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New catalysts for poly(butylene terephthalate) synthesis. 2. Kinetic comparison using model compounds

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Abstract

A kinetic study of poly(butylene terephthalate) polymerization from dimethyl terephthalate and butanediol, using a catalyst mixture composed of titanium tetrabutoxide and hafnium acetylacetonate, in 1:3 molar ratio, was performed and compared to the standard titanium only catalyst. Arrhenius parameters were obtained from model reactions for both stages of polymerization. The mixed catalyst showed a consistently higher pre-exponential factor (A) and a higher activation energy (E_a) in the Arrhenius equation compared to the industrially used catalyst. For this reason the mixed catalyst, as observed in actual polymerizations, is more active at high temperature. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(butylene terephthalate); Kinetics; Model compounds

1. Introduction

Current poly(butylene terephthalate) (PBT) [1] production is based on the reaction of dimethyl terephthalate (DMT) with 1,4-butanediol (BD) catalyzed by an organotitanate (e.g. $Ti(OBu)_4$). The polymerization process is performed in two steps; the first step is called ester interchange (EI) and is generally performed at 170–215°C at atmospheric pressure, the second step, called transesterification (TE) or polycondensation, is performed at 245–255°C under dynamic vacuum in order to remove excess BD. While this is a well-known and widely practiced reaction system, it has a few limitations. In particular, the rate of transesterification catalyzed by titanates during polycondensation, while sufficient, is relatively slow. Thus during industrial scale production long residence times and high temperatures are required to prepare high molecular weight resins; these high temperatures combined with the presence of titanium based catalysts gives rise to the formation of carboxylic acid end-groups (that affect the thermal stability of the final product) and of unrecoverable side products (mainly tetrahydrofuran (THF)) [2].

Recent work carried out by our group, devoted to develop more effective catalysts for polyester synthesis, have led to the discovery that mixtures of titanium alkoxides with hafnium derivatives or lanthanide derivatives result in faster polymerizations [3]. A recent patent [4] has shown that several different catalyst mixtures (e.g. titanium with hafnium or lanthanide metals) are capable of delivering higher reactivity during PBT polymerization. Among those catalysts the titanium tetrabutoxide/hafnium acetylacetonate in a 1:3 molar ratio afforded the best results. In particular, a 25% decrease in EI reaction time and a 45% decrease in TE reaction time were obtained with respect to TBT. The Ti–Hf catalytic system also reduces the amount of THF formed during both polymerization stages. On the basis of these very interesting results, we decided to perform an extensive study of the kinetics of this new catalytic system.

While the results from the complete polymerizations are very useful on a relative basis, the data presented in the patent on titanium–hafnium catalytic system are derived from non-isothermal, *batch*-type reactions. Batch PBT polymerizations are typically run with a temperature gradient due to the increasing melting point of the product and the need to remove higher boiling materials as the reaction proceeds. This type of experiment does not yield true activation parameters which would be useful for the prediction of the performance of these catalysts in a continuous reaction facility, such as that used for the production of PBT, where there are discreet operating points of temperature, pressure and conversion. Activation (Arrhenius-type) parameters can be used for predictions of continuous operations

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through a computer model previously developed for PBT production. Arrhenius parameters are also very useful to evaluate the reaction mechanism and in fact, most of the previous works on ester interchange reaction mechanisms are based on this kind of study [5].

Due to the continuous increase in the melting point, which occurs during PBT polymerization, suitable model reactions must be chosen to represent the reactions involved. Model reaction studies of EI have been reported in the literature by Pilati [6] and others [7]. However, all of these previous studies have used unsubstituted benzoate esters and have consequently failed to account for the electronic effects operating on the aromatic ring of DMT.

In this paper we report the kinetic study of the hafnium/titanium catalyst system in PBT synthesis using model compounds for both stages of the polymerization reaction.

