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Kinetic Studies of Polyethylene Terephthalate Synthesis with Titanium-Based Catalyst

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Summary: Thermogravimetric analysis and stirred tank reactor techiques were used to study the kinetic of polycondensation of bis-hydroxy ethylene terephthalate catalyzed by titanium tetrabutylate. Polycondensation reaction can be modelled best with a second order reaction with respect to hydroxyl end groups concentration. Titanium tetrabutylate is a precursor and needs preactivation for polycondensation catalysis. Kinetic data depends on the mode of operation in thermogravimetric analysis. In nonisothermal mode, the overall activation energy was determined by model-free method and the pre-exponential factor was found to be affected by catalyst concentration. The kinetic study of isothermal reaction in thermogravimetric analysis is complex due to lack of a precise way to reach desired isothermal temperature and high activity of the catalyst. Titanium catalyst shows higher activity and lower selectivity than antimony catalyst but its activity is affected by the nature of ligands.

Keywords: kinetics; polyethylene terephthalate; thermogravimetric analysis; titanium tetrabutylate

Introduction

Polyethylene terephthalate (PET), one of the fast growing thermoplastic polymers, is manufactured via step growth polymerisation. Now a days, PET is synthesized in two steps, esterification of pure terephthalic acid (PTA) with ethylene glycol (EG) to bis-hydroxy ethylene terephthalete (BHET) followed by polycondensation to PET.[1] Polycondensation of BHET and its oligomers is catalyzed in general by antimony compounds mainly in form of oxide and acetate. The use of heavy metal antimony as catalyst can be a possible source of health risks especially in the food packaging application. Beside that, the tendency to increase the catalyst activity caused various PET producers to concentrate on the development of antimony-free and environmentally safe catalyst system. The best alternatives for antimony replacement are based on titanium but the main drawback of these catalysts is their low selectivity.[2] Although many activities in developing new titanium based catalysts with high activity and selectivity are occurring in the research center of industrial companies,[3] little is published about kinetics and mechanism of this kind of catalysts. The few kinetic studies of titanium-based catalysts had been done mostly by application of monofunctional model molecule like ethylene glycol monobenzoat to simplify the reaction analysis.[3,4] Kinetic data reported like activation energy and rate constant strongly depended on experimental conditions and procedures which are in the range of 48 to 80 $\mathrm{kJ \cdot mol^{-1}}$ and 1.5×10^{-4} to $2 \times 10^{-3} \mathrm{l \cdot mol^{-1} \cdot min^{-1}}$ respectively.[4,5]

Thermogravimetric analysis (TGA) was introduced as a technique for catalyst screening for the first time by Bhatty et al.,[6] in 1986. They used the temperature at which initial mass loss occurs (onset temperature T_o) as activity index. In 1997, Zimmerer et al.[7] applied TGA to examine

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the kinetics of polycondensation reaction in order to estimate the mass transfer influence and optimize reaction condition. They considered also monomer evaporation in their mathematical model. Moreover, they studied diffusion of EG within the melt by changing the thickness of the polymer layer. Rieckmann et al.[8] also applied TGA to study the kinetic of PET synthesis and tried to consider mass transfer effects. El-Toufaili et al.[9] studied the kinetics of hydrotalcite catalyzed BHET polycondensation by TGA and applying nonisothermal mode of operation.

The aim of this study is to elucidate the kinetics of BHET polycondensation catalyzed by titanium tetrabutylate (TTB) and using mainly TGA as data acquisition technique.

Experimental Part

Chemicals

BHET (>99%) was from Aldrich, EG (>99%) and Butanol (>99%) were from Merck, Titanium tetrabutylate (>98%) was from Fulka, Oligomer with chain length of 5 and hydroxyl end groups concentration of 2.9 mol l^{-1} from Equipolymers GmbH. All the applied chemicals were used without further purification.

Sample Preparation

The preliminary studies of different sample preparation methods showed that the most reliable and reproducible method of sample preparation is the following: 1 μl of TTB was added to appropriate amount of molten BHET (5–25 g) for desired concentration at 110 °C and stirred at this temperature for 15 min. The product was cooled down and ground to fine powder and used for TGA measurements. All catalyst concentrations expressed in ppm are based on molar ratio of TTB to BHET.

