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Study of various catalysts in the synthesis of poly(propylene terephthalate) and mathematical modeling of the esterification reaction

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Abstract

Pure terephthalic acid (TPA) was esterified with 1,3-propanediol (1,3-PDO) in the presence of various catalysts, in order to find the most effective one for this esterification reaction. The prepared oligomers were polycondensated in a second step under high vacuum and using the same catalyst ($Sb(OCOCH_3)_3$, $Ti(OC_4H_9)_4$, GeO_2) as before, or the well known catalyst for poly(ethylene terephthalate) (PET) production technology Sb_2O_3. The esterification reaction was monitored by measuring the distilled water as a function of time and from these data the modeling of this process was carried out. The received poly(propylene terephthalate) (PPT) samples were characterized by viscometry, carboxyl end-group content and color measurement. From this study, tetrabutoxytitanium was proved to be the most effective catalyst for the esterification reaction. When this catalyst was used in the second step a PPT polymer with the highest molecular weight was received.

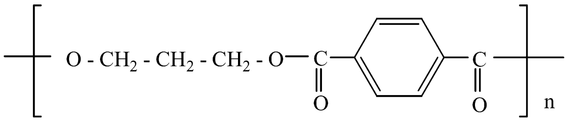
Keywords: Poly(propylene terephthalate); Poly(trimethylene terephthalate); 1,3-Propanediol

1. Introduction

Poly(propylene terephthalate) (PPT) is a relatively new semicrystalline thermoplastic polyester, since one of its monomer propyleneglycol or 1,3-propanediol (1,3-PDO) was not available in sufficient quantity and purity in the past [1–3]. However, in the last years more attractive processes have been developed for the production of 1,3-PDO including selective hydration of acrolein, followed by catalytic hydrogenation of the intermediate 3-hydroxypropionaldehyde [2,4] and hydroformylation of ethylene oxide [4,5]. Currently, Du Pont's fiber-grade or apparel-grade 1,3-PDO has successfully been prepared by a fermentation process based on corn sugar, a renewable resource [6]. Shell also announced the production of 1,3-PDO via an enzymic fermentation of glycerine [7].

The main application field of poly(propylene terephthalate) is that of fibers, because it combines the advantageous properties of polyamides and polyesters. PPT fibers are distinguished for their high elasticity, excellent recovery rate, excellent dyeing in boiling water without carriers, stain resistance, high UV stability, low water absorption and low electrostatic charging [6,8].

Poly(propylene terephthalate) fibers are offered today in the market under the trade name Corterra produced by Du Pont de Nemours and Sorona by Shell. The repeating unit of their macromolecules has the chemical structure:



PPT

In most of the papers published in the last years, this polymer is called briefly as 3GT or PTMT or mainly PTT, derived from the empirical name 'poly(trimethylene terephthalate)', but this polyester should have a more suitable acronym harmonized with its homologues (PET and PBT) and which is PPT, as it is shown here: poly(ethylene terephthalate), PET; poly(propylene terephthalate), PPT; poly(butylene terephthalate), PBT.

Besides, if someone wants to call poly(butylene terephthalate) as poly(tetramethylene terephthalate), he has to give the same acronym PTT.

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The synthesis of PPT can be achieved in principle by transesterification of the dimethylester of terephthalic acid (TPA) similarly to PET and PBT or by direct esterification of TPA. Until now, polyesters are synthesized mainly via DMT-route, which is by using the dimethylester of terephthalic acid, but nowadays there is a tendency for the synthesis via TPA-route, which is more economic. So, in this work, efforts will be made for PPT to be synthesized via TPA-route, with the method of melt-polymerization in two steps: the esterification and the polycondensation. In both steps catalysts are necessary. The use of metal compounds as catalysts in the industrial production of PET gave strong interest in the study and comparison of their activity as well as their effectiveness on the polymerization reactions and properties of the final polymers. In the literature various catalysts are described for the transesterification and the polycondensation steps. On the contrary, only few information are available for the direct esterification of TPA.

Also, to our knowledge, there is not any model published in the literature on the direct esterification of terephthalic acid with propyleneglycol for the poly(propylene terephthalate) synthesis. Therefore, the simulation model derived in this paper is based on previous works on the poly(ethylene terephthalate) synthesis. These models are reviewed next.

The direct esterification of terephthalic acid with ethyleneglycol (EG) has been mainly studied by two groups of investigators, namely: Yamada and co-workers [9–12] and Kang et al. [13,14]. Yamada et al. [9,10] developed a simulation model for the three phase continuous esterification process of TPA with EG that could express the oligomer properties and the concentration of each composition in the vapor and liquid phase. Furthermore, they extensively studied the effect of several reaction conditions (i.e. temperature, pressure, etc.) on the characteristics of oligomer [11,12].

Kang et al. presented a comprehensive kinetic model for the direct esterification reaction of PET synthesis in semi-batch and continuous reactors using the functional group analysis [13,14].

In this work, 1,3-propanediol is used to prepare polyesters directly from terephthalic acid in presence of various catalysts. The effect of catalysts is studied and a comprehensive kinetic model is developed in a semi-batch esterification reactor based on the polymer segment approach.

2. Experimental

2.1. Materials

PPT samples were synthesized from TPA and 1,3-PDO using 10 different catalytic systems (Table 1). The catalysts were of commercial grade and were used without further purification. TPA was obtained from Fluka (Purum ≥99%) and 1,3-PDO (CAS Number 504-63-2) was a gift from Du Pont de Nemours, suitable for polyester synthesis.

2.2. Synthesis of polyester samples

TPA (0.30 mol) and 1,3-PDO (0.36 mol) in a molar ratio of TPA/1,3-PDO $= 1/1.2$ and the catalyst (5×10^{-4} mol catalyst/mol TPA) were charged into the reaction tube of the polyesterification apparatus, which was similar to that used by Zachmann and Günther [15]. The reaction mixture (catalyzed or uncatalyzed) was heated at 260 °C under an argon atmosphere, in atmospheric pressure and stirred at a constant speed (500 rpm). This first step (esterification) is considered to be completed after the collection of 8 ml of H_2O approximately, which was removed from the reaction mixture by distillation and collected in a graduated cylinder.

