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Aspects of the Chemistry of Poly(ethylene Terephthalate). III. Transesterification of Dimethyl Terephthalate with Ethylene Glycol in the Presence of Various Catalytic Systems

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ABSTRACT

The transesterification of dimethyl terephthalate has been studied by measuring the amount of methanol formed as a function of time. The influence of various catalytic systems was investigated with regard to the nature and concentration of the metal ion and temperature. The order of decreasing activity was found to be Pb, Zn, Mn, Sn, Sb, Ti, and mixtures of Zn plus Pb and Zn plus Sb were found to be synergistic. The postulate that there is a correlation between the metal oxygen bond and the activity of the catalyst is discussed.

INTRODUCTION

Poly(ethylene terephthalate) (PET) is produced by polycondensation of bis(hydroxyethyl) terephthalate or its oligomers. These were originally formed by transesterification of dimethyl terephthalate (DMT) with ethylene glycol. The later availability of terephthalic acid of high purity made the preparation possible by direct esterification with ethylene glycol, but the first route to the monomer formation is still widely used. A knowledge of the catalyst behavior in the transesterification of dimethyl terephthalate with ethylene glycol is important for the polyester industry. In the present study, transesterification of DMPT with ethylene glycol was carried out in the presence of various catalysts and at various temperatures.

EXPERIMENTAL

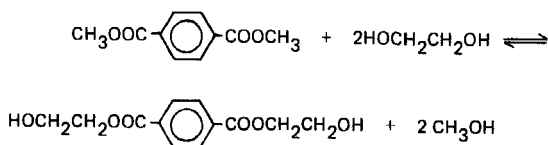
All the materials used in this study were of commercial grade and they were used without further purification.

The transesterification of DMT with ethylene glycol was carried out in a well-lagged, 3-necked polymerization tube. The appropriate mixtures of dimethyl terephthalate (0.25 mol), the catalyst, and ethylene glycol (1.0 mol) were introduced into the reaction vessel. Dimethyl terephthalate was allowed to melt to form a homogeneous mixture with the catalyst and ethylene glycol, then nitrogen was bubbled through the mixture at a rate of approximately 50 mL/min. The temperature of the reaction was maintained with a thermostated ethylene glycol bath.

The reaction was considered to have started when the first drop of the methanol formed appeared in the receiver. The transesterification reaction was followed by measuring the volume of methanol distilled over several intervals of time.

RESULTS AND DISCUSSION

The transesterification of dimethyl terephthalate (DMT) with ethylene glycol (EG) may be represented by the following equation where methanol and bis(hydroxyethyl) terephthalate (BHET) are formed:



The transesterification is a reversible reaction. Therefore, to obtain a high yield of BHET, efficient removal of formed methanol is necessary.

The formation of BHET is considered to be a two-step process. The first step is the formation of p-methoxycarbonyl-2-hydroxyethyl benzoate, which then reacts with another molecule of ethylene glycol and yields BHET. An important problem in the kinetic treatment of the transesterification reaction is whether there is a difference between the rate constant of the first step and that of the second step.

Challa [1] argued that both rate constants are essentially the same. On the other hand, the presence of a difference was maintained by Peebles and Wagner [2]. From experiments with model compounds, Tomita and Ida [3] have concluded such a difference is negligible. Consequently, it may be assumed from the above evidence that the rate constants of the first step and that of the second step are much the same. Thus, BHET formation may be regarded as being simply the reaction between a methyl ester group and a hydroxyl group in ethylene glycol.

Effect of Catalyst Concentration

The dependence of the rate of transesterification reaction of dimethyl terephthalate with ethylene glycol on the catalyst concentration using zinc, tin, and titanium compounds as catalysts forms the subject of this part of the investigation. The data from such a series of experiments are presented in Figs. 1-3.

The volume of methanol formed during the transesterification reaction is represented as the extent of the reaction by considering the theoretical amount of methanol which may be evolved if the reaction is taken to completion.

The results illustrated in Figs. 1-3 show that the effect of catalyst concentration is highly dependent upon the nature of the catalyst employed.

Figure 3 shows the effect of zinc acetate concentration on the extent of the transesterification reaction.

It can be seen that as the catalyst concentration was increased from 5×10^{-5} up to 1×10^{-3} mol/mol DMT, the velocity of the transesterification was enhanced, especially in the initial stages of the reaction.