2. Experimental

Preparation of hafnium acetylacetonate. A solution of $HfCl_4$ (3.00 g; 9.37 mmol) in 50 ml of H_2O was added dropwise to a solution of acetylacetone (5.63 g; 56.2 mmol) in 50 ml of H_2O under stirring at room temperature. The pH was then increased to 7 by addition of 2N KOH solution and the reaction mixture, with precipitated hafnium acetylacetonate, was stirred for 6–8 h. The hafnium acetylacetonate was filtered and dried at 60°C under vacuum overnight (yield 65%). ^1H NMR ($CDCl_3$): δ (ppm downfield from TMS) 5.5 (1H, s); 2.1 (6H, s).

Titanium tetrabutoxide (TBT) (from Aldrich) was distilled under reduced pressure twice and stored in closed bottles under nitrogen at 0°C. Methyl *p*-chlorobenzoate (ClBzMe) (from Aldrich), DMT, phenyl ether (Ph_2O), (all from Aldrich) were high purity products and were not purified prior to use. BD was dried over 4 Å sieves prior to use.

2.1. Model compounds synthesis

Preparation of 4-octyloxy-1-butanol (BDE). BD (115.8 g; 1.28 mol), NaOH (20.7 g; 0.52 mol) and tetrabutylammonium chloride (1.80 g; 0.006 mol) were placed in a three neck round bottom flask immersed in a silicon oil bath. (25.0 g; 0.129 mol) of 1-bromooctane were added dropwise to the stirred solution. The temperature was increased to 80°C and the reaction mixture was kept at this temperature for 4 h. The reaction mixture was then dissolved in 300 ml of ether and the organic solution was washed twice with water and brine to eliminate any unreacted BD. The ether solution was dried over $MgSO_4$ and the solvent was then removed under reduced pressure. The crude mixture was then distilled under reduced pressure (15 mmHg) at 155°C to give BDE (yield 65%). ^1H NMR ($CDCl_3$): δ (ppm downfield from TMS) 3.53 (2H, t), 3.37 (4H, m), 1.5–1.2 (16H, m), 0.96 (3H, t).

Preparation of 1,4-bis (p-chlorobenzoyloxy)butane (BzBDBz). BD (25 ml; 0.282 mol) and 200 ml of ethyl ether were placed into a 1 l round bottom flask provided with magnetic stirrer and a water-cooled reflux condenser bearing a N_2 inlet. *p*-Chlorobenzoyl chloride (83.21 g; 0.592 mol) and triethylamine (79.6 ml; 0.592 mol) were then added to the stirring solution. The mixture was left to react overnight at 80°C. After cooling to room temperature, ethyl acetate and 400 ml of water were added to the clear crude product. The water layer was removed and the remaining organic layer washed twice each with water, 5% NaOH (aq.), and brine. The ether solution was dried over $MgSO_4$ and the solvent was then removed under reduced pressure (yield 90%). The product was analyzed by ^1H NMR ($CDCl_3$): δ (ppm downfield from TMS) 7.88 (4H, d), 7.36 (4H, d), 4.21 (4H, t), 1.70 (4H, t).

Preparation of 1-(p-chlorobenzoyloxy)-4-butanol (BzBD). BD (506.3 ml; 5.70 mol) was placed into a 1 l round bottom flask provided with magnetic stirrer and a water-cooled reflux condenser bearing a N_2 inlet. *p*-Chlorobenzoyl chloride (89.46 g; 0.57 mol) and triethylamine (79.6 ml; 0.57 mol) were then added to the stirring butanediol. The mixture was left to react overnight at 80°C. After cooling the flask to room temperature, 400 ml of ethyl acetate and 400 ml of water were added to the clear crude product. The water layer was removed and the remaining organic layer washed twice each with water, 5% NaOH (aq.), and brine. The ether solution was dried over $MgSO_4$ and the solvent was then removed under reduced pressure. The product was then purified with great difficulty from the diester (BzBDBz) by flash chromatography using methylene chloride and ethyl acetate as eluents. The solvent was then removed under reduced pressure (yield 45%). The product was analyzed by ^1H NMR ($CDCl_3$): δ (ppm downfield from TMS) 7.91 (2H, d), 7.38 (2H, d), 4.25 (2H, t), 3.53 (2H, m), 1.75 (2H, m), 1.48 (2H, m).

