

## Synthesis of poly(alkylene succinate) biodegradable polyesters, Part II: Mathematical modelling of the polycondensation reaction

D.N. Bikiaris, D.S. Achilias\*

Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Macedonia, Greece

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### ABSTRACT

In this investigation, synthesis of three biodegradable aliphatic polyesters, namely poly(ethylene succinate) (PESu), poly(propylene succinate) (PPSu) and poly(butylene succinate) (PBSu), is presented using the appropriate diols and succinic acid in the presence of tetrabutoxytitanium as catalyst. A theoretical mathematical model for the polycondensation reaction is developed and applied successfully in the simulation of all experimental data. From measurements of intrinsic viscosity (IV) at four polycondensation temperatures (210, 220, 230 and 245 °C) and different times from 15 min to 3 h, it was concluded that PESu exhibits higher values followed by PBSu and finally PPSu. Using additional measurements on the carboxyl content and the simulation model results, it was found that when ethylene glycol is used as reactant, both esterification and transesterification reaction rates are promoted resulting thus in lower carboxyl concentrations and higher IV values. However, the transesterification reaction rate constant of PPSu is much lower compared to PBSu leading to higher carboxyl and hydroxyl end groups and therefore finally lower IV values. Moreover, the esterification rate constant was estimated always to be much larger compared to the rate constant of the transesterification reaction, meaning that the former reaction proceeds much faster compared to the later, resulting thus in very low values of the carboxyl end groups compared to corresponding hydroxyl end groups. Finally, from measurements of the mechanical properties of the polyesters produced it was found that concerning the tensile strength and the elongation at break, PBSu exhibits the larger values followed by PESu in the order: PBSu > PESu > PPSu, whereas PESu exhibits higher Young's Modulus in the order: PESu > PBSu > PPSu.

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### 1. Introduction

In recent years, biodegradable polymers have attracted considerable attention as green materials and biomaterials in pharmaceutical, medical and biomedical engineering applications, including drug delivery systems, artificial implants and functional materials in tissue engineering. Among synthetic polymers, aliphatic polyesters have attracted considerable attention as they combine the features of biodegradability, biocompatibility and physical or chemical properties comparable with many traditional and non-biodegradable polymers such as low-density polyethylene (LDPE) and polypropylene (PP). Biodegradable final products made from these polymers find a variety of end-uses especially as films for packaging and in agricultural applications [1–3].

Synthesis of aliphatic polyesters by polycondensation reactions of diols with different dicarboxylic acids or their esters is dated back to 1930s [4]. However, the low melting points of the most produced polyesters in combinations with the difficulty to obtain

high molecular weight materials has prevented their usage for long time. High molecular weight polyesters are an essential request for producing materials with appropriate processability and acceptant mechanical properties capable for producing fibres, bottles, films, etc. Techniques like solid-state polycondensation that used in other polyesters like poly(ethylene terephthalate) (PET) are not possible to be implementing due to the low melting point of aliphatic polyesters which makes very difficult the removal of by-products formed during polycondensation [5].

In polyester preparation it is known that reaction kinetics are mostly affected by the monomer(s) chemical structure, type and amount of catalyst used, polymerisation temperature and reaction time [6–9]. However, an extensive and more detailed study about synthesis of aliphatic polyesters and the dependence of their molecular weight on several parameters has not been reported so far in the literature. To this direction, three polyesters of succinic acid were prepared by using ethylene, propylene and butylene glycols by the two-stage melt polycondensation method, esterification and polycondensation. The advantage of these polyesters is that despite their low melting point they have very high thermal stability, which is similar to aromatic polyesters [10–12]. Their decomposition temperature is higher than 400 °C. Comparative biodegradability

\* Corresponding author. Tel.: +30 2310 997822; fax: +30 2310 997769.  
E-mail address: [axilias@chem.auth.gr](mailto:axilias@chem.auth.gr) (D.S. Achilias).

studies, as well as the crystallization and melting behaviour of the three polyesters, namely poly(ethylene succinate) (PESu), poly(propylene succinate) (PPSu) and poly(butylene succinate) (PBSu), have already been carried out in our laboratory [8,13–15]. It should be noticed that PPSu synthesis has been reported only recently [16] due to difficulties encountered in the production of one of its comonomers (1,3-propanediol) in sufficient quantity and purity. Thus, available literature data about its synthesis and characterization are limited [8].

In Part I, a theoretical mathematical model, based on the functional group analysis, was developed to predict the kinetics of the esterification reaction of the three poly(alkylene succinate)s (PESu, PPSu and PBSu) [17]. In this work, the kinetics of the second step, meaning the polycondensation reaction of these polyesters, are investigated and a simple theoretical model is proposed to simulate both esterification and transesterification reactions taking place during polycondensation. The effect of the monomer chemical structure, polycondensation temperature and time on the reaction kinetics is elucidated. According to our knowledge, there is not any work published in literature on modelling of the polycondensation reaction of poly(alkylene succinate)s. Finally, mechanical properties of the polyesters produced are measured and the Young's modulus, the tensile strength and the elongation at break are estimated as a function of polycondensation temperature.

## 2. Experimental

### 2.1. Materials

Succinic acid (purity 99%), ethylene glycol (purity 99%) and 1,3-propanediol (purity >99.7%) were purchased from Fluka, while butylene glycol (purity 99%) was purchased from Aldrich Chemical Co. Tetrabutoxytitanium (TBT) used as catalyst was of analytical grade and purchased from Aldrich Chemical Co. Polyphosphoric acid (PPA) used as heat stabilizer was supplied from Fluka. All other materials and solvents used for the analytical methods were of analytical grade.

### 2.2. Synthesis of polyesters

Synthesis of aliphatic polyesters was performed following the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor [18]. In brief, the proper amount of succinic acid (1.4 mol) and appropriate glycols (ethylene glycol, 1,3-propanediol and butylene glycol) in a molar ratio 1/1.2 and the catalyst TBT ( $3 \times 10^{-4}$  mol TBT/mol SA) were charged into the reaction tube of the polycondensation apparatus [19]. The apparatus with the reagents was evacuated several times and filled with argon in order to remove the whole oxygen amount. The reaction mixture was heated at 190 °C under argon atmosphere and stirring at a constant speed (400 rpm) was applied. This first step (esterification) is considered to complete after the collection of almost the theoretical amount of H<sub>2</sub>O, which was removed from the reaction mixture by distillation and collected in a graduate cylinder. In order to ensure that all glycols vaporized totally returned to the reactor, in the side condenser a closed tub was used containing water, as it was described in the apparatus used by Günther and Zachmann [20]. This tube acts as a stopper, entrapping the glycol while the volatile water can pass and be removed from the reactor.