Using the catalyst concentration of 5×10^{-5} mol/mol DMT, the time required for 50% of the reaction to occur was about 2 h, whereas using 5×10^{-4} mol/mol DMT this value (extent of reaction = 0.5) was reached in only 10 min. The increase in the catalyst concentration beyond 5×10^{-4} mol/mol DMT does not affect the rate of the transesterification reaction as dramatically as in the lower concentration region. It is also seen in Figs. 1 and 2 that the extent of reaction against time plots at lower catalyst concentrations are almost linear. As the catalyst con-

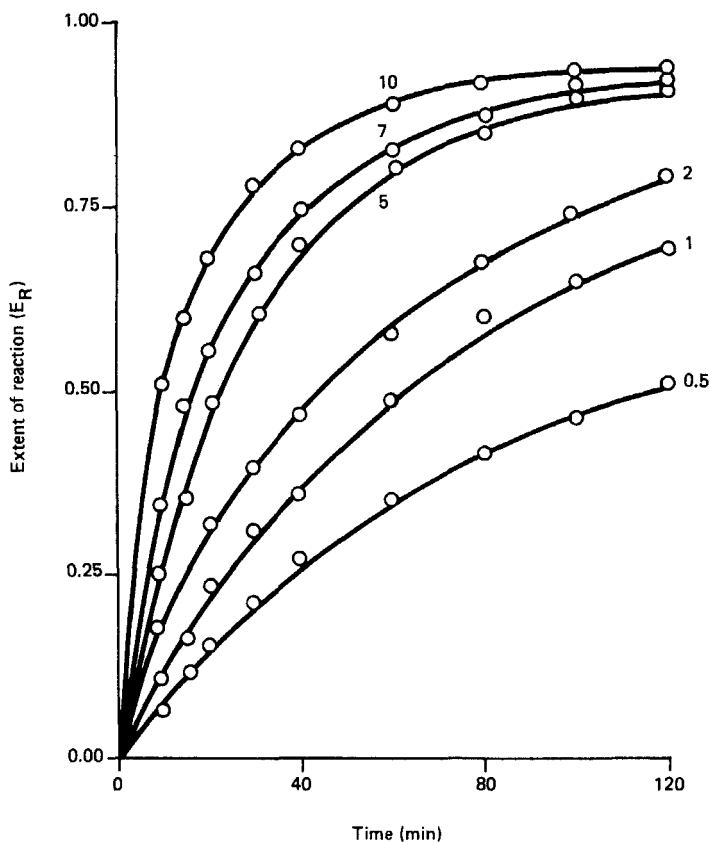


FIG. 1. The effect of zinc acetate concentration (range 0.5 to 10×10^{-4} mol/mol DMT) on the transesterification of DMT with EG at 197°C .

centration was increased, deviation of these plots from linearity became more pronounced.

Figure 3 illustrates the results for similar experiments using dibutyl tin oxide as the catalyst in transesterification. The effect of increasing the catalyst concentration followed a pattern of behavior similar to zinc acetate catalysts but was not as pronounced. The plots obtained (Fig. 2) at lower concentrations are very good straight lines and the deviation from linearity at higher catalyst concentration is not as marked as that for the data plotted for zinc acetate catalyzed transesterifications.

