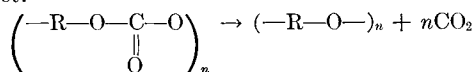


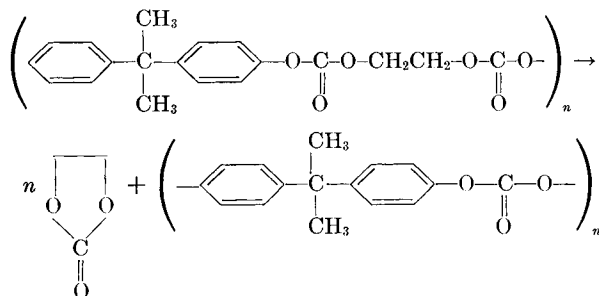
NOTES

Elimination of Ethylene Carbonate from Poly[ethylene *co* 2,2-bis(4-phenylene)propane Carbonate]

Pyrolysis of polycarbonates can, in some instances, yield polyethers. Thus J. W. Hill pyrolyzed poly(decamethylene carbonate) and obtained poly(decamethylene oxide) as one product:¹



Attempts to apply the same reaction to the polycarbonate derived from ethylene bischloroformate and diphenylolpropane did not give a polyether, but instead ethylene carbonate was rapidly and quantitatively eliminated leaving diphenylolpropane polycarbonate. The overall reaction was thus:



The residual diphenylolpropane polycarbonate was light yellow, clear, and tough, apparently of high molecular weight. Films were prepared either by dry casting from chloroform or by the usual melt pressing techniques. That the residual polymer was diphenylolpropane polycarbonate was conclusively shown by identity of its infrared spectrum to that of General Electric's Lexan* polycarbonate resin and to the same polymer prepared by interfacial polymerization² from diphenylolpropane and diphenylolpropane bischloroformate.

EXPERIMENTAL: Pyrolysis of Poly[ethylene *co* 2,2-bis(4-phenylene)propane Carbonate]

Poly[ethylene *co* 2,2-bis(4-phenylene)propane carbonate] was prepared from diphenylolpropane and ethylene bischloroformate by interfacial polymerization using methyl ethyl ketone as the organic phase and aqueous sodium hydroxide as acid acceptor. The polymer thus obtained was soluble in dimethylformamide and melted at 170°C. on a Dennis temperature gradient bar. This polycarbonate (η_{inh} 0.9 at 0.5% concentration and 30°C. in tetrachloroethane/phenol, 40/60 by weight) was heated at 280°C. and 1 mm. Hg pressure for 1 hr. Vigorous effervescence occurred and a colorless liquid distilled, which was identified as ethylene carbonate. The polymeric residue was cooled under nitrogen, dissolved in chloroform, and reprecipitated into methanol. The precipitate was then filtered and dried at 60°C. *in*

vacuo. Clear tough films were obtained by pressing the polymer at 240°C. in a Carver press or by dry casting from chloroform. The polymer melted at 240°C. on a Dennis temperature gradient bar and had an inherent viscosity at 0.5% concentration in tetrachloroethane/phenol (40/60) of 0.45. The polymer was shown to be diphenylolpropane polycarbonate.

References

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Stabilization of Polyethylene by Antioxidants of Large Particle Size

Carbon blacks which are used to inhibit photo-oxidation of polyolefins also function as mild thermal antioxidants. It has been suggested¹ that carbon black functions as a radical trap in terminating thermal oxidation. Antioxidant effectiveness has also been attributed to the presence of reactive groups on the particle surface.² The latter hypothesis is substantiated by the fact that effectiveness in chain termination increases with the concentration of these functional groups. Various investigators³⁻⁵ have identified these groups as hydroxyl, carbonyl, carboxyl, and lactone.

The effect of temperature on the oxidation rate of polyethylene inhibited with carbon black is different from that observed with the uninhibited polymer or with polyethylene containing molecularly dispersed antioxidants.⁶ With carbon black as the antioxidant, protection of the solid polymer is far greater than the extrapolated value based on accelerated oxidation above the polymer melting range. This results in a nonlinear relationship between oxidation temperature ($1/T$) and degree of protection (expressed as the logarithm of the induction period) in the temperature range of 80-160°C. Increased protection in the solid polymer has been confirmed by the observation that addition of 1% carbon black prevented significant loss in the physical properties of polyethylene during outdoor exposure in Florida for more than 18 years.¹

Oxidation of semicrystalline polymers has been assumed to occur principally in the amorphous regions.⁶ Also, it has been shown by density and x-ray studies that the overall crystalline content of polyethylene is not reduced by addition of 3% carbon black. Thus, there is an apparent increase in carbon black concentration with respect to the amorphous (oxidation-susceptible) region which results in greater protection in the solid polymer. Molecularly dis-

* Trademark for General Electric's polycarbonate resin.