Crystallization and melting behavior of three biodegradable poly(alkylene succinates). A comparative study

George Z. Papageorgiou, Dimitris N. Bikiaris *

Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Macedonia, Greece

Abstract

Polyesters based on succinic acid and respective aliphatic diols, with 2–4 methylene groups were synthesized by melt polycondensation. Crystallization and melting behaviour of samples having the same molecular weight were studied. The odd–even effect was observed for the melting temperatures of these polymers. Poly(propylene succinate) exhibited the slower crystallization rates and lower degree of crystallinity, among these polyesters. In contrast poly(butylene succinate) showed the faster crystallization rates and higher degree of crystallinity. Multiple melting of the isothermally crystallized samples was attributed to partial melting re-crystallization and re-melting, as was revealed by MTDSC measurements and observations at fast DSC heating scans. The equilibrium melting points were found to be 114, 133.5 and 58 °C for PESu, PBSu and PPSu respectively. Also, the corresponding values for enthalpy of fusion were 180, 210 and 140 J/g. Spherulitic growth rates were analysed and the regime transition of PESu and PBSu was studied.
© 2005 Elsevier Ltd. All rights reserved.

Keywords: Poly(propylene succinate); Poly(ethylene succinate); Poly(butylene succinate)

1. Introduction

Biodegradable polymers have received much attention during last two decades. Among biodegradable polymers aliphatic polyesters have attracted considerable attention due to their combination of biodegradability, biocompatibility and physical or chemical properties, which are comparable with some of the extensively used polymers like LDPE, PP, etc. Poly(butylene succinate) (PBSu) and poly(ethylene succinate) (PESu) are two of the most important biodegradable polyesters and they are also commercially available. However, relatively few works dealing with poly(butylene succinate) (PBSu) have been reported [1–9]. Also a limited number of papers on poly(ethylene succinate) (PESu) have been published [10–14]. Synthesis of poly(propylene succinate) (PPSu) oligomers was only recently described in two papers [15,16].

In our previous work we found that poly(propylene succinate) exhibits enhanced enzymatic degradation rates comparing to PESu and PBSu [17]. It has been reported that the distance between ester groups in polyesters affects their

degradation rates [18–20]. Furthermore, degradation rates are affected by the degree of crystallinity, spherulite size and lamellar structure [21–24].

Early studies on PESu and PBSu reported multiple melting for these polymers [8,12]. Multiple melting has been observed for polyesters and other polymers [25–33]. Interpretation of multiple melting endotherms in differential scanning calorimeter (DSC) traces of semi-crystalline polymers is difficult. The most common concepts concerning multiple melting behaviors of polymers are the melting of crystals of different stability (dual morphology mechanism) [34], and the melting recrystallization, remelting process (reorganization mechanism) [35]. The dual morphology mechanism is based on the evidence of two or more different crystalline structures existing in the crystallized polymers, i.e. (a) two or more crystal modifications [36], (b) at least two populations of lamellae of different stabilities [37], or (c) different crystalline morphologies [38]. These entities have already been formed during the isothermal crystallization before DSC heating scan. Structures like secondary (thinner) lamellae may melt at lower temperature than primary lamellae, giving rise to multiple endotherms in DSC traces. There are two variants of this model: the dual-lamellar stack model and the insertion model. The dual-lamellar stack model suggests that the thin and thick lamellae exist in different stacks [39]. According to the lamellar insertion model the thin lamellae appear between

* Corresponding author. Tel.: +30 231 099 7812; fax: +30 231 099 7769.
E-mail address: dbic@chem.auth.gr (D.N. Bikiaris).

thick lamellae in the same stack [40]. The reorganization mechanism suggests that the crystallization produces initially crystals of a lower degree of perfection or thinner lamellae, which can melt and recrystallize during heating, scan to yield crystals of better perfection or greater thickness [41].

In this work, PESu, PBSu and PPSu samples of the same molecular weight were prepared in order to study their properties in a comparative manner, and to correlate crystalline morphology with biodegradation, since there are differences in biodegradation rates of the polymers. Crystallization rates, as well as the melting behavior of the isothermally crystallized samples during subsequent heating was analyzed with standard DSC, and step scan modulated temperature DSC, wide angle X-ray diffraction (WAXD) and polarizing optical microscopy (POM). High rates can be applied in power compensated DSC, since superheating effects are minimized, especially by using ultra-low polymer masses. Changes in polymer morphology during scanning can be prevented at fast scanning rates and thus the original morphology of the specimens can be effectively detected [42]. Modulated temperature DSC techniques like step scan DSC, which applies true isothermal steps between short heating steps, is appropriate to distinguish endothermic phenomena like melting, from exothermic ones like re-crystallization. Finally, thermodynamic data of the polymers were calculated and spherulitic growth rates were analyzed.

