

# Study on the Macrokinetics of Poly(trimethylene terephthalate) Polycondensation Reaction

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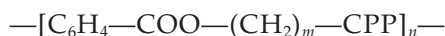
**ABSTRACT:** The macrokinetics of poly(trimethylene terephthalate) (PTT) polycondensation reaction during the high-vacuum process was studied. The results showed that PTT polycondensation reaction may be considered as a second-order reaction and thermal degradation is negligible in mathematical handling. The intrinsic viscosity versus time undergoes two different processes according to temperature. The apparent reaction rate constants and apparent activation energy of PTT polycondensation reaction are

smaller than those of PET. Under efficient stirring, PTT polycondensation reaction is still reaction-controlled and the role of devolatilization could be neglected even during the high-vacuum process. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1765–1770, 2004

**Key words:** poly(trimethylene terephthalate); catalysts; kinetics; polycondensation

## INTRODUCTION

Poly(trimethylene terephthalate) (PTT) is of renewed interest because of a new process for an economical monomer synthesis by Shell Chemical Co.<sup>1–4</sup> PTT has already shown its outstanding qualities in the fiber industry especially, where it is used in carpet fibers for its outstanding resiliency and stain resistance. PTT is a member of the aromatic polyesters family with the structural formula:



The best known members of this series are poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), which have been studied extensively. PTT can be made from either pure terephthalic acid (PTA) by direct esterification or dimethyl terephthalate (DMT) by transesterification. Similar to PET, the most competitive technical way to produce PTT is by direct esterification and polycondensation reaction with PTA and 1,3-propanediol (1,3-PDO) as monomers. For direct esterification and polycondensation reaction process of PTT, the preferred catalysts including compounds of titanium or tin, such as titanium butoxide,<sup>5–7</sup> a mixture of both titanium and silicon oxide, such as C-94,<sup>8</sup> were reported. We also invented a highly efficient complex catalyst for PTT polycondensation.<sup>9</sup>

To disclose the kinetic characteristics of PTT polycondensation reaction, we studied the macrokinetics of PTT polycondensation reaction with C-94, complex catalyst, and molybdenum oxide, *A*, as catalyst, respectively, so as to direct theoretically the technique of PTT polycondensation reaction.

## EXPERIMENTAL

### Materials and catalysts

Oligomer bis-1,3-hydroxypropyl terephthalate (BHPT) was used as a raw material for the kinetic study of PTT polycondensation reaction, which was made from direct esterification of PTA and 1,3-PDO. The reactor was pressurized to 0.2 MPa with nitrogen and heated to a temperature of 220°C. The direct esterification reaction was finished when the esterification rate was above 98%. C-94 was kindly provided by Acordis Co. (Germany); the added amount of it was 350 ppm to PTT. Complex catalyst, made by our laboratory, is a mixture of C-94 and molybdenum oxide, *A* (supplied by the Shanghai Chemical Reagents Co., Shanghai, China); the added amount of C-94 and *A* were 280 and 5 ppm to PTT, respectively. *A* as a catalyst alone was added 50 ppm to PTT. They are all by weight. For the sake of simplification of the study, the concentrations of catalysts used were fixed.

### Determination of intrinsic viscosity

The intrinsic viscosity ( $[\eta]$ ) of PTT was measured with a Ubbelohde viscometer in a concentration of 0.5 wt % by using phenol/1,1,2,2-tetrachloroethane (1 : 1 w/w) as solvent at  $25 \pm 0.1^\circ\text{C}$ .

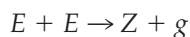
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## Experimental procedures

In view of the complexity of the mechanism of PTT polycondensation reaction and difficulties in determining the rates of individual steps, macrokinetics is proposed to meet the industrial requirement. In addition to chemical reaction, the effects of diffusion and mass transformation should also be considered in the macrokinetic study of PTT polycondensation reaction. The experiment was done in a 500-mL four-necked glass flask with efficient stirring. The needed amount of oligomer and catalyst was weighed accurately and charged to the four-neck flask, installed with stirring paddle, condenser, and thermometer. When heating to the a set temperature with a stirring of 600 rpm, vacuum pumping was started to a pressure of 0.02 MPa for 60 min. Then, sampling began every 15 to 30 min during the high-vacuum process under the pressure of less than 50 Pa. The intrinsic viscosity of each PTT sample was measured. Four to eight sets of samples were taken according to the polycondensation process.