In the second step of polycondensation, PPA was added ( $5 \times 10^{-4}$  mol PPA/mol SA), which is believed to prevent side reactions such as etherification and thermal decomposition. A vacuum (5.0 Pa) was applied slowly over a time period of about 30 min, to avoid excessive foaming and to minimise oligomer sublimation, which is a potential problem during the melt polycondensation. For each polyester prepared, several polycondensation temperatures

were used such as 210, 220, 230 and 245 °C while stirring speed was slowly increased to 720 rpm. The polycondensation reaction time was ranged for each temperature from 15 min up to 3 h and afterwards the polyesters maintained at room temperature in order to be cooled.

### 2.3. Measurements

#### 2.3.1. Intrinsic viscosity

Intrinsic viscosity  $[\eta]$  measurements were performed by using an Ubbelohde viscometer at 25 °C in chloroform. All polyesters were dissolved at room temperature in order to prepare solutions of 1 wt% and filtered through a disposable membrane filter (0.2  $\mu$ m; Teflon). Intrinsic viscosity was calculated after the Solomon–Ciuta equation [21]:

$$[\eta] = [2\{t/t_0 - \ln(t/t_0) - 1\}]^{1/2}/c \quad (1)$$

where  $c$  is the concentration of the solution,  $t$  is the flow time of solution and  $t_0$  is the flow time of pure solvent.

The number-average molecular weight ( $\bar{M}_n$ ) of the samples was calculated from intrinsic viscosity  $[\eta]$  values, using the Berkowitz equation:

$$\bar{M}_n = 3.29 \times 10^4 [\eta]^{1.54} \quad (2)$$

#### 2.3.2. End-group analysis

Carboxyl end-group content (C.C.) of the resins was determined as follows. About 0.1 g of polyester was dissolved in chloroform at room temperature and the solution was titrated using a standard solution of NaOH in methanol ( $N/10$ ) and phenol red as indicator.

#### 2.3.3. Mechanical properties

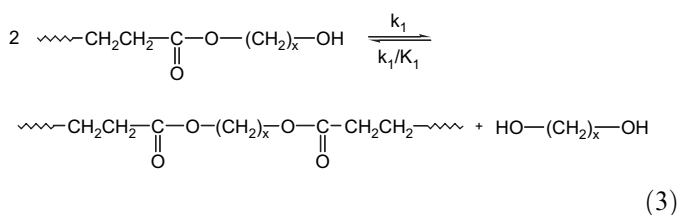
Measurements of the mechanical properties, such as tensile strength and elongation at break, were performed on an Instron 3344 dynamometer, in accordance with ASTM D638 using a cross-head speed of 50 mm/min. Prior to measurements, the samples were conditioned at  $50 \pm 5\%$  relative humidity for 36 h by placing them in a closed chamber containing a saturated Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O solution in distilled water (ASTM E-104). Five measurements were conducted for each sample, and the results were averaged to obtain a mean value.

## 3. Modelling of the polycondensation reaction kinetics for the poly(alkylene succinate) synthesis

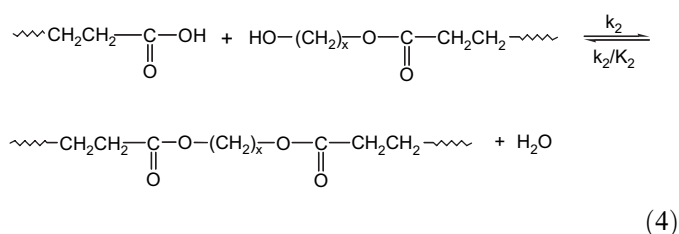
### 3.1. Reaction scheme

During polycondensation it is well known that two main reactions are taking place:

- the transesterification or polycondensation where a glycol (i.e. EG, PG, or BG) is produced and
  - the esterification where water is eliminated as by-product.
- (a) Transesterification/polycondensation:



(b) Esterification:



Herein,  $k_1$ ,  $K_1$  and  $k_2$ ,  $K_2$  are the forward and equilibrium rate constants of transesterification and esterification reactions, respectively, the subscript  $x$  stands for the number of methylene units used and takes the values  $x = 2, 3$  and  $4$  for the ethylene, propylene or butylene ester, respectively.

The forward reactions are facilitated by the by-product removal either by flow of an inert gas or by maintaining reduced pressure, or a combination of the two. The overall reaction rate is influenced by a combination of the intrinsic reaction kinetics, diffusion of the reactive end groups, change of polymer degree of crystallization and diffusional limitations on account of desorbing volatile by-products (i.e. glycol and water) [22–24]. Several models have been developed in literature describing the rate of change of the concentration of the species present during polycondensation of PET as a function of time and distance from the interface [22–27]. Having two independent variables, partial differential equations must be set and solved including the number of kinetic, diffusional and crystallization parameters [22–24]. Furthermore, the results of these models are used to fit only a few experimental data points. Therefore, in order to keep the modelling as simple as possible and not use more adjustable parameters than the experimental data points (five at each experimental condition), in this investigation a simple modelling approach is followed after Agarwal and coworkers [25–27]. This approach was originally developed for the solid-state polycondensation (SSP) of PET and successfully applied by our group in modelling the SSP of PET with activated carbon black nanoparticles [28].

### 3.2. Development of the mathematical model

In order to develop the mathematical model the following assumptions are made:

- Polymer-end reactivity and as a result all kinetic rate constants are independent of polymer chain length.
- The removal of glycol and water produced is assumed very fast, due to the application of high vacuum (ca. 5 Pa).
- In the absence of water and EG inside the reaction mixture, backward reactions in Eqs. (3) and (4) are eliminated.
- No side reactions for the formation of diethylene glycol or acetaldehyde or degradation of diester end groups are considered [10,11].
- Diffusional limitations on account of desorbing volatile species are neglected.

Then, the rate of change of hydroxyl and carboxyl end groups is described by the following expressions [27]:

$$\frac{d[\text{OH}]_t}{dt} = -2k_1[\text{OH}]_t^2 - k_2[\text{COOH}]_t[\text{OH}]_t \quad (5)$$

$$\frac{d[\text{COOH}]_t}{dt} = -k_2[\text{COOH}]_t[\text{OH}]_t \quad (6)$$

where  $[\text{OH}]_t$  and  $[\text{COOH}]_t$  denote the actual 'true' hydroxyl and carboxyl end-group concentration, respectively.

