Kinetics of Phthalic Anhydride/Ethylene Carbonate Reactions

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Synopsis

The kinetics of the polymerization of phthalic anhydride with ethylene carbonate to give poly(ethylene phthalate) were studied to elucidate the reaction mechanism. Zero-order kinetics were observed to varying degrees of reaction depending upon reaction temperature. Although no clear-cut overall reaction order could be established, previously proposed mechanisms involving decomposition of the carbonate as the first step of the reaction were ruled out. The chain propagation step was on the order of or faster than the initiation step of the reaction. Virtually no ether–glycol species were formed during the polymerization. A new mechanism was proposed for the polymerization.

INTRODUCTION

In 1960, Fischer[1] described the synthesis of some polyesters via the reaction of a dicarboxylic acid anhydride and an epoxide. The reaction was strongly catalyzed by trialkylamines. Polymer molecular weights were reported to be up to ca. 18,000. Titration of reaction mixtures indicated a zero-order dependence of the reaction on glycidyl ether concentration for the first portion of the reaction. Later, Schwenk and co-workers[2] and Hilt and co-workers[3] extended this reaction by replacing epoxides, which have very long reaction times, with cyclic carbonates; the polymer molecular weights obtained were higher than those obtained in the work of Fischer. They also measured the CO_2 evolved in the reaction and reported an initial zero-order dependence on carbonate.

Hilt and co-workers proposed a reaction mechanism for the anhydride–carbonate system involving decomposition of the carbonate as the first step. In their work, however, they reported indications of catalyst insolubility which made it difficult to do a kinetic analysis.

We have recently reported work[4] with a model reaction of benzoic acid and ethylene carbonate, which showed the previously suggested mechanisms for that reaction to be in error and which would now indicate that the carbonate decomposition is probably not the first step of the anhydride–carbonate reaction. We now report the results of kinetic studies on the reaction of phthalic anhydride and ethylene carbonate with a tributylamine catalyst. The kinetic studies were directed at elucidation of the mechanism of this reaction.

EXPERIMENTAL

Ethylene carbonate obtained from Union Carbide was vacuum distilled (bp 147°C/36 torr) prior to use. Reagent-grade phthalic anhydride, 3-chlo-
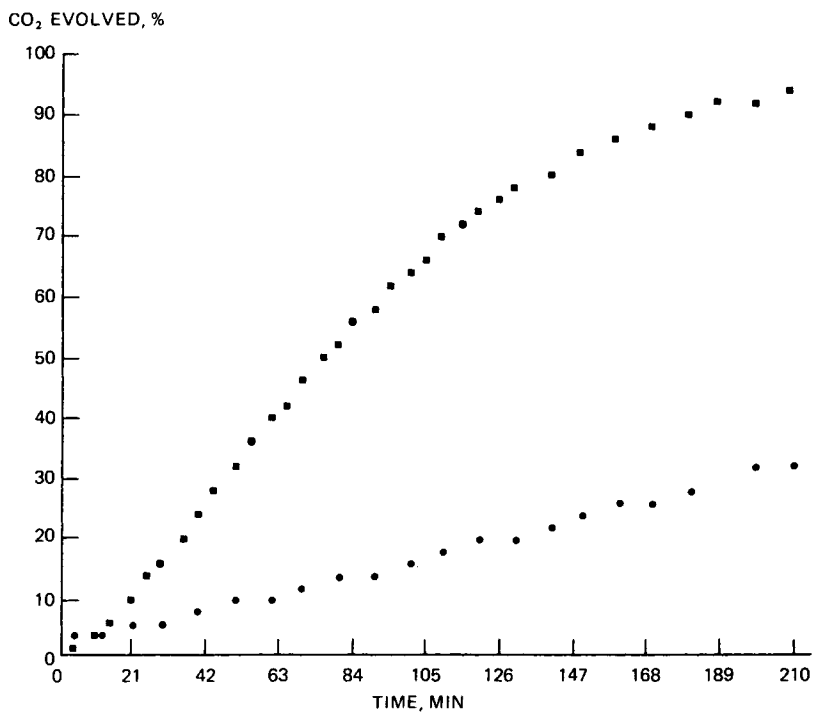
CCC 0021-8995/84/124287-09$04.00