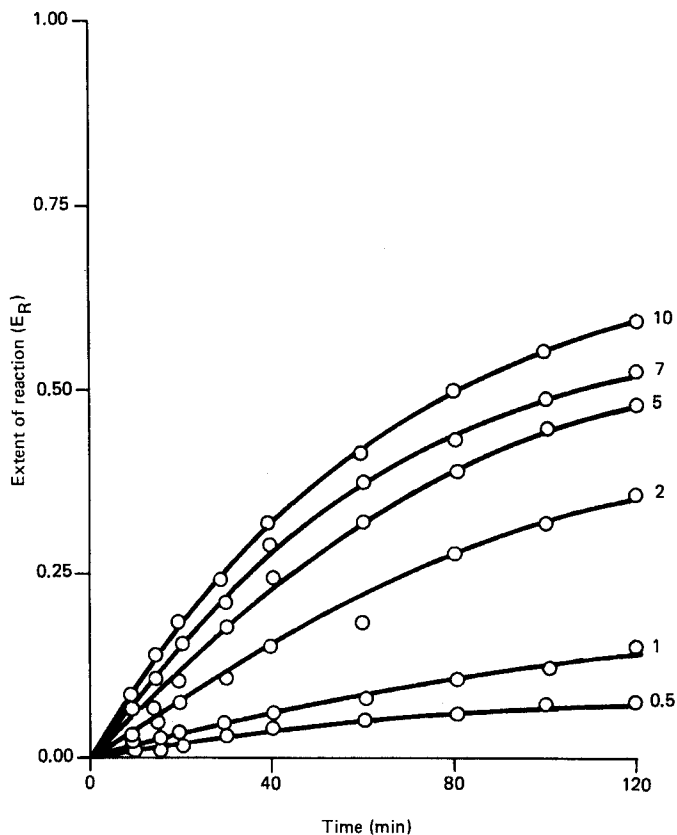


FIG. 2. The effect of dibutyl tin oxide concentration (range 0.5 to 10×10^{-4} mol/mol DMT) on the transesterification of DMT with EG at 197°C.

The least active of the three transesterification catalysts employed was potassium titanium oxalate. Increasing the catalyst concentration in this case had very little effect on the rate of methanol evolution and, as depicted in Fig. 3, the plots are all linear.

When zinc acetate and tin oxide were used as catalysts, the velocity of the transesterification reaction was enhanced in the early stages and then it leveled off. In the case of the transesterification catalyzed by the titanium compound, the increase in the rate of reaction was constant throughout the experiment. A change in the catalyst concentration did not affect this pattern of behavior, and straight line plots were obtained (Fig. 3) at all the concentrations used.

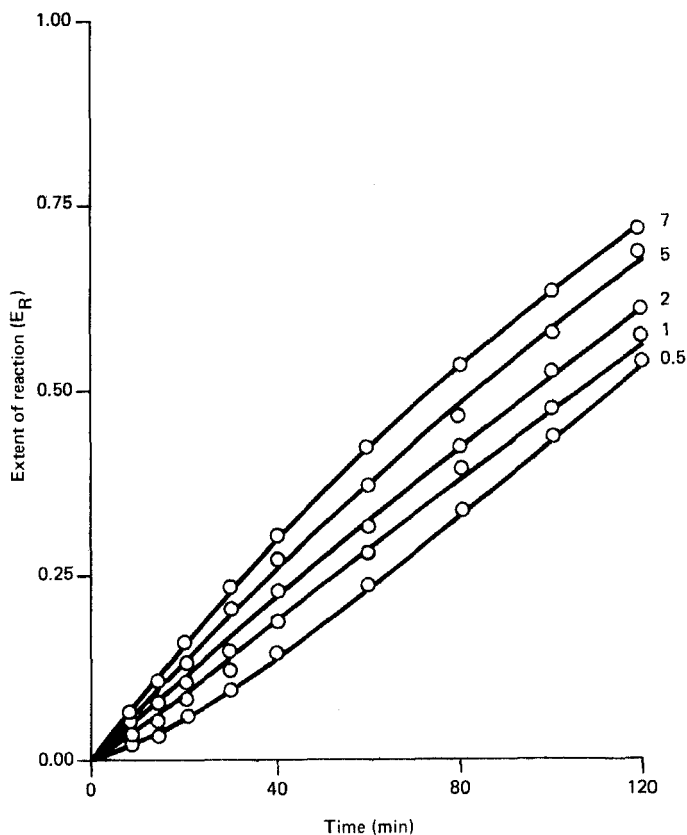


FIG. 3. The effect of potassium titanium oxalate concentration (range 0.5 to 10×10^{-4} mol/mol DMT) on the transesterification of DMT with EG at 197°C .

Effect of Catalyst Nature

The rate of transesterification of dimethyl terephthalate with ethylene glycol in the presence of various metal compounds and their mixture as catalysts at 197°C were determined from the quantity of methanol produced. From these results, catalytic activities of these compounds were evaluated.

Figure 4 illustrates the effect of various metal compounds (2×10^{-4} mol/mol DMT) on the transesterification reaction. It is interesting to note that the catalysts which are least effective in polycondensation reactions [4] show the greatest catalytic activity in the transesterification process though it is not known how general this behavior is.