According to Agarwal et al. [25,27], the rapid slowdown in SSP kinetics at high  $[\eta]$  values can be represented by the transesterification and esterification reactions (Eq. (3) and (4)) only when accounting for a part of the carboxyl ( $[\text{COOH}]$ ) and hydroxyl end groups ( $[\text{OH}]$ ) to be rendered temporarily inactive. Then, the actual concentration of OH and COOH in Eqs. (5) and (6) are expressed as:

$$[\text{OH}]_t = [\text{OH}] - [\text{OH}]_i \quad (7)$$

$$[\text{COOH}]_t = [\text{COOH}] - [\text{COOH}]_i \quad (8)$$

where  $[\text{OH}]$ ,  $[\text{COOH}]$  and  $[\text{OH}]_i$ ,  $[\text{COOH}]_i$  denote the concentration of the total and temporarily inactivated OH and COOH end groups, respectively.

The apparent inability of a fraction of OH and COOH groups to participate in the polycondensation reactions can be due to chemical degradation leading to unreactive chain ends (such as vinyl end groups), side reactions, or to the reactive ends being unable to approach each other due to diffusional limitations [25, 29]. Such limited extent of mobility of some chain ends could be a result of their being restricted by relatively short chain segments linking them to crystalline parts, or a result of their having been incorporated in crystalline parts as defects. Duh [30] also accounted for such inactive groups in his modelling approach.

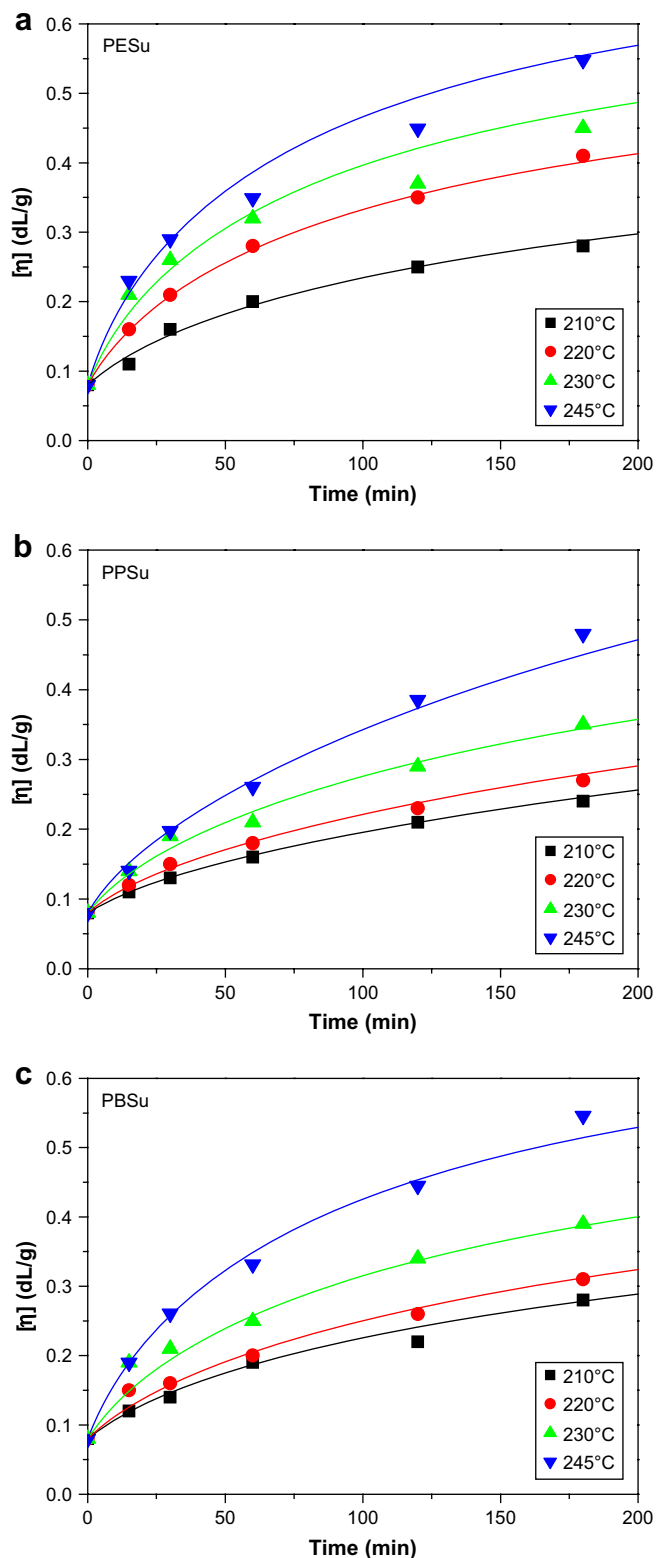
Furthermore, the number-average molecular weight is expressed as:

$$\bar{M}_n = \frac{2}{[\text{COOH}] + [\text{OH}]} \quad (9)$$

Then, Eqs. (5) and (6) together with Eqs. (2) and (7)–(9) constitute a set of ordinary differential equations which can be easily solved numerically using a varying step-size Runge–Kutta method to give intrinsic viscosity, as well as concentration of hydroxyl and carboxyl end groups as a function of time. Four adjustable parameters, namely  $k_1$ ,  $k_2$ ,  $[\text{OH}]_i$  and  $[\text{COOH}]_i$ , are estimated at each temperature and glycol used by simultaneous fitting of the values of all three variables to the experimental data points as a function of time.