Thermogravimetric Analysis

Thermogravimetric analysis setup, TGA-209 F3 Tarsus, from Netzsch was applied in this investigation. 10 mg of prepared sample was filled in the aluminium crucible with 80 μl volume which was located on the sample holder of TGA. Nitrogen was used as purging gas with purging rate of 20 ml min^{-1}. The vertical construction of sample holder provided efficient purging. The oven of the TGA was first evacuated and then purged with nitrogen before each run. Isothermal polycondensation of BHET was investigated at 220, 230, 240 and 250 °C for 40 min reaction time. Non-isothermal runs were performed at heating rates of 1, 5 and 20 K min^{-1} starting at 30 °C and ending at 300 °C.

Polycondensation in Lab Scale Stirred Tank Reactor

Polycondensation was also run in a lab scale stirred tank reactor (STR) made of glass with a volume of 250 ml equipped with a special helical type of stirrer. Polycondensation was performed with 120 g monomer and 10 ppm TTB catalyst at different temperature 250, 255, 260 °C and 0.5 mbar with stirring speed of 200 rpm for different reaction time 2, 3 and 4 h.

FTIR Spectroscopy

FTIR spectroscopic investigations were done on an attenuated total reflection Fourier transform (ATR/FTIR) spectrometer of the type Spectrum One from Mettler Toledo.

Results and Discussion

Optimization of TGA for Quantitative Study

The micro-scale of the TGA crucibles provides micro-scale diffusion path length and thereby mass transfer limitations might be avoided. The main draw back of this system is absence of effective mixing of reaction mass, however it can be seen that reaction mixture within the TGA crucible is moving very strongly and stimulates self-mixing thereby. Another problem can be the catalytic activity of the crucible itself. It was found that aluminium crucibles have least catalytic activity.[10] Moreover, monomer evaporation is present during polycondensation of BHET,[7,9] since polycondensation of BHET in an open crucible led to mass loss much higher than expected for complete conversion equal to 24.4 wt%. To reduce monomer evaporation, a lid with a hole in the centre covered the aluminium crucible in all polycondensation runs. Another important point in application of TGA is the mode of operation. Running the reaction merely isothermal was not possible. Since the heating rate and heating time from ambient to reaction temperature have effect on mass loss and consequently concentration of hydroxyl end groups. These effects however were considered in the kinetic studies.

Figure 1, represents the thermogram of BHET polycondensation in quasi-isothermal mode of operation with different initial heating rates. At high heating rate the thermal lag between sample and oven is highest and at lower heating rate, higher conversion is achieved before reaching to isothermal regime. Therefore, 20 $K \cdot min^{-1}$ was chosen as optimal heating rate for isothermal runs in TGA.

Nonisothermal runs were performed by heating up the reaction mixture at 1, 5 and 20 $K \cdot min^{-1}$. Figure 2, represents the thermograms of nonisothermal runs. Heating rate has significant effect on the onset temperature of reaction. The reason is that the true sample temperature lags behind recorded temperature caused by heat transfer effects. Furthermore, time effect should also be considered. A low heating rate has the advantages of overcoming of temperature lag. However, in this case, the melt solidifies partially due to increase in molecular weight of product and kings are formed in the thermogram of polycondensation as can be seen in Figure 2. Therefore, 5 $K \cdot min^{-1}$ was used as optimal heating rate for nonisothermal mode of TGA operation.

Kinetics

Quantitative evaluation of thermogarms which is corresponding to calculation of hydroxyl end groups concentration with respect to mass loss in TGA was done according to the method of El-Toufaily[9] by considering volume change during reaction. The concentration of hydroxyl end groups in lab scale reactor was calculated by analysis of intrinsic viscosity and carboxyl end groups concentration of polymer product.

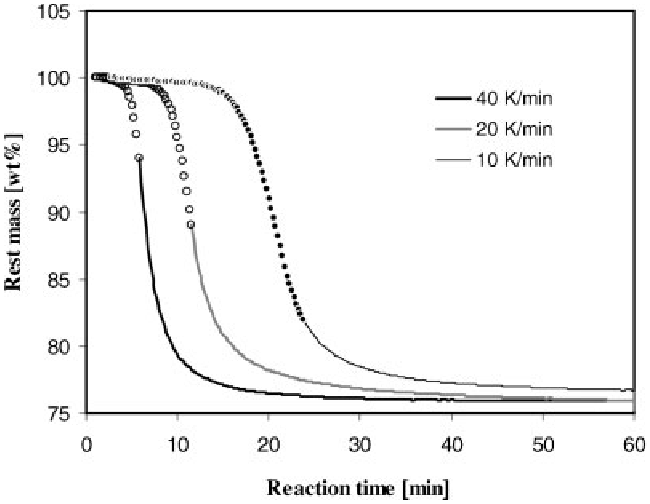

Figure 1.
Effect of initial heating rate on mass loss of reaction mixture of BHET polycondensation at 250 °C, [Ti]: 10 ppm. Dots indicate nonisothermal and lines isothermal regimes. Heating rate: 10 K min^{-1} [——], 20 K min^{-1}[——], 40 K min^{-1} [▬].