In the second step, the polycondensation catalyst was added (5×10^{-4} mol/mol TPA). Also, polyphosphoric acid was added in the reaction tube (5×10^{-4} mol polyphosphoric acid/mol TPA). Polyphosphoric acid is believed that blocks the esterification catalyst and prevents side reactions such as etherification, thermal decomposition and acrolein and allyl alcohol formation [1,2,4]. A vacuum (≈5 Pa) was applied slowly over a period of time of about 30 min, to avoid excessive foaming and to minimize oligomer sublimation, which is a potential problem during the melt polycondensation. The temperature was again 260 °C. The polycondensation was continued for 90 min for all preparations, in order to be able to compare the final polymers. After the polycondensation reaction was completed, the reaction tube had to be broken to receive the product. All polyester samples, which had a white color, were washed with methanol and dried at 110 °C for 24 h.

2.3. Measurements

Intrinsic viscosity $[\eta]$ measurements were performed using an Ubbelohde viscometer at 25 °C in a mixture of phenol/1,1,2,2-tetrachloroethane (60/40, w/w). The sample was maintained in the above mixture of solvents at 120 °C for some time to achieve a complete solution. The solution then cooled to room temperature and filtered through a disposable membrane filter made from Teflon. Intrinsic viscosity was calculated after the Solomon–Ciuta equation [16].

Carboxyl end-group content (CC) of the resins was determined according to Pohl's method [17] by titrating a solution of the resin in benzyl alcohol/chloroform with standard NaOH in benzyl alcohol in the presence of phenol red as indicator.

Color measurements were performed on homogeneous 'spot' areas of 4 mm in diameter, under diffuse reflectance and *d*/8° geometry, using a MINOLTA CM-2022 portable spectrophotometer supplied with a memory card for data storage, a CM A32 zero calibration box and a CM-1 color data software. Color measurements representation was

Table 1
Catalysts used in the esterification and polycondensation reactions

Polyester sample	Esterification catalyst	Polycondensation catalyst
PPT (blank)	None	None
PPT 1	$Mg(OCOCH_3)_2 \cdot 2H_2O$	Sb_2O_3
PPT 2	$Mn(OCOCH_3)_2 \cdot 4H_2O$	Sb_2O_3
PPT 3	$Zn(OCOCH_3)_2 \cdot 2H_2O$	Sb_2O_3
PPT 4	$Sn[OCO(C_2H_5)CH(CH_2)_3CH_3]_2$	Sb_2O_3
PPT 5	$Sb(OCOCH_3)_3$	$Sb(OCOCH_3)_3$
PPT 6	$Ti(OC_4H_9)_4$	Sb_2O_3
PPT 7	$Ti(OC_4H_9)_4$	$Ti(OC_4H_9)_4$
PPT 8	GeO_2	GeO_2
PPT 9	$Zr(OC_4H_9)_4$	Sb_2O_3
PPT 10	$Ti(OC_4H_9)_4 + Zr(OC_4H_9)_4$	Sb_2O_3

realized on a a^*, b^* diagram, of the CIELAB (1976) uniform color system.

3. Mathematical modeling of the esterification reaction for the poly(propylene terephthalate) synthesis

3.1. Reaction scheme

As it was reported earlier by Kang et al. [13], two main modeling approaches can be applied in representing the polymerization kinetics: the molecular species models and the functional group models. In the first approach, all the molecular species present in the reactor, including oligomers with varying degree of polymerization, should be considered, although in the second, only functional groups are treated as special entities. Molecular species models are more comprehensive while leading to a large number of equations to be solved. On the other hand, the functional group models still provide enough information on the polymerization mixture, while the number of equations to be solved is very much shortened.

In this paper the polymer segment approach, which is in the framework of functional group approaches was used [13]. According to this approach, the polymerization reaction is regarded as a reaction between two functional groups. The molecular structure of the components considered in the reaction scheme, is presented in Table 2.

Five different oligomeric segments are used: tTPA, tPG, bTPA, bPG and bDPG (the term t and b refer to the terminal functional group and bound monomeric repeating unit, respectively). The acronym PG that is derived from propylenglycol will be used instead of 1,3-PDO for short.

Based on these functional groups, the mechanism shown in Table 3 is assumed to represent the kinetics of the esterification process. Reactions 1–4 represent the typical esterification reactions, while reaction 5 is the polycondensation reaction, occurring mainly in the second step of PPT formation. Reaction 6 is a side reaction resulting in dipropylene glycol repeating units in the oligomeric chain. In this table, k_i $(i = 1,6)$ represent the ‘effective’ rate constants (l/mol min), K_i $(i = 1,5)$ denote the equilibrium rate constants.

3.2. Development of the mathematical model

In order to develop a mathematical model for the esterification reaction for the production of the poly(propylene terephthalate) the following assumptions are made:

- Reactions occur only in the liquid phase hence only the dissolved TPA participates in the reaction.
- All kinetic rate constants are independent of the polymer chain length.
- There exist no mass transfer limitations during the dissolution of TPA in PG, therefore the rate determining step is not the dissolution of TPA, but the reaction of TPA.
- All the water produced during the reaction is instantaneously vaporized and removed.
- All PG vaporized is totally returned to the reactor.

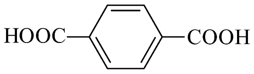
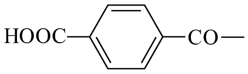
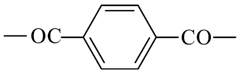
Based on the reaction mechanism presented in Table 3 the reaction rates can be expressed in terms of the different functional groups present in the reactor and the corresponding rate constants (Table 4) [13]. All the terms in parentheses denote mole numbers of every component in the liquid phase.

Furthermore the material mole balance equations for a semi-batch reactor can be written and are shown in Table 5. F_W is used to represent the flow rate of the water vaporized and removed from the reactor.