CO$_2$ EVOLVED, %

Fig. 1.   CO$_2$ evolution vs. time for 155℃ reaction temperature (■) anhydride plus carbonate (●) carbonate alone.
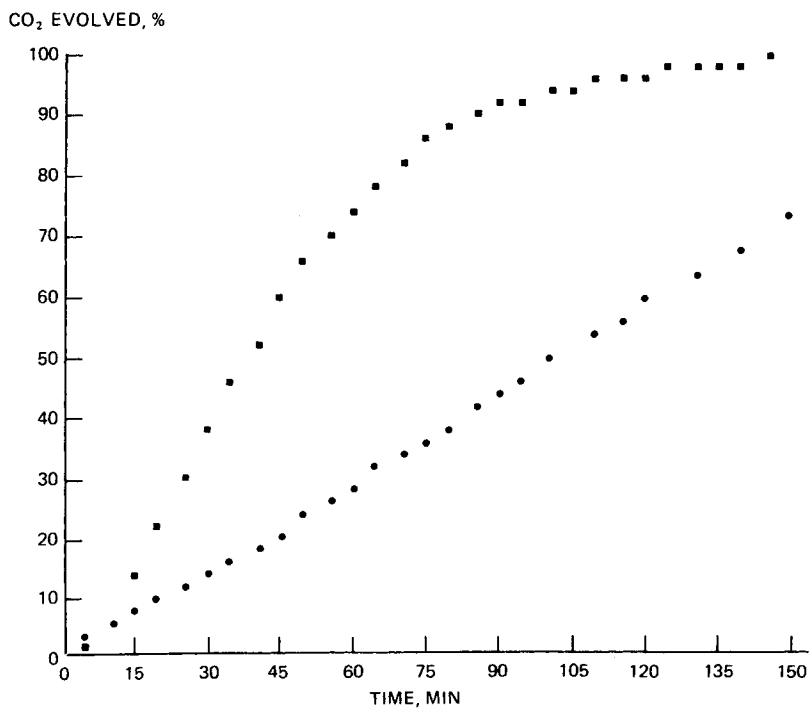
CO$_2$ EVOLVED, %