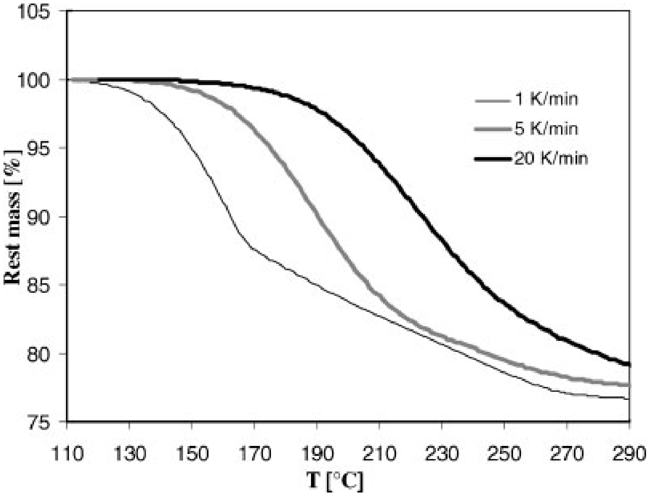

Figure 2.
Effect of heating rate on mass loss of reaction mixture of BHET polycondensation, [Ti]: 10 ppm · 1 K min^{-1} [——], 20 K min^{-1} [——], 40 K min^{-1} [▬].

Kinetic studies are based on following assumption:

1- Polycondensation is considered as a reaction between hydroxyl end groups.
2- All hydroxyl end groups have the same activity irregardless of the chain length of the parent molecules.
3- Polycondensation reaction is considered as irreversible reaction due to fast and efficient removal of EG (Figure 3). Side reactions are negligible in TGA since the IR spectra of evolved gas of polycondensation reaction, represented no IR bands corresponding to side products and was mainly showing bands corresponding to EG.
4- Mass transfer limitations in polycondensation reaction are neglected.

Fitting of nonisothermal data to different reaction models results in widely varying Arrhenius parameters. This problem had been addressed by different authors.[11–14] The way of obtaining trustworthy kinetic parameter is to extract them in a way that is independent of the reaction model. A viable alternative method is based on the model–free isoconversional method and allows obtaining unambiguous values of activation energy by considering of its dependency on reaction conversion. Friedman isoconversional method[11] applied in these studies (equation 2), is derived by taking the logarithm of reaction rate

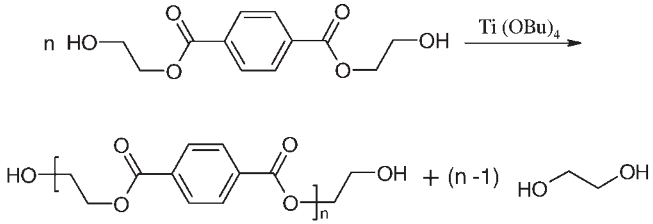

Figure 3.
Scheme of polycondensation of BHET.

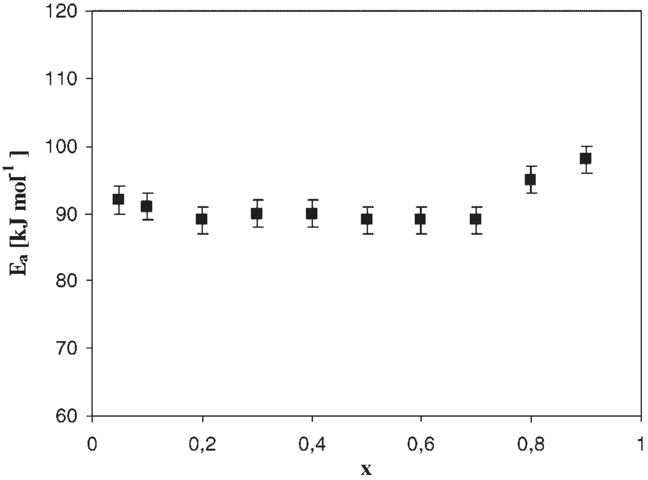

Figure 4.
Dependency of activation energy on conversion of nonisothermal reaction evaluated by Friedman method.[11]