As the esterification reaction proceeds, the volume of the liquid phase changes due to the dissolution of solid TPA into liquid that participates in the reaction as well as the continuous removal of water. The volume of the reaction mixture can then be expressed as

$$V = \frac{(\mathrm{TPA})\mathrm{MW}_{\mathrm{TPA}}}{\rho_{\mathrm{TPA}}} + \frac{(\mathrm{PG})\mathrm{MW}_{\mathrm{PG}}}{\rho_{\mathrm{PG}}} + \frac{W_{\mathrm{OLIG}}}{\rho_{\mathrm{OLIG}}} - \frac{N_{\mathrm{W}}\,\mathrm{MW}_{\mathrm{W}}}{\rho_{\mathrm{W}}} \quad (1)$$

Table 2
Molecular structure of components considered

Symbol	Description	Molecular structure
TPA	Terephthalic acid	
PG	Propylene glycol	$HOCH_2CH_2CH_2OH$
W	Water	H_2O
tTPA	TPA end group	
tPG	PG end group	$HOCH_2CH_2CH_2O{-}$
bTPA	TPA repeating unit	
bPG	PG repeating unit	$-OCH_2CH_2CH_2O-$
bDPG	Dipropylene glycol repeating unit	$-OCH_2CH_2CH_2OCH_2CH_2CH_2O-$

where MW and ρ represent the molecular weight and density of the corresponding material. Values are tabulated in Table 6. W_{OLIG} is used to express the weight of all oligomers presented in the reaction mixture, i.e. (tTPA), (tPG), b(TPA), (bPG) and (bDPG). N_{W} denote the total moles of water removed up to time t and can be calculated from:

$$N_{\mathrm{W}} = \int_0^t F_{\mathrm{W}}\,\mathrm{d}t \qquad (2)$$

Conversion according to the water produced and removed was calculated according to the following equation:

$$X_{\mathrm{W}} = \frac{N_{\mathrm{W}}\,\mathrm{MW_W}}{10.8} \qquad (3)$$

The value 10.8 in the denominator is used to express the total weight of water that should be produced when all 0.3 mol of TPA will be reacted.

Because the solubility of TPA in PG like in EG is extremely low and the esterification is taking place in the liquid phase, the concentration of TPA dissolved in PG should be calculated. According to the assumptions made the mean solubility of TPA in the reaction mixture is given by the following expression [12,13]

$$\alpha = \alpha_{\mathrm{PG}} W_{\mathrm{PG}} + \alpha_{\mathrm{OLIG}} W_{\mathrm{OLIG}} \qquad (4)$$

where α denote moles of TPA dissolved in the liquid phase, α_{PG} and α_{OLIG} the solubility of TPA in PG and oligomers, respectively, in terms of mol of TPA per kg of material and W_{PG} is the weight of propylene glycol ($\mathrm{MW_{PG}}$(PG)). For the calculation of α_{OLIG} we used the value proposed by Yamada [12]. In order to calculate α_{PG} the arithmetic mean value between the corresponding values reported for the solubility of TPA in EG [12] and of TPA in butanediol [18] was used. The numerical values used are shown in Table 5.

Table 3
Reaction mechanism of the esterification process

No.	Reaction	Rate constants
1	$\mathrm{TPA} + \mathrm{PG} \underset{k_1''}{\overset{k_1}{\rightleftharpoons}} \mathrm{tTPA} + \mathrm{tPG} + W$	$k_1, k_1'' = k_1/K_1$
2	$\mathrm{tTPA} + \mathrm{PG} \underset{k_2''}{\overset{k_2}{\rightleftharpoons}} \mathrm{bTPA} + \mathrm{tPG} + W$	$k_2, k_2'' = k_2/K_2$
3	$\mathrm{TPA} + \mathrm{tPG} \underset{k_3''}{\overset{k_3}{\rightleftharpoons}} \mathrm{tTPA} + \mathrm{bPG} + W$	$k_3, k_3'' = k_3/K_3$
4	$\mathrm{tTPA} + \mathrm{tPG} \underset{k_4''}{\overset{k_4}{\rightleftharpoons}} \mathrm{bTPA} + \mathrm{bPG} + W$	$k_4, k_4'' = k_4/K_4$
5	$\mathrm{tPG} + \mathrm{tPG} \underset{k_5''}{\overset{k_5}{\rightleftharpoons}} \mathrm{bPG} + \mathrm{PG}$	$k_5, k_5'' = k_5/K_5$
6	$\mathrm{tPG} + \mathrm{tPG} \xrightarrow{k_6} \mathrm{bDPG} + W$	k_6

Table 4
Reaction rates

$R_1 = \{4k_1(\mathrm{TPA})(\mathrm{PG}) - (k_1/K_1)(\mathrm{tTPA})(W)\}/V^2$
$R_2 = \{2k_2(\mathrm{tTPA})(\mathrm{PG}) - 2(k_2/K_2)(\mathrm{bTPA})(W)\}/V^2$
$R_3 = \{2k_3(\mathrm{TPA})(\mathrm{tPG}) - (k_3/K_3)(\mathrm{tTPA})(W)\}/V^2$
$R_4 = \{k_4(\mathrm{tTPA})(\mathrm{tPG}) - 2(k_4/K_4)(\mathrm{bTPA})(W)\}/V^2$
$R_5 = \{k_5(\mathrm{tPG})(\mathrm{tPG}) - 4(k_5/K_5)(\mathrm{bPG})(\mathrm{PG})\}/V^2$
$R_6 = \{k_6(\mathrm{tPG})(\mathrm{tPG})\}/V^2$

Compounds in paranthesis denote moles.

Table 5
Detailed material mole balance equations

$$\frac{1}{V}\frac{d(TPA)}{dt} = -R_1 - R_3$$

$$\frac{1}{V}\frac{d(PG)}{dt} = -R_1 - R_2 + R_5$$

$$\frac{d(W)}{dt} = V(R_1 + R_2 + R_3 + R_4 + R_6) - F_w$$

$$\frac{1}{V}\frac{d(tTPA)}{dt} = R_1 - R_2 + R_3 - R_4$$

$$\frac{1}{V}\frac{d(tPG)}{dt} = R_1 + R_2 - R_3 - R_4 - 2R_5 - 2R_6$$

$$\frac{1}{V}\frac{d(bTPA)}{dt} = R_2 + R_4$$

$$\frac{1}{V}\frac{d(bPG)}{dt} = R_3 + R_4 + R_5$$

$$\frac{1}{V}\frac{d(bDPG)}{dt} = R_6$$

3.3. Kinetic rate constants

The kinetic rate constants depend on temperature, catalyst type and concentration [12]. In the literature [13,19,20] it has been proposed that the esterification and polycondensation reactions are acid-catalyzed and that the corresponding rate constants can be expressed as:

$$k_i = k_i' C_{acid} \qquad (i = 1-5) \tag{5}$$

where k_i' are the 'true' rate constants in l^2/mol^2 min, and C_{acid} denote the concentration of acid groups defined as the sum of the concentration of carboxylic end groups (tTPA) and the carboxylic groups of the free acid (2 TPA), i.e.

$$C_{acid} = \{2(TPA) + (tTPA)\}/V \tag{6}$$

It should be noticed that the acid catalysis influenced both the forward and the reverse reactions and is not considered for the DPG formation.