Fig. 2.   CO$_2$ evolution vs. time for 170℃ reaction temperature (■) anhydride plus carbonate (●) carbonate alone.
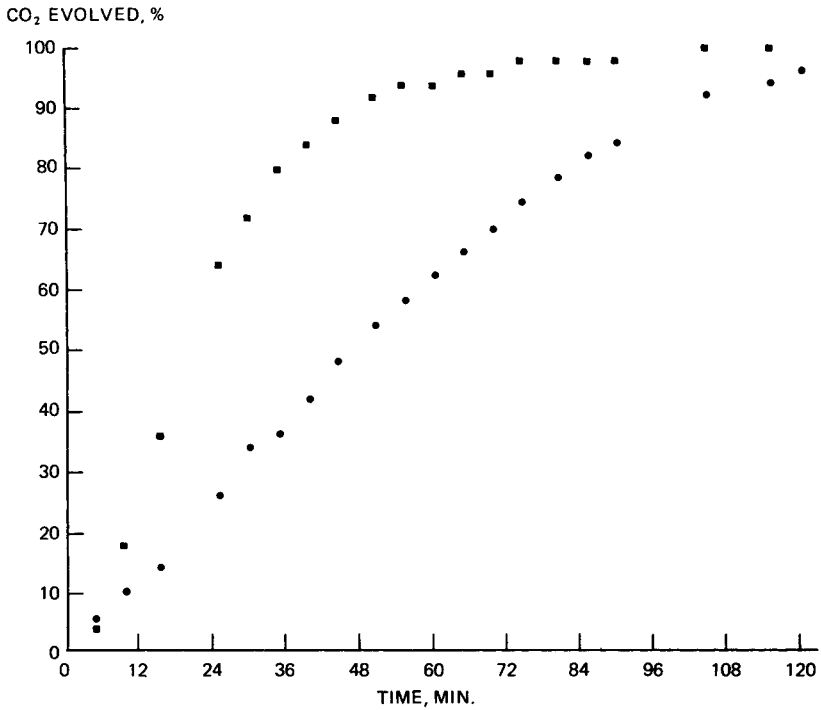
Fig. 3. CO_2 evolution vs. time for 185°C reaction temperatures (■) anhydride plus carbonate (●) anhydride alone.
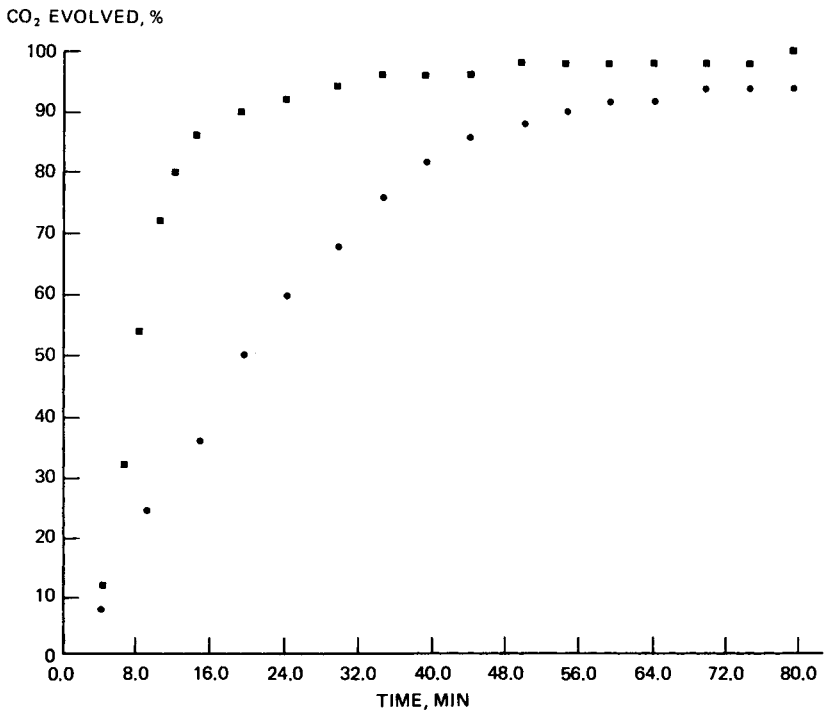

Fig. 4. CO_2 evolution vs. time for 200°C reaction temperature (■) anhydride plus carbonate (●) carbonate alone.
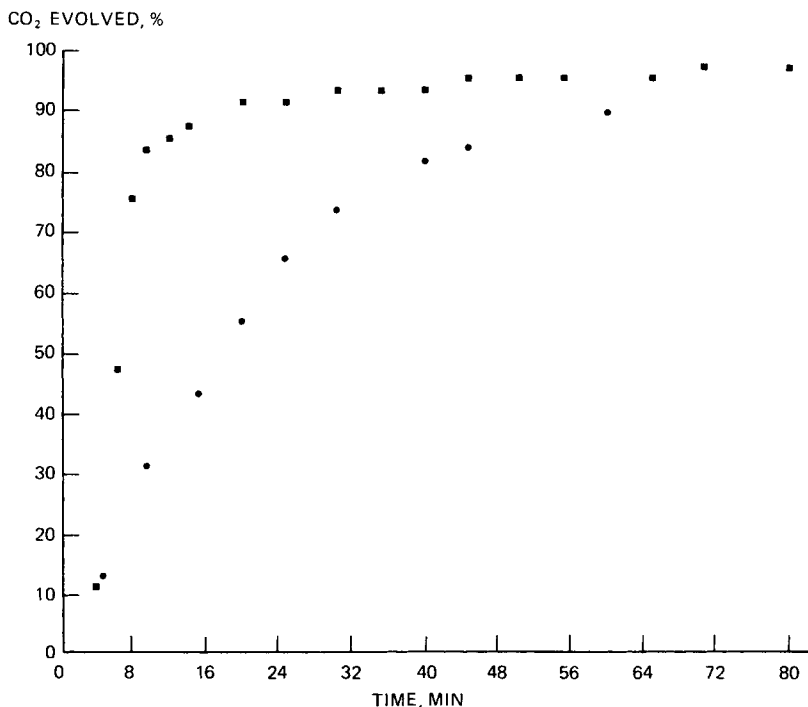
CO$_2$ EVOLVED, %

Fig. 5.   CO$_2$ evolution vs. time for 215°C reaction temperature (■) anhydride plus carbonate (●) anhydride alone.

rophthalic anhydride, and 3-nitrophthalic anhydride (all obtained from Eastman Organic Chemicals) were recrystallized from toluene. Reagent-grade tributylamine obtained from Eastman Organic Chemicals was used without further purification.