EI kinetic experiments. For each kinetic experiment, a $20.0 \times 0.75\ cm^2$ test tube was filled with ClBzMe (4.265 g; 0.025 mol), BDE (0.510 g; 0.0025 mol) and 0.850 g of phenyl ether as internal standard. Tubes were allowed to thermally equilibrate at the desired temperature for at least 30 min. The head of the tube was cooled and the catalyst (0.0207 mmol, corresponding to the molar concentration used in the pilot plant [3]) was carefully transferred into the tube. During this time, the tube was kept closed with a rubber septum. For each experiment, from eight to ten samples were drawn at predetermined times so that each reaction would proceed to at least 50% conversion. Samples were drawn from the reaction, dissolved in 1 ml of CH_2Cl_2 and the mixtures were analyzed by gas chromatography employing a 30 m (ID 0.53 mm, film thickness 1.2 μm) Alltech EC-Wax (Carbowax) column. Response factors for the FID detector were determined from the analysis of standard solutions of ClBzMe, BDE and phenylether. The data obtained from the GC were automatically converted into Microsoft Excel spreadsheets and fitted with pseudo first order kinetic equations.

Isothermal TE kinetic experiments. For each kinetic

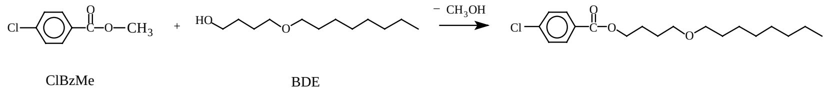

Fig. 1. EI model reaction.

experiment, a $20.0 \times 0.75\ \text{cm}^2$ test tube was filled with 4.501 g (0.050 mol) of BD and 1.836 g (0.0050 mol) of BzBDBz, and a stir bar to ensure good mixing. The head of the tube was cooled with cold water. Tubes were allowed to thermally equilibrate at the desired temperature for at least 30 min. The catalyst (0.0236 mmol) was carefully introduced into the tube. During this time, the tube was kept closed with a rubber septum. For each experiment, from eight to ten samples were drawn at predetermined times so that each reaction would proceed to at least 50% conversion. Samples were drawn from the reaction tubes and dissolved in 2 ml of THF. The THF mixture was filtered and analyzed by HPLC on a Perkin Elmer instrument employing a 4.6 mm × 25 cm Zorbax SB C18 reverse-phase column. A water/THF mixture with the following gradient was implemented: initial: 50:50 THF/H_2O, 1.5 ml/min. Step 1: 2 min, 1.5 ml/min 75:25 THF/H_2O. Step 2: 6 min, 1.5 ml/min, 100% THF. Step 3: 15 min, 1.5 ml/min 50:50 THF/H_2O. Response factors for the UV detector at 254 nm were determined from an analysis of standard solutions of BzBD and BzBDBz.

3. Results and discussion

As reported above, several aspects of ester interchange chemistry must be considered when developing a model system, including the electronic effects on the aromatic ring of dimethyl terephthalate. Thus, this kinetic study was designed to account for these effects on esterification reactions. Because isothermal kinetics are required to generate activation parameters, and the melting point of PBT oligomers increases rapidly with the degree of polymerization, pairs of difunctional monomers could not be used simultaneously in these studies. In addition, the use of monofunctional reagents simplifies the analysis of the kinetics.

Previous work involving β-elimination reactions demonstrated that methyl *p*-chlorobenzoate was an appropriate model compound to mimic the electronic effects on the aromatic ring [8]. That study used the Hammet [9] equation (Eq. (1)) in order to find a good model for the β-elimination reaction.

$$\log \frac{k}{k_0} = \sigma_p \rho \tag{1}$$

where k is the rate constant of the reaction of a substituted compound, k_0 is the value for the unsubstituted substance, σ_p is a constant characteristic of a substituent and ρ is a constant for a particular reaction and is a measure of the sensitivity of the reaction to substituent changes.