Table 6
Numerical values of the physical properties

Property	Value	Units	Reference
ρ_{TPA}	1.371	g/ml	[13]
ρ_{PG}	1.053	g/ml	[13]
ρ_{OLIG}	1.110	g/ml	[14]
MW_{TPA}	166.13	g/mol	
MW_{PG}	76.09	g/mol	
MW_W	18.02	g/mol	
α_{EG}	0.962 (260 °C)	mol TPA/kg EG	[12]
α_{BD}	0.650 (260 °C)	mol TPA/kg BD	[18]
α_{OLIG}	0.283 (260 °C)	mol TPA/kg OLIG	[12]

3.4. Molecular characteristics of the oligomers produced

Using the polymer segment approach the number average degree of polymerization of the oligomers produced can be expressed as [13]:

$$\overline{DP}_n = \frac{(tTPA) + (bTPA) + (tPG) + (bPG) + (bDPG)}{(tTPA) + (tPG)} \tag{7}$$

3.5. Integration of the system of differential equations and estimation of kinetic parameters

The system of differential equations (Table 4) was integrated by applying the Runge–Kutta fourth order method with varying step size. In order to have the mole number of every component in the reaction mixture as a function of time the kinetic rate constants have to be evaluated. According to the reaction presented in Table 3, 11 rate constants (k_i, $i = 1-6$ and K_i, $i = 1-5$) should be determined. Since there are not any experimental data in the literature on the PPT polymerization all these parameters were estimated according to the following assumptions. In PET polymerization it was assumed that the reactivity of the acid end group on TPA is equivalent to the reactivity on oligomer chain (tTPA), whereas the reactivity of hydroxyl end group on EG was twice of the reactivity on half-esterified EG (tEG) [13,14,21–24]. Since in the polymerization of PG the end groups are identical, we used the same assumption, i.e. $k_1 = k_2 = 2k_3 = 2k_4$. In order to simplify further the calculations it was assumed that $k_5 = k_3 = k_4$ [13]. Kang et al. [13] proposed that the polycondensation reaction involving the attack of a hydroxy end group (tPG) on an ester link near the end of an oligomeric chain is quite similar to the esterification reaction between a hydroxyl end group (tPG) and a carboxyl end group (tTPA). This assumption was used in every catalytic esterification reaction, while when the reaction was carried out without a catalyst the value $k_5 = 0$ was used to fit the experimental data best. The equilibrium constants K_i, $i = 1-4$ need not to be evaluated since according to the assumptions made the reverse reaction rates (R_i, $i = 1-4$) are zero ((W) = 0 in the liquid phase). For K_5 the value proposed by Kang et al. [13] (i.e. $K_5 = 0.5$) was used. From the above analysis the number of parameters that need to be evaluated is only two, k_1 and k_6. The values of these parameters were calculated for every different catalyst system from fitting to the experimental data. The final values are reported in Table 7. Notice that these values are correct only for the specific catalyst concentration.

4. Results and discussion

The synthesis of poly(propylene terephthalate) samples was performed by the two-step melt polymerization method,

Table 7
Numerical values of the kinetic rate constants

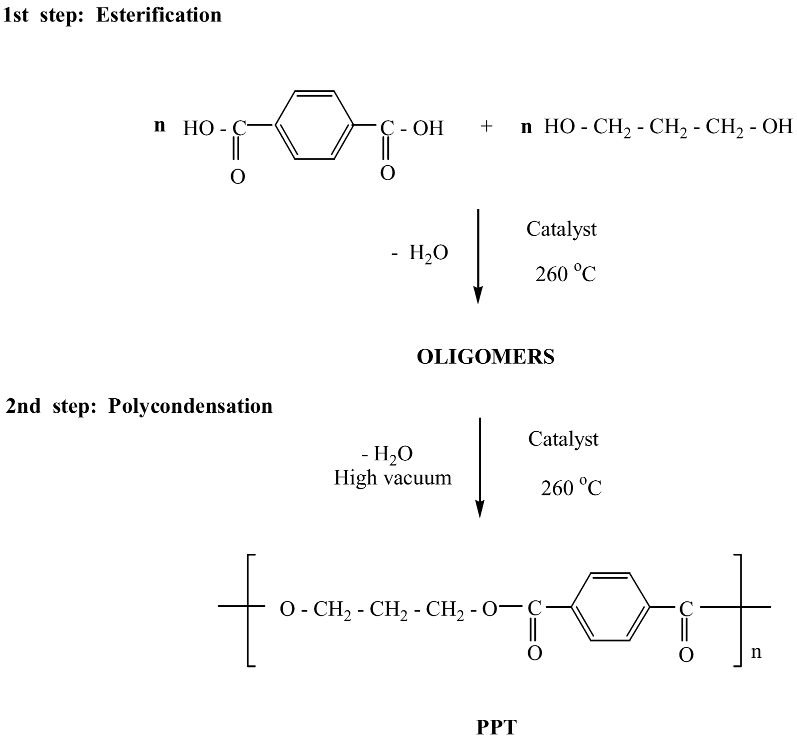
	$k'_1 = k'_2$ (10^4 l^2/mol^2 min)	$k'_3 = k'_4$ ($\times 10^4$ l^2/mol^2 min)	k'_5 ($\times 10^4$ l^2/mol^2 min)	k_6 ($\times 10^3$ l/mol min)
No catalyst	1.4	0.7	0.7	0.01
$Mg(OCOCH_3)_2 \cdot 2H_2O$	1.1	0.55	0.55	0.80
$Mn(OCOCH_3)_2 \cdot 4H_2O$	1.4	0.7	0.7	0.25
$Zn(OCOCH_3)_2 \cdot 2H_2O$	2.2	1.1	1.1	0.70
$Sn[OCO(C_2H_5)CH(CH_2)CH_3]_2$	1.8	0.9	0.9	0.15
$Sb(OCOCH_3)_3$	1.6	0.8	0.8	0.90
$Ti(OC_4H_9)_4$	2.6	1.3	1.3	1.00
$Zr(OC_4H_9)_4$	1.5	0.75	0.75	0.80
GeO_2	0.9	0.45	0.45	0.20