2. Experimental

The polyesters studied in this work were synthesized from succinic acid and proper diol. 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. Tetrabutyl titanate catalyst of analytical grade and polyphosphoric acid (PPA) used as heat stabilizer were purchased from Aldrich Chemical Co. All the other materials and solvents which were used for the analytical methods were of analytical grade.

The aliphatic polyesters were prepared by the two-stage melt polycondensation method (esterification and polyconden-sation) in a glass batch reactor. In brief, the proper amount of succinic acid and appropriate glycols in a molar ratio 1/1.1 and the catalyst Ti(OBu)$_4$ were charged into the reaction tube of the polyesterification apparatus. 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). This first step (esterification) is considered to complete after the collection of theoretical amount of H$_2$O, which was removed from the reaction mixture by distillation and collected in a graduate cylinder.

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 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 slowly increased to 230 °C while stirring speed was increased at 720 rpm. The polycondensation continued for about 60 min for all prepared polyesters. After the polycondensation reaction was completed, the polyesters were easily removed, milled and washed with methanol.

Intrinsic viscosity [η] was measured using an Ubbelohde viscometer at 25 °C in chloroform. Among a series of polyester samples three polyesters with intrinsic viscosity [η] = 0.28 dL/g were selected. Thus, influence of molecular weight variation on the polyester behaviour was diminished. In practice polyesters had average molecular weight M_n of 6800–6900 g/mol, as was measured by GPC.

A Perkin–Elmer, Pyris 1 differential scanning calorimeter (DSC), calibrated with indium and zinc standards, was used. Samples of 5 ± 0.1 mg were used in tests. They were sealed in aluminium pans and heated to 30 °C above the melting point at a heating rate 20 °C/min. The samples were held at that temperature for 5 min in order to erase any thermal history. For isothermal crystallizations the sample was rapidly cooled to 20 °C above the crystallization temperature and finally cooled to that at a rate 50 °C/min, to achieve equilibration of the instrument. Heating rate was in most tests 20 °C/min. If some other rate was used this will be discussed in the specific section. Fresh sample was used in each run.

Modulated temperature DSC experiments were also carried out using the same Pyris 1 DSC and the Perkin Elmer step scan software. Step-Scan DSC is a temperature modulated DSC technique that operates, in conjunction with the power compensation DSC. The approach applies a series of short interval heating and isothermal steps to cover the temperature range of interest. This requires a DSC with very fast responsiveness to achieve short interval linear and isothermal steps. The use of ultra low mass furnaces with the power compensation DSC ensures very fast response time. With the step scan DSC approach, two signals are obtained. Thermo-dynamic C_p signal represents the reversible aspects of the material, while the isothermal signal reflects the irreversible nature of the sample during heating. Because the sample is either heated or held isothermally (true isothermal), the step scan DSC approach is straightforward. High rate DSC is also applicable with power compensation DSC, since high resolution and low thermal lag is required. High rates of 100 °C/min up to 500 °C/min minimize time for changes in morphologies of the samples during scanning and thus the original morphology can be effectively detected [42].

The crystalline structure of the polyester samples was investigated by wide angle X-ray diffraction (WAXD) using a PW 1050 powder diffractometer with Cu K$_\alpha$ radiation (λ = 0.154 nm).

The spherulite growth rates of polyester samples were recorded using a polarizing optical microscope (POM) (Nikon, Optiphot-2) equipped with a Linkam THMS 600 heating stage and a TP 91 control unit. Heating rates were 10 °C/min. Microphotographs were taken using a JVC TM-1500 E (CV) colour video monitor and a SONY UP-1200 AEPM video

printer. For the isothermal crystallization experiments the conditions were very similar as for the DSC ones, i.e. thin polyester films were initially sandwiched between two microscopic cover glasses melted on the hot stage to 30 °C above melting temperature, rapidly cooled to the crystallization temperatures and then held at that temperature to crystallize. The sizes of spherulites during crystallization were recorded and the crystal growth rates were calculated from the slopes of the plots of spherulite radius vs time.