Reactions were conducted as previously described[4] with 0.25 mol each of anhydride and carbonate and with a 1 mol % catalyst concentration. Reaction mixtures were dried via azeotroping for ca. 1 h with toluene followed by catalyst addition. Gel permeation chromatography was performed in m-cresol at 100°C by using a Waters 200 instrument. Calibration was with narrow molecular weight distribution polystyrene standards according to a universal calibration approach.

RESULTS AND DISCUSSION

Consistent with previous work,[2,3] plots of CO$_2$ evolution vs. time over the range of temperatures studied (155–215°C) gave initial portions of the curves

TABLE I

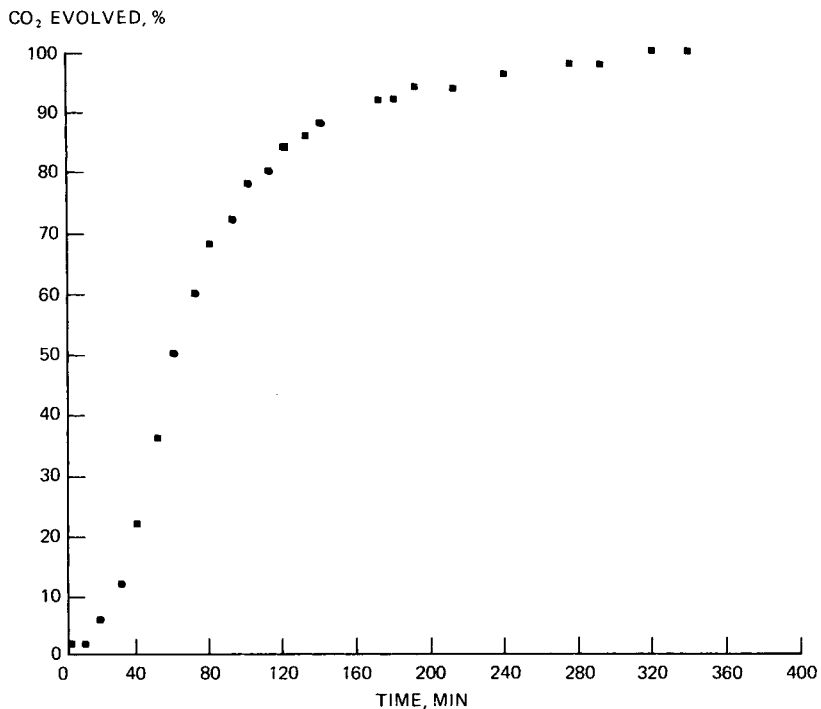| Reaction temp (°C)	% of reaction, apparently zero order
155	55
170	60
185	64
200	72
215	76

Fig. 6. CO_2 evolution vs. time at 200°C reaction temperature in the presence of NMP solvent.
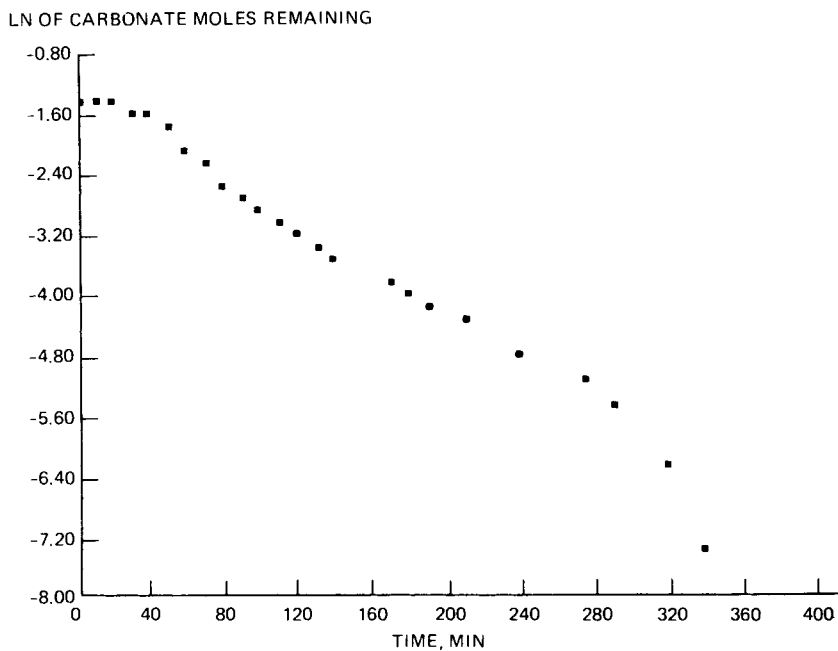