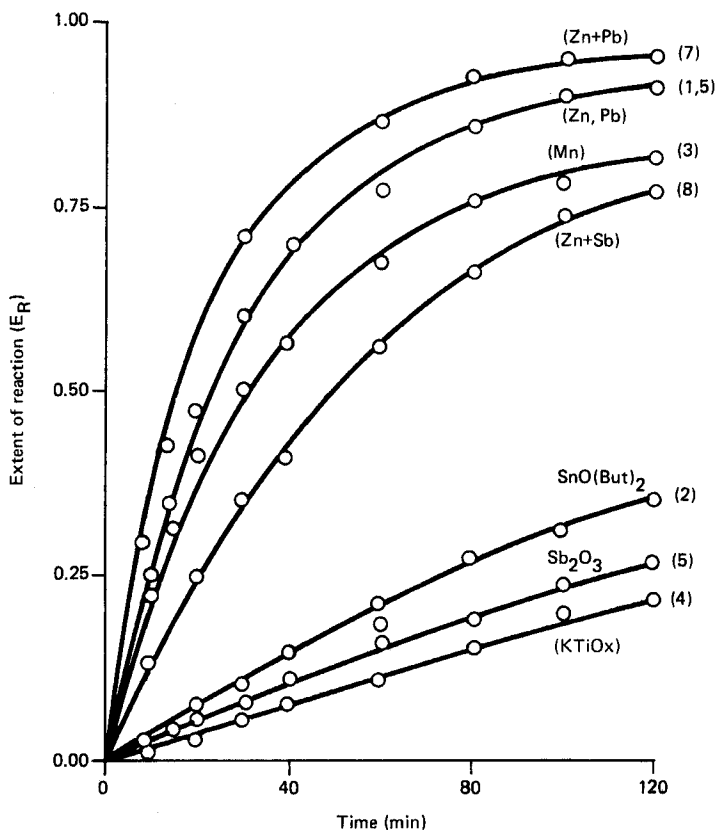


FIG. 4. The effect of various catalysts (concentration 2×10^{-4} mol/mol DMT) on the transesterification of DMT with EG at 197°C .

The mechanism of catalyzed transesterification is similar to that of catalyzed polycondensation. The reaction intermediate is regarded as a complex formed by coordination of the ester carbonyl group to the metal species [5]. This coordination lowers the electron density of the carbonyl carbon atom and facilitates the nucleophilic attack of the hydroxyl group upon the positively charged carbon atom. The extent of metal-carbonyl group coordination may depend on the endgroups attached in the ester.

The mixtures of these compounds have greater catalytic influence on the transesterification reactions than individual catalysts. For example, an equimolar mixture of the zinc acetate and lead acetate (2×10^{-4} mol/mol DMT) showed greater catalytic activity than both zinc acetate and lead acetate on their own (Fig. 4).

Kimoto et al. [6] have proposed that the electronegativity of each metal species is the ordering factor of catalytic activity. Tomita [5] determined rate constants of transesterification reactions in the presence of various metal acetates as catalysts and then plotted these rate constants logarithmically against electronegativities proposed by Gordy et al. [7].

Tomita's results suggest that optimum catalytic activity is shown by metal species with intermediate electronegativities. Yoda [8] showed that in a series of metal acetates, those salts of metals having electronegativity lying between 1.0 and 1.7 (that is calcium, manganese, zinc, lead, and cobalt) were most catalytically active for the esterification reactions studied.

An important feature of the catalysis of transesterification is the interaction between the metal complex and the negatively charged oxygen of the carbonyl group of the ester. Thus, the strength of the M-O bond formed must also play a part in the rate-determining step of the transesterification process.

The M-O bond lengths for various cations used as catalytic agents are given in Table 1.

The metal-oxygen bond lengths given in Table 1 have been determined by various workers [9-14] using x-ray diffraction techniques. This table is drawn up from the values of M-O bond lengths given for various organometallic complexes. M-O lengths tabulated are for the metal-oxygen bonds where metal has a similar environment to that when it forms a transition complex with the ester group of DMT during the catalysis. The valencies of the metal ions listed in Table 1 are the same as those they have in the catalytic compounds used.

The order of M-O distances is essentially similar to that of the catalytic activities of the cations. Since bond lengths and strengths are related to each other in that the shorter the bond the stronger it is, therefore the bond strength must be considered an important parameter in determining the catalytic activity of the cations employed in the transesterification reaction.