A previous study [8] revealed that although the Hammett σ_p value (0.23) for the *p*-chloro substituent is half that of a *p*-carboxymethyl substituent (0.45), the electronic effect upon the rates of reaction was minimal. This was due to the low sensitivity of the β-elimination reaction of primary esters to electronics effects. However, another work [10] on the esterification reaction of benzoic acid with methanol catalyzed by acid reports that there is a slight dependence on electronic factors ($\rho = -0.229$). Therefore the *p*-chloro derivative could be considered an acceptable model for the catalyzed reactions.

3.1. EI model kinetics

The model reaction chosen to simulate EI is shown in Fig. 1. ClBzMe was employed to mimic DMT, and 4-hydroxybutyl octyl ether (BDE) was chosen to simulate BD. The reactions were conducted using a 10 fold excess of ClBzMe with respect to BDE and the same catalyst molar concentration used in the previous work [3] in the laboratory scale pilot plant (0.81 mmol/mol of terephthalic unit).

The model kinetic reactions were performed over a 30°C span at four temperatures: 160, 170, 180 and 190°C. The total molar concentration of the catalysts was the same in both series of experiments. The reactions were repeated twice for the three lower temperatures and three times for the 190°C condition. It was assumed, in agreement with the literature [11], that the EI reaction is first order with respect to the concentration of both reagents (Eq. (2)).

$$v_{EI} = k[\text{BDE}][\text{ClBzMe}] \tag{2}$$

The rate constants were obtained from the slope of the pseudo first order plots of $\ln([\text{BDE}]_0/[\text{BDE}])/[\text{ClBzMe}]$ versus time, of which a sample is shown in Fig. 2.

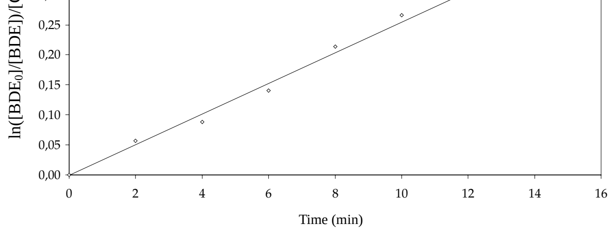

Fig. 2. EI model kinetics pseudo first order linear fit.

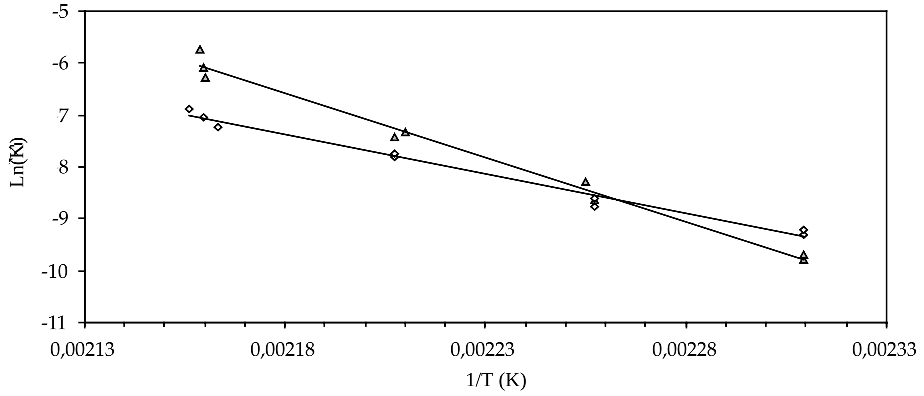

Fig. 3. EI Arrhenius plot for the Ti (◇) and the Ti–Hf (△) catalyzed reactions.

As reported in Fig. 2 there is a good agreement between experimental data and the kinetic equation used. The activation parameters were determined from the Arrhenius plot, shown in Fig. 3, of ln k versus $1/T$(K).