equation of nonisothermal experiment (equation 1) with constant heating rate, $\beta = dT/dt$:

$$\frac{dx}{dT} = \frac{k_0}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(x) \tag{1}$$

$$\ln\left(\frac{dx}{dt}\right)_x = \ln[k_{0,x} f(x)] - \frac{E_a, x}{RT_x} \tag{2}$$

where x is conversion and $f(x)$ represents the reaction progress as function of conversion. The linear plots between $\ln(dx/dt)_x$ and $1/T_x$ determine the value of E_a (activation energy, $kJ \cdot mol^{-1}$) at different conversion. The software package, Thermokinetic from Netzsch company was used for determination of activation energy of nonisothermal experiments. Figure 4, represents dependency of overall activation energy of nonisothermal reaction on conversion. It is observed that in the conversion range of 0 to 80%, activation energy remains constant with a value of 92 ± 4 $kJ \cdot mol^{-1}$. Increasing of activation energy at higher conversion might be due to the presence of side reactions which affect overall activation energy. This value of activation energy (92 $kJ \cdot mol^{-1}$) was used for the determination of pre-exponential factor by application of simulation software.

The reaction order with respect to hydroxyl end groups concentration, was determined with integration method. Best fitting was achieved by plotting of experimental data with a second order reaction. Therefore the reaction rate, R [$mol \cdot l^{-1}$ min^{-1}], can be written as following:

$$R = -\frac{1}{2}\frac{d[OH]}{dt} = k_0 \exp\left[\frac{-E_a}{RT}\right][OH]^2 \tag{3}$$

k_0 is overall pre-exponential factor [$l \cdot mol^{-1}$ min^{-1}] and E_a is overall activation energy.

The PREDICI[15] software package was used for detailed kinetic modelling. It was applied to fit experimental conversion-time curves. The fitting parameter was pre-exponential factor for fixed overall activation energy of 92 $kJ \cdot mol^{-1}$. Figure 5 shows experimental and simulated data by second order kinetic for nonisothermal run. The fitting quality indicates second order kinetic is able to predict polycondensation progress.

The overall pre-exponential factor is depending on catalyst concentration and it is increasing linearly with increasing initial catalyst concentration (Figure 7).

Therefore the reaction rate should be rewritten in the following form:

$$R = -\frac{1}{2}\frac{d[OH]}{dt} = (k_{0,cat}[Ti] + k_0) \times \exp\left[\frac{-E_a}{RT}\right] \quad [OH]^2 \tag{4}$$

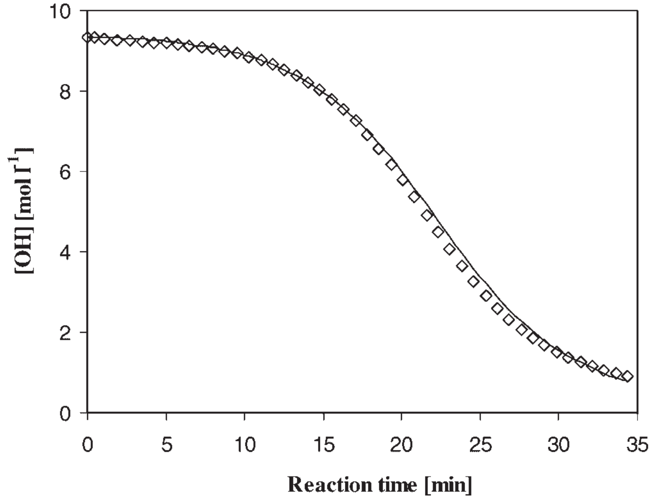

Figure 5.
Fitting of experiments (dots) with model, [Ti]:0.000051 mol l^{-1}, nonisothermal run.

in which $k_{0,cat}$, is frequency factor of catalyzed path of reaction and k_0 is expressing frequency factor of uncatalyzed path of reaction. According to the nonisothermal studies, the following values could be substituted in the reaction equation:

$$R = -\frac{1}{2}\frac{d[OH]}{dt} = (4 \times 10^{11}[Ti] + 7 \times 10^{7}) \times \exp\left[\frac{-92000}{RT}\right][OH]^2 \tag{5}$$

It is assumed that the initial concentration of titanium is equal to the concentration of catalyst active sites. However the IR spectra of TTB/BHET mixture at 110 °C shows bands which are probably due to the complexation of BHET with titanium species indicating that TTB is just a precatalyst (Figure 7).

