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Synthesis of poly(alkylene succinate) biodegradable polyesters I. Mathematical modelling of the esterification reaction

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Abstract

Synthesis of three biodegradable aliphatic polyesters, namely poly(ethylene succinate), poly(propylene succinate) and poly(butylene succinate) is presented using the appropriate diols and succinic acid in the presence of tetrabutoxytitanium as catalyst. A theoretical mathematical model for the esterification reaction, based on the functional group approach, is developed and applied successfully in the simulation of all experimental data. Values for the kinetic rate constants are proposed for different catalyst molar ratios and comonomer chemical structure. It was found that the presence of the metal catalyst used leads to a poor activity of self-catalyzed acid and the main kinetic rate constant of the esterification reaction correlates well with the square root of the catalyst concentration. Different glycols do not influence much the number average degree of polymerization (NADP) values of the oligomers produced, even thought they slightly affect esterification rates in the order BG > PG > EG. In contrast, these values are affected by the amount of catalyst, with larger catalyst molar ratio giving polymer with bigger average molecular weight. These results were verified from measurements of the final polyester average molecular weight obtained at different polycondensation temperatures. Finally, from theoretical simulation results it was found that although higher initial ratios of glycol to succinic acid are useful to increase the esterification rate, they lower the NADP of the oligomers formed at a fixed conversion of acid end groups.

Keywords: Aliphatic polyesters; Biodegradable polymers; Mathematical modelling

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].

Carothers first studied the synthesis of aliphatic polyesters by polycondensation reactions of diols with different dicarboxylic acids or their esters back in 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 fibers, 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, polymerization temperature and reaction time [6–9]. However, an extensive and more detailed study about synthesis of aliphatic polyesters and the dependence of 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.

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The advantage of these polyesters is that despite of their low melting point they have very high thermal stability (decomposition temperature higher than 400 °C), which is similar to aromatic polyesters [10–12]. Comparative biodegradability studies, as well as the crystallization and melting behavior 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]. It should be noticed that PPSu synthesis has been reported only recently [14] 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].

Moreover, concerning the theoretical modelling of the polyesterification reaction, although it is well-known for about 50 years since the work of Flory [15], the models published in literature on the direct esterification for the poly(alkylene succinates) production are very limited. In fact, to our knowledge, only one work dealing with modelling of the PBSu reaction has been published [16]. The Flory's self-catalyzed reaction model was used for unanalyzed reactions, together with a new complex model suitable for catalyzed esterification. The ability of the diacid used to act as a self-catalyst was addressed there [16]. Therefore, the aim of this work is to develop a theoretical mathematical model to predict the kinetics of the esterification reaction of the three poly(alkylene succinates) (PESu, PPSu and PBSu). The model is based on the functional group analysis, which had originally developed for the PET synthesis by Kang et al. [17,18] and extended by our group in the production of poly(propylene terephthalate) [19]. The effect of the catalyst molar ratio, monomer chemical structure and glycol/acid molar ratio on the esterification kinetics is elucidated. Finally, some results on the effect of the polycondensation temperature on the average molecular weight of the polyesters produced are presented.

2. Experimental

2.1. Materials

Succinic acid (purum 99%), ethylene glycol (purum 99%) and butylene glycol (purum 99%) were purchased from Aldrich Chemical Co. 1,3-Propanediol (CAS Number: 504-63-2, Purity: >99,7%) was kindly supplied by Du Pont de Nemours Co. Tetrabutoxy-titanium (TBT) used as catalyst was 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 [19]. In brief, the proper amount of succinic acid (0.55 mol) and appropriate glycols (ethylene glycol, 1,3-propanediol and butylene glycol) in a molar ratio 1/1.1 and the catalyst TBT (3×10^{-4} mol TBT/mol SA) were charged into the reaction tube of the polycondensation apparatus [20]. TBT was selected as a proper catalyst leading to high reaction rates as it was observed in poly(propylene terephthalate) esterification [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 (500 rpm) was applied. This first step (esterification) is considered to complete after the collection of almost the theoretical amount of H_2O, which was removed from the reaction mixture by distillation and collected in a graduate cylinder. In order to ensure that all glycol vaporized totally returned to the reactor, in the side condenser a closed tube was used containing water, as it was described in the apparatus used by Günther and Zachmann [21]. This tube acts as a stopper, entrapping the glycol while the volatile water can pass and be removed from the reactor.

In the case of PPSu two additional catalyst concentrations, namely 1.5×10^{-4} and 6×10^{-4} mol TBT/mol SA were used in order to study the effect of catalyst amount on esterification and polycondensation reactions.

In the second step of polycondensation, PPA was added (5×10^{-4} mol PPA/mol SA), which is believed that prevents side reactions such as etherification and thermal decomposition. A vacuum (5.0 Pa) was applied slowly over a period time 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 140, 170, 200, 230 and 250 °C while stirring speed was slowly increased to 720 rpm. The polycondensation reaction time was always kept constant at 1 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 1 wt% and filtered through a disposable membrane filter 0.2 μm (Teflon). Intrinsic viscosity was calculated after the Solomon–Ciuta equation [22]

$$[\eta] = \left[2\left\{\frac{t/t_0}{\ln(t/t_0)} - 1\right\}\right]^{1/2} /c \qquad (1)$$

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

2.3.2. Gel permeation chromatography (GPC)

GPC analysis was performed using a Waters 150C GPC equipped with differential refractometer as detector and three ultrastyragel (10^3, 10^4, 10^5 Å) columns in series. $CHCl_3$ was used as the eluent (1 ml/min) and the measurements were performed at 35 °C. Calibration was performed using polystyrene standards with a narrow molecular weight distribution.

2.3.3. 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.