The activation energy (E_a) and pre-exponential factor (A) were deduced from a linear fit of the Arrhenius plot, along with the activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) from the corresponding Eyring equation (Eq. (3)) and all of the parameters are reported in Table 1.

$$k = K\frac{k_B T}{h}e^{-\Delta G^{\ddagger}/RT} \tag{3}$$

where k is the rate constant, K is the transmission coefficient, h and k_B are the Planck and Boltzman constants, and $\Delta G^{\ddagger}$ is the free energy of activation that is equal to $\Delta H^{\ddagger} - T\Delta S^{\ddagger}$.

It is clear from these results that the activation energies for the two catalyst systems are very different, which helps to explain why significant differences have been observed in pilot plant distillation curves during batch polymerizations (see part 1 in Ref. [3]). In that case the reaction catalyzed by the titanium/hafnium mixture was slower compared to the reaction catalyzed by only titanium when the temperature was below 190°C, but became faster at higher temperatures. As can be seen in the Arrhenius plot, titanium is clearly superior at lower temperatures to the mixed 3:1 catalyst for ester interchange. However, there is a crossing-over in rates that occurs at approximately 168°C, above which the mixed catalyst is superior. These results are in good agreement with the results reported in the patent [4] and in part 1 in Ref. [3].

The activation parameters derived from the Eyring equation can also help in understanding the differences between the catalyst systems. One observation that can be made is that there is a large reduction in the entropic requirements in the transition state for EI for the mixed catalyst system (compare $\Delta S^{\ddagger}$ for each catalyst in Table 1) over titanium. This can be ascribed to the smaller ionic radius of Ti^{+4} (0.68 Å) compared to Hf^{+4} (0.78 Å), which necessitates a very tight packing of both reactant and product species at the metal center.

Table 1
EI model kinetics activation parameters

Catalyst	E_a (kcal/mol)	A (l/mol s)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
Ti control	30.1	1.37×10^{11}	29.2	−10.4
Ti(1)–Hf(3)	49.2	3.87×10^{20}	48.3	32.9

3.2. TE model kinetics

For the same reasons stated above for the EI kinetics, a model compound reaction must also be used for the measurement of the activation parameters for the TE reaction. The reaction scheme used for the TE model kinetics is shown in Fig. 4.

The reaction studied is the reverse of the normal TE reaction, which would consist of the reaction between two BzBD molecules to form BzBDBz and BD. The reverse reaction was chosen because of the highly problematic purification of BzBD. The forward reaction rate (k_f) was calculated through Eq. (4), as the equilibrium constant for this reaction in a closed system was previously measured to be equal to one.

$$K_{eq} = \frac{k_r}{k_f} = 1 \tag{4}$$

The results obtained at high conversion in these open system reactions confirmed the previously measured equilibrium constant value.

The BzBDBz and the BzBD concentrations were measured by HPLC using UV detection. No internal standard was employed because it was verified by ^{1}H NMR spectroscopy that no loss of aromatic species and that no side reactions occurred, due to the lower temperature used for TE model compound reactions respect to the second stage of polymerization. The kinetic equation used is

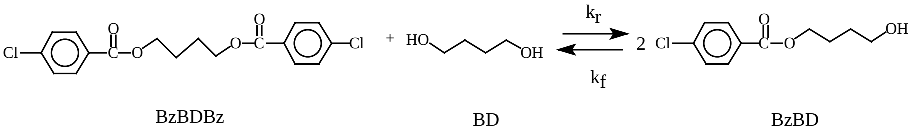

Fig. 4. TE model reaction.