that is, by the direct esterification of terephthalic acid with 1,3-PDO and subsequent polycondensation of the oligomers produced. In the first step the reactants were heated at 260 °C with continuous stirring. After the removal and collection of a definite amount of water (≈ 8 ml), this stage was supposed to be completed. In the second step high vacuum (≈ 5 Pa) was applied and the temperature remained again at 260 °C, while fresh catalyst was added. This step was completed in 90 min (Scheme 1).

In order to compare the activity of the esterification catalysts used, a blank PPT sample (without catalyst) was firstly prepared. As it is shown in Table 8 this sample is a PPT with low molecular weight. For all other samples the same esterification conditions were used except the kind of catalyst. A number of important catalysts were used, known from the PET production technology, to clarify their effect on the molecular weight, carboxyl content, and the color of the final product.

During esterification of TPA with 1,3-PDO, water was released the amount of which was measured as a function of time (Table 8). These data were used for the modeling of the esterification reaction, while the total time consumed for the removal of 8 ml of water was used as a criterion for the suitability of the catalyst for this first step. As it is shown in Table 8, the removal of the aforementioned amount of water was not completed in some experiments even after a prolonged period of time.

From all the catalysts that were used in the esterification step the faster one (the catalyst that lead faster the removal of H_2O) was tetrabutoxytitanium (TBOT) (Fig. 2). The concentration of catalysts used was 5×10^{-4} mol/mol TPA, however, in the case of TBOT three other concentrations



Scheme 1. Reactions for the preparation of PPT.

Table 8
Intrinsic viscosity, esterification time, carboxyl content and color of the PPT samples prepared

Polymeric sample	[η] (dl/g)	Esterification time (min)	$\bar{M}_w$ (g/mol)	[COOH] (μequiv./g)	Sample color		
					L^*	a^*	b^*
PPT (blank)	0.36	1060[a]	12510	70.0	85.385	−0.945	12.705
PPT 1	0.52	705	21320	15.3	87.445	0.035	4.055
PPT 2	0.60	545[b]	26230	47.5	81.740	0.295	3.040
PPT 3	0.16	600[c]	3860	290.1	79.580	−0.490	4.170
PPT 4	0.38	540[d]	13530	14.4	85.170	0.125	8.160
PPT 5	0.50	510	20140	9.6	82.915	0.020	4.985
PPT 6	0.64	230	28800	44.5	81.980	−0.030	4.770
PPT 7	0.74	215	35550	17.0	78.515	−0.045	4.060
PPT 8	0.21	645[e]	5730	51.4	85.710	−0.010	6.300
PPT 9	0.40	610	14575	20.0	87.575	−0.365	5.790
PPT 10	0.69	240	32120	12.6	82.100	0.335	3.895

[a] After collection of 6.9 ml H_2O.
[b] After collection of 5.7 ml H_2O.
[c] After collection of 6.0 ml H_2O.
[d] After collection of 7.0 ml H_2O.
[e] After collection of 7.1 ml H_2O.

(7×10^{-5}, 1×10^{-4} and 4×10^{-4} mol/mol TPA) were examined, but with poorer results.

In the second step, as it is shown in Table 1, in most of the samples the catalyst was the same (Sb_2O_3), except the three samples PPT 5, 7 and 8 where antimony triacetate, TBOT and germanium oxide was used, respectively. So, the properties of the final product could be seriously due to the catalyst of the first step.

So far as we know, the constants K and α for PPT of Mark–Houwink–Sakurada equation, are cited for a phenol/tetrachloroethane 60/40 w/w solvent only in one paper [25]. The values of these constants were used in this work in order to estimate the weight average molecular weight of the samples.

It is of interest, that when zinc acetate was used as esterification catalyst, a polymer (PPT 3) with the lowest molecular weight (3860 g/mol) was obtained, while this catalyst was considering as the best one for the industrial

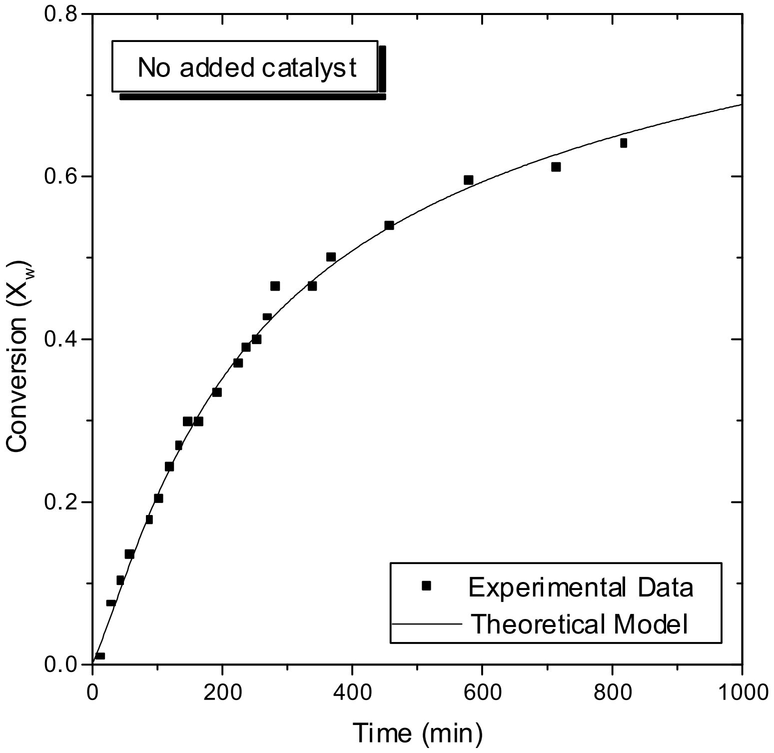


Fig. 1. Conversion (X_w) versus time for the esterification reaction with no added catalyst.