3. Mathematical modeling of the esterification reaction for the poly(alkylene succinate) synthesis

3.1. Reaction scheme

Two main modeling approaches can be applied in representing the esterification reaction kinetics: the molecular species model and the functional group model [17–19]. 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 [17] following our previous article on modeling of the poly(propylene terephthalate) esterification kinetics [19]. 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 1.

As it was reported earlier the esterification reaction of succinic acid (SA) with three glycols is considered here. The general acronym G derived from glycol, is used to represent the three different glycols used in this study (i.e. EG ethylene glycol, PG propylene glycol and BG butylene glycol). Five different oligomeric segments are used: tSA, tG, bSA, bG and bDG (the term t and b refer to the terminal functional group and bound monomeric repeating unit, respectively).

Based on these functional groups, the following mechanism is assumed to represent the kinetics of the esterification process [19].

$$\mathrm{SA} + \mathrm{G} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \mathrm{tSA} + \mathrm{tG} + \mathrm{W} \tag{2}$$

$$\mathrm{tSA} + \mathrm{G} \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} \mathrm{bSA} + \mathrm{tG} + \mathrm{W} \tag{3}$$

$$\mathrm{SA} + \mathrm{tG} \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} \mathrm{tSA} + \mathrm{bG} + \mathrm{W} \tag{4}$$

$$\mathrm{tSA} + \mathrm{tG} \underset{k_4'}{\overset{k_4}{\rightleftharpoons}} \mathrm{bSA} + \mathrm{bG} + \mathrm{W} \tag{5}$$

$$\mathrm{tG} + \mathrm{tG} \underset{k_5'}{\overset{k_5}{\rightleftharpoons}} \mathrm{bG} + \mathrm{G} \tag{6}$$

$$\mathrm{tG} + \mathrm{tG} \xrightarrow{k_6} \mathrm{bDG} + \mathrm{W} \tag{7}$$

Reactions (2)–(5) represent the typical esterification reactions, while reaction (6) is the polycondensation reaction, occurring mainly in the second step of polyester formation. Finally, reaction (7) is a side reaction resulting in di-glycol repeating units, with ether linkages in the oligomeric chain. k_i ($i=1, 6$) and k_i' ($i=1, 5$) represent the kinetic rate constants of the six elementary reactions (L mol^{-1} min^{-1}).

3.2. Development of the mathematical model

In order to develop a mathematical model for the esterification reaction the following assumptions are made:

Table 1
Molecular structure of components considered

Material	Symbol	Description	Molecular structure
Monomers	SA	Succinic acid	HOOC–CH_2–CH_2–COOH
	G	Ethylene glycol	HO–CH_2–CH_2–OH
		Propylene glycol	HO–CH_2–CH_2–CH_2–OH
		Butylene glycol	HO–CH_2–CH_2–CH_2–CH_2–OH
Product	W	Water	H_2O
Oligomers	tSA	SA end group	HOOC–CH_2–CH_2–CO–
	tG	EG end group	HO–CH_2–CH_2–O–
		PG end group	HO–CH_2–CH_2–CH_2–O–
		BG end group	HO–CH_2–CH_2–CH_2–CH_2–O–
	bSA	SA repeating unit	–OC–CH_2–CH_2–CO–
	bG	EG repeating unit	–O–CH_2–CH_2–O–
		PG repeating unit	–O–CH_2–CH_2–CH_2–O–
		BG repeating unit	–O–CH_2–CH_2–CH_2–CH_2–O–
	bDG	Diethylene glycol repeating unit	–O–CH_2CH_2–O–CH_2CH_2–O–
		Dipropylene glycol repeating unit	–O–$CH_2CH_2CH_2$–O–$CH_2CH_2CH_2$–O–
		Dibutylene glycol repeating unit	–O–$CH_2CH_2CH_2CH_2$–O–$CH_2CH_2CH_2CH_2$–O–

- All kinetic rate constants are independent of polymer chain length.
- All the water produced during the reaction is instantaneously vaporized and removed.
- All glycol vaporized is totally returned to the reactor. This assumption is correct according to the specially designed experimental device used [21].

Based on the reaction mechanism (Eqs. (2–7), the reaction rates can be expressed in terms of the different functional groups present in the reactor and the corresponding rate constants [17]. All the terms in parentheses denote mole numbers of every component.

$$R_1=\{4k_1(\mathrm{SA})(\mathrm{G})-(k_1/K_1)(\mathrm{tSA})(\mathrm{W})\}/V^2 \tag{8}$$

$$R_2=\{2k_2(\mathrm{tSA})(\mathrm{G})-2(k_2/K_2)(\mathrm{bSA})(\mathrm{W})\}/V^2 \tag{9}$$

$$R_3=\{2k_3(\mathrm{SA})(\mathrm{tG})-(k_3/K_3)(\mathrm{tSA})(\mathrm{W})\}/V^2 \tag{10}$$

$$R_4=\{k_4(\mathrm{tSA})(\mathrm{tG})-2(k_4/K_4)(\mathrm{bSA})(\mathrm{W})\}/V^2 \tag{11}$$

$$R_5=\{k_5(\mathrm{tG})(\mathrm{tG})-4(k_5/K_5)(\mathrm{bG})(\mathrm{G})\}/V^2 \tag{12}$$

$$R_6=\{k_6(\mathrm{tG})(\mathrm{tG})\}/V^2 \tag{13}$$

where, $K_i=k_i/k_i'$ $(i=1,5)$ denote the equilibrium rate constants and the volume of the reaction mixture can be expressed as

$$V=\frac{(\mathrm{SA})\mathrm{MW}_{\mathrm{SA}}}{\rho_{\mathrm{SA}}}+\frac{(\mathrm{G})\mathrm{MW}_{\mathrm{G}}}{\rho_{\mathrm{G}}}+\frac{W_{\mathrm{OLIG}}}{\rho_{\mathrm{OLIG}}}-\frac{(\mathrm{W})\mathrm{MW}_{\mathrm{W}}}{\rho_{\mathrm{W}}} \tag{14}$$

where MW and ρ represent the molecular weight and density of the corresponding material. W_{OLIG} is used to express the weight of all oligomers presented in the reaction mixture, i.e. (tSA), (tG), (bSA), (bG) and (bDG).

