Effect of Different Catalysts on the Synthesis of Bis(2-Hydroxyethyl) Terephthalate

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Transterification of Ethylene Glycol and DiMethyl Terephthalate, through the use of different acetates as catalysts, for producing Bis(2-HydroxyEthyl)Terephthalate under isothermal conditions, was studied from the point of view of the kinetics involved. Best results were obtained by employing zinc acetate and a second order reaction was determined from the experimental data.

Keywords: Bis(2-Hydroxyethyl)Terephthalate; synthesis catalysts; polymerization kinetics

INTRODUCTION

Bis(2-HydroxyEthyl)Terephthalate (BHET) is a very important compound for the synthesis a number of engineering polymeric materials, ranging from unsaturated polyester resins [1] and PolyEthylene

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Terephthalate (PET) [2] to novel biocompatible systems. BHET is also employed as a plastifying agent for unsaturated polyester resins [3] and has been crystallized for purification and compounding purposes [4], just to mention few of the important practical uses of this substance, which represents a very important market worldwide.

The most popular route, industrially speaking, to synthesize BHET is *via* the esterification of DiMethyl Terephthalate (DMT) and Ethylene Glycol (EG) by using different catalysts, among which Cd, Ca, Zn and other acetates have been preferred in the various technologies available. The general synthesis scheme is represented by the following equation:

$$DMT + EG \underset{catalyst}{=} BHET + MeOH$$
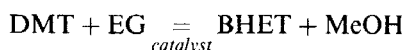
where MeOH stands for Methanol. In this regard, Cadmium and Silver acetates have been reported to yield the best results in terms of efficiency of the above reaction, as compared to other less expensive substances such as Calcium acetate, and the relationship between the quality of the final BHET produced in terms of the chemistry of the reaction involved is well known and industrially applied already. Nevertheless, very scarce information is available on the details of the kinetics of the aforementioned reaction, key factor if a more profound understanding of the process for producing such an important substance is to be achieved. Accordingly, in this present contribution, a study of the effect of employing different acetates as catalysts for the sterification of DMT to yield BHET, from the point of view of the corresponding kinetics, has been carried out.

EXPERIMENTAL

Reactive grades DMT (Baker), Ethylene Glycol (Baker), and zinc, lead, sodium and calcium acetates (Baker) were employed for preparing the BHET, according to the reaction route mentioned above. The experimental set-up is schematically depicted in Figure 1, where 1 mol of DMT, 2 mols of EG and 2.4×10^{-4} mols of the corresponding acetate are utilized, following the literature [5]. First, EG is heated up to 80°C and the acetate is added, mixing until complete

HO-CH₂-CH₂-OOC —⟨◯⟩— COO-CH₂-CH₂-OH
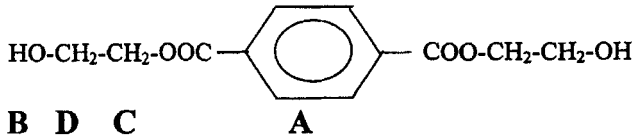
B D C   A

FIGURE 1   Schematic diagram of the chemical structure of the BHET molecule.

dissolution is reached. Meanwhile, the DMT is melted at 140°C in the reactor of Figure 1, adding then the EG-acetate solution and heating up the reaction temperature, between 175°C and 195°C, under permanent stirring [6]. Once the BHET is formed a special crystallization procedure, previously reported [4], is carried out to purify the product.

FTIR was carried out in a Nicolet 910 bench, within the spectral range $4000 - 300 \, cm^{-1}$ and by using the ATR technique, so no KBr was necessary. RMN-H spectra were obtained in a Varian Gemini 200 MHz machine, using Deuterated Chloroform ($CDCL_3$), as solvent, and TetraMethylSilane (TMS), as reference. DSC was taken in a Dupont 2100 apparatus from room temperature up to 250°C, under N_2 atmosphere and a heating rate of 10°C/min.