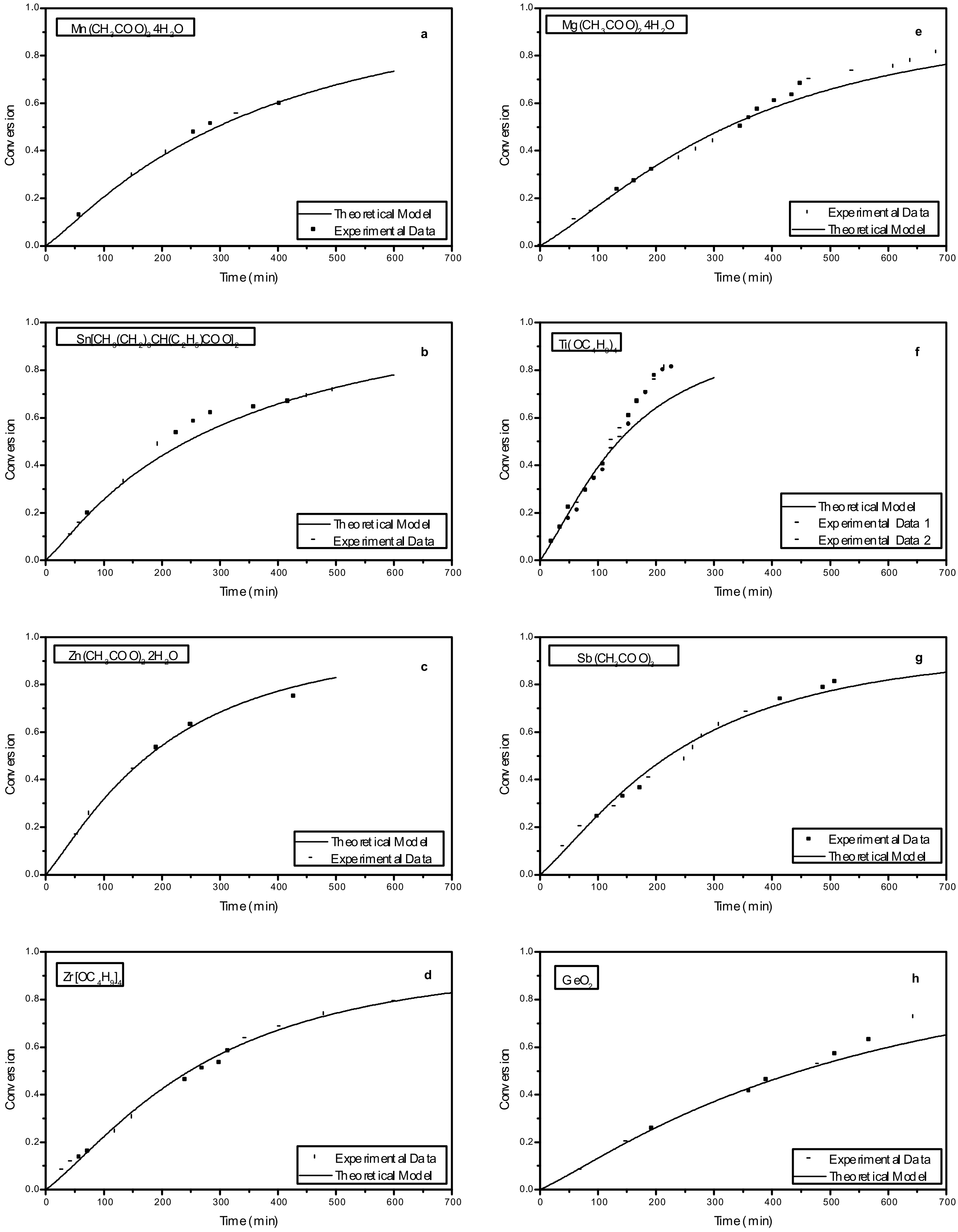


Fig. 2. Conversion (X_w) versus time for the esterification reaction with different kinds of catalysts.

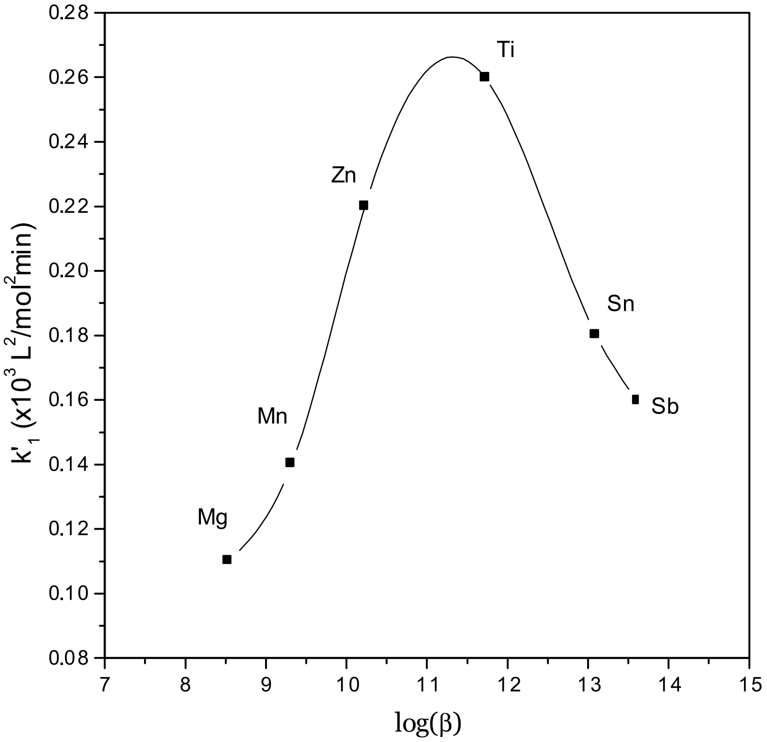


Fig. 3. Effect of the acidity of the metals on the kinetic rate constant, k'_1.

production of PET via DMT route. So, PPT 3 as an oligomeric sample showed reasonably the highest carboxyl content (290 μequiv./g).