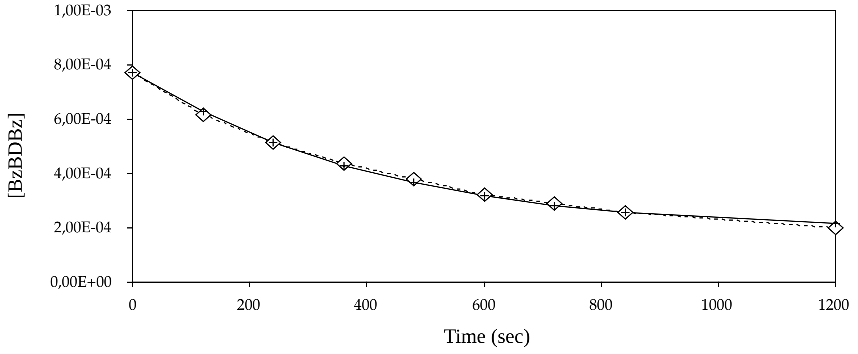

Fig. 5. Example of second order equilibrium reaction fit for the TE model reaction ((◇) experimental; (+) predicted).

reported in Eq. (5).

$$\frac{\mathrm{d[BzBDBz]}}{\mathrm{d}t} = k_\mathrm{f}[\mathrm{BzBD}]^2 - k_\mathrm{r}[\mathrm{BD}][\mathrm{BzBDBz}] \tag{5}$$

Considering that the reaction was performed using a 10 fold excess of BD respect to BzBDBz the concentration of BD during the reaction is:

$$[\mathrm{BD}] = 9[\mathrm{BzBDBz}]_0 + [\mathrm{BzBDBz}] \tag{6}$$

where [BzBDBz($_0$ is the initial concentration of BzBDBz. Taking into account that $k_\mathrm{f} = k_\mathrm{r}$ and that the BzBD concentration is equal to:

$$[\mathrm{BzBD}] = 2([\mathrm{BzBDBz}]_0 - [\mathrm{BzBDBz}]) \tag{7}$$

Eq. (5) can be written as a function of BzBDBz concentration:

$$\mathrm{d[BzBDBz]} = k_\mathrm{r}(\{2([\mathrm{BzBDBz}]_0 - [\mathrm{BzBDBz}])\}^2 - (9[\mathrm{BzBDBz}]_0 + [\mathrm{BzBDBz}])[\mathrm{BzBDBz}])\mathrm{d}t \tag{8}$$

Numerical integration was employed to extract the TE rate constant by fitting, using Eq. (8), the experimental curves of the concentration of BzBDBz.

As reported in Fig. 5, the fit of the experimental results to a second order equilibrium reaction was excellent.

The model kinetic reactions were performed at four temperatures: 160, 170, 180 and 190°C. An Arrhenius plot was generated from these data (Fig. 6) and the activation energy and pre-exponential factor were deduced. Similarly, the activation enthalpy and entropy, deduced from the Eyring plot, are reported in Table 2. As seen previously in the EI reaction, titanium is the superior catalyst at lower

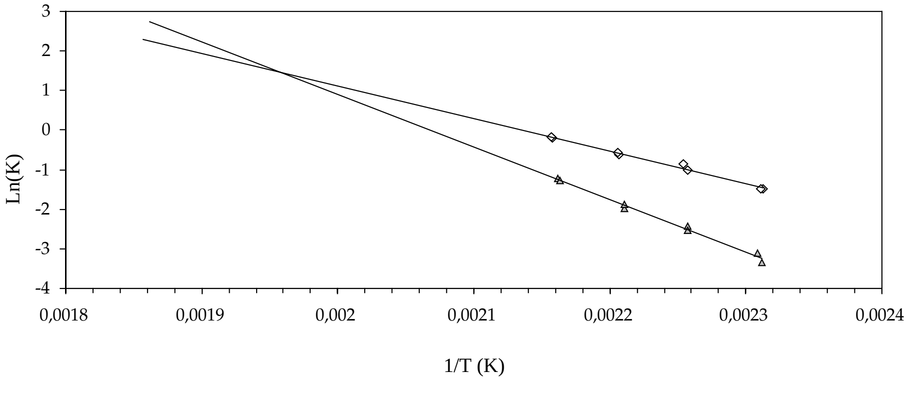

Fig. 6. TE Arrhenius plot for the Ti (◇) and the Ti–Hf (△) catalyzed reactions.