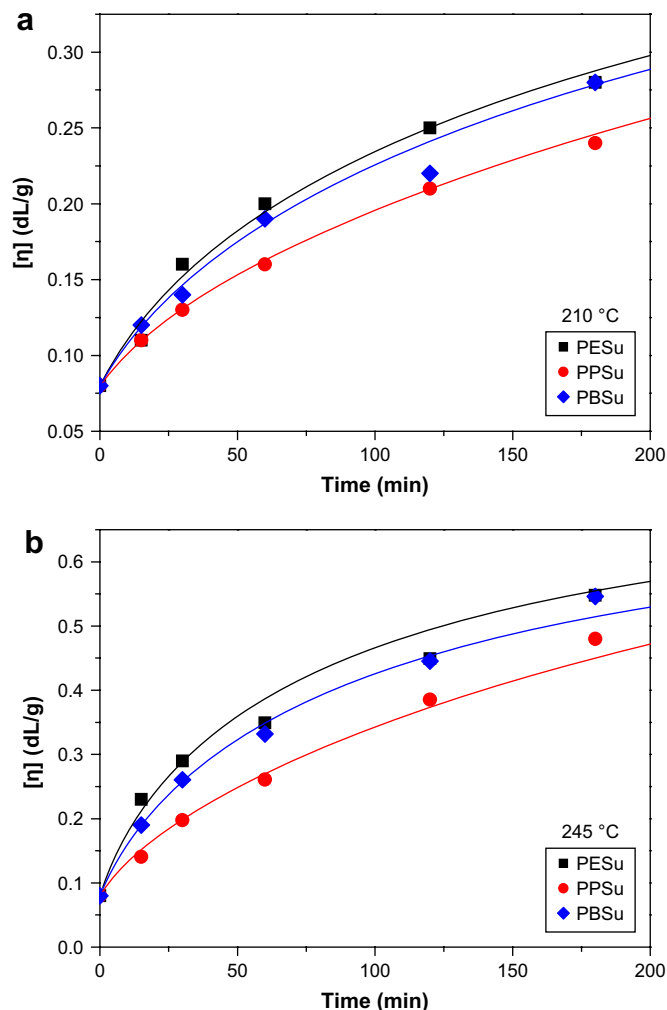
## 4. Results and discussion

In order to evaluate the effect of the glycol type and temperature on the polycondensation kinetics, the intrinsic viscosity values of all samples were measured and are presented in Fig. 1a–c. As it was expected the increase of intrinsic viscosity is time as well as temperature depending. For the PESu samples, using an initial oligomer with IV = 0.08 dL/g, the intrinsic viscosity increased to 0.28, 0.41, 0.45 and 0.55 dL/g after 3 h of polycondensation at 210, 220, 230 and 245 °C, respectively. A great increase of IV with temperature was observed with the value at 245 °C, almost double that at 210 °C. This is a result of higher esterification and transesterification reactions rates obtained at increased temperatures, as well as higher diffusion rates of by-products produced (i.e. water and ethylene, propylene or butylene glycol). The same effect of temperature on the reaction was also observed in the cases of PPSu and PBSu. During synthesis of PPSu the intrinsic viscosity increased from 0.08 dL/g to 0.24, 0.27, 0.35 and 0.48 dL/g after 3 h of polycondensation at 210, 220, 230 and 245 °C, respectively, and the corresponding increase of IV during polycondensation of PBSu was from 0.08 dL/g to 0.28, 0.31, 0.39 and 0.55 dL/g. In addition, an increase in polycondensation time increases also the IV at each temperature and polyester produced. This increase of IV with time is smoother at low temperatures (e.g. 210 °C), while more abrupt at higher temperatures (e.g. 245 °C).



**Fig. 1.** Variation of intrinsic viscosity with time during polycondensation of PESu (a), PPSu (b) and PBSu (c) at different temperatures. Continuous lines represent the theoretical kinetic model simulation results.

The effect of the type of glycol used on the time evolution of the polymer intrinsic viscosity is presented in Fig. 2a,b at temperatures 210 and 245 °C, respectively. From this figure it is clear that in the PPSu samples, at all temperatures and reaction times, the intrinsic viscosity and as a result the average molecular weight of the



**Fig. 2.** Effect of glycol type on the variation of intrinsic viscosity with time during polycondensation of PESu, PPSu and PBSu at 210 (a) and 245 °C (b). Continuous lines represent the theoretical kinetic model simulation results.

polymer formed showed lower values compared to PESu or PBSu. Furthermore, PESu exhibited slightly higher IV values compared to PBSu. The same trend was also observed when comparing the corresponding number-average molecular weights of the PESu, PPSu and PBSu. These values were estimated using Berkowitz equation (Eq. (2)) and are presented in Table 1. The higher IV values of PESu samples may be explained either by increased reaction rates or by an increased diffusion of condensates. Concerning the later, indeed higher diffusion rates of by-products from PESu synthesis (i.e. ethylene glycol and water) would be expected since EG is more volatile compared to butanediol, or propanediol. However, this would result in higher IV values of PPSu compared to PBSu, which is not the case. Therefore, it appears that synthesis of PPSu is somehow decelerated compared to PBSu.

In order to clarify this effect on the reactions taken place during polycondensation, end-group analysis was performed on the prepared samples. The measured carboxyl end groups of the studied samples are illustrated in Fig. 3a–c. As it was expected, carboxyl end groups decrease constantly with time at all temperatures studied with higher rates at increased temperatures. Thus, at all temperatures the carboxyl groups for PESu decrease from 475 eq/10<sup>6</sup> g (initial sample) to 12 eq/10<sup>6</sup> g after 3 h of polycondensation. This decrease is in accordance with the corresponding increase of intrinsic viscosity at these temperatures. A similar reduction was also observed in PPSu from 365 eq/10<sup>6</sup> g to 11 eq/10<sup>6</sup> g and for PBS from

**Table 1**  
Number-average molecular weight of poly(alkylene succinate) samples at different polycondensation temperatures and times

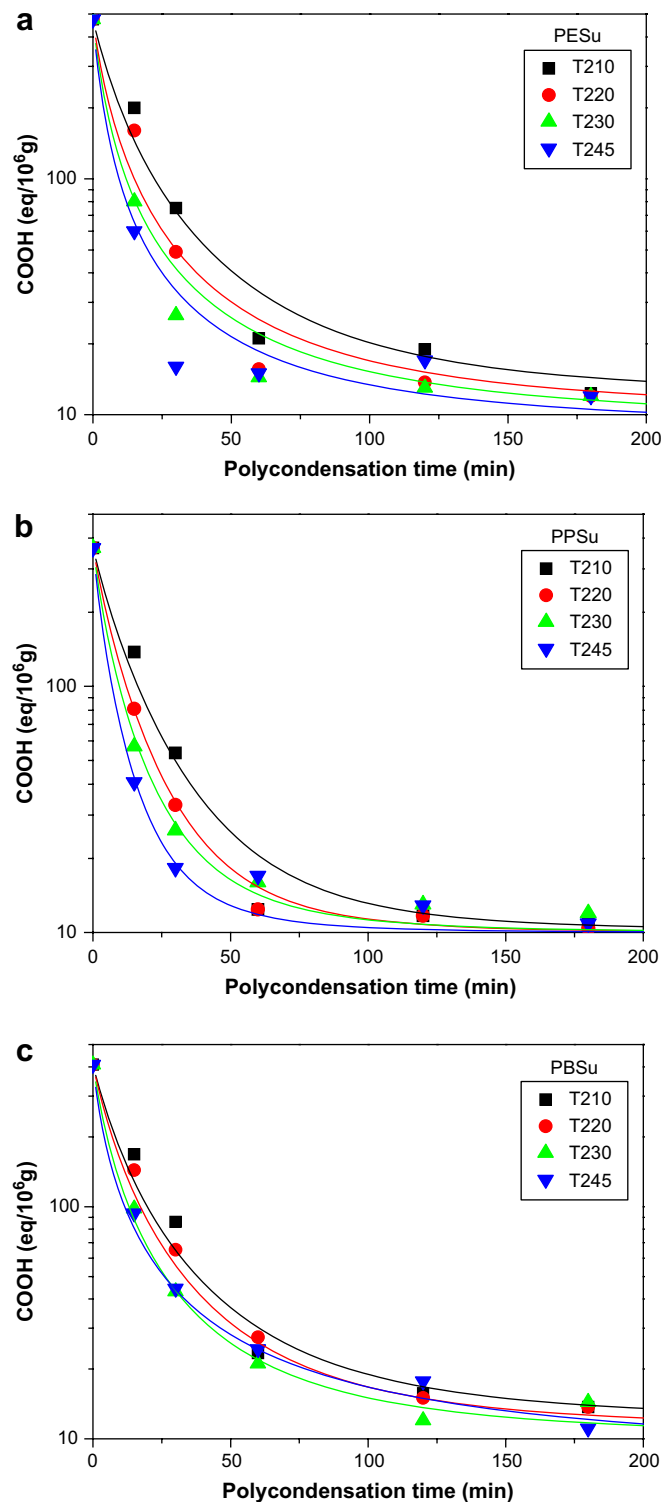
Sample	Time (min)	Temperature (°C)			
		210	220	230	245
PESu	0	670	670	670	670
	15	1100	1960	2970	3420
	30	1960	2970	4130	4890
	60	2760	4630	5690	6510
	120	3890	6530	7120	9590
	180	4630	8340	9620	13,030
PPSu	0	670	670	670	670
	15	1100	1260	1590	1610
	30	1420	1770	2550	2710
	60	1960	2350	2970	4150
	120	2970	3420	4890	7580
	180	3650	4380	6530	12,020
PBSu	0	670	670	670	670
	15	1260	1770	2550	2550
	30	1590	1960	2970	4150
	60	2550	2760	3890	6010
	120	3190	4130	6250	9460
	180	4630	5420	7720	12,960