Kinetic studies of isothermal experiments in TGA are not easy task. The reason is the preheating of reaction mixture to reach the isothermal regime which has

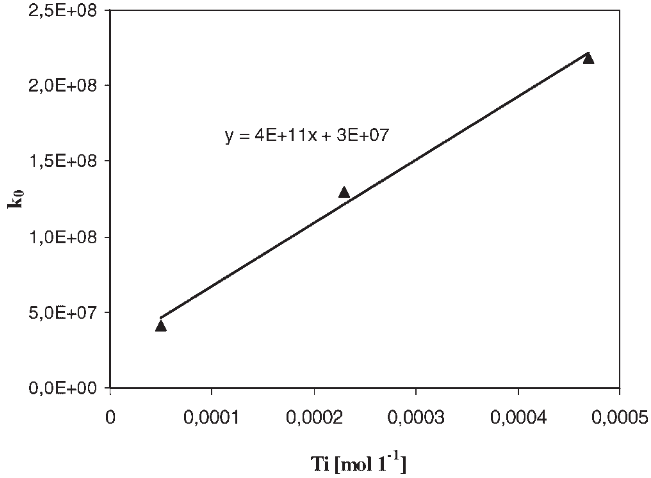

Figure 6.
Effect of catalyst concentration on overall pre-exponential factor.

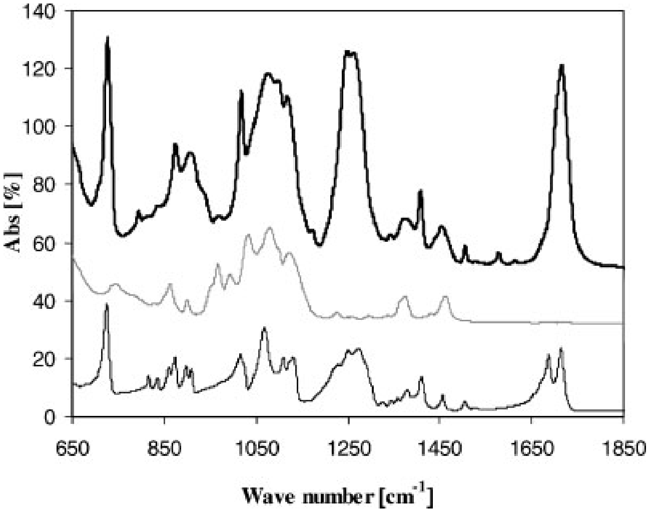

Figure 7.
FTIR spectra of BHET and TTB at room temperature and mixture of TTB/BHET at 110 °C (molar ration 1:2). BHET [___]", TTB [___], molten BHET-TTB [___].

severe effect on hydroxyl end groups concentration before reaching to isothermal temperature. Further more this effect is more pronounce with increasing catalyst concentration. The investigation is only possible at very low catalyst concentration ($0.000051\ \mathrm{mol \cdot l^{-1}}$), which led to the results of $89 \pm 4\ \mathrm{k\ J \cdot mol^{-1}}$ for overall activation energy and $4.5 \times 10^7\ \mathrm{l \cdot mol^{-1} \cdot min^{-1}}$ of overall pre-exponential factor.

In order to check the kinetic results of TGA, polycondensation was run at 250, 255 and 260 °C in lab scale STR. Due to low temperature of the reaction and efficient vacuum to remove by-product, kinetics of polycondensation was assumed to be

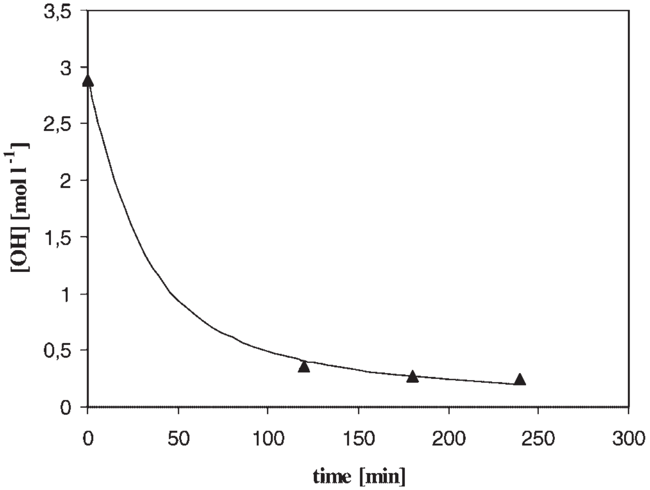

Figure 8.
Fitting of experiments (dots) with model, [Ti]:0.000051, in STR at 255 °C under vacuum.