It should be noted here that Eq. (14), describing the volume change during the reaction, should be a differential equation with respect time. The continuous removal of water, as well as evaporation and reflux of the glycol will definitely lead to a continuously changing reaction volume. However, in order to keep the model as simple as possible, an algebraic equation is used for the calculation of the reaction volume in which the instantaneous production of water and consumption of monomers is taken into account.

Furthermore, the material mole balance equations for a semi-batch reactor can be written as:

$$\frac{1}{V}\frac{\mathrm{d(SA)}}{\mathrm{d}t}=-R_1-R_3 \tag{15}$$

$$\frac{1}{V}\frac{\mathrm{d(G)}}{\mathrm{d}t}=-R_1-R_2+R_5 \tag{16}$$

$$\frac{\mathrm{d(W)}}{\mathrm{d}t}=V\left(R_1+R_2+R_3+R_4+R_6\right)-F_{\mathrm{W}}=0 \tag{17}$$

$$\frac{1}{V}\frac{\mathrm{d(tSA)}}{dt}=R_1-R_2+R_3-R_4 \tag{18}$$

$$\frac{1}{V}\frac{\mathrm{d(tG)}}{\mathrm{d}t}=R_1+R_2-R_3-R_4-2R_5-2R_6 \tag{19}$$

$$\frac{1}{V}\frac{\mathrm{d(bSA)}}{\mathrm{d}t}=R_2+R_4 \tag{20}$$

$$\frac{1}{V}\frac{\mathrm{d(bG)}}{\mathrm{d}t}=R_3+R_4+R_5 \tag{21}$$

$$\frac{1}{V}\frac{\mathrm{d(bDG)}}{\mathrm{d}t}=R_6 \tag{22}$$

In Eq. (17), F_{W} is used to represent the flow rate of the water vaporized and removed from the reactor. Then, the total moles of water removed up to time t, N_{W}, can be calculated from:

$$N_{\mathrm{W}}=\int_0^t F_{\mathrm{W}}\mathrm{d}t \tag{23}$$

Finally, conversion according to the water produced and removed can be calculated according to the following equation:

$$X_{\mathrm{W}}=\frac{N_{\mathrm{W}}\mathrm{MW}_{\mathrm{W}}}{19.8} \tag{24}$$

The value 19.8 in the denominator is used to express the total weight of water that should be produced when all 0.55 mol of SA will be reacted.

3.3. Molecular characteristics of the oligomers produced

Using the polymer segment approach the number average degree of polymerization of oligomers produced can be expressed as [17]:

$$\overline{DP}_n=\frac{(\mathrm{tSA})+(\mathrm{bSA})+(\mathrm{tG})+(\mathrm{bG})+(\mathrm{bDG})}{(\mathrm{tSA})+(\mathrm{tG})} \tag{25}$$

3.4. Kinetic rate constants

The kinetic rate constants usually depend on temperature, as well as catalyst type and concentration [23]. In literature [17,24,25], it has been proposed that the esterification and polycondensation reactions are acid-catalyzed and that the corresponding rate constants can be expressed as

$$k_i=k_{i,0}C_{\mathrm{acid}};\quad i=1\text{–}5 \tag{26}$$

where $k_{i,0}$ are the ⟨true⟩ rate constants in $\mathrm{L}^2\ \mathrm{mol}^{-2}\ \mathrm{min}^{-1}$, and C_{acid} denote the concentration of acid groups defined as the sum of the concentration of carboxylic end groups (tSA) and the carboxylic groups of the free acid (2SA), i.e.

$$C_{\mathrm{acid}}=\{2(\mathrm{SA})+(\mathrm{tSA})\}/V \tag{27}$$

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

The assumption whether kinetic rate constants used in the esterification of the poly(alkylene succinates) are indeed acid-catalyzed is investigated in the results and discussion section.

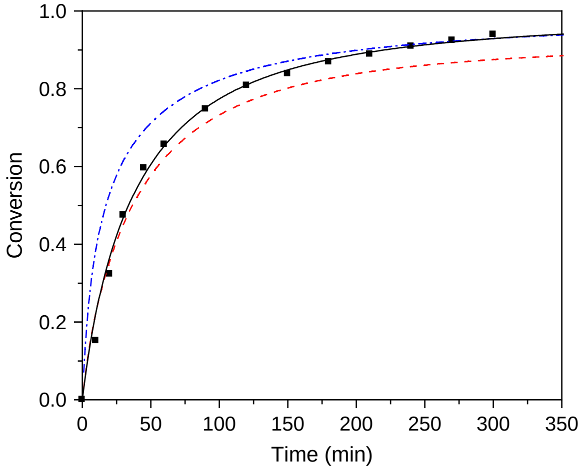

Figure 1. Conversion (X_w) versus time for the esterification reaction of PPSu at 190 °C and 3×10^{-4} mol TBT/mol SA. Experimental data (■) and simulation results using non-acid catalyzed kinetics with $k_1=2.2\times10^{-3}$ L mol^{-1} min^{-1} and $k_6=0.8\times10^{-3}$ L mol^{-1} min^{-1} (—) and acid catalyzed according to Eqs. (26) and (27) with $k_{1,0}=0.2\times10^{-3}$, $k_{6,0}=2\times10^{-3}$ L mol^{-1} min^{-1} (– – –) and $k_{1,0}=0.5\times10^{-3}$, $k_{6,0}=0.8\times10^{-3}$ L mol^{-1} min^{-1} (–.–.–).

