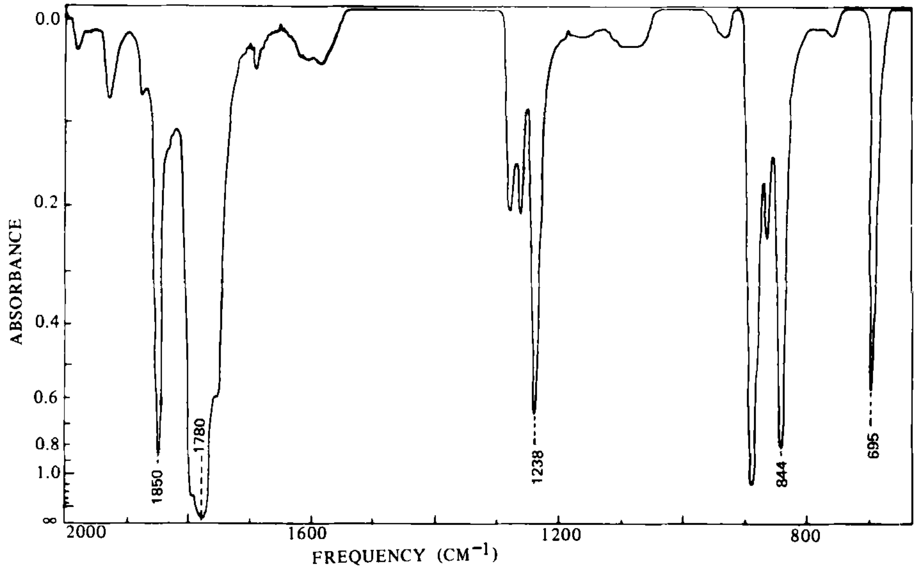

FIG. 1. Infrared spectrum of maleic anhydride solution (0.5% in acetonitrile).

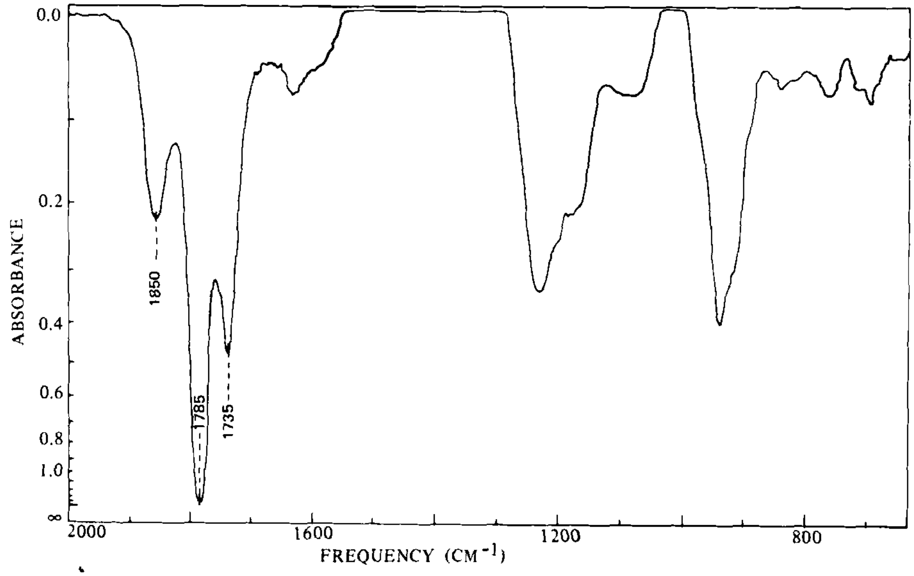

FIG. 2. Infrared spectrum of poly(maleic anhydride) solution (0.5% in acetonitrile).

When the polymerization was carried out in tetrahydrofuran, no polymer could be isolated. Also, when 2,2-azobisisobutyronitrile initiator was used, no polymer was obtained.

A literature survey revealed that poly(maleic anhydride) was prepared in bulk polymerization of the molten anhydride [2] or by using drastic conditions and a high catalyst concentration in acetic anhydride solvent [3]. With the sweeping technique described above, poly(maleic anhydride) was obtained under mild conditions and relatively low initiator concentration.

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