Table 2
TE model kinetics activation parameters

Catalyst	E_a (kcal/mol)	A ($\mathrm{l\ mol^{-1}\ s^{-1}}$)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
Ti control	16.4	4.01×10^{7}	15.5	−60.9
Ti(1)–Hf(3)	26.5	9.39×10^{11}	25.6	−6.57

temperatures and there was again a predicted crossing-over in the rate of TE.

The crossover temperature, 232°C, is below the operating temperature of the TE reactor in the continuous plant. At 245°C, which is the TE temperature in the pilot plant and in the last part of the industrial process, the reaction rate of the Ti/Hf catalyzed reaction is 1.30 times higher with respect to the titanium-catalyzed reaction. This prediction does not match completely the results obtained in the pilot plant [3], where the TE rate for the mixed catalyst was 1.75 times the rate for the TBT catalyzed reaction. One reason of this discrepancy can be attributed to the absence of acid groups at the beginning of model compounds reactions, while in the pilot plant at the starting of TE stage they are already present.

It is interesting to note that the titanate catalyst is even more strongly sensitive to entropic effects during TE. The activation entropy is a remarkable −60.9 e.u., which is 20 e.u. lower than several reported secondary S_N2 reactions [12], and more than 55 e.u. lower than that of the mixed-catalyst system (−6.6 e.u.). This result is suggestive of an even more highly constrained transition state for titanium during TE than EI, which is plausible due to the increased size of the butyl ester over the methyl ester. There is also the possibility for bidentate binding of the BD molecule, making the approach of a required BzBDBz molecule more difficult.

4. Conclusions

The kinetic investigation on the hafnium/titanium mixed catalyst has shown that this catalyst is faster compared to the standard titanate catalyst at elevated temperatures in both stages of PBT polymerization. The mixed catalyst presents an Arrhenius activation energy and a pre-exponential factor consistently higher compared with the titanate and for this reason is favored at higher temperature. These results suggest that the titanium, due to its smaller ionic radius, necessitates a very tight packing of both reactant and product species at the metal center. The results obtained using model compounds are in good agreement with those obtained in the pilot plant and are able to explain the differences observed between the two catalytic systems tested in PBT batch polymerizations.

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References

[1] Whinfield JR, Dickson JT. US Patent 2,465,319, 1949.

[2] Passalacqua V, Pilati F, Zamboni V, Fortunato B, Manaresi P. Polymer 1976;17:1044.

[3] Pilati F, Berti C, Colonna M, Marianucci E, Messori M, Toselli M, Fiorini M, Banach TE. New catalysts for poly(butylene terephthalate) synthesis. Part 1. Titanium–lanthanides and titanium–hafnium systems, submitted for publication.

[4] Banach TE, Pilati F, Berti C, Colonna M, Marianucci E, Messori M, Toselli M, Fiorini M. US patent 5,902,873, 1999.

[5] Leverd F, Fradet A, Marechal E. Eur Polym Sci 1987;23(9):695.

[6] Pilati F, Manaresi P, Fortunato B, Munari A, Passalacqua V. Polymer 1981;22:79.

[7] Asua JM, Yurramendi L, Barandiaran MJ. J Macromol Sci Chem 1987;22:799.

[8] Banach TE, Baghdassarian MA. General Electric Company Internal Report.

[9] Gordon AJ, Ford RA. The chemist's companion. New York: Wiley, 1972 (for a review on σ_p and ρ values in Hammet Equation), p. 143.

[10] Leffler JE, Grunwald E. Rates and equilibrium of organic reactions. New York: Wiley, 1963.

[11] Pilati F. In: Allen G, editor. Polyesters, Comprehensive polymer science, vol. 5. Oxford: Pergamon Press, 1989. p. 275 [Chapter 17].

[12] Wiberg KB. Physical organic chemistry. New York: Wiley, 1964 p. 380.