410 eq/10<sup>6</sup> g to 14 eq/10<sup>6</sup> g after 3 h of polycondensation. Since carboxyl end groups are reducing only by esterification it is thus confirmed that this reaction is accelerated by increased temperatures. It is interesting to note that after the first polycondensation hour a plateau in the carboxyl end-group values is almost reached in all polyesters studied. These values, although small enough, are not zero. This will be explained later in this section. In addition, the constant COOH end groups after 1 h of polycondensation would result also in constant IV values. However, this was not observed experimentally. Therefore, the effect of temperature and glycol used (i.e. EG, PD or BD) in the transesterification reaction was examined next. To this direction, the hydroxyl end groups were calculated in terms of the number-average molecular weight and carboxyl content, using Eq. (9) and assuming that only hydroxyl and carboxyl end groups are present in all poly(alkylene succinate)s investigated.

The calculated hydroxyl groups of all poly(alkylene succinate)s are presented in Fig. 4a–c. From these diagrams, an initial abrupt reduction of hydroxyl groups was realized in all samples during the first 30 min of polycondensation, while afterwards this reduction levelled off. This reduction was more pronounced at higher temperatures. This reduction of the hydroxyl content was from 2497 eq/10<sup>6</sup> g to 420, 228, 196 and 141 eq/10<sup>6</sup> g for PESu, from 2607 eq/10<sup>6</sup> g to 536, 446, 294 and 177 eq/10<sup>6</sup> g for PPSu and from 2562 eq/10<sup>6</sup> g to 418, 355, 245 and 143 eq/10<sup>6</sup> g for PBSu after 3 h of polycondensation at temperatures 210, 220, 230 and 245 °C, respectively. The values of the hydroxyl end groups measured do not show the plateau observed in COOH end groups instead they continuously decrease. Thus, the continuous increase of IV even after the first polycondensation hour is explained through only the consumption of hydroxyl end groups after the point where the number of carboxyl end groups is so small that they could react no more. This is an expectable result since the values of OH is much larger compared to corresponding COOH values.

Comparing the change of hydroxyl groups between the samples, any certain perceptible difference was not revealed at first sight. For this reason it was decided to compare the absolute values of hydroxyl-groups' reduction at different temperatures. These absolute values were calculated by subtracting the values of each sample from the initial hydroxyl group values, [OH]<sub>0</sub>. Thus, the change of hydroxyl end groups due to transesterification can be expressed as:

$$[\text{OH}]_0 - [\text{OH}] - ([\text{COOH}]_0 - [\text{COOH}])$$



**Fig. 3.** Variation of the carboxyl content with time during polycondensation of PESu (a), PPSu (b) and PBSu (c) at different temperatures. Continuous lines represent the theoretical kinetic model simulation results.

where the last term is included to take into account the change of hydroxyl group concentration due to esterification and [COOH]<sub>0</sub> denotes the initial carboxyl end groups.

The change of hydroxyl groups due to the transesterification reaction is shown in Fig. 5a,b. From this figure it was realized that at 220 °C PESu results in higher values followed by PBSu and then PPSu. However, this tendency was not clear at other temperatures.