## Model of macrokinetics of PTT polycondensation reaction

According to Ravindranath,<sup>10</sup> if the volumes of reactants in the reaction process remain constant, polyester polycondensation reaction behaves as a second-order reaction. With efficient stirring, transformation of small molecules through PTT melt should be taken as sufficient. The water product was rapidly removed from the flask so that the backward reaction of PTT polycondensation reaction could be neglected. Forward reaction and thermal degradation become a competition reaction in PTT polycondensation reaction during the high-vacuum process. For the sake of ease of mathematical handling, PTT polycondensation reaction during the high-vacuum process was simplified as PET (i.e., only forward reaction of PTT polycondensation reaction was considered and thermal degradation was neglected); then, the second-order reaction can be expressed as



where  $E$  in the formula is the end group,  $Z$  represents ester group in PTT macromolecules, and  $g$  denotes small molecules. Thus, the equation of forward reaction can be expressed as

$$-dC_e/dt = kC_e^2 \quad (1)$$

where  $C_e$  is the total number of molarity of end groups at time  $t$ , and  $k$  is the apparent reaction rate constant.

After integration and rearrangement, the following equation is obtained

$$1/C_e - 1/C_{e0} = kt \quad (2)$$

where  $C_{e0}$  is the total number of molarity of end groups at the beginning of the polycondensation reaction.

According to Moore,<sup>11</sup> there exists a relation of  $[\eta] = 4.08 \times 10^{-4} M_n^{0.79}$  between  $[\eta]$  and  $M_n$  (i.e.,  $M_n = 19,512[\eta]^{1.266}$ ).

As PTT is a bifunctional group molecule, the number of molarity of 1 unit mass (1 kg) of PTT sample is  $n = 1000/M_n$  and the total number of molarity of end groups is twice that of PTT (i.e.,  $C_e = 2n = 0.1025[\eta]^{1.266}$ ). After substituting the formula into eq. (2), eq. (3) is obtained

$$[\eta]_t^{1.266} = 0.1025kt + [\eta]_0^{1.266} \quad (3)$$

where  $[\eta]_0$  and  $[\eta]_t$  are the intrinsic viscosity at the beginning and at time  $t$  of the high-vacuum process in PTT polycondensation reaction, respectively.

Under isothermal conditions, the corresponding  $[\eta]_t$  at different times were measured and the linear regression of eq. (3) was done by using the least-squares method. The apparent reaction rate constant  $k$  can be obtained from the rectilinear slope of  $[\eta]_t^{1.266}$  versus  $t$ .

According to Arrhenius eq. (4):

$$k = k_0 \exp(-E/RT) \quad (4)$$

Equation (5) is obtained after logarithmic treatment of both sides of eq. (4):

$$\ln k = -E/RT + \ln k_0 \quad (5)$$

where  $E$  is the apparent activation energy,  $k_0$  is preexponential factor, and  $R$  is gas constant taken as 8.314 J mol/K.

The apparent reaction rate constant was measured under different temperatures of 240, 250, 260, 268, and 276°C, respectively. Linear regression with the least-squares method was performed to eq. (5). The apparent activation energy  $E$  of PTT polycondensation reaction can be obtained from the rectilinear slope of  $\ln k$  versus  $1/T$ .

## The significance test for regressive equations

### F test

All the equations involved in the present study can be converted into monovariant linear regressive equations with only one independent variable. The correlation between independent and dependent variables can be evaluated with correlation coefficient  $r$ . At the same time,  $F$  test and correlation coefficient test were also used in testing significance.

