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INVESTIGATION OF THE REACTION OF SOME UNSATURATED DICARBOXYLIC ACID ANHYDRIDES WITH CYCLIC CARBONATES

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ABSTRACT

This work reports attempts to extend to unsaturated anhydrides the rapid reaction of dicarboxylic acid anhydrides with ethylene carbonate to form polymer directly. The reaction of unsaturated diacid anhydrides with two cyclic carbonates, ethylene and propylene carbonate, leads to gelled products whenever the anhydride is capable of Michael addition, while an anhydride without such unsaturation gave linear polymer instead. The GC/MS results, along with efforts to trap radical reactions, support Michael addition as an explanation of gelation in these systems.

INTRODUCTION

We have previously reported on the reaction kinetics of two carboxylic acids [1, 2] and phthalic anhydride [3] with ethylene carbonate, and also of terephthalic acid with some alkyl-substituted ethylene carbonates [2]. Reactions with phthalic anhydride were notable for their overall short reaction time and direct production of polymer. We now report on efforts to extend this reaction to aliphatic anhydrides, in particular to unsaturated anhysrides, such as maleic anhydride, in order to determine the utility of these reactions for possible rapid production of polymers of the alkyd resin type. There is a patent literature report of the synthesis of such polymers with ethylene carbonates and acid or basic catalysts [4].

EXPERIMENTAL

The diacid anhydrides, maleic, 4-cyclohexenedicarboxylic, itaconic, and 5-norbornene-2,3-dicarboxylic, were all obtained from Eastman Organic Chemicals, as were the quaternary ammonium salts, propylene carbonate, *p*-toluenesulfonic acid, and fumaric acid. Ethylene carbonate was obtained from Union Carbide and was purified by vacuum distillation (bp 113°C/7 torr). The benzyltriphenylphosphonium chloride was obtained from M and T Chemicals, while the sodium borate, sodium stannate, and potassium acetate were obtained from Mallinckrodt. Irganox 1010 was obtained from Ciba-Geigy, and hydroquinone was photo-grade from Eastman Chemicals.

Reactions were run and polymerization kinetics determined by CO_2 evolution vs time as described previously [3]. A catalyst concentration of 0.4 mol% based on moles of carbonate was generally employed.

Analysis of the gelled polymer typical of the runs reported in this work was carried out by Soxhlet extraction of the gelled mass for 8 h with methylene chloride, followed by Soxhlet extraction for 8 h with chloroform. One gram of the thus extracted gel residue was then heated in 100 mL methanol for 4 h at 200°C in an autoclave in the presence of 0.1 g titanium tetraisopropoxide. The dark solution was filtered and then analyzed on a Finnegan GC/MS instrument using a 30M DB-5 capillary column and ammonia as a carrier gas in the chemical ionization mode of analysis.

RESULTS AND DISCUSSION

In attempting to reproduce the patent literature [4], we found, in the reaction of maleic anhydride with ethylene carbonate, that use of concentrated sulfuric acid as a catalyst gave a slow reaction and highly colored product. For the less acidic *p*-toluenesulfonic acid, the reaction was slow enough that it appeared to cease for all practical purposes at ~15% of CO_2 evolution. With any basic catalysts, however, severe darkening of the reaction mass occurred within 5 min of placing the reaction flask in the preheated metal bath. This was followed by eventual gelation of the reaction mixture. In order to determine what role the catalyst system played in the darkening and gellation, a series of reactions was run employing the catalysts, with and without poten-

TABLE 1. Catalyst Systems for Ethylene Carbonate/Maleic Anhydride Reaction

Catalyst	Inhibitor
Tri-*n*-butylamine	–
Tri-*n*-butylamine	Pennstop[a]
Ethyltrimethylammonium chloride	–
Ethyltrimethylammonium chloride	Irganox 1010[b]
Ethyltrimethylammonium chloride	Hydroquinone[c]
Potassium acetate	–
Benzyltriphenylphosphonium chloride	–
Tetraethylammonium fluoroborate	–
Sodium borate	–
Sodium stannate	–

[a] *N,N*-Bis(hydroxyethyl)aminobenzene, 0.01 wt% concentration.

[b] A hindered phenol antioxidant, at 0.1 and 1.0 wt% concentration.

[c] At 0.1 wt% concentration

tial inhibitors, shown in Table 1. All systems experienced gelation although a variety of cations and anions were employed. Although some catalysts were slower to gel than others, gelation always occurred at ~70% reaction of the carbonate as determined by CO_2 evolution. Addition of radical trapping agents did not seem to prevent gelation.

The strong bases gave rapid reaction. Both salts with chloride ion caused rapid reaction. Although not normally thought of as a strong base, Cl^- probably functions as such in the very polar carbonate medium, by analogy to chlorides dissolved in DMF, which are known to be basic enough to promote dehydrohalogenation [5]. Catalysts having very weakly basic anions, such as tetraethylammonium tetrafluoroborate, sodium stannate, and sodium borate, also yielded gelled reaction mixutres, albeit the CO_2 evolution was very slow.