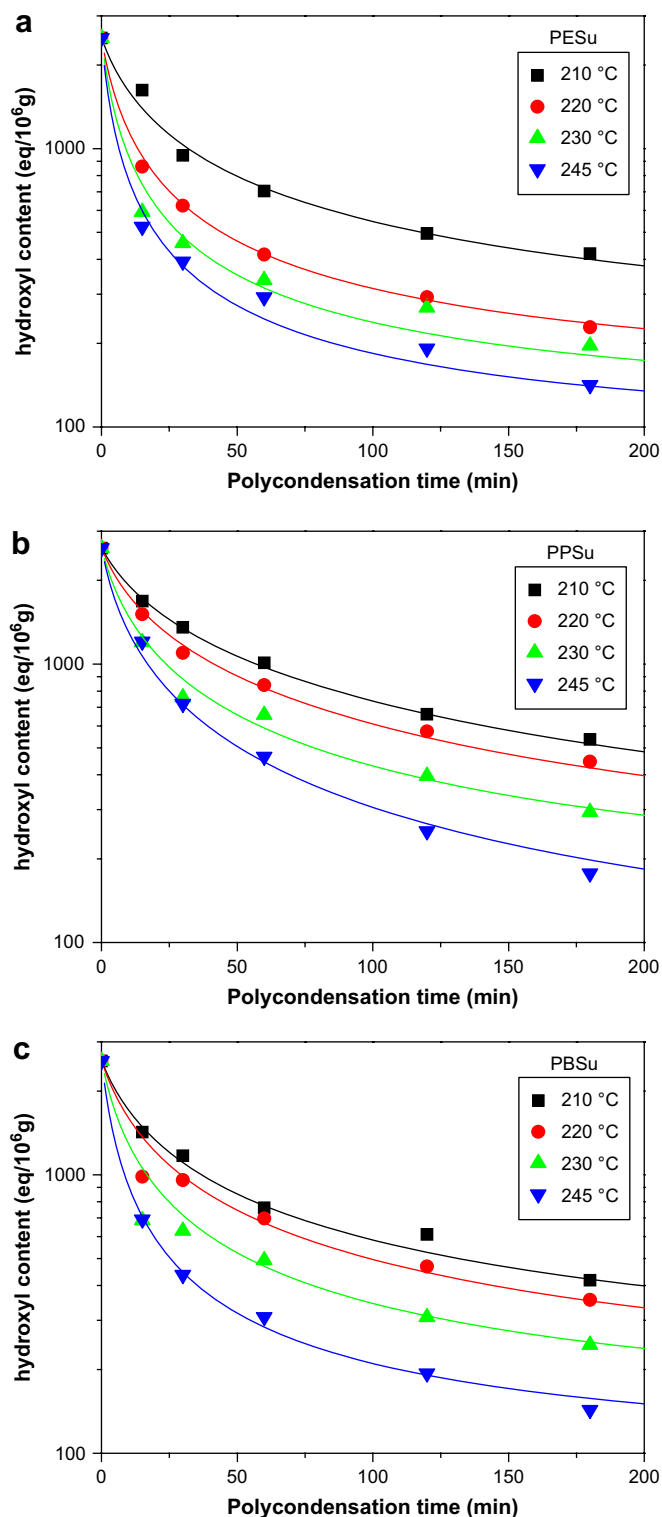


Fig. 4. Variation of the hydroxyl content with time during polycondensation of PESu (a), PPSu (b) and PBSu (c) at different temperatures. Continuous lines represent the theoretical kinetic model simulation results.

In order to clarify all these experimental measurements and come into a safe conclusion, the theoretical kinetic model presented in the previous section was employed. Differential Eqs. (5) and (6) were solved numerically together with Eqs. (2), (7)–(9) and IV values, as well as the concentration of hydroxyl and carboxyl end groups were obtained as a function of polycondensation time. The best set of the four parameters (i.e.  $k_1$ ,  $k_2$ ,  $[\text{OH}]_i$  and  $[\text{COOH}]_i$ )

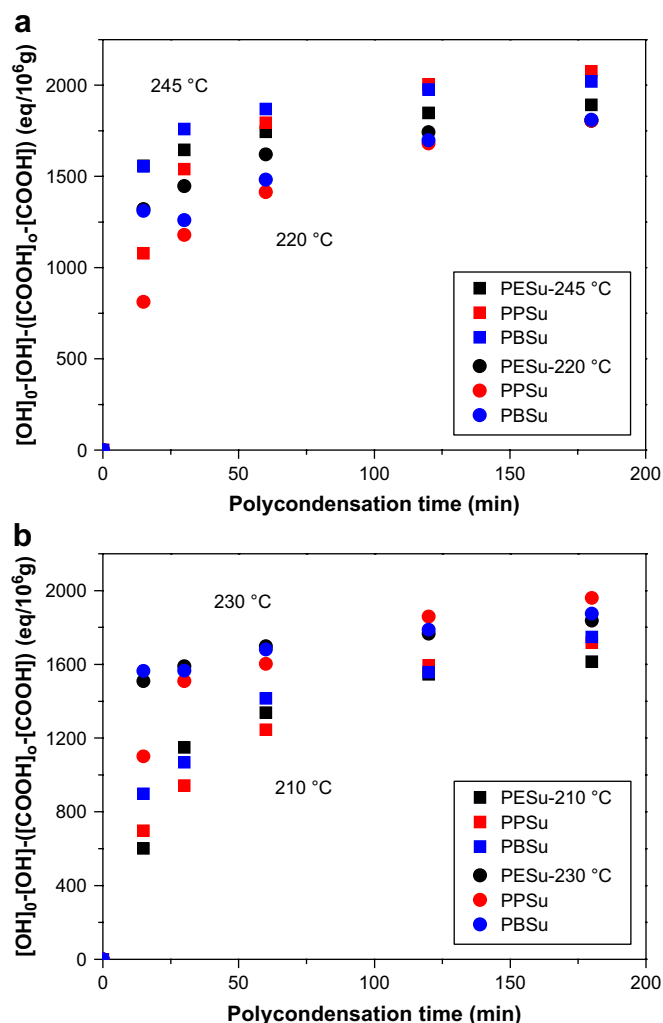


Fig. 5. Change of the concentration of hydroxyl groups due to transesterification with time during polycondensation of PESu, PPSu and PBSu at different temperatures.

estimated after simultaneous fitting of the experimental data presented in Figs. 1, 3 and 4, appears in Table 2 for all poly(alkylene succinate)s (i.e. PESu, PPSu and PBSu). Results of the theoretical simulation curves are presented as continuous lines in the above-mentioned figures. As it can be seen, although the theoretical model used was very simple, the simulation model fits very well the experimental data at all different temperatures and polyesters produced.

Table 2

Kinetic rate constants of the transesterification and esterification reaction and concentration of temporarily inactivated OH and COOH end groups at different polycondensation temperatures for all poly(alkylene succinate)s

Sample	Temperature (°C)	$k_1$ (kg/meq) $\text{h}^{-1}$	$k_2$ (kg/meq) $\text{h}^{-1}$	$[\text{OH}]_i$ (meq/kg)	$[\text{COOH}]_i$ (meq/kg)
PESu	210	$5.4 \times 10^{-4}$	$30 \times 10^{-4}$	150	12
	220	$12.4 \times 10^{-4}$	$50 \times 10^{-4}$	120	10
	230	$18.0 \times 10^{-4}$	$65 \times 10^{-4}$	100	9
	245	$24.4 \times 10^{-4}$	$84 \times 10^{-4}$	80	8.5
PPSu	210	$3.2 \times 10^{-4}$	$26 \times 10^{-4}$	110	10
	220	$4.4 \times 10^{-4}$	$35 \times 10^{-4}$	110	10
	230	$7.6 \times 10^{-4}$	$47 \times 10^{-4}$	110	10
	245	$9.6 \times 10^{-4}$	$62 \times 10^{-4}$	40	10
PBSu	210	$5 \times 10^{-4}$	$28 \times 10^{-4}$	150	12
	220	$6 \times 10^{-4}$	$32 \times 10^{-4}$	120	11
	230	$10.4 \times 10^{-4}$	$45 \times 10^{-4}$	110	10
	245	$20 \times 10^{-4}$	$60 \times 10^{-4}$	85	8