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

The system of differential Eqs. (15–22), together with Eqs. (8–14) was integrated by applying the Runge–Kutta 4th 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 mechanism presented in Eqs. (2–7), 11 rate constants (k_i, $i=1$–6 and $k_i^{\prime}$, $i=1$–5) should be determined. Since there are not any experimental data in the literature on the polymerization of SA with either EG, PG or BG, 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 (terephthalic acid) 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) [17–18,26–27]. Since, in the polymerization of either PG or BG the end groups are identical, we used the same assumption, i.e. $k_1=k_2=2k_3=2k_4$. This assumption was employed also successfully in modeling the poly(propylene terephthalate) esterification reaction [19]. In order to simplify further the calculations it was assumed that $k_5=0$, i.e. that the poly-condensation reaction is not carried out in a great extent during the esterification step. This assumption is justified by the following reasons: (a) From initial runs of the simulation kinetic model, it was observed that the values of k_5 that fitted best the experimental data were always very low (less than three orders of magnitude compared to k_1, or k_6); (b) in this investigation, the esterification reaction is only modeled, therefore it sounds reasonable to assume negligible the contribution of the polycondensation reaction; (c) the adjustable parameters must be always kept as few as possible and (d) in the basic and only reference that has been published on the esterification of PBSu [16], the polycondensation reaction was also omitted. The equilibrium constants K_i, $i=1$–5 (or the $k_i^{\prime}$, $i=1$–5) need not to be evaluated since according to the assumptions made the reverse reaction rates are zero [$(W)=0$ in the liquid phase]. From the above analysis the number of parameters that need to be evaluated is only two, namely k_1 and k_6.

4. Results and discussion

Initially, the assumption is tested that succinic acid can act as its own catalyst in the esterification reaction. In Fig. 1, the experimental results on the esterification of PPSu are compared to the theoretical model predictions using kinetic rate constant that are either acid-catalyzed (dashed and dotted lines) or not (solid line). As it can be seen, the simulation of the experimental data by the theoretical model is very good when the kinetic rate constants used are not acid catalyzed. However, when the kinetic rate constants are assumed to be acid catalyzed using Eqs. (26) and (27) the experimental data are not predicted equally well. Using values to accurately predict the initial rate data, the final data are underestimated. In contrast, when such values are used to predict the final experimental data, the initial data are overestimated. Thus, it was concluded that in the synthesis of the poly(alkylene succinates) studied here the presence of the metal catalyst TBT leads to a poor activity of self-catalyzed acid. This was also observed for PBSu by Park et al. [16]. Therefore, for the rest of the paper Eqs. (26) and (27) are not used and only parameters k_1 and k_6 need to be estimated. The values of these parameters were calculated for every different system studied from fitting to the experimental data. The final values are reported in Table 2. Notice that these values are correct only for the specific catalyst type.

The effect of the catalyst molar ratio on the rate of the PPSu esterification reaction is examined next. Fig. 2, shows the variation of extent of the esterification reaction measured from the amount of water collected, versus time at several molar ratios of TBT/SA. TBT was selected as an esterification

Table 2
Numerical values of the kinetic rate constants

Polymer	Symbol used	Catalyst amount ($\times 10^4$ mol TBT/mol SA)	$k_1=k_2$ ($\times10^3$ L/mol min)	$k_3=k_4$ ($\times10^3$ L/mol min)	k_6 ($\times10^3$ L/mol min)
Poly(propylene succinate)	PPSu(H)	1.5	1.5	0.75	1.0
Poly(propylene succinate)	PPSu(T)	3.0	2.2	1.1	0.8
Poly(propylene succinate)	PPSu(D)	6.0	3.0	1.5	0.7
Poly(ethylene succinate)	PESu	3.0	1.8	0.9	0.6
Poly(butylene succinate)	PBSu	3.0	2.7	1.35	1.1

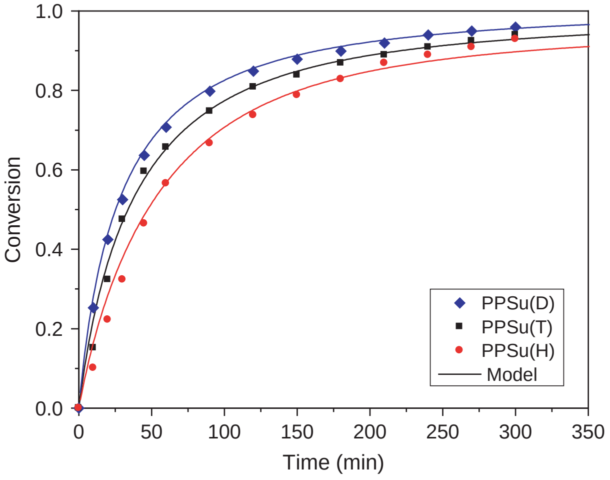

Fig. 2. Conversion (X_w) versus time for the esterification reaction of PPSu at 190 °C with different amounts of added catalyst. Experimental data (discrete points) and theoretical model simulation results.

catalyst since it was observed that it was the most effective catalyst in the synthesis of poly(propylene terephthalate) [19]. The best-fitting values of the parameters k_1 and k_6 are reported in Table 2. From Fig. 2, it is obvious that the theoretical model simulates the experimental data very well at all catalyst amounts. As it was also reported for PBSu [16], an increase in the catalyst concentration leads to increased reaction rates. Also the time required for 50% completion of the reaction decreases with the increase of the concentration of TBT. The values measured were approximately 47, 33 and 25 min for 1.5×10^{-4}, 3×10^{-4} and 6×10^{-4} mol TBT/mol SA, respectively. Furthermore, a correlation between the kinetic rate constant of the basic esterification reaction, k_1 and the catalyst concentration is presented in Fig. 3. It was observed that when plotting k_1 versus the catalyst concentration in a double logarithmic plot a very good straight line was obtained. The slope of the straight line was approximately equal to 0.5 and the equation thus calculated was: $k_1 = 10^{-0.91}(\text{mol TBT/mol SA})^{0.5}$. Therefore, it seems that k_1 correlated with the square root of the catalyst concentration. Very interesting to note, that