TABLE 1

Metal-oxygen bond	Bond length (Å)	Ref.
Pb(II)-O	2.44	9
Zn(II)-O	2.26	10
Mn(II)-O	2.24	11
Sb(III)-O	2.17	12
Sn(IV)-O	2.08	13
Ti(IV)-O	1.73	14

It may be concluded from the above discussion that the cations which form weaker bonds with the carboxyl oxygen of DMT show greater catalytic activity, and the converse is true of the stronger M-O bond-forming cations.

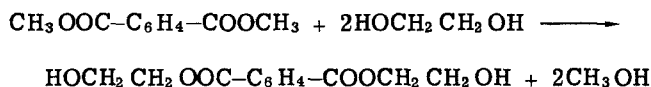
The mixtures of various compounds were studied as catalytic agents and the results are shown in Fig. 4 by Curves 7 and 8.

These results show that when two of the most active transesterification catalysts, lead acetate and zinc acetate, were employed in combination with each other (1:1 molar ratio), the rate of transesterification was enhanced as shown by Curve 7 in Fig. 4. On the other hand, when zinc acetate was used in equimolar combination with antimony trioxide, the methanol evolution Curve 8 (Fig. 4) was obtained, which shows that a mixture of zinc acetate and antimony trioxide gives an activity which is intermediate of the activities of the two catalysts employed (cf. Curves 1 and 5).

EFFECT OF TEMPERATURE

Transesterification of DMT with ethylene glycol was carried out in the presence of zinc acetate catalyst (2×10^{-4} mol/mol DMT) in the temperature range of 155 to 197°C. The results from these experiments are illustrated in Figs. 5-7. Figure 6 is a representation of the results as plots of extent of the reaction against time at various temperatures.

On the basis that for every 2 mol of methanol formed, 1 mol of DMT is lost for the reaction mixture, the following equation can be formulated:



Thus, from knowledge of the volume and density of methanol formed, the number of DMT moles disappearing from the system can be calculated. Consequently, from this the number of DMT moles remaining in the mixture (C_1) may be determined. In the same way the number of moles of ethylene glycol remaining in the mixture (C_2) can also be determined.

Figure 6 shows that when $\log(C_1/C_2)$ was plotted against time for various temperatures (155-197°C), straight line graphs were obtained. These plots suggest that the transesterification of DMT with ethylene glycol is a second-order reaction in the presence of a catalyst.

The Arrhenius plot was obtained by plotting $\log k$ against $1/T$ (Fig. 7). The activation energy was calculated from this plot as $E = 52.12$ kJ/mol. This value is higher than that determined by Tomita [3]

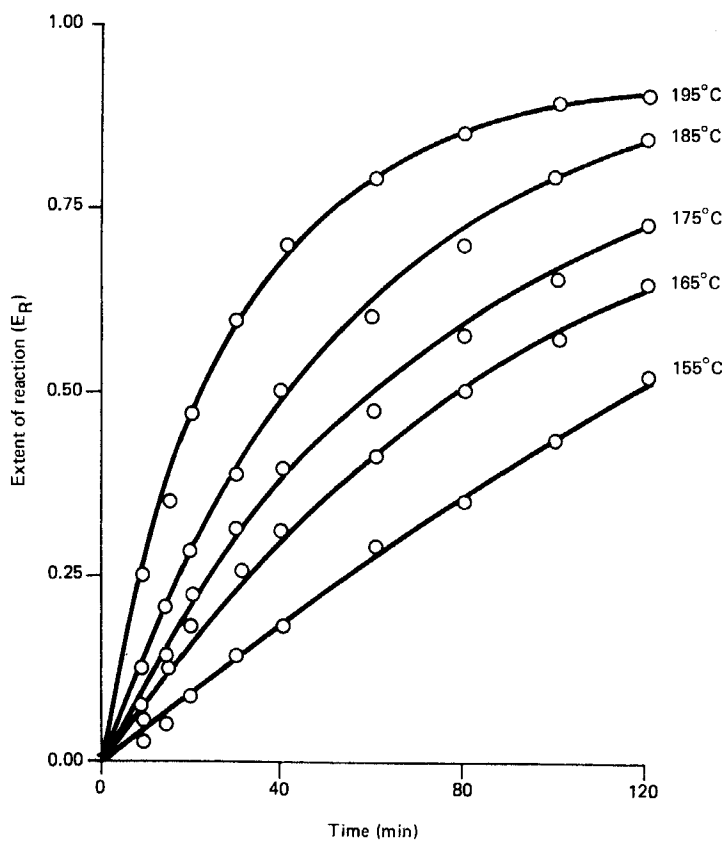


FIG. 5. The effect of temperature on the transesterification of DMT with EG using zinc acetate (concentration 2×10^{-4} mol/mol DMT).