Table 1.
Overall reaction rate constant at different temperature obtained by modelling.

T [°C]	k [l mol^{-1} · min^{-1}]
250	9×10^{-3}
255	1.1×10^{-2}
260	1.3×10^{-2}

Table 2.
Activity comparison of different titanium based catalysts, [Cat]: 800 ppm.

Catalyst	Relative Activity [$g_{product}$ mg^{-1}_{cat} h^{-1}]
Titanium tetrabutylate	38
Potassium titanium oxide oxalate. dihydrate	19
Lactic acid titanate chelate, ammonium salt	17

chemistry controlled. Furthermore, the analysis of polymeric product showed that the side products are negligible. However the concentration of side products like carboxylic end groups is increasing at higher temperature. Moreover, polycondensation at 250 °C for longer time (more than 180 min) leads to polymer precipitation because the melting point of reaction product is higher than reaction temperature.

Kinetic studies had been done by fitting of experimental data with second order kinetic by application of PREDICI. Fitting parameter was overall reaction rate constant. Figure 8 represents fitting of decay of hydroxyl end groups concentration of experiment and model at 255 °C. By plotting of Arrhenius equation, ln k versus 1/T, reported in Table 1, the overall activation energy and overall pre-exponential factor of polycondensation was achieved as $E_a = 84 \pm 4$ kJ mol^{-1} and $k_0 = 1.9 \times 10^6$ l · mol^{-1} · min^{-1} respectively (Figure 9). However it should be considered that these values are overall kinetic parameters and contain effects of catalyst and temperature inclusively. But the difference between the kinetic results of polycondensation in TGA and lab scale reactor is not big and is comparable.

Additionally, concentration of catalyst can also strongly affect the reaction rate. The details of catalyst effect on polycondensation kinetic in lab scale stirred tank reactor at low and high conversion regime including of spectroscopic studies is still under investigation.

Moreover, comparative activity studies of titanium based catalysts with different ligands showed that the catalyst activity depends on ligands nature and activity reduces when bidendate ligands are used

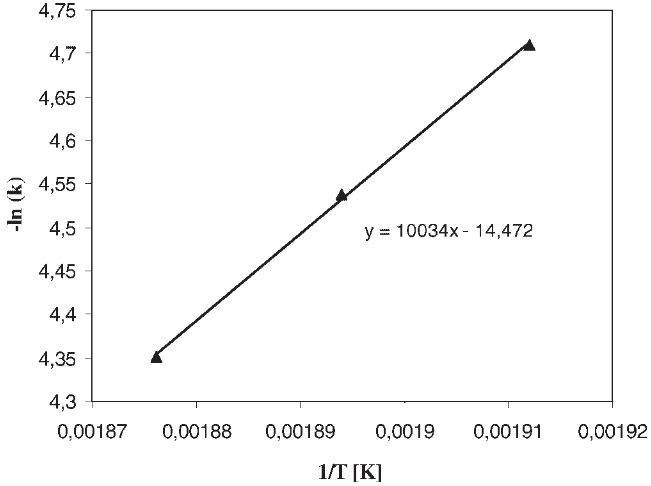

Figure 9.
Ahrrenius plot of polycondensation at [Ti]:0.000051 mol l^{-1}, till 98% conversion.

due to formation of chelating complexes, which might have effect on transition state formation (Table 2).

Conclusion

Thermogravimetric analysis is a suitable method for fast screening of catalyst of polycondensation reaction, since reaction is characterized by mass loss. However, the method of thermogravimetry for quantitative kinetic studies of polycondensation reactions should be used only if another independent method is confirming the thermogravimery and to the method of data evaluation.

The activity of titanium based catalysts in polycondenstion of bis-hydroxy ethylene terephthalate depends on the nature of the ligands attached to titanium. This phenomenon will give opportunities to modify titanium based catalyst in such a way that they will show high activity and high selectivity simultaneously.

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