Fig. 7. Natural log of remaining carbonate moles vs. time at 200°C in presence of NMP solvent.
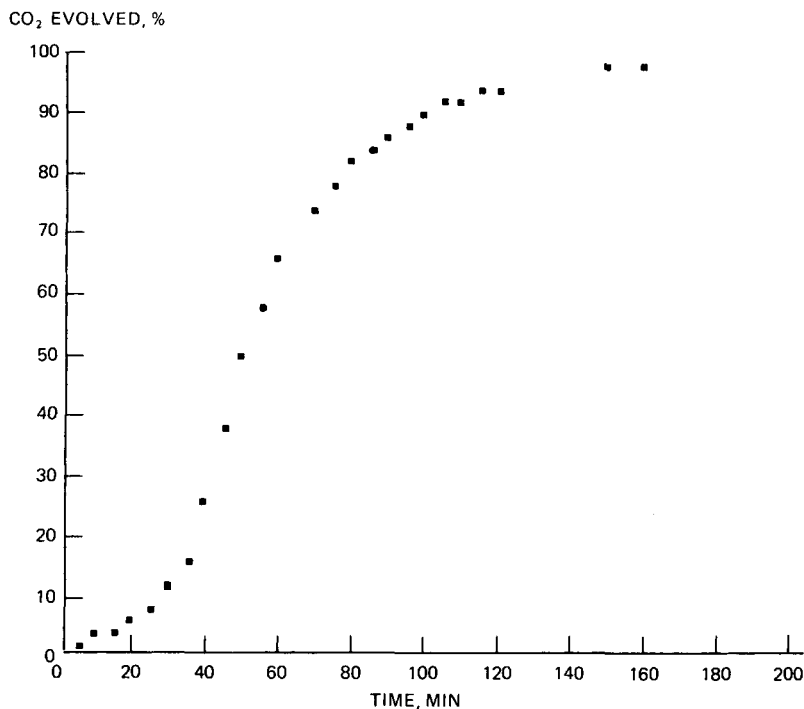
CO₂ EVOLVED, %

Fig. 8.   CO$_2$ evolution vs. time at 200°C reaction temperature for undried reaction mixture.

which appeared to be zero order (Figs. 1–5). The portion of each curve which was zero order was an apparent function of temperature (Table I). Even after extensive mathematical manipulation, an overall rate order was not obtainable at any temperature.

It was initially postulated that the observation of differing inflection points from a zero-order reaction might be due to viscosity effects. A rate deceleration due to high viscosity was postulated. Therefore, the reaction was run with two volumes of N-methylpyrrolidone (NMP) (dielectric constant at 25°C, 32.0)[5] added as a solvent. The shapes of the CO$_2$ evolution vs. time plot (Fig. 6) and a plot of the natural log of the ethylene carbonate moles vs. time (Fig. 7) were the same with or without solvent, although the reaction was much slower in the presence of NMP. Thus the observed

TABLE II
Effect of Polar Substituents
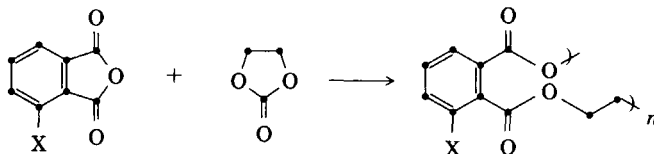
X	Rate constant (%/min)
H	1.93
Cl	1.44
NO$_2$	1.07