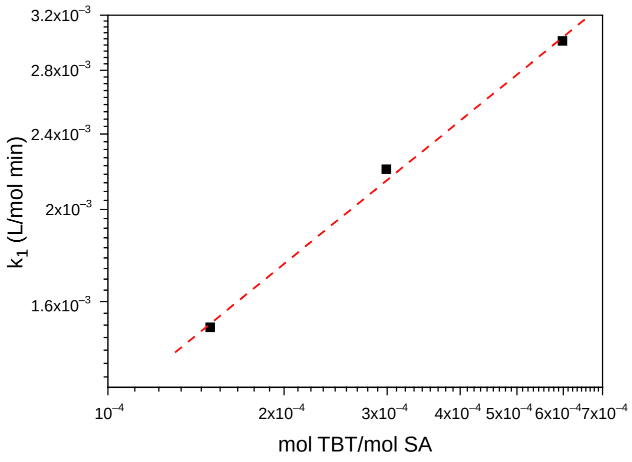

Fig. 3. Kinetic rate constant of the main esterification reaction, k_1, as a function of the molar ratio of TBT/SA for the esterification of PPSu at 190 °C.

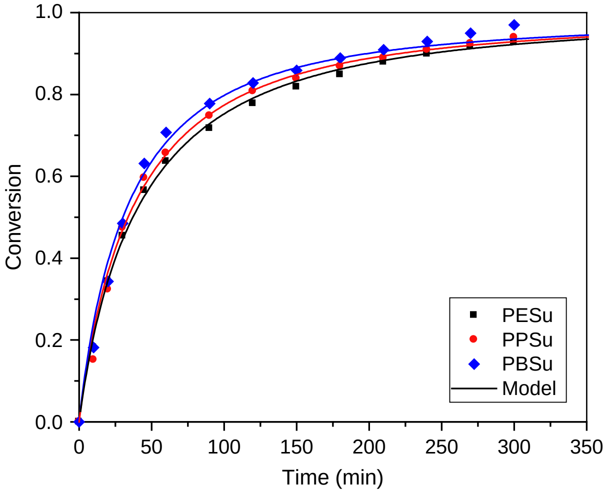

Fig. 4. Conversion (X_w) versus time for the esterification reaction of PESu, PPSu and PBSu at 190 °C and 3×10^{-4} mol TBT/mol SA. Experimental data (discrete points) and simulation results.

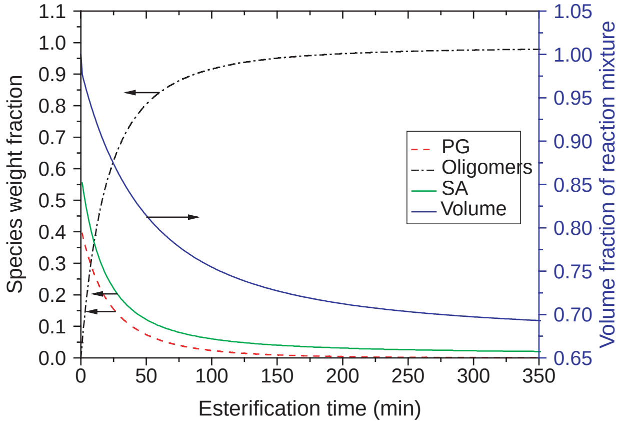

Fig. 5. Normalized weight fraction of SA, PG and oligomers, as well as volume fraction of reaction mixture as a function of time for the esterification of PPSu at 190 °C.

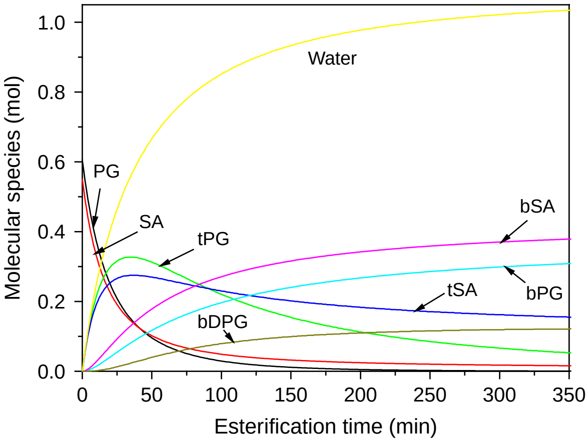

Fig. 6. Mole number of all molecular species present in the reactor as a function of time for the esterification of PPSu at 190 °C.

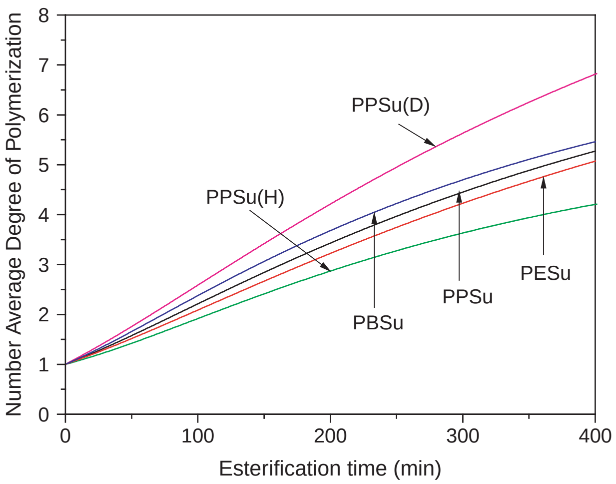

Fig. 7. Number average degree of polymerization as a function of esterification time for all poly(alkylene succinates) studied.

for PBSu an almost equal catalyst dependence (i.e. 0.51 from Fig. 11 in Ref. [16]) was observed in literature.

The effect of the type of glycol used (i.e. EG, PG or BG) on the esterification reaction is examined next. Results on the water conversion as a function of time appear in Fig. 4. It is seen that use of BG leads to slightly higher reaction rates than PG, which in turn is also slightly faster compared to EG. Again the theoretical simulation model fits the experimental data very well. The kinetic parameters evaluated are reported in Table 2. As it was expected k_1 increases in the order PBSu > PPSu > PESu.

Some typical simulation results from the solution of the theoretical model are presented next. In Fig. 5 the normalized weight fraction of SA, PG and oligomers during the PPSu esterification reaction is plotted, as a function of time. It is noted that PG is consumed first, while an amount of SA remains finally unreacted. The amount of oligomers initially increases fast, while afterwards it reaches a plateau. In the same figure, the change in the reaction volume during esterification is presented as a fraction relative to the initial volume. A decrease in volume is observed as a result of the continuous removal of water. Furthermore, the change in moles of all molecular species present in the reactor as a function of time is plotted in Fig. 6. It is interesting to note that the moles of tSA and tPG initially increase with time but then gradually decrease leading to the production of bSA and bPG, which are not initially produced. The amount of bDPG produced is rather low while it begins to appear only after 20 min of reaction time.

Theoretical results coming from Eq. (25) of the model on the average degree of polymerization as a function of esterification time is shown in Fig. 7 for all different polyesters studied. From this figure it is evident that only oligomers are produced during the esterification reaction (first step in polyester synthesis), since the maximum number average degree of polymerization reached is in between 4 and 7. It is interesting to point that different glycol used does not influence

Table 3
Intrinsic viscosity, IV, number average molecular weight, $\bar{M}_n$, polydispersity, $\bar{M}_w/\bar{M}_n$ and carboxyl number, [–COOH], of PPSu prepared using different catalyst amounts at different polycondensation temperatures

Polycondensation temperature (°C)	PPSu (H)				PPSu (T)				PPSu (D)			
	IV (dL/g)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	[–COOH] (equiv/10^{-6})	IV (dL/g)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	[–COOH] (equiv/10^{-6})	IV (dL/g)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	[–COOH] (equiv/10^{-6})
T_{in}[a]	0.08	–	–	996	0.08	–	–	1301	0.09	–	–	948
140	0.09	–	–	787	0.10	–	–	952	0.12	–	–	877
170	0.16	4250	2.6	279	0.17	4450	2.4	522	0.18	5350	2.0	573
200	0.32	10170	2.0	67	0.33	11380	2.6	82	0.34	12540	1.8	85
230	0.44	13440	2.0	75	0.46	14450	2.1	22	0.48	15480	1.9	18

[a] T_{in} refers to experimental data measured after the esterification step and before the start of polycondensation.

Table 4
Intrinsic viscosity, IV, number average molecular weight, $\bar{M}_n$, polydispersity, $\bar{M}_w/\bar{M}_n$ and carboxyl number, [–COOH], of PESu and PBSu prepared at different polycondensation temperatures

Polycondensation temperature (°C)	PESu				PBSu			
	IV (dL/g)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	[–COOH] (equiv/10^{-6})	IV (dL/g)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	[–COOH] (equiv/10^{-6})
T_{in}[a]	0.08	–	–	942	0.08	–	–	755
170	0.15	3560	2.8	178	0.15	3650	2.8	325
200	0.35	11,250	2.2	39	0.34	11,100	2.1	19
230	0.53	17,100	2.6	16	0.51	16,530	2.5	18
250	0.66	21,480	2.5	21	0.65	22,370	2.4	26

[a] T_{in} refers to experimental data measured after the esterification step and before the start of polycondensation.

much the number average degree of polymerization values of the oligomers produced during the esterification step. In contrast, these values are affected much from the amount of catalyst used, with larger catalyst molar ratio giving polymer with bigger average molecular weight.

In order to test these findings the average molecular weight of the final polyesters produced after the polycondensation step, was measured using either the intrinsic viscosity, or the gel permeation chromatography. From the results presented in Table 3 it is obvious that an increase in the catalyst concentration (or better the molar ratio of catalyst over SA) leads to increased values of the final polyester intrinsic viscosity as well as number average molecular weight. The same trend was observed at all different polycondensation temperatures examined. The polydispersity of the molecular weight distribution does not seem to follow any clear tendency with values in the vicinity of 2.0. This is a value required by Flory's most probable distribution for step polymerization at large extents of reaction [15]. Values very different than 2 are rather attributed to experimental measurement errors. Also, the results of the carboxyl number values cannot be exploited since in some temperatures they seem to increase with the amount of catalyst (e.g. 170 or 200 °C) and in others to decrease (e.g. 230 °C). A comparison of the average molecular weight values of the final polyester, PESu, or PBSu produced at different polycondensation temperatures is illustrated in Table 4. As it can be seen there is not a clear trend of these values coming thus to the conclusion that within experimental error approximately the same average molecular weight is obtained independent of the diol used. In contrast, polycondensation temperature affects very much polyester average molecular weight with $\bar{M}_n$ values to increase from approximately 3500 at 170 °C to as high as 22,000 at 250 °C. This is readily understood because the polycondensation rate increases with increasing temperature [15]. As the temperature is increased, the mobility and activity of the chain ends are also increased, resulting in an increased overall forward reaction rate and eventually an increase in the polymer average molecular weight. This was observed in all different polyesters examined in this study.

Finally, the predictive capabilities of the model developed are illustrated by examining the effect of the monomer initial molar ratio on the conversion of SA and PG, the number average degree of polymerization of the oligomers formed and the molar fraction of dipropylene glycol produced. Fig. 8 shows how the fractional conversion of total acid end groups (8a), and mole fraction of the unreacted succinic acid (8b) and propylene glycol (8c) varies with reaction time at five different initial monomer feed ratios (PG/SA = 1.1, 1.3, 1.5, 2.0 and 3.0). It is observed that as the PG/SA ratio is increased SA is completely consumed at shorter reaction times, while a large amount of PG remains unreacted. Moreover, as the PG/SA ratio increases the conversion of total acid end groups gradually increases, as it was reported for similar systems (e.g. transesterification of dimethyl terephthalate with ethylene glycol [28] and terephthalic acid with ethylene glycol [17]). This indicates that more PG is available for the esterification reactions. It is also shown that the higher the ratio, the higher the final conversion reached. However, more PG hinders the polycondensation reactions and lowers the number average degree of polymerization (NADP) at a fixed conversion of acid end groups, as it is illustrated in Fig. 9. At 85% conversion of acid end groups NADP decreases from a value of approximately 6 at a PG/SA ratio equal to 1.1 to only 1.5 at a value of

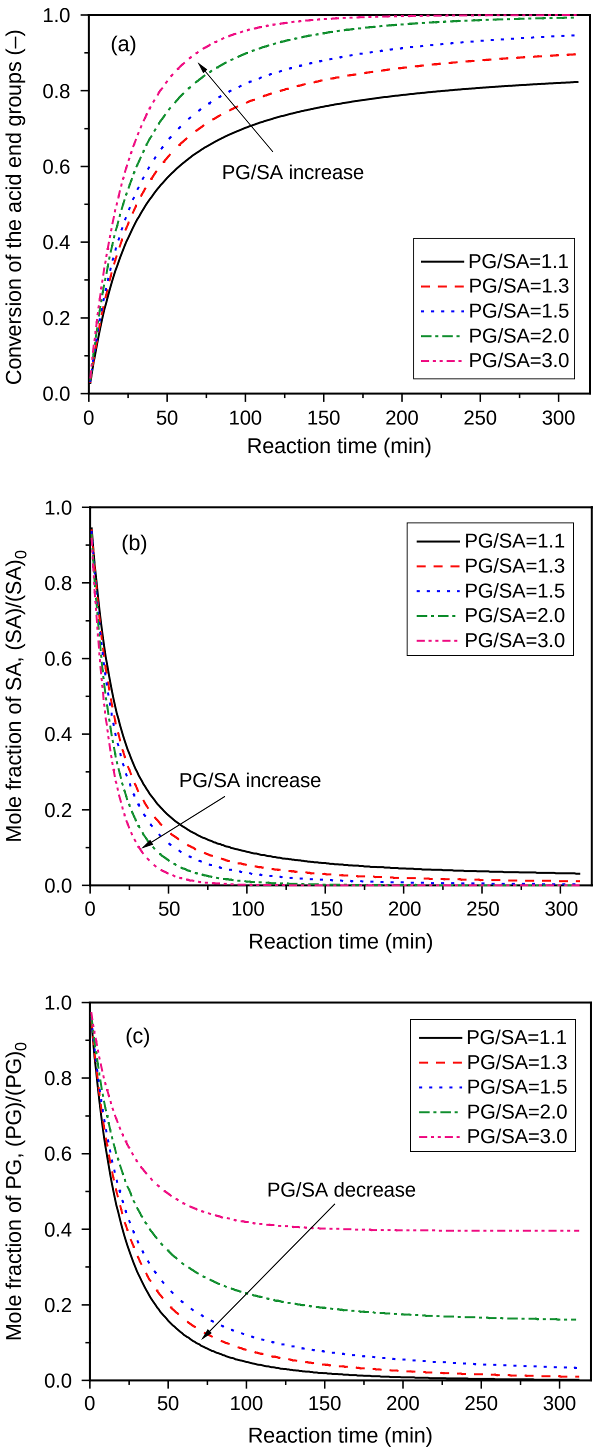

Fig. 8. Effect of the monomer feed ratio on the conversion of the acid end groups (a), molar fraction of unreacted succinic acid (b) and propylene glycol (c) as a function of time in the esterification of PPSu at 190 °C.

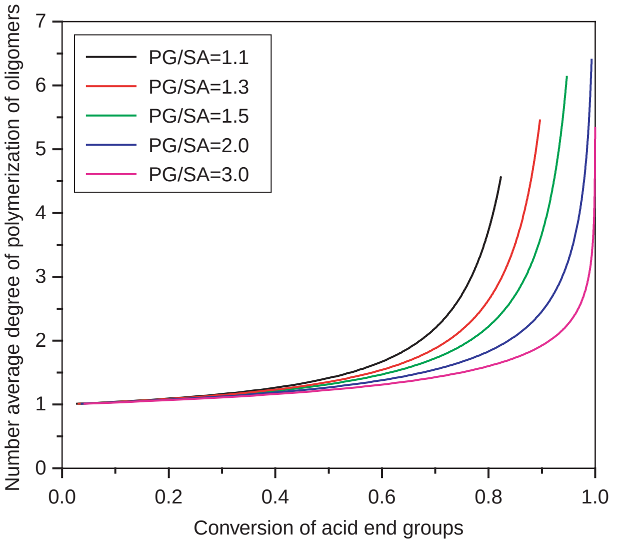

Fig. 9. Effect of the monomer feed ratio on the number average degree of polymerization of the oligomers produced plotted versus the conversion of the acid end groups (PPSu at 190 °C).

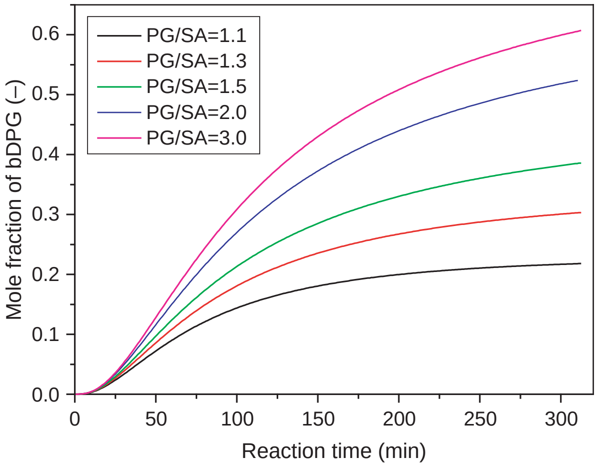

Fig. 10. Effect of the monomer feed ratio on the bDPG formation for PPSu at 190 °C. The mole fractions are normalized with respect to the initial moles of SA.

PG/SA = 3.0. This is a crucial factor that must be taken into consideration in the polycondensation of aliphatic polyesters since a low NADP results in polyesters with very low average molecular weight and thus having inferior mechanical properties. Besides, an increase in the PG/SA molar ratio leads to the formation of polymers containing an increased amount of groups with ether linkages (bDG) produced from the side reaction (7). As it is seen in Fig. 10 the mole fraction of bDPG increases from 0.2 to 0.6 as the PG/SA ratio increases from 1.1 to 3.0.

5. Conclusions

In this investigation, three poly(alkylene succinates) 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 esterification reaction has been developed and applied successfully in the simulation of all experimental data. Values for the kinetic rate constants are proposed for different catalyst molar ratios and comonomer chemical structure. Also, the effect of the polycondensation temperature on the average molecular weight of the polyesters produced is examined.

It was found that in the synthesis of the poly(alkylene succinates) studied the presence of the metal catalyst TBT leads to a poor activity of self-catalyzed acid. Also, the main kinetic rate constant of the esterification reaction k_1, seems to correlate well with the square root of the catalyst concentration.

Different glycol used does not influence much the number average degree of polymerization values of the oligomers produced during the esterification step. In contrast, these values are affected by the amount of catalyst used, with larger catalyst molar ratio giving polymer with bigger average molecular weight. These results were also verified from measurements of the final polymer average molecular weight obtained at different polycondensation temperatures.

Finally, from theoretical simulation results it was found that higher initial ratios of PG to SA are useful to increase the esterification reaction rates. However, they lower the NADP of the oligomers formed at a fixed conversion of acid end groups and also increase the amount of bDPG produced. Therefore, an optimum value can be selected.

References

[1] Guillet J. In: Scott G, Gilead D, editors. Degradable polymers, principles and applications. London: Chapman and Hall; 1995.
[2] Albertsson A-C, Ljungquist O. J Macromol Sci Chem 1986;A23:411.
[3] Ferré T, Franco L, Rodríguez-Galán A, Puiggalí J. Polymer 2003;44:6139.
[4] Carothers WH. J Am Chem Soc 1929;51:2548.
[5] Karayannidis G, Sideridou I, Zamboulis D, Stalidis G, Bikiaris D, Lazaridis N, et al. Angew Makromol Chem 1991;192:155.
[6] Rafler G, Dahlamann J. Acta Polym 1992;43:91.
[7] Seretoudi G, Bikiaris D, Panayiotou C. Polymer 2002;43:5405.
[8] Bikiaris DN, Papageorgiou GZ, Achilias DS. Polym Degrad Stab 2006;91:31.
[9] Yang J, Zhang S, Liu X, Cao A. Polym Degrad Stab 2003;81:1.
[10] Chrissafis K, Paraskevopoulos KM, Bikiaris DN. Thermochim Acta 2005;435:142.
[11] Chrissafis K, Paraskevopoulos KM, Bikiaris DN. Polym Degrad Stab 2006;91:60.
[12] Roupakias CP, Bikiaris DN, Karayannidis GP. J Polym Sci, Part A: Polym Chem 2005;43:3998.
[13] Papageorgiou GZ, Bikiaris DN. Polymer 2005;46:12081.
[14] Liu Y, Ranucci E, Soderqvist, Lindblad M, Albertsson A-C. J Polym Sci, Polym Chem 2001;39:2508.
[15] Flory PJ. Principles of polymer chemistry. Ithaca, New York: Cornell University Press; 1953.
[16] Park SS, Jun HW, Im SS. Polym Eng Sci 1998;38(6):905.
[17] Kang CK, Lee BC, Ihm DW. J Appl Polym Sci 1996;60:2007.
[18] Kang CK, Lee BC, Ihm DW, Tremblay DA. J Appl Polym Sci 1997;63:163.

[19] Karayannidis GP, Roupakias CP, Bikiaris DN, Achilias DS. Polymer 2003;44:931.
[20] Iwaya Y, Mukai K, Kawanishi M, Nishinohara M., US patent 5504148, 1996.
[21] Günther B, Zachmann HG. Polymer 1983;24:1008.
[22] Solomon OF, Ciuta IZ. J Appl Polym Sci 1962;6:683.
[23] Yamada T. Polym React Eng 1996;4(1):1.
[24] Rieckmann Th, Volker S. Chem Eng Sci 2001;56:945.
[25] Otton J, Ratton S. J Polym Sci, Polym Chem Ed 1988;26:2183.
[26] Lei GD, Choi KY. Ind Eng Chem Res 1992;31:769.
[27] Ravindranath K, Mashelkar RA. Chem Eng Sci 1986;41:2969.
[28] Choi KY. Polym Eng Sci 1987;27:1703.