RESULTS AND DISCUSSION

(a) Characterization of the Produce

Figure 1 shows schematic diagram of the BHET chemical structure, which helps to understand the RMN-H spectrum of the BHET formed, shown in Figure 2. As observed, a single signal corresponding to the hydrogen atoms of the benzene ring appears at 8.1231 ppm. This signal is located at low field because of the delocalized electrons of the benzene ring. A signal is found a 4.875 ppm, corresponding to the hydrogen – oxygen bond. Two triplets are attributed to the coupling of the methylene groups. The first triplet at 4.252, 4.4016 and 4.37 ppm correspond to the bonding of methylene to a carboxyl group. The second triplet at 3.8868, 3.8612, and 3.8378 ppm correspond to the bonding to the —OH group.

Figure 3 shows a typical FTIR spectrum of the BHET. A strong band at $3557 \, cm^{-1}$ corresponds to the end —OH group, forming
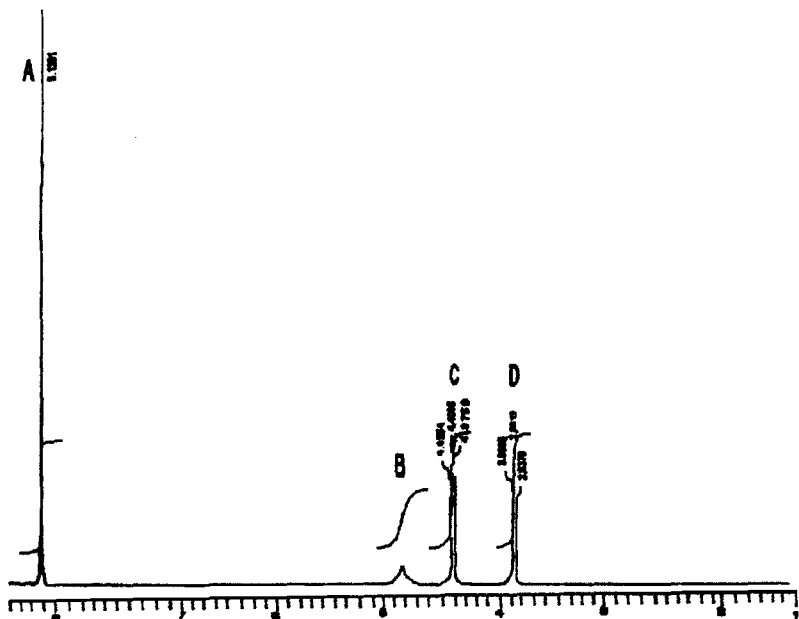
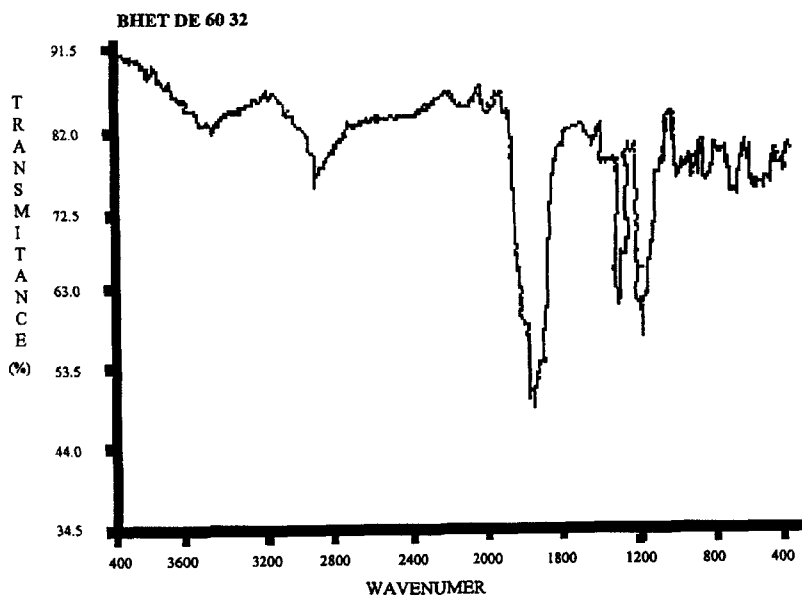FIGURE 2 Typical NMR-H spectrum of the BHET prepared.