The reactions conducted in the presence of hydroquinone or Irganox 1010 evolved CO_2 and gelled just like those not containing these additives. This

TABLE 2. Effect of Diacid Unsaturation Position on Reaction with Ethylene Carbonate

Diacid anhydrides	Results
Maleic	Gelled
Itaconic	Gelled
4-Cyclohexene-1,2-dicarboxylic	0.21 dL/g[a]
5-Norbornene-2,3-dicarboxylic	Gelled

[a] Inherent viscosity measured in 60:40 phenol:1,1,2,2-tetrachloroethane at 0.5 g/100 mL.

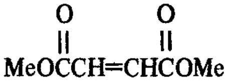
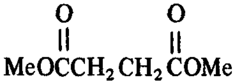
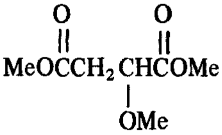
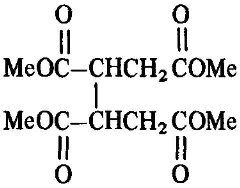
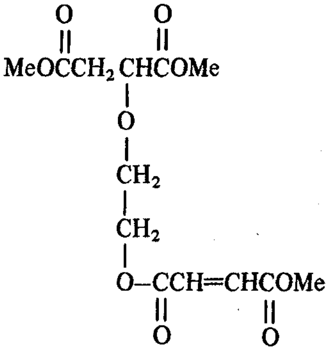
tended to indicate that radical crosslinking was probably not the cause of gelation although that possibility cannot be ruled out solely on such evidence. Propylene carbonate also behaved the same as ethylene carbonate in these reactions.

Additionally, three other anhydrides were used to probe the reaction. The results (Table 2) showed that gelation occurred whenever unsaturation was in conjugation with the carbonyl functionality or in a position to promote Michael addition. On the other hand, when conjugation was not present, a soluble polymer resulted. This would indicate possible Michael addition of

TABLE 3. Ions Observed by Mass Spectrometry of Methanolysis Products

Fumaric/ethylene carbonate	Maleic/ethylene carbonate
144	144
174	146
176	176
216	
288	290
290	344
318	432
400	

TABLE 4. Possible Structures of Some Mass Spectrograph Ions

m/e	
144	 $\mathrm{MeO\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}OMe}$
146	 $\mathrm{MeO\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}OMe}$
176	 $\mathrm{MeO\overset{O}{\overset{\|}{C}}CH_2\underset{\underset{OMe}{\|}}{CH}\overset{O}{\overset{\|}{C}}OMe}$
290	 $\begin{array}{l}\mathrm{MeO\overset{O}{\overset{\|}{C}}{-}CHCH_2\overset{O}{\overset{\|}{C}}OMe} \\ \qquad\ \ \mathrm{|} \\ \mathrm{MeO\underset{O}{\underset{\|}{C}}{-}CHCH_2\underset{O}{\underset{\|}{C}}OMe}\end{array}$
318	 $\begin{array}{l}\mathrm{MeO\overset{O}{\overset{\|}{C}}CH_2CH\overset{O}{\overset{\|}{C}}OMe} \\ \qquad\quad\ \mathrm{|} \\ \qquad\quad\ \mathrm{O} \\ \qquad\quad\ \mathrm{|} \\ \qquad\quad\ \mathrm{CH_2} \\ \qquad\quad\ \mathrm{|} \\ \qquad\quad\ \mathrm{CH_2} \\ \qquad\quad\ \mathrm{|} \\ \qquad\quad\ \mathrm{O{-}\underset{O}{\underset{\|}{C}}CH{=}CH\underset{O}{\underset{\|}{C}}OMe}\end{array}$

some species in the reaction mixture to form species with three or more groups. An alkoxy intermediate has been proposed from the anhydride-carbonate reaction [3] and would be expected to undergo Michael addition readily to a double bond conjugated with a carbonyl group. This mechanism of gelation is also in accord with the observation that strong-acid catalysis (see above) did not produce gelled polymer.

In order to gain further evidence for such a side reaction, a gelled mixture from the reaction of maleic anhydride and ethylene carbonate and one from fumaric acid and ethylene carbonate were analyzed by extraction and methanolysis of the residue (see Experimental section). The gels showed major peaks as summarized in Table 3 with some possible structures shown in Table 4. It is apparent that the results are not completely in agreement but that some of the structures would seem to indicate the presence of Michael addition products. Products were observed that could result from radical reactions but they could be equally well explained as incomplete fragments of the compounds in question if the masses observed are not the parent ions. It is well known that mass spectrometry of ethers often does not give good molecular ions, and since these proposed addition products are ethers, that may account for the observed results.

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