From an inspection of the values reported in Table 2 it seems that the values of  $k_1$  estimated are higher in the case of PESu followed by PBSu and then by the corresponding values of PPSu. Thus, it seems that the transesterification reaction is favoured in PESu synthesis followed by PBSu and finally PPSu. This result confirms the experimental findings on the change of hydroxyl groups presented in Fig. 5. A great increase in the esterification kinetic rate constant values,  $k_2$ , was also observed at all temperatures in the production of PESu, which this time was followed by PPSu and then PBSu. Furthermore, the best-fitting values of the concentration of hydroxyl inactive groups were lower in PPSu, compared to those of PESu and PBSu, which presented similar values. This could be considered as physically correct if it would be attributed to the less crystalline structure of PPSu compared to other two poly(alkylene succinate)s [13]. Hydroxyl inactive groups could be considered as groups trapped in the crystalline phase and therefore a less amount of crystalline phase would result in lower values of  $[OH]_i$ . Furthermore, an increase in temperature does not favour the side reactions since it increases the main reaction rate constants and therefore the values of  $[OH]_i$  decrease with temperature. Moreover, the best fit values of the  $[COOH]_i$  estimated are the same or slightly lower to the values experimentally measured after 3 h of polycondensation. The theoretical simulation model thus is able to predict the constant COOH end-group values measured at the final stages of polycondensation.

With these findings on the kinetic rate constants the experimental data points measured can be explained as follows. During synthesis of PESu, use of a glycol with lower molecular weight and therefore more flexible leads to increased values of both  $k_1$  and  $k_2$  which means faster transesterification and esterification rates and as a result lower carboxyl concentrations at all temperatures and higher amounts of hydroxyl consumption. As a result, the polyesters produced exhibit higher intrinsic viscosities meaning higher average molecular weights. Accordingly use of a larger glycol (i.e. PG and consequently BG) leads to lower esterification kinetic rate constant, following the number of methylene units. However, the transesterification reaction rate constant of PPSu is much lower compared to PBSu leading to higher carboxyl and hydroxyl end groups and therefore eventually lower IV values meaning lower average molecular weights.

In addition, the values of the esterification rate constant,  $k_2$ , estimated are always much larger compared to the corresponding  $k_1$  in all three poly(alkylene succinate)s. This signifies that esterification proceeds in a much faster rate compared to transesterification. Since carboxyl end groups are only consumed through the esterification reaction, this explains the very low values of COOH end groups measured and as a result the stop of their reaction after a point and the continuation of the reaction only through transesterification (consumption of OH end groups).

Finally, the kinetic rate constants were correlated with temperature using an Arrhenius-type expression. As it is expected the values of all rate constants increase with SSP temperature. As the temperature is increased the mobility and activity of the chain ends are also increased leading to increased forward reaction rate constants. Fig. 6a,b shows such a plot of the kinetic rate constants  $k_1$  and  $k_2$ , respectively, for all three polyesters studied. Good straight lines were always obtained with correlation coefficients greater than 0.90 (Table 3). From the slope of these straight lines the activation energies for the transesterification and esterification reactions were determined and are illustrated in Table 3. Results are in accordance with previous statements, meaning that the activation energy of the esterification reaction decreases with increasing methylene units in glycols (i.e. PESu > PPSu > PBSu). However, the activation energy of the transesterification reaction was larger in PESu followed by PBSu and significantly lower in PPSu.

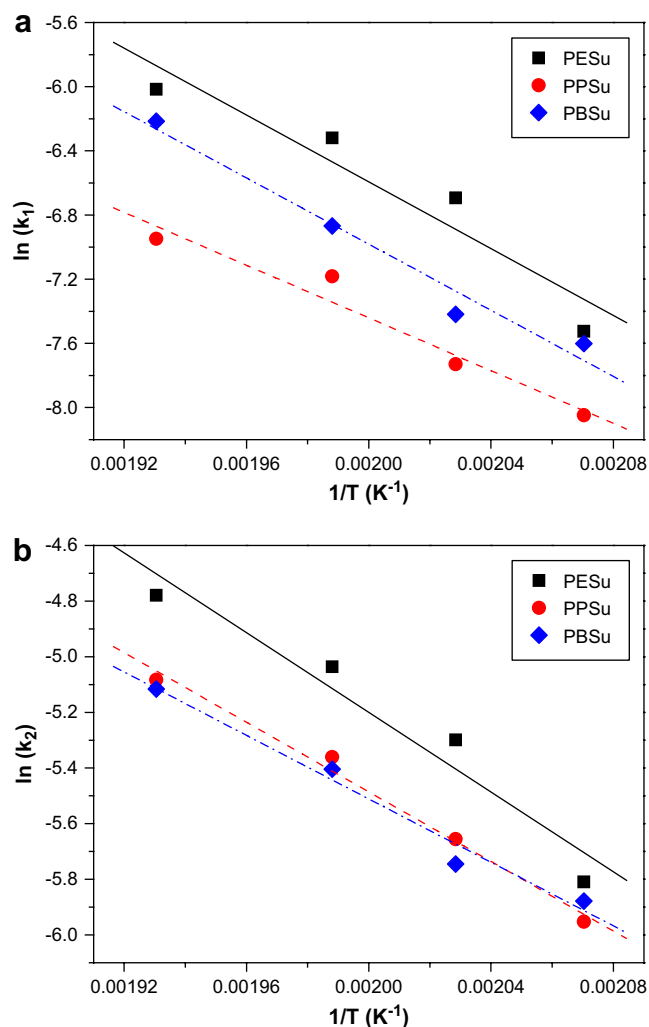


Fig. 6. Arrhenius plots of the kinetic rate constants for transesterification,  $k_1$  (a) and esterification,  $k_2$  (b) estimated for the polycondensation of PESu, PPSu and PBSu.