3. Results and discussion

3.1. Characteristic transitions and enthalpy of fusion

In order to study the thermal behaviour of PESu PBSu and PPSu first the transition temperatures were measured using DSC. To observe the glass transition of the polyesters, amorphous samples were obtained by melt quenching in liquid nitrogen. As can be seen in Fig. 1, traces of the amorphous samples showed clear glass transition. The glass transition temperature of the polymers decreased with increasing the number of methylene groups of the respective monomer diol used in synthesis. Thus, the T_g for PESu was -11.5 °C, while it was found to be -35 and -43.9 °C for PPSu and PBSu respectively, for a heating rate 20 °C/min. No cold-crystallization was observed for PPSu at heating the amorphous sample at this rate, since its crystallization is very slow, and thus no melting was recorded till 70 °C. However, the melting

Fig. 1. DSC traces for quenched samples of PESu, PBSu and PPSu. Heating rate 20 °C/min.

temperature for a series of semi-crystalline PPSu samples was found to range between 42 and 50 °C, depending on the thermal history of the samples. On the other hand, PESu showed a broad cold-crystallization exothermic peak from 30 up to 75 °C, which was accompanied by a second exothermic peak, probably due to re-crystallization. Quenched PBSu showed a sharp cold-crystallization peak beginning at about -18 °C. This crystallization process seemed to be almost completed before reaching 10 °C, but some slower exothermic phenomena, were also observed till final melting. These should probably be attributed to some supplementary crystallization or reorganization process. The melting temperatures of the cold-crystallized PESu and PBSu were 102 and 112 °C respectively. Consequently, referring to the melting temperature of poly(alkylene succinate)s, the well-known odd-even effect holds. Also, these first DSC traces for the quenched polymers indicate that crystallization rates become faster as the methylene groups of the respective diol increase from 2 to 4.

As one can see at Table 1, different values of heat of fusion were measured for isothermally crystallized samples of the three polymers. In general PPSu showed lower heat of fusion, in contrast to PBSu. The enthalpies of fusion for the pure crystalline polymers were calculated. For this purpose a series of samples having different degrees of crystallinity were prepared by isothermal treatment and WAXD and DSC were used to determine their crystallinities (X_c) and heats of fusion (ΔH), respectively. The crystallinity values were calculated from WAXD patterns using the relative areas under the crystalline peaks, A_c, and the amorphous background, A_{am}, using

$$X_c = \left(1 + \frac{A_{am}}{A_c}\right)^{-1} \tag{1}$$

according to Hay et al. [43].

Fig. 2 shows the WAXD patterns observed for three of these semi-crystalline samples. WAXD patterns for PESu and PBSu corresponded to the α-crystal structures of these polymers reported in literature [2,10]. However, there is no bibliographic report for the crystalline structure of PPSu up to know, as proved by our survey. We will not discuss the crystal structure of PPSu in this paper, since this study is not completed yet. Finally, from the above study it was concluded that the heat of fusion for pure crystalline PESu is about 180 ± 10 J/g (or 25.9 ± 1.4 kJ/mol), comparing to 140 ± 10 J/g (or 22.2 ± 1.6 kJ/mol) for PPSu and 210 ± 10 J/g (or 36 ± 1.7 kJ/mol) for PBSu. This ΔH_m^0 value for PBSu is close that of 200 J/g reported by others [4]. The variation of ΔH_m^0 with methylene units is similar to that for the melting points.

3.2. Crystallization rates

To compare the crystallization behaviours of poly(alkylene succinate)s, for each polymer isothermal tests in the DSC were performed at various temperatures between the respective melting and glass transition temperature, after cooling from the melt. After completion of the crystallization the relative
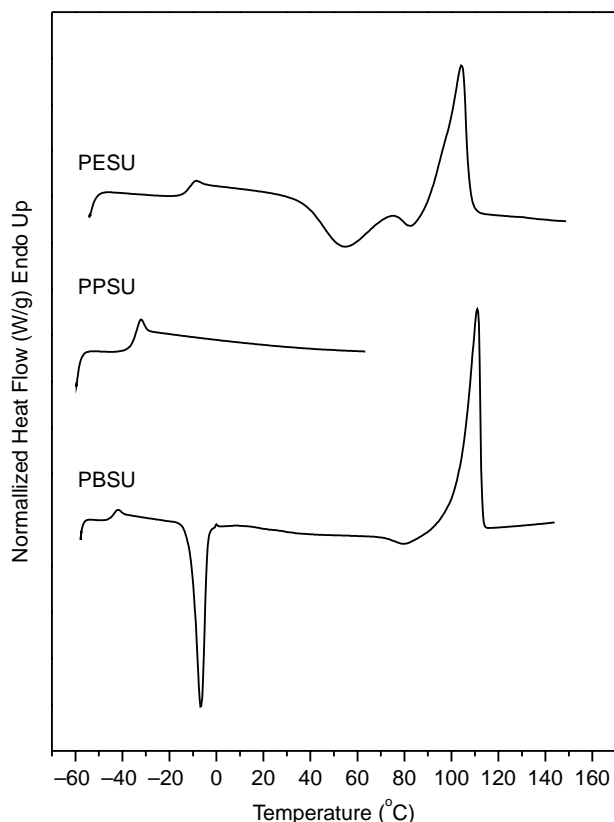
Table 1
Heats of fusion (ΔH) and crystallinity (X_c %), for isothermally crystallized samples