FIGURE 3 Typical FTIR spectrum of the BHET prepared.

hydrogen bridges. The 2976 and 2885 cm^{-1} bands are identified as corresponding to the symmetric and asymmetric modes of the — CH$_2$— group, respectively. The 720 cm^{-1} vibration is reported to belong to the —(CH$_2$)$_n$— group, with $n°4$, as indeed is the BHET case. Moreover, it is known that the intensity is maximum for $n = 4$, which is precisely the case of the structure of the BHET. The 3147 and 3082 cm^{-1} bands correspond to the —CH— group in the aromatic ring. Finally, the 1704 and 1671 cm^{-1} bands correspond to the carbonyl group, free in the first band and forming hydrogen bridges in the latter.

The DSC thermogram of Figure 4 shows a melting temperature of 106°C, which agrees with previous reports [7, 8] on BHET.

(b) Kinetics

The reaction was followed by taking at different intervals, samples from the reactor and by measuring the methanol (MeOH) content,
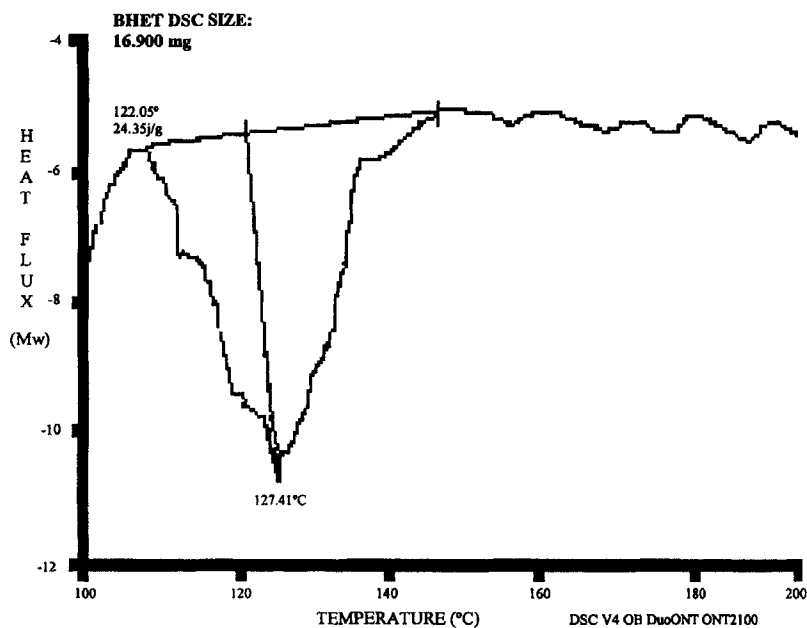

FIGURE 4 DSC thermogram of the BHET formed.

which, according to the reaction described above, provides a direct
measure of how much product has been formed. Figure 5 shows plots
of the amount of MeOH formed *vs.* the reaction time for the different
acetates used as catalysts. As observed there, the zinc and lead acetates
present obvious advantages over the other acetates and the their
corresponding kinetics was evaluated more carefully. Figures 6 and 7
show the plots of the amount of MeOH formed as a function of time
for the zinc and lead acetates at different temperatures, respectively.

As mentioned, BHET is produced from DMT and EG. More
specifically, the monomer is produced from the condensation stage
according to the following scheme:

$$HOCH_2CH_2OOC - \langle \bigcirc \rangle - COOCH_2CH_2OH \; + \; CH_2OH$$
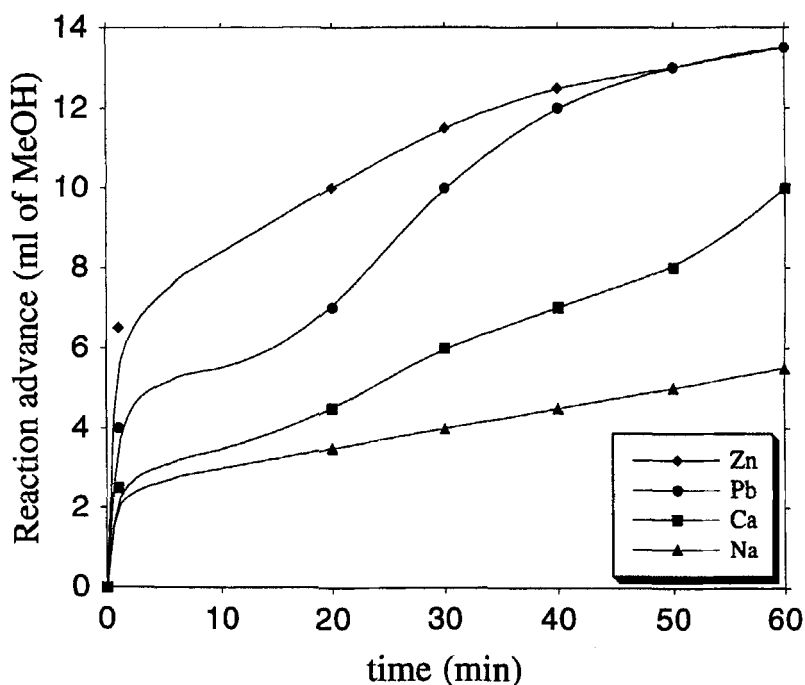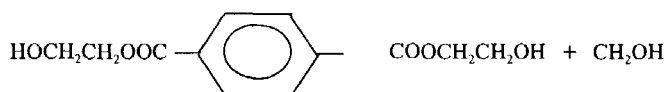

FIGURE 5   Plots of the amount of MeOH formed against reaction time for all the
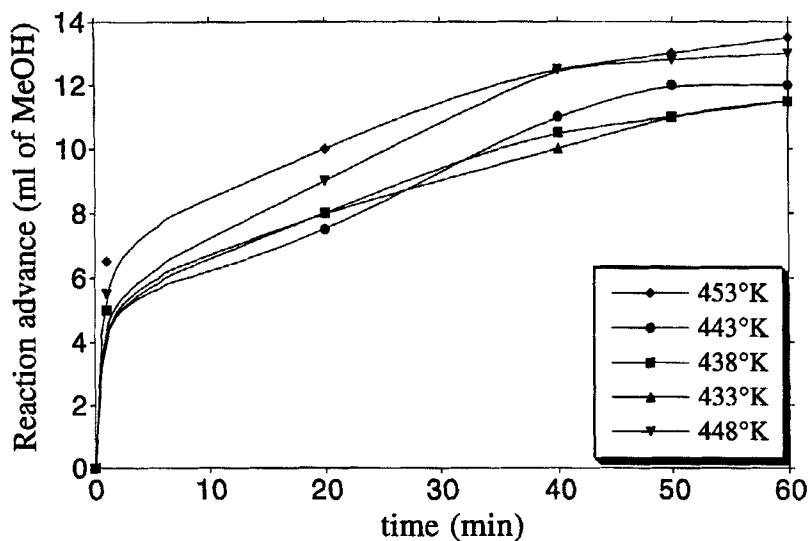catalysts tested.

FIGURE 6 Plots of the amount of MeOH formed as a function of time for the zinc acetate at different temperatures.
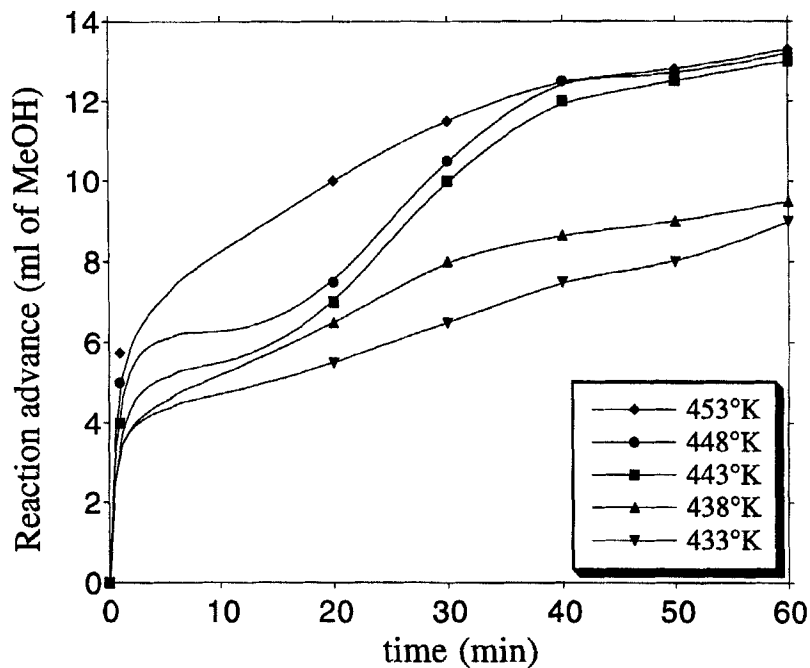

FIGURE 7 Plots of the amount of MeOH formed as a function of time for the lead acetate at different temperatures.

However, it is possible, due to the different reaction routes, that some oligomers could be formed, as has been described in the literature [9, 10], according to the following scheme:

$$R_m + g = R_g + m \qquad (1)$$

$$R_m + R_g = R_g + m \qquad (2)$$

$$R_g + R_g = R_gR + g \qquad (3)$$

w h e r e $R_m = $ —COOCH$_3$; $R_g = $ —COOCH$_2$CH$_2$OH; $R_gR = $ —COOCH$_2$CH$_2$COO—; g = EG; m = MeOH; R = monomer and Ki the corresponding reaction constant of each reaction.

In some previous works [10], the use of a slight EG excess indicated that the reaction was described by a first order model, if a constant volume reactor was assumed:

$$-dC_A/dt = kN_cC_A$$

where C_A is the DMT concentration and N_c the number *f* moles of the catalyst. However, other authors [8 – 10] have questioned seriously these results and the assumption of a constant volume reactor and have even proposed a fractional reaction order. In any case, the arguments on the specific reaction order and, moreover, on the effect of the acetate as catalyst, still persist and no comparative work has been carried out.

By assuming a discontinuous reactor of variable volume as a model [11] and a second order reaction, one obtains for the reactant r_A:

$$r_A = (1/V)(dN_A/dt) = (C_{A0}/(1 - e_AX_A))(dX_A/dt)$$

where V is the total volume of the reactor, N_A the number of moles of reactant A, C_{A0} the initial concentration, X_A the conversion degree and e_A the relative variation of the volume of the system, that is the relation between complete conversion ($X_A = 1$) and no conversion at all ($X_A = 0$), as follows:

$$e_A = (X_{A=1} - X_{A=0})/X_{A=0}$$

Upon integration and after straightforward algebra, one obtains that:

$$C_A \int_0^{X_A} \frac{dX_A}{(1 + \varepsilon_A X_A)(-r_A)} = t$$

Which means that, by plotting the right hand side of the above equation *vs.* the reaction time, a straight line must be obtained, if the assumption of a variable volume reactor is indeed correct.

Figure 8 shows the plot of the above equation for the case of the zinc acetate at 433°K, as an example, since similar plots were obtained for all temperatures measured, with excellent statistical correlation between the experimental data and the fitting. Figure 9 shows the equivalent plot for the lead acetate, also at 433°K. From this, and by using the Arrhenius equation, it is possible to obtain the corresponding activation energies as being 13,315.45 and 36,308 cal/mole for zinc and lead acetates, respectively, which lie within the range reported by various authors [5, 9, 10].

Finally, it is important to point out that, in all cases, the degree of conversion achieved was relatively high, of the order of 70%.
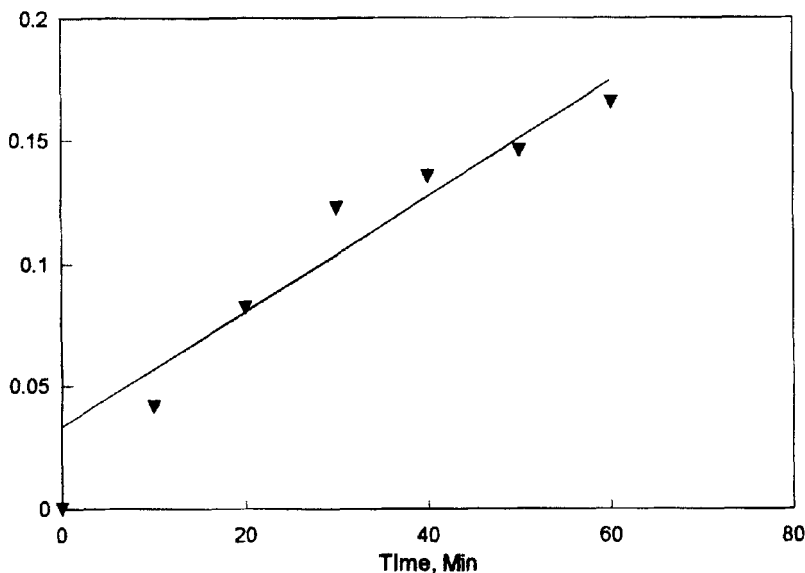

FIGURE 8   Plot of $C_A \int_0^{X_A} \frac{dX_A}{(1+\varepsilon_A X_A)(-r_A)}$ *vs.* Reaction time for the zinc acetate at 433°K.
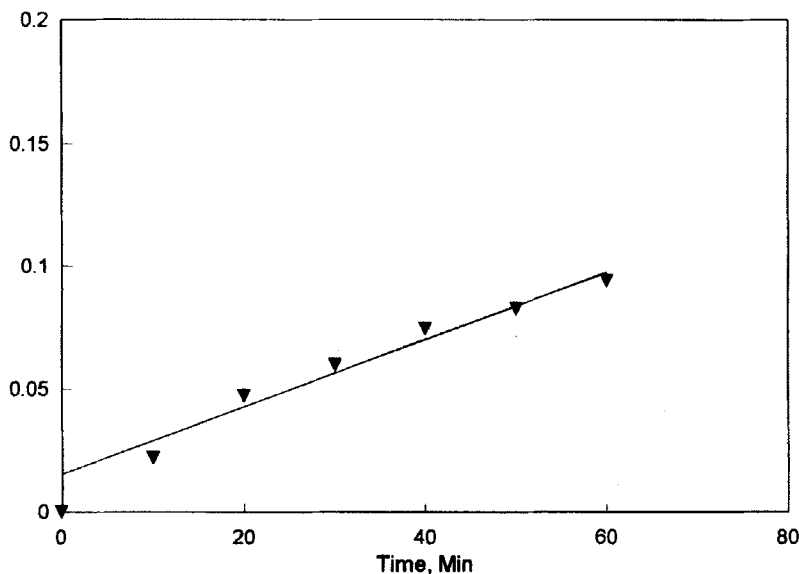
FIGURE 9   Plot of $C_A \int_0^{X_A} \frac{dX_A}{(1+\varepsilon_A X_A)(-r_A)}$ *vs.* Reaction time for the lead acetate at 433°K.

CONCLUSIONS

A second order reaction was found to best describe the experimental results of a number of different acetates employed as catalysts for the BHET production from DMT and EG. Also, the corresponding kinetics is well described by assuming a variable volume reactor, rather than a constant volume one, as was reported previously. Among all the acetates studied, the zinc acetate showed the best results, offering an interesting alternative to the much more expensive cadmium acetate, commonly utilized for this reaction. The product of the reaction route followed is a good quality BHET, as demonstrated by the FTIR, NMR-H and DSC characterizations performed.

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