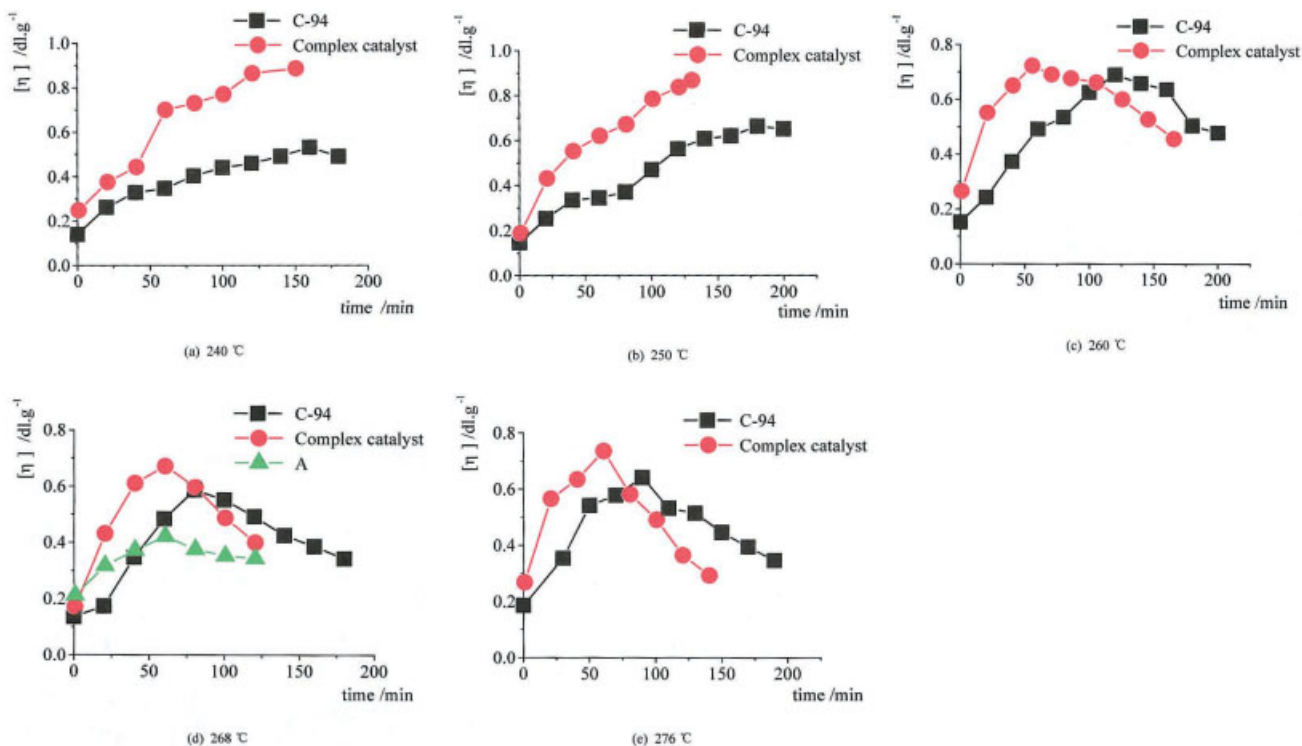


Figure 1 Effect of reaction temperature on intrinsic viscosity of PTT with different catalysts.

The following formula was used in the estimation of statistical value  $F$ :

$$F = r^2(n - 2)/(1 - r^2) \quad (6)$$

At the given significance of  $\alpha$ , in the case of  $F > F_\alpha(1, n - 2)$ , the linear correlation between independent and dependent variables can be considered significant; otherwise, the linear correlation should be considered not significant. In the present study,  $\alpha$  is taken as 0.05.

#### Correlation coefficient test

In the correlation coefficient test, the correlation coefficient  $r$  of two variables was chosen as a statistical quantity. At the given significance of  $\alpha$ , when  $r$  is greater than the critical value of  $r_\alpha(n - 2)$ , the correlation coefficient between independent and dependent variables can be considered significant; otherwise, the linear correlation should be considered not significant. In the present study,  $\alpha$  is taken as 0.05.

## RESULTS AND DISCUSSION

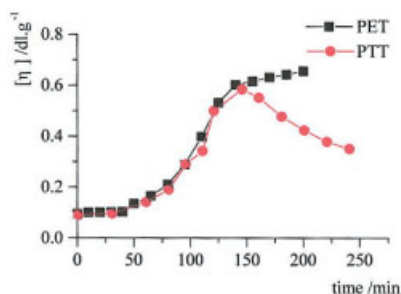
### Effect of reaction time on intrinsic viscosity

The rate of PTT polycondensation reaction during the high-vacuum process depends not only on the competition of polycondensation reaction and thermal degradation of PTT but also on the mass transfer of

small molecules through PTT melt, that is, the rate of devolatilization. It is shown in Figure 1 that the intrinsic viscosity versus time undergoes two different processes according to reaction temperature no matter what catalyst is used.

Within the temperature range between 240 and 250°C, with the increase of reaction time, the intrinsic viscosity of PTT increases gradually, which is not accompanied by a significant thermal degradation of PTT shown in Figure 1(a, b). The rate of PTT polycondensation reaction is greater than that of thermal degradation of PTT so as to neglect thermal degradation. With mathematical handling, PTT polycondensation reaction behaves as a second-order reaction.