TABLE III
Gel Permeation Chromatography of Poly(ethylene Phthalate)

Solution IV (dL/g)	0.574	0.513	0.246
$\overline{M}_n$	34,100	29,200	16,100
$\overline{M}_w$	64,500	54,000	26,300
$\overline{M}_z$	108,900	91,100	44,300
$\overline{M}_w/\overline{M}_n$	1.89	1.85	1.63
$\overline{M}_z/\overline{M}_n$	3.19	3.12	2.74

change with temperature of the inflection point from a zero-order reaction is not consistent with viscosity affecting the reaction progress.

The reaction was also run by using two volumes of diphenyl ether (dielectric constant at 30°C, 3.69)[5] as a solvent. Carbon dioxide evolution was extremely slow ($< 45\%$ reaction in 360 min). The results from using NMP and diphenyl ether as solvents compared to the results from using neat reactants indicated that a very polar transition state is involved in the reaction.

Since rate-order analysis was not possible for these reactions, the decomposition of ethylene carbonate in the presence of catalyst was run in order to determine if it is possibly involved in the reaction. The CO_2 evolution vs. time data for the carbonate alone is given in the figures for the appropriate temperature of the anhydride-carbonate reaction (see Figs. 1–5). It is apparent that the carbonate decompositions are uniformly too slow by a large factor to be in the main reaction path.

It should be noted that the drying of the reaction mixtures by the toluene azeotroping procedures is essential. Otherwise, a CO_2 evolution curve that is even more difficult to interpret is obtained. Figure 8 shows an example of data obtained when the drying procedure is omitted.
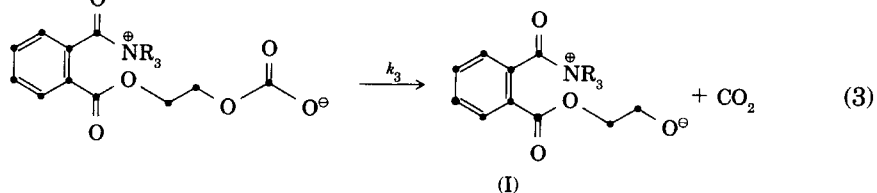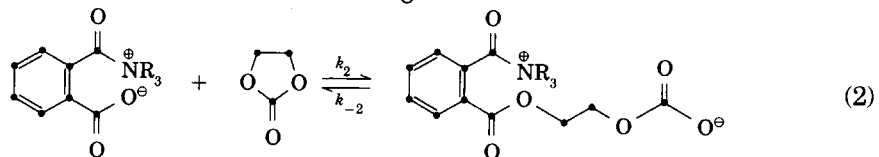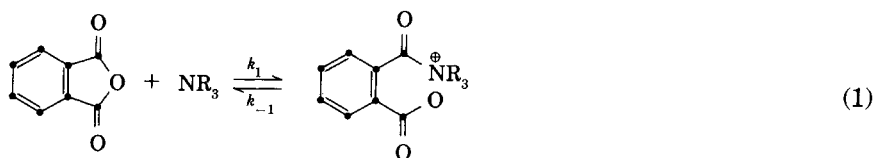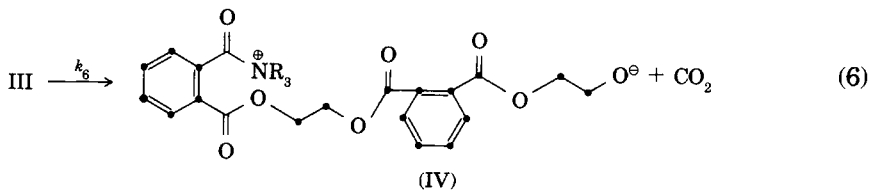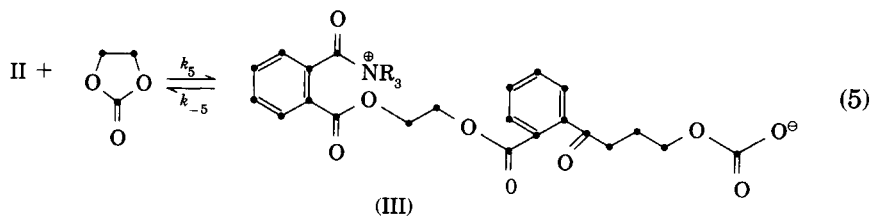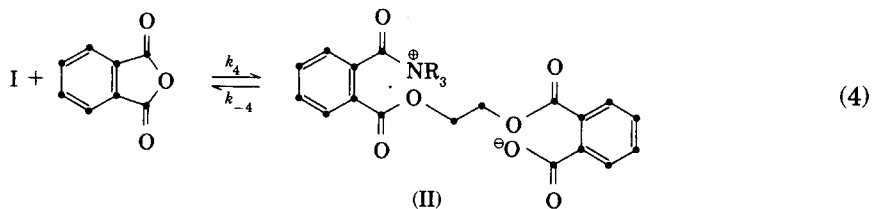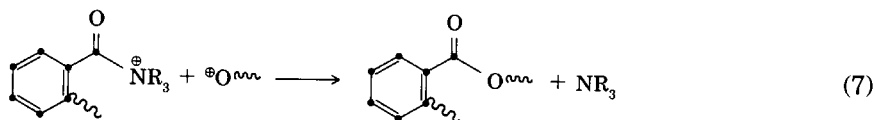
Reactions of phthalic anhydride, 3-chlorophthalic anhydride, and 3-nitrophthalic anhydride with ethylene carbonate were run at 200°C. The initial slopes of the plots of CO_2 evolution vs. time gave rate constants as shown in Table II. The low sensitivity of reaction rate to the polar groups indicates that the ring character is not important in the transition state.