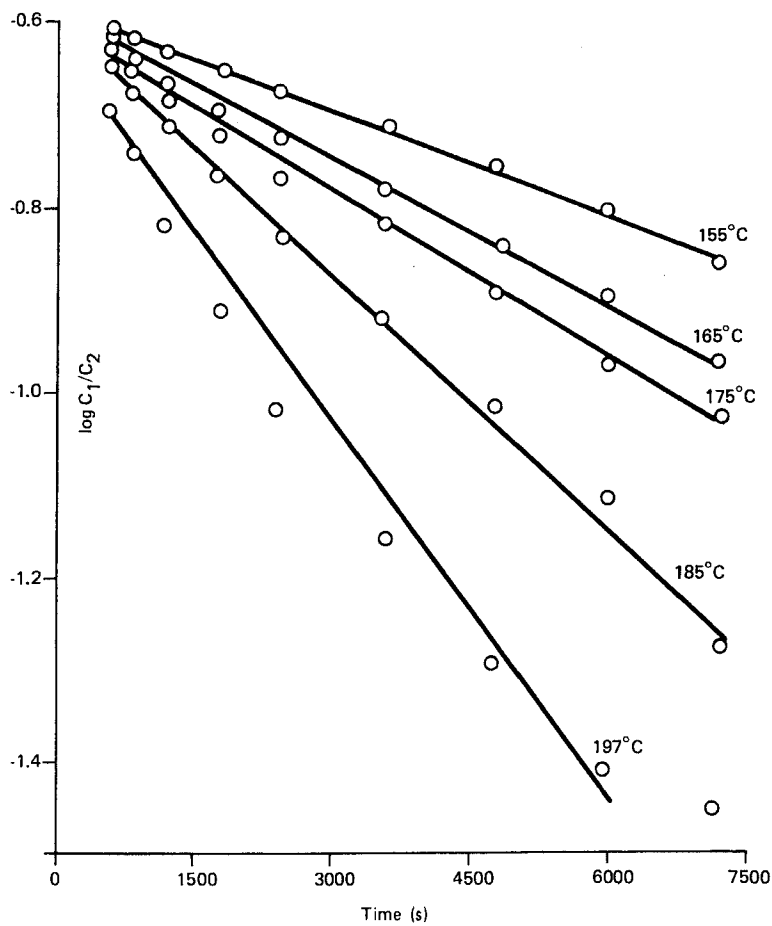


FIG. 6. Second-order plots of $\log C_1/C_2$ against time for determination of rate constant of the transesterification reaction at various temperatures.

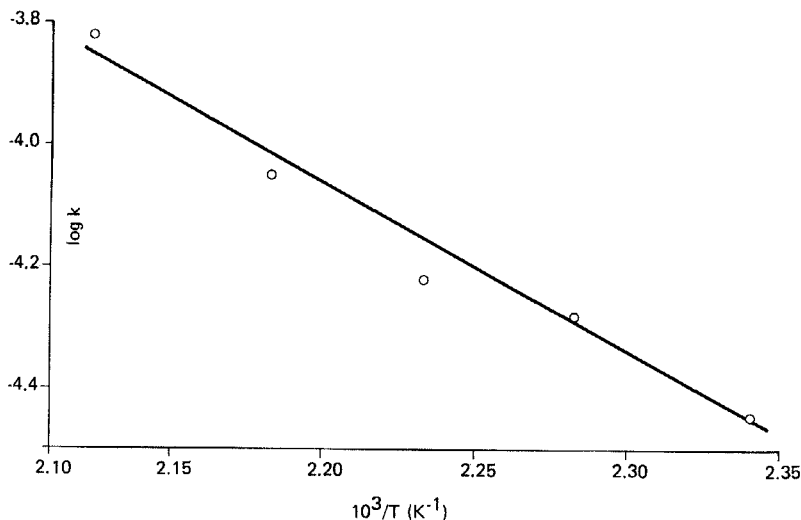


FIG. 7. The Arrhenius plot for the transesterification of DMT with EG.

which is 39.5 kJ/mol for the catalyzed transesterification and much lower than that obtained by Challa [1] for the uncatalyzed polycondensation of bis(hydroxyethyl) terephthalate.

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