When reaction temperature  $\geq 260^\circ\text{C}$ , the intrinsic viscosity of PTT versus  $t$  undergoes two different stages. The intrinsic viscosity of PTT increases at first, reaches an ultimate value, that is, a peak of the intrinsic viscosity, and then decreases rapidly. In the first stage, the intrinsic viscosity of PTT is low enough so that PTT polycondensation reaction becomes the main reaction. The intrinsic viscosity of PTT increases gradually with the increase of reaction time. In the second stage, the intrinsic viscosity of PTT becomes very high so that the rate of devolatilization and thermal degradation of PTT should play an important role. Because of an efficient stirring of 600 rpm, sufficiently to devolatilize small molecules even if at a higher intrinsic viscosity, PTT polycondensation reaction is a reac-



**Figure 2** The intrinsic viscosity versus reaction time of PTT and PET.

tion-controlled process and the role of devolatilization may still be neglected. However, the tendency of thermal degradation of PTT increases so as to be greater than that of polycondensation reaction. Thermal degradation of PTT plays a more important part than PTT polycondensation reaction, which is quite different from that of PET polycondensation reaction shown in Figure 2, so that it is important to terminate PTT polycondensation reaction promptly when the intrinsic viscosity of PTT reaches the values needed to decrease thermal degradation of PTT.

#### Variance test for regressive equations

Linear regressions were performed to eq. (3),  $[\eta]_t^{1.266}$  versus  $t$ , based on the data obtained from the experi-

ment with the least-squares method. Linear regressive equations were obtained and listed in Table I. Fairly good correlation between two variables can be judged from the values of correlation coefficient  $r$ . The results of the  $F$  test and the correlation coefficient test for regressive equations are shown in Table II. By using either the  $F$  test or the correlation coefficient test at the given significance of  $\alpha$ , the linear regressive equations of PTT polycondensation at different temperatures are very significant (i.e., the linear correlation between  $[\eta]_t^{1.266}$  and  $t$  is fairly good).

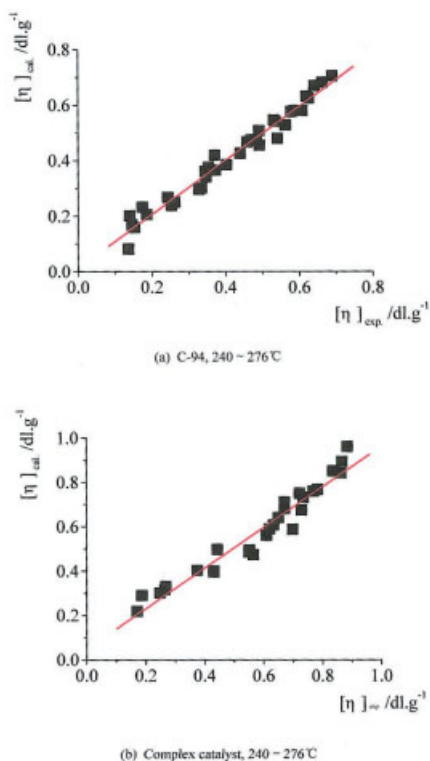
Figure 3 shows the relationship between the values of  $[\eta]_t$  calculated from regressive equations and the experimental values with the temperature range between 240 and 276°C. Both the calculated and the experimental values accumulate near the line by 45° in the coordinate, which denotes that the calculated values are very close to the experimental values no matter what catalyst is used. Thus, it is accepted that the assumption of PTT polycondensation reaction is a second-order reaction during the high-vacuum stage. Forward reaction of PTT polycondensation reaction can be taken as the main reaction in this period. Negligence of thermal degradation of PTT and backward reaction of PTT polycondensation reaction during data handling does not result in significant error. It indicates that the above-mentioned hypothesis is rational.

**TABLE I**  
Linear Regression Equations for PTT Polycondensation with Different Catalysts

Catalyst	Temp (°C)	Regression equation	$r$
C-94	240	$[\eta]_t^{1.266} = 2.07 \times 10^{-3} t + 0.1313$	0.9790
	250	$[\eta]_t^{1.266} = 2.83 \times 10^{-3} t + 0.1056$	0.9871
	260	$[\eta]_t^{1.266} = 4.53 \times 10^{-3} t + 0.0977$	0.9950
	268	$[\eta]_t^{1.266} = 5.74 \times 10^{-3} t + 0.0422$	0.9851
	276	$[\eta]_t^{1.266} = 5.18 \times 10^{-3} t + 0.1345$	0.9778
Complex catalyst	240	$[\eta]_t^{1.266} = 4.87 \times 10^{-3} t + 0.2186$	0.9620
	250	$[\eta]_t^{1.266} = 5.06 \times 10^{-3} t + 0.2085$	0.9807
	260	$[\eta]_t^{1.266} = 8.40 \times 10^{-3} t + 0.2330$	0.9679
	268	$[\eta]_t^{1.266} = 8.40 \times 10^{-3} t + 0.1454$	0.9747
	276	$[\eta]_t^{1.266} = 7.71 \times 10^{-3} t + 0.2470$	0.9546