Gel permeation chromatography (Table III) showed a molecular weight distribution that is probably not significantly different from that theoretically expected of condensation polymers, indicating that the initiation portion of the reaction is slower than or at least comparable to the overall rate of chain propagation.

The above observations are consistant with the type of mechanism previously proposed in the reexamination of the benzoic acid-ethylene carbonate reaction.[4] The mechanism is analogous to that of Fisher.

TABLE IV
Hydrolysis/GC Analysis of Poly(ethylene Phthalate)

Glycol	Wt %
Ethylene	32.45
Diethylene	0.07
Triethylene and higher	None detected

Initiation:

$$\text{(1)}$$

$$\text{(2)}$$

$$\text{(3)}$$

Propogation:

$$\text{(4)}$$

$$\text{(5)}$$

$$\text{(6)}$$

Termination:

$$\text{(7)}$$

$$\text{~~~} O^{\ominus} + HA \longrightarrow \text{~~~} OH + A^{\ominus} \qquad \text{(8)}$$

The species IV will, of course, react with more anhydride to continue chain growth. From this sort of mechanism, it is easy to understand how protonic impurities could interfere with the reaction since alkoxy intermediates would be rapidly converted to an alcohol whose reactivity would be expected to be lower toward anhydride than that of the alkoxide. Additionally, carboxylate end groups would be converted to carboxy groups that would probably have lower reactivity toward carbonate.

That the relative rate constants of the reaction of I with anhydride must be very much faster than that of I reaction with carbonate was shown by a GC analysis of the glycols from hydrolyzed polymer (1N KOH in refluxing 2-ethoxyethanol) (Table IV). For the reaction of I with carbonate to be appreciable, much larger amounts of diethylene and higher ether glycols would be expected. Instead, essentially insignificant amounts were observed.

CONCLUSIONS

Although no simple rate order was followed, the kinetics of the phthalic anhydride–ethylene carbonate reaction was more consistent with a mechanism like that proposed for the benzoic acid–ethylene carbonate reaction than the previously proposed reaction mechanism. The reaction was found to be very specific in its propagation, giving essentially no ether–glycol species. The rate of the initiation portion of the polymerization reaction was comparable to or slower than the overall rate of propagation.

References

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3. Von A. Hilt et al., *Makromol. Chemie*, **89**, 177–198 (1965).
4. D. R. Fagerburg, *J. Macromol. Sci. Chem.*, **A21**, 142–155 (1984).
5. R. L. Schneider, *Eastman Org. Chem. Bull.*, **47**, (1975).