According to Tables 1 and 8, when antimony trioxide (PPT 6) and TBOT (PPT 7) were used as catalysts in the polycondensation reaction, a higher intrinsic viscosity (0.74 dl/g) for PPT 7 was observed, while PPT 6 showed a lower intrinsic viscosity (0.64 dl/g).

It is worthwhile noting, that when titanium compounds are used for the production of PET, the polymer becomes

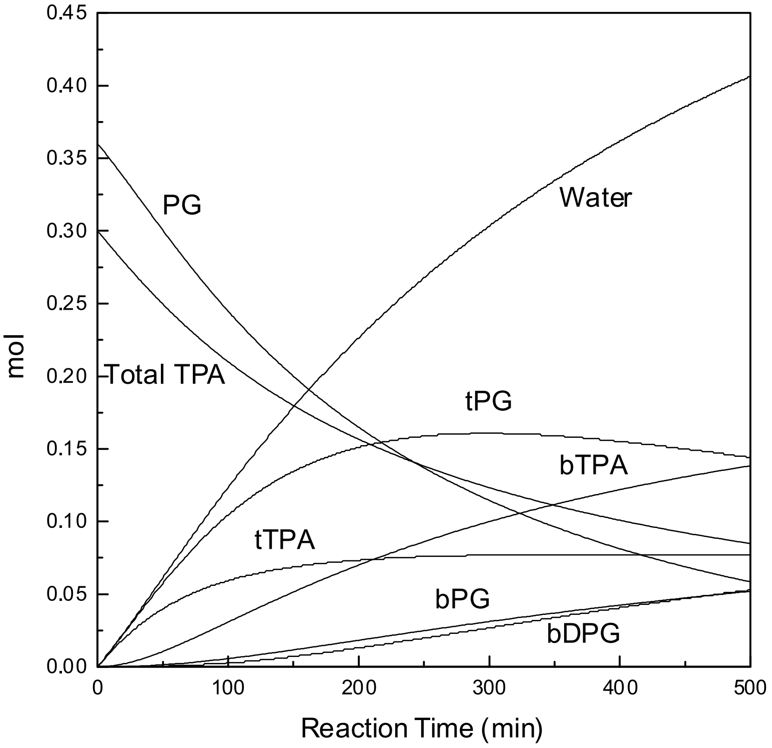


Fig. 4. Mole number of all molecular species present in the reactor as a function of time.

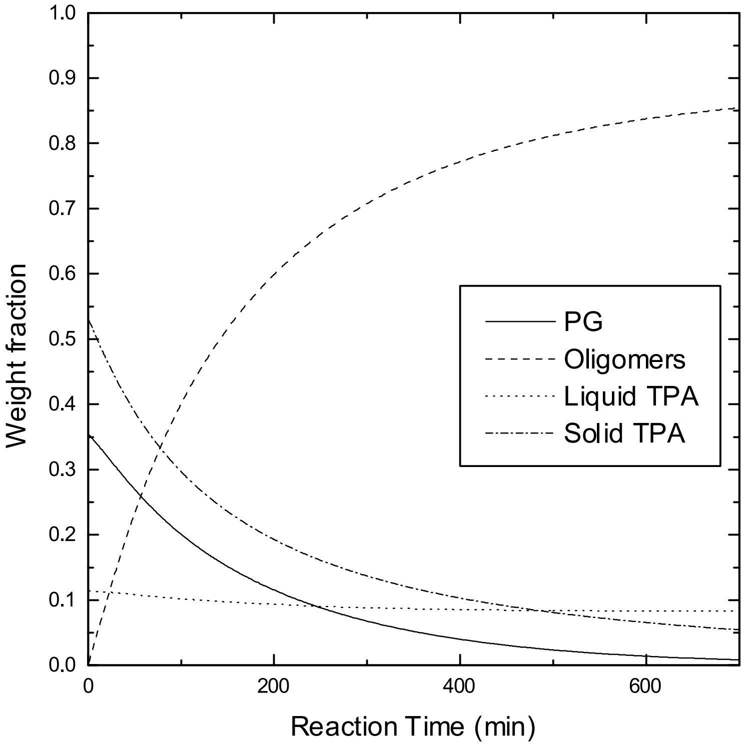


Fig. 5. Normalized weight fraction of TPA (solid and liquid), PG and oligomers as a function of time.

markedly yellowish [1]. From b^* values of color measurement of PPT samples of this work (Table 8), the PPT blank sample showed a clear visible yellow discoloration ($b^* = 12.705$) due to higher reaction time. Also, a visible yellow discoloration showed the samples with b^* values >4.5 (PPT 4, PPT 5, PPT 6, PPT 8 and PPT 9), while all other samples did not show any sensible discoloration. So, tetrabutoxytitanium worked better in the case, where it was common catalyst for both steps.

The experimental data together with the simulation

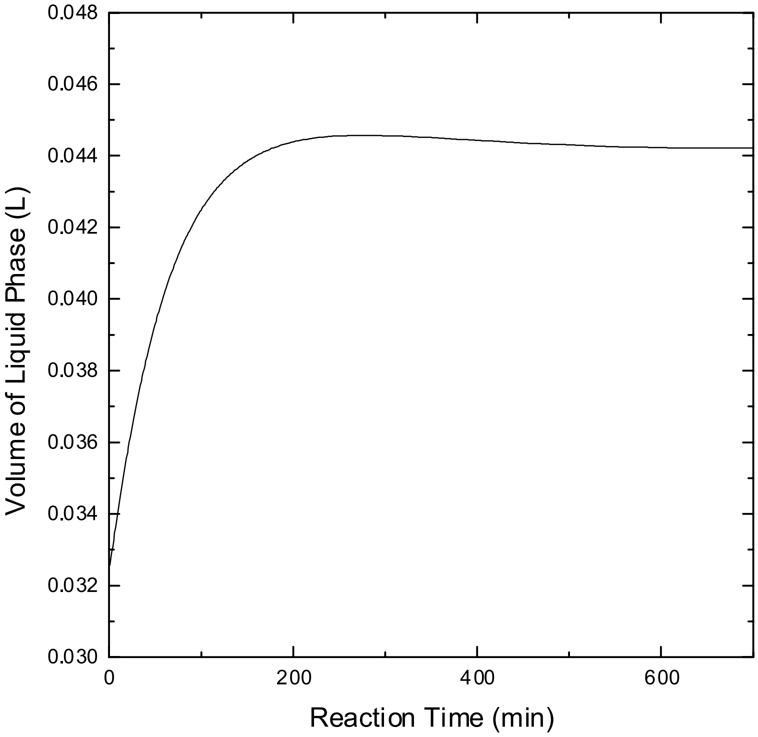


Fig. 6. Volume of the reaction mixture liquid phase with respect to time.