**TABLE II**  
Variance Test for Linear Regressive Equations

Catalyst	Temp. (°C)	$n$	$F$ test ( $\alpha = 0.05$ )			Correlation coeff. test ( $\alpha = 0.05$ )		
			$F$	$F_a(1, n-2)$	Significance	$r$	$r_a(n-2)$	Significance
C-94	240	9	161.44	5.59	Significant	0.9790	0.6664	Significant
	250	10	304.09	5.32	Significant	0.9871	0.6319	Significant
	260	7	496.25	6.61	Significant	0.9950	0.7545	Significant
	268	5	98.43	10.13	Significant	0.9851	0.8783	Significant
	276	5	65.33	10.13	Significant	0.9778	0.8783	Significant
Complex catalyst	240	8	74.48	5.99	Significant	0.9620	0.7067	Significant
	250	8	150.96	5.99	Significant	0.9807	0.7067	Significant
	260	4	29.66	18.51	Significant	0.9679	0.9500	Significant
	268	4	38.03	18.51	Significant	0.9747	0.9500	Significant
	276	4	20.54	18.51	Significant	0.9546	0.9500	Significant



**Figure 3** Correlation between calculated and experimental  $[\eta]$  data of PTT.

### Effect of catalyst on PTT polycondensation reaction

The effects of the three catalysts on PTT polycondensation reaction are shown in Figure 1. Figure 1 shows that at the high-vacuum condition, and, within the temperature range between 240 and 276°C, the catalytic activity of complex catalyst on PTT polycondensation reaction is more efficient than that of C-94. Under similar temperatures and times, the rate of reaction by the former is significantly quicker than that of the latter, which indicates that the addition of a small amount of *A* can significantly increase the rate of PTT polycondensation reaction, whereas *A* added alone is inferior to that of C-94 even if 10-fold is added in the complex catalyst, as shown in Figure 1(d). This indicates that *A* does not exert significant catalytic activity alone on PTT polycondensation reaction but plays a catalyst promoting role. It is also shown in Figure 1(d) that the intrinsic viscosity of PTT reaches higher by complex catalyst than by C-94 under the same conditions. Promoter *A* added in the complex catalyst can significantly increase PTT polycondensation reaction but has no significant action to thermal degradation of PTT.

### Effect of reaction temperature on PTT polycondensation reaction

It is also shown in Figure 1 that in the above two catalysts, reaction temperature exerts a remarkably

large effect on PTT polycondensation reaction. Within the temperature range between 240 and 250°C, with the increase of reaction time, the intrinsic viscosity of PTT increases gradually, which is not accompanied by significant thermal degradation of PTT, whereas at temperatures  $\geq 260^\circ\text{C}$ , with the increase of reaction time, the intrinsic viscosity of PTT increases at first, reaches an ultimate peak, and then decreases rapidly.

With the increase of reaction temperature, the decrease of the intrinsic viscosity is more rapid, and the more rapid the reaction rate of the catalyst, the more prompt the decrease of the intrinsic viscosity of PTT. Thus, in the mechanism of PTT polycondensation reaction, the reaction temperature exerts significant influence that differs remarkably with the mechanism of PET polycondensation reaction shown in Figure 1. Under lower temperatures, both PTT polycondensation reaction and thermal degradation of PTT are slow. It is predominant in PTT polycondensation reaction, so at the latter stage thermal degradation is not significant and the intrinsic viscosity of PTT still increases with the increase of time. In macrokinetic study, thermal degradation of PTT may be neglected in the whole reaction process. Under higher temperatures, the rates of both PTT polycondensation reaction and thermal degradation of PTT are increased. PTT polycondensation reaction is still predominant at the earlier stage and the intrinsic viscosity of PTT increases with the increase in time; only forward reaction of PTT polycondensation reaction should be considered in mathematical handling at that time. Because the thermal degradation occurs easily in long macromolecular chains, the higher the intrinsic viscosity of PTT, the easier the thermal degradation of PTT occurs. Consequently, the negligence of thermal degradation of PTT is feasible at an earlier stage even though under a high temperature. That is why the data from an earlier stage of the high-vacuum period could be used when applying eq. (3) in data handling. However, at the latter stage, the rate of thermal degradation of PTT is significantly increased, which is not negligible.