Moreover, it was observed that the inactive end-group concentrations  $[OH]_i$  and  $[COOH]_i$  of PESu and PBSu decrease with increasing temperature. This can be attributed to two reasons [30]. First, as the temperature is increased some of the inactive end groups are sufficiently activated and become active. In other words, some of the end groups, trapped in the crystalline phase, are rejected into the amorphous phase as a result of the increasing “fractionating” action of polymer crystallization at a higher temperature. Second, as the temperature is increased, the diffusion resistance, which is accounted for mainly by the apparent inactive end-group concentration according to this model, decreases. As a result of increased by-product diffusivities, by-product concentration decreases. This, in turn, decreases the backward reaction rates and increases the net polycondensation rate. The increased diffusion rates and decreased backward reaction rates are accounted for by the decreased  $[OH]_i$  and  $[COOH]_i$  values. When plotting the inactive hydroxyl and carboxyl concentrations as a function of

Table 3

Activation energies and correlation coefficients of the transesterification and esterification reactions of PESu, PPSu and PBSu

Sample	$E_1$ (kJ/mol)	$R^2$	$E_2$ (kJ/mol)	$R^2$
PESu	86.5	0.904	59.5	0.941
PPSu	68.3	0.953	52.0	0.990
PBSu	85.7	0.970	47.4	0.978

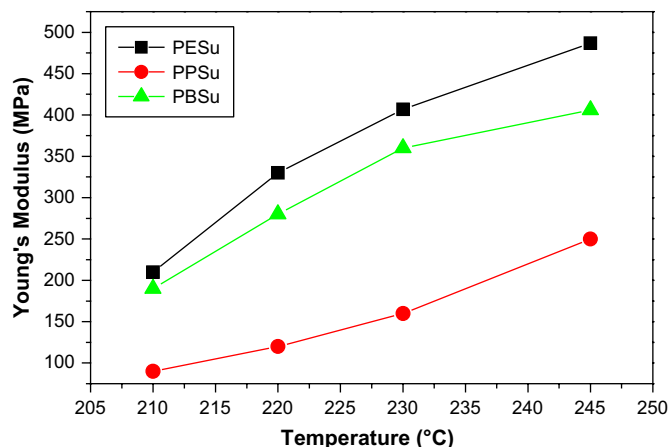


Fig. 7. Young's modulus versus polycondensation temperature of the three aliphatic polyesters studied.

1/T, good straight lines were observed, with the following equations in the case of PESu and PBSu:

$$[\text{OH}]_i = -877 + 493,550/T \quad \text{PESu}$$

$$[\text{OH}]_i = -773 + 443,648/T \quad \text{PBSu}$$

and

$$[\text{COOH}]_i = -39 + 24,312/T \quad \text{PESu}$$

$$[\text{COOH}]_i = -47 + 28,507/T \quad \text{PBSu}$$

Finally, the mechanical properties of the poly(alkylene succinate)s synthesized were studied in relation to the effect of the diol type used as well as polycondensation temperature. From the stress-strain curves of the three polyesters, PESu and PBSu were characterized as 'hard and tough' materials whereas PPSu as a 'brittle' material.

The effect of temperature and glycol type on the Young's modulus, tensile strength at break and elongation at break are shown in Figs. 7–9, respectively. As it can be seen the mechanical properties are both temperature and polyester type dependent. The low tensile strength of PPSu together with its low Young's modulus

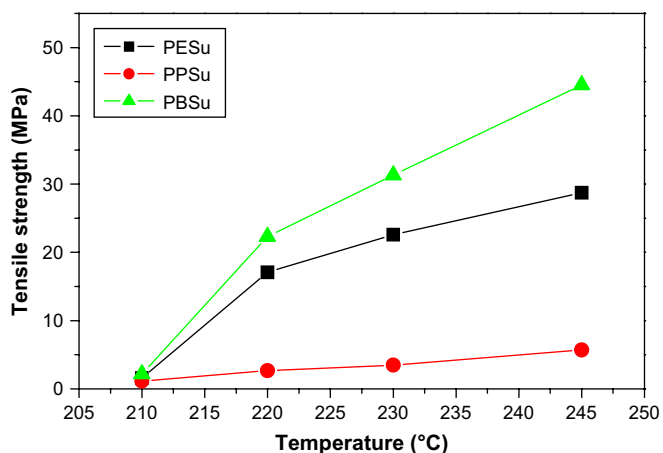


Fig. 8. Tensile strength versus polycondensation temperature of the three aliphatic polyesters studied.

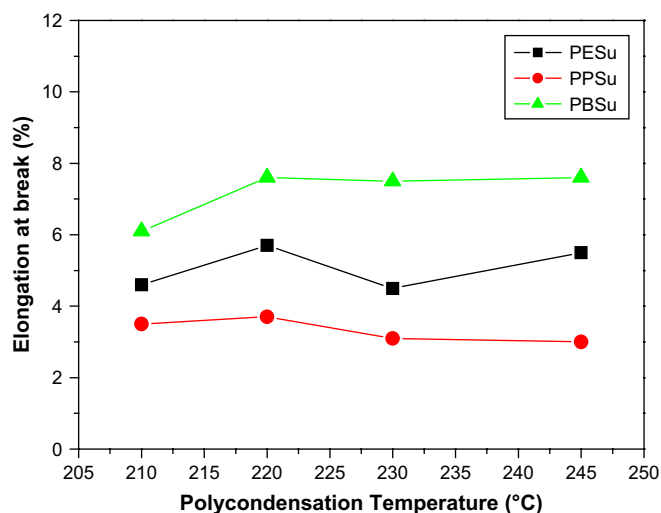


Fig. 9. Elongation at break versus polycondensation temperature of the three aliphatic polyesters studied.

explain the brittleness of this material. An increase in temperature leads to higher tensile strengths and Young's modulus which is a result of the higher average molecular weight of the samples produced. Furthermore at the same temperature, PPSu exhibits the lower tensile strength, elongation at break and Young's modulus compared to PESu and PBSu. Comparing PESu to PBSu the former exhibits higher Young's modulus following its higher IV, although the latter exhibits higher tensile strength especially at high temperatures and higher elongation at break values at all temperatures.

## 5. Conclusions

In this investigation, three poly(alkylene succinate)s have been synthesized using succinic acid and either ethylene glycol, 1,3-propanediol, or butylene glycol in presence of tetrabutoxytitanium as catalyst. A theoretical mathematical model for the polycondensation reaction has been developed and applied successfully in the simulation of all experimental data. Values for the kinetic rate constants are proposed for different temperatures and comonomer chemical structure. Also, the activation energy of the transesterification and the esterification reactions are estimated. Poly(ethylene succinate) was found to exhibit the higher IV values followed by PBSu and finally PPSu with much lower values. The transesterification rate constants were found to follow the order: PESu > PBSu > PPSu, while the esterification rate constant is in the order: PESu > PPSu > PBSu. In addition, the values of the esterification rate constant,  $k_2$ , estimated are always much larger compared to the corresponding  $k_1$  in all three poly(alkylene succinate)s resulting thus in very low values of COOH end groups compared to corresponding OH end groups.

Finally, from measurements of the mechanical properties of the polyesters produced it was found that, concerning the tensile strength and the elongation at break, PBSu exhibits the larger values followed by PESu in the order: PBSu > PESu > PPSu, whereas PESu exhibits the higher Young's Modulus in the order: PESu > PBSu > PPSu.

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