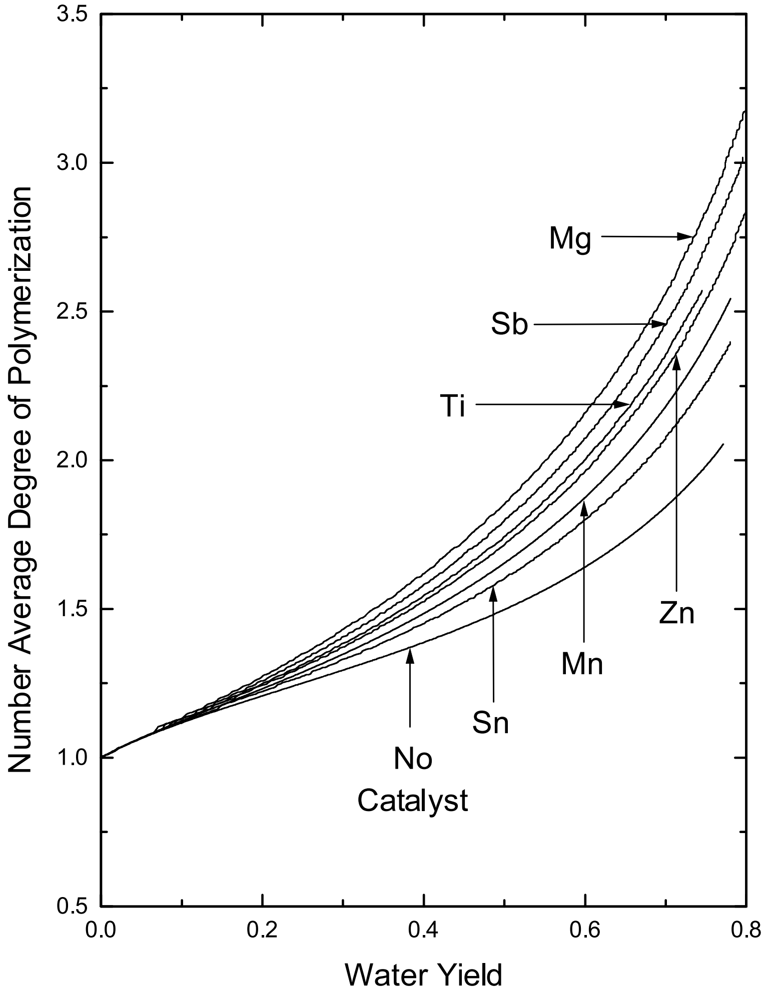


Fig. 7. Number average degree of polymerization as a function of the water removed conversion.

results on the water removal with no added catalyst is shown in Fig. 1. As it can be observed the theoretical model very well simulates the experimental data. The effect of different types of catalyst on the water removal is shown in Fig. 2(a)–(h). As it can be seen in most cases, the experimental data are fitted well by the theoretical model. The most effective catalyst seems to be the TBOT. It is interesting to note that when no catalyst is added it takes about 900 min to reach a conversion of approximately 65% while with the TBOT catalyst this conversion is reached in 170 min.

If the numerical values of the k_1 kinetic rate constant are plotted as a function of the acidity of the metals, using the factor β introduced by Tomita and Ida [26], a volcano shaped trend is obvious (Fig. 3), as other authors also observed it [26,27]. As it can be seen the optimal acidity level corresponds to the TBOT catalyst.

Some typical simulation results from the solution of the theoretical model are presented next. The change in moles of all molecular species present in the reactor as a function of time is plotted in Fig. 4. Furthermore, in Fig. 5 the normalized weight fraction of TPA (solid and liquid), PG and oligomers is plotted, as a function of time. It is interesting to note that the amount of liquid TPA is almost unchanged until the complete dissolution of solid TPA. This implies that the solid TPA acts as a reservoir supplying the liquid TPA molecules, which will be consumed in the esterification reaction.

Fig. 6 shows variation in the liquid volume of the reaction melt with respect to reaction time. As it can be easily seen the dissolution of solid TPA increases the volume of the liquid phase. However, after a certain point the volume of the liquid phase slightly decreases due to the continuous removal of water. Finally, the degree of polymerization with water yield is shown in Fig. 7 for all different catalyst types. From this figure it is evident that only oligomers are produced during the esterification reaction (first step in PTT synthesis), since at 80% water yield the maximum number average degree of polymerization reached is only 3. Furthermore, the absence of catalyst leads to lower number-average chain lengths.

5. Conclusions

A series of poly(propylene terephthalate)s have been synthesized using terephthalic acid (not the dimethylester) and 1,3-propanediol in presence of various catalysts.

A colorless PPT polymer was prepared with high molecular weight ($\bar{M}_w = 35,550$ g/mol) and low carboxyl content (17 μequiv./g), when TBOT was used as catalyst for both esterification and polycondensation steps.

The use of TBOT as catalyst has the major advantage to be effective in both esterification and polycondensation steps. Hence, no addition of another catalyst is necessary. Furthermore, this catalyst does not give any rise to environmental problems and is available at reasonable cost.

Finally, a theoretical mathematical model for the esterification reaction has been developed and applied successfully in the simulation of all experimental data under different kinds of catalysts used. Values for the kinetic rate constants are proposed based on a good fitting of the experimental data at given catalyst concentration of 5×10^{-4} mol/mol TPA.

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