From the slope of regressive equations listed in Table I, the apparent reaction rate constant  $k$  of various catalysts under isothermal conditions are calculated and the results are listed in Table III and Figure 4. Under identical temperatures, the apparent reaction rate constant of complex catalyst is significantly higher than that of C-94. Within the temperature range of the present study, the apparent reaction rate constant of the complex catalyst is 1.46- to 2.36-fold to that of C-94 and with the increase in reaction temperature the difference between the apparent reaction rate constant of above two catalysts decreases. Obviously, application of complex catalyst can increase the rate of PTT polycondensation reaction remarkably.

TABLE III  
Effect of Catalyst and Temperature on Apparent Reaction Rate Constant and Apparent Activation Energy of PTT

Catalyst	Temp. (°C)					$E$ (KJ mol <sup>-1</sup> )	$k_0$ (Kg mol <sup>-1</sup> min <sup>-1</sup> )
	240	250	260	268	276		
C-94	0.0202	0.0276	0.0442	0.0560	0.0506	67.66	$1.65 \times 10^5$
Complex catalyst	0.0475	0.0494	0.0819	0.0819	0.0752	38.33	$3.81 \times 10^2$

According to the Arrhenius equation, the linear correlation of  $\ln k$  versus  $1/T$  can be obtained and the apparent activation energy  $E$  can be calculated from rectilinear slope. The data listed in Table III show that the apparent activation energy of C-94 is significantly higher than that of the complex catalyst. It indicates that temperature exerts a prominent influence on PTT polycondensation reaction catalyzed by C-94. The pre-exponential factor of C-94 is rather high. The rate of transformation from active monomer molecules to PTT macromolecules in the reaction catalyzed by C-94 is very fast, which results in the promotion of PTT polycondensation reaction. Therefore, it is very important to strictly control the reaction temperature while applying C-94 in the PTT polycondensation reaction.

The effect of reaction temperature was studied in the temperature range of 240–276°C on the apparent reaction rate constant. Higher reaction temperature will reduce the reaction time. The apparent reaction rate constants are elevated significantly with the elevation of temperature, with the exception of temperature of 276°C. The tendency of thermal degradation of PTT at high temperature is obviously greater than that at lower temperature. Higher reaction temperature promotes thermal degradation of PTT so as to reduce the apparent reaction rate constant in a reaction temperature of 276°C.

## CONCLUSION

The macrokinetics of PTT polycondensation reaction was studied by using a stirring glass reactor. The

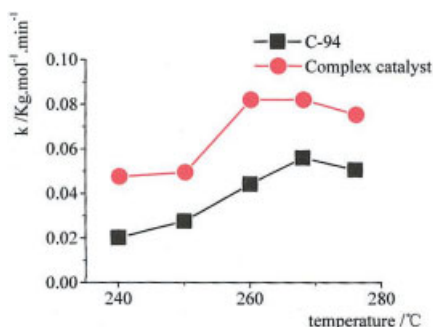


Figure 4 The apparent reaction rate constant versus temperature with different catalysts.

results showed that the hypotheses concerning the second-order reaction and negligence of thermal degradation in mathematical handling are rational.

The intrinsic viscosity versus reaction time experiences two different processes according to temperature. Reaction temperature exerts a remarkably large effect on PTT polycondensation process. Within the temperature range of 240 and 250°C, with the increase of reaction time, the intrinsic viscosity of PTT increases gradually, which means that PTT polycondensation reaction plays an important role and the negligence of thermal degradation of PTT is feasible in data handling. When the temperature is above 260°C, with the increase of reaction time, the intrinsic viscosity of PTT increases at first, reaches an ultimate peak, and then decreases rapidly, which indicates that thermal degradation of PTT is not negligible at the latter stage.

The catalytic activity of the complex catalyst on PTT polycondensation reaction is more efficient than that of C-94. The addition of a small amount of *A* can significantly increase the rate of PTT polycondensation reaction. However, *A* added alone is inferior to that of C-94, which means that *A* does not exert a significant catalytic activity alone on PTT polycondensation reaction but plays a catalyst promoting role.

Because of efficient stirring, PTT polycondensation reaction is still reaction-controlled and the role of devolatilization could be neglected even during the high-vacuum process no matter what catalysts are used.

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