PESu sample	ΔH (J/g)	X_c %	PBSu sample	ΔH (J/g)	X_c %	PPSu sample	ΔH (J/g)	X_c %
20 °C, 90 min	40.7	23.7	72.5 °C, 30 min	80.6	38.3	0 °C, 90 min	13.2	9.9
30 °C 60 min	44.3	26.5	75 °C, 30 min	82.3	38.6	5 °C, 120 min	21.1	15.6
40 °C, 60 min	58.4	33.8	80 °C 60 min	86.3	40.9	10 °C, 90 min	28.0	19.3
50 °C, 60 min	53.3	30.1	85 °C, 60 min	79.7	37.5	15 °C, 90 min	23.2	15.8
60 °C, 60 min	57.4	33.4	90 °C, 180 min	86.1	40.6	20 °C, 120 min	25	18.3
70 °C, 80 min	54.1	31.0	95 °C, 480 min	73.4	34.7	25 °C, 180 min	33.4	33.4

crystallinity (X_c) vs time (t_c) plot was obtained by integration of the heat flow evolved during crystallization. Then the crystallization half-time ($t_{1/2}$) for every test, was directly measured from the X_c vs t_c plot. In Fig. 3 the isothermal crystallization half-times ($t_{1/2}$) of PESu, PPSu and PBSu as a function of crystallization temperature are compared. It is obvious that the crystallization half-times of PBSu are less than those of PESu, which in turn are shorter than those for PPSu. As can be seen, PESu and PPSu half times showed a minimum, corresponding to the faster crystallization rates. This appeared in the range between 30 and 60 °C for PESu, while for PPSu it was close to 0 °C. In contrast PBSu crystallizes rather rapidly and it is difficult to perform isothermal tests for PBSu at T_cs lower than 70 °C, since cooling from the melt in the instrument cannot effectively prevent crystallization. The enhanced crystallization rates of PBSu, comparing to the other two polymers, is

attributed to its chemical structure, and especially to its flexible butylene units. On the other hand retardation in PPSu crystallization is due to its reduced symmetry caused by the propylene units. As a matter of fact crystallization rates follow the order of the melting points of the polyesters discussed previously.

3.3. Multiple melting

For PESu and PBSu multiple melting behaviour of isothermally crystallized samples has been reported in the literature [6,7,12,44]. In this work melting behaviour of PPSu in parallel to that of PESu and PBSu is studied.

Multiple melting was observed for all of the above polymers after isothermal crystallization. WAXD study showed that for each polyester only crystals of one crystal form were generated after isothermal crystallization at a wide range of temperatures (T_cs). Thus, multiple melting cannot be related with different crystal modifications.
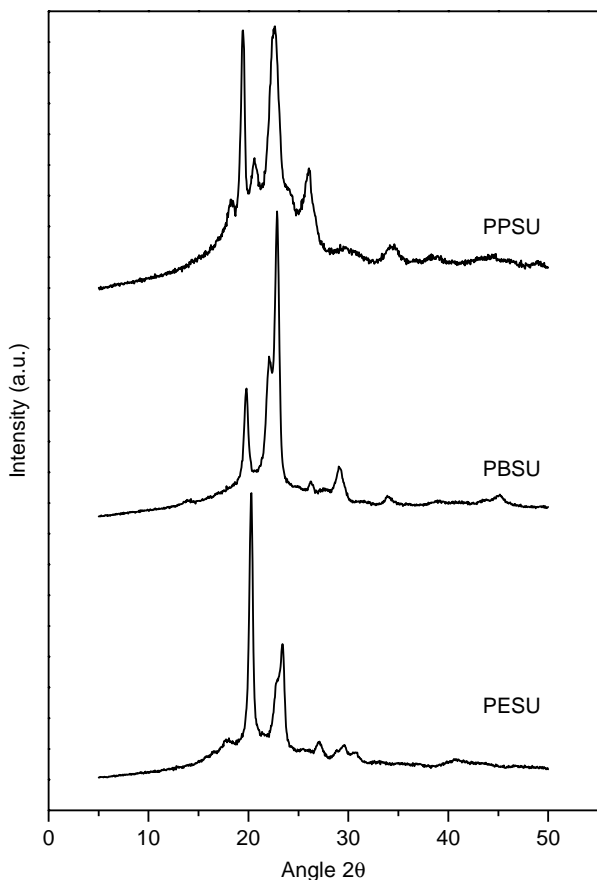

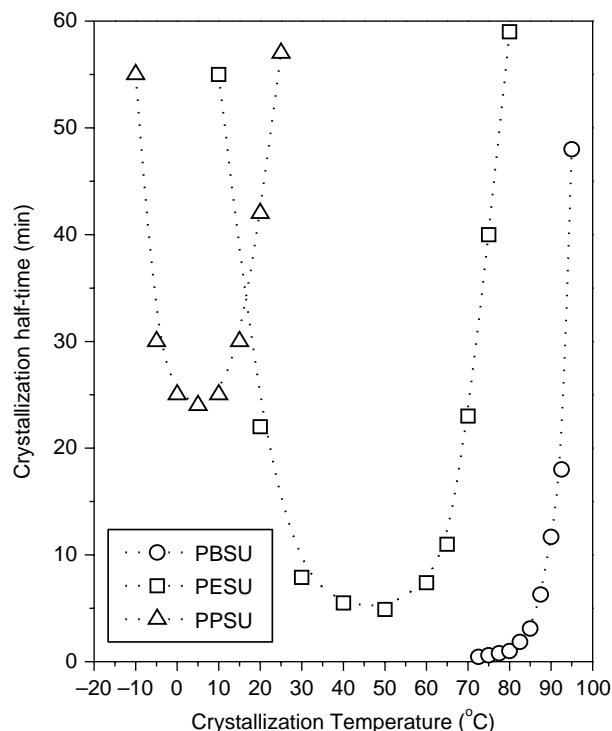Fig. 2. WAXD patterns for PESu, PBSu and PPSu.

Fig. 3. Crystallization half-time as a function of crystallization temperature for PESu, PBSu and PPSu. Data obtained directly from DSC measurements.
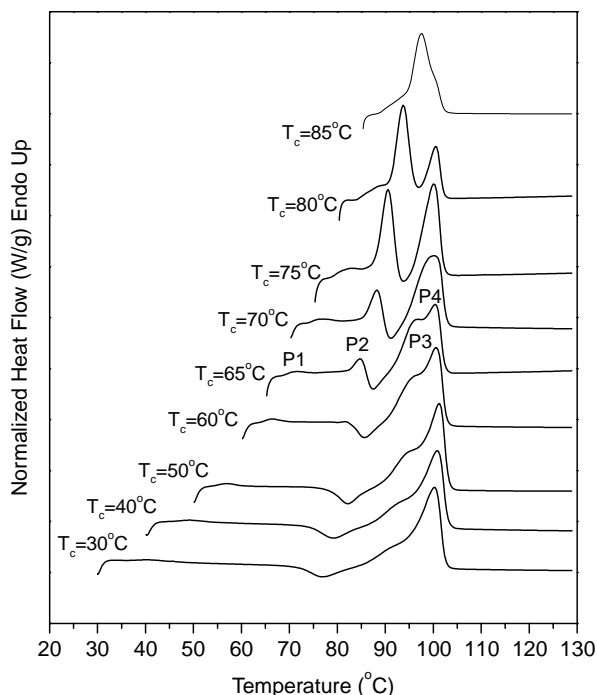
Fig. 4. DSC traces for PESu samples after isothermal crystallization at various temperatures. Heating rate 20 °C/min.

The number of melting peaks in DSC traces depended on the crystallization temperature. In Figs. 4–6 DSC heating scans recorded at 20 °C/min for PESu, PBSu and PPSu samples respectively, are shown. The samples, prior to melting, were crystallized under isothermal conditions, till the practical end of the phenomenon. As can be seen in Fig. 4, for PESu samples
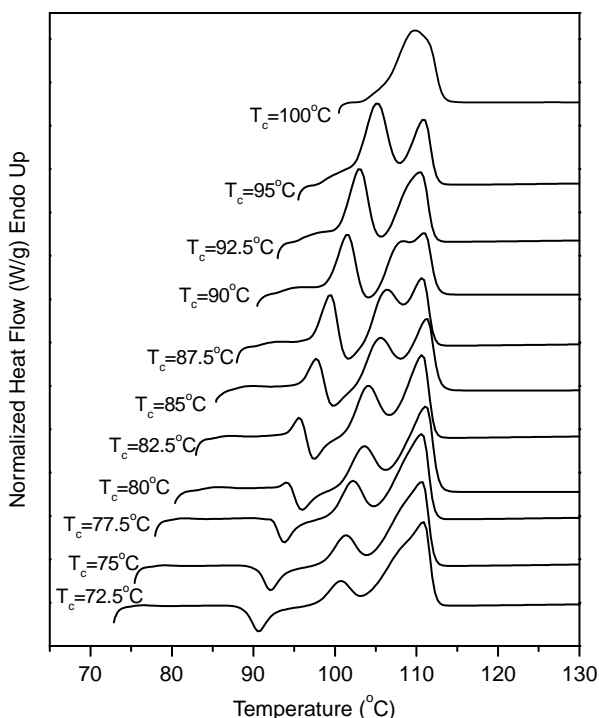

Fig. 5. DSC traces for PBSu samples after isothermal crystallization at various temperatures. Heating rate 20 °C/min.
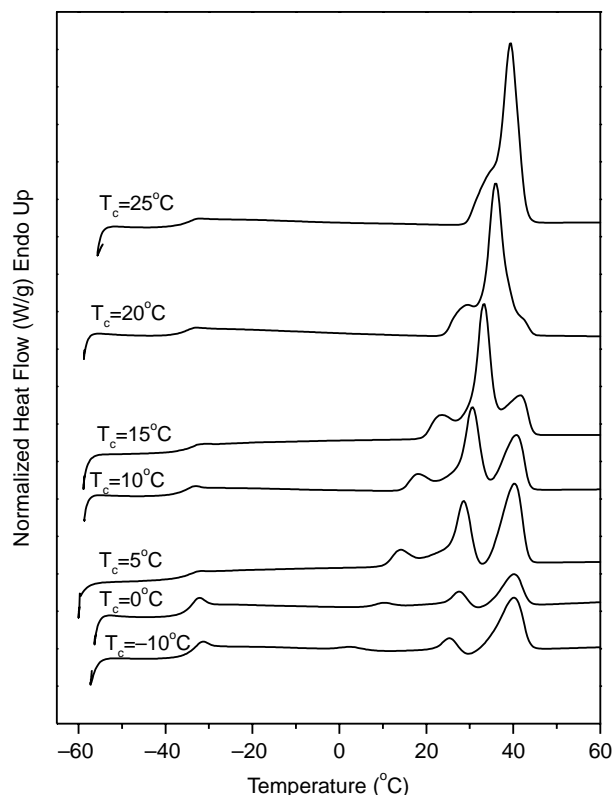

Fig. 6. DSC traces for PPSu samples after isothermal crystallization at various temperatures. Heating rate 20 °C/min.

crystallized below 65 °C, even a forth-fold melting should be supposed, though the picture is not so clear because of overlapping of melting and re-crystallization peaks. For example in the trace corresponding to $T_c = 65$ °C, from low to high temperature, the first peak is observed at about 8 °C above T_c. Usually, such a peak is referred to as annealing peak, and it is related to secondary crystals melting. However, according to Schick et al. there was no evidence for different crystal populations in PET, but instead such a peak should be associated with the balance of melting re-crystallization processes [45]. This, hereinafter, will be referred to as peak 1 and the respective peak temperature will be referred to as T_{m1}. A second melting peak marked as peak 2 appears just before re-crystallization. Two other peaks follow, the one just after re-crystallization (it is marked as peak 3), and an ultimate peak corresponding to final melting. This will be signed as peak 4. For samples crystallized at T_cs higher than 65 °C, peaks 3 and 4 coincided. This is because peak 3 increase in peak temperature with increasing T_c, while peak 4 was not affected, and is always observed at the same position. Peaks 1 and 2, increased in peak temperature, with increasing T_c. Also, peaks 3 and 4 reduced in heat of fusion with increasing T_c, in contrast to peak 2, which finally (see trace for $T_c = 80$ °C) dominated. On the other hand for samples crystallized at low T_c, re-crystallization was more pronounced and thus in fact melting peak 2 could not be easily observed. Finally, there was also a trend all the melting peaks to coincide with increasing T_c. This was because crystals of increased perfection and stability were generated at elevated temperatures and then reorganization and re-crystallization

could not take place upon heating. Since PESu did not crystallize during fast cooling, crystallizations over a wide range could be performed. Thus, under very large super-coolings (equivalently $T_c < 50\,°C$) crystallization was slow and reduced number of melting peaks was observed. At T_cs in the range between 50 and 70 $°C$, the faster crystallization rates were obtained for PESu and fourth-fold melting was observed. Crystallization at T_cs above 70 $°C$ but lower than 85 $°C$, resulted in slow rates and triple melting. At higher temperatures crystallization was very slow and melting peaks coincided and finally only one peak remained.

Similar conclusions can be extracted for the melting behaviour of PBSu, by studying traces presented in Fig. 5. Up to four peaks can be observed for that polymer. Rapid crystallization rates did not permit tests at temperatures lower than 70 $°C$.

As was referred in the above sections PPSu has very slow crystallization. In Fig. 6 the DSC heating scans of PPSu samples crystallized from the melt at temperatures ranging between -10 and 25 $°C$ are shown. In these traces the glass transition was also clearly observed even after prolonged crystallization, and this was a proof that always, low crystallinity can be achieved for PPSu. Three peaks were present in traces recorded after crystallization at low $T_c <$ 20 $°C$. The peaks, in ascending order from the view of peak temperature, will be referred to as peak 1, 2 and 3, respectively. Peak 1 is like in the case of PESu and PBSu the result of the melting re-crystallization balance. Peak 2 was the middle peak, and increased in height and heat of fusion with increasing T_c. On the other hand heat of fusion of peak 3 decreased as T_c increased, in favour of peak 2. Its location was not affected by T_c increase. However, peak temperature for both peaks 1 and 2 increased with T_c. Thus, as for the other two poly(alkylene succinate)s the peaks finally coincided.

To estimate the extent of possible re-crystallization, the effect of heating rate on peak multiplicity is usually studied for samples crystallized at a given T_c. The respective thermograms for PESu are shown in Fig. 7. In this figure it is obvious that slow heating rates resulted in extended re-crystallization and increased multiplicity of melting peaks. The peaks were well resolved. Furthermore, for slow heating rates, the peak temperature of the ultimate peak was increased as a consequence of the longer time available for crystal perfection above the T_c during heating scan. For heating at 100 $°C$/min the ultimate peak disappeared. In fact a peak was observed at about the same temperature with that of the ultimate peak 4 at heating at 20 $°C$/min. However, its peak temperature shifted upwards due to superheating effects, and thus the observed peak for heating at 100 $°C$/min corresponds to peak 3 and not peak 4 of the trace for 20 $°C$/min. This is a proof that peak 4 was associated with melting of re-crystallized material and thus it should not be related with the initial morphology generated during the isothermal stage. In contrast peak 1 should be attributed to melting of less stable crystals formed during the isothermal test. Peak 2 should be related to primary crystals generated at the isothermal step. As for the origin of crystals melting at peak 3, it is important to keep in mind that in traces
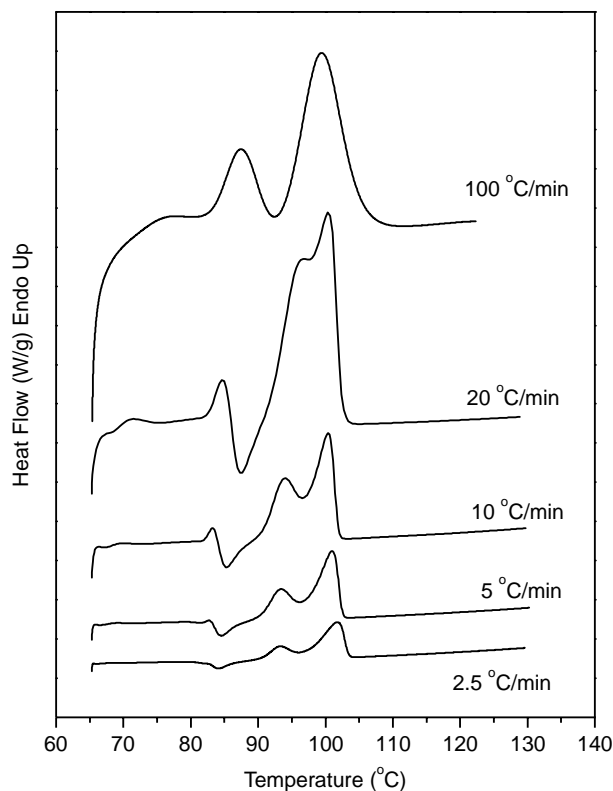

Fig. 7. Effect of heating rate on melting of PESu. All samples were crystallized at 65 $°C$ for 30 min.

for high T_c in Fig. 4, peak 3 was minimized. Thus, it was also associated with the heating process. In other words, both crystal populations melting at peak 3 and 4, appeared after a perfection process, taking place during heating scan, but they differ in stability.

Findings for PBSu were similar and will be not discussed more for briefness.

As for the effect of heating rate on the melting of PPSu samples this can be seen in Fig. 8 where thermograms obtained at different heating rates for samples crystallized at 0 $°C$ for 120 min are presented. For slow heating rates even four melting peaks were observed, as well as a re-crystallization peak. This was an evidence that re-crystallization during heating scan plays an important role in the melting behaviour of PPSu, though for this polyester re-crystallization rates are slower than for PESu and PBSu. Scanning at a rate 100 $°C$/min showed only two peaks, namely peak 1 and 2, while peak 3 disappeared. Thus, the higher temperature peak like for the other two polymers was due to melting of re-crystallized material. In contrast peak 2 is attributed to melting of primary crystals formed during isothermal crystallization.

To study the influence of time on the heat of fusion of each melting peak, the heating scans of PESu samples crystallized at 70 $°C$ for different durations are shown, in Fig. 9. For short times peak 2 as well as peaks 3 and 4 are present in traces. After prolonged crystallization peak 1 appeared, and peaks 3 and 4 coincided. Furthermore, the observed exothermic peak between peaks 2 and 3 increased in area with increasing time. This is a proof that it is due to re-crystallization and not
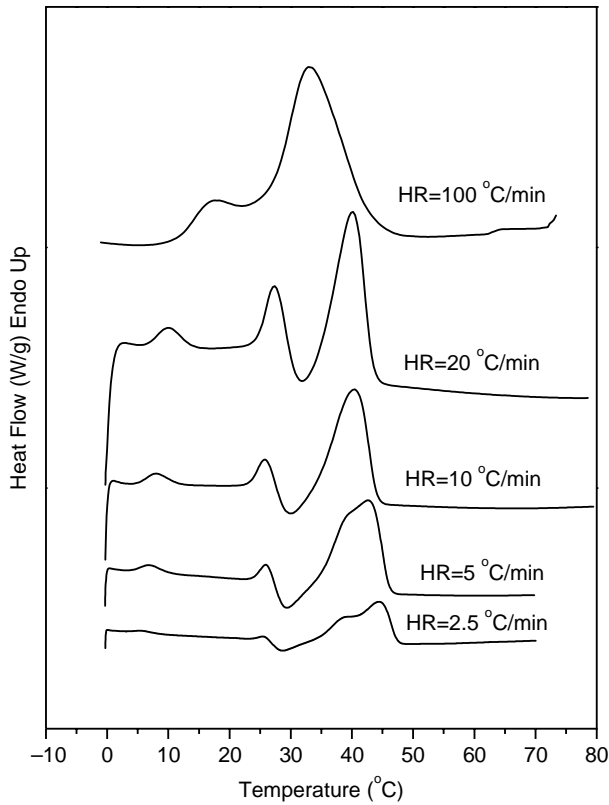
Fig. 8. Effect of heating rate on melting of PPSu. All samples were crystallized at 0 °C for 1 h.
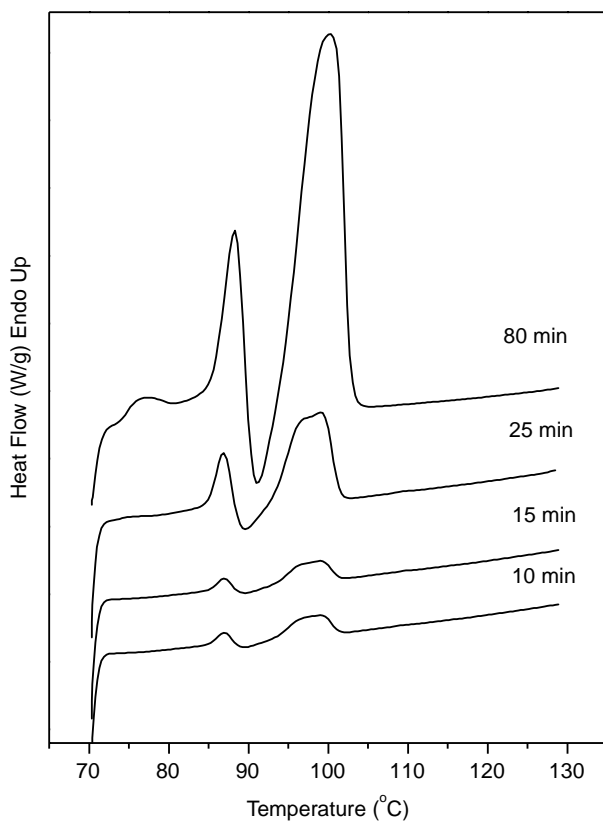

Fig. 9. Effect of crystallization time on melting of PESu. All samples were crystallized at 70 °C. Heating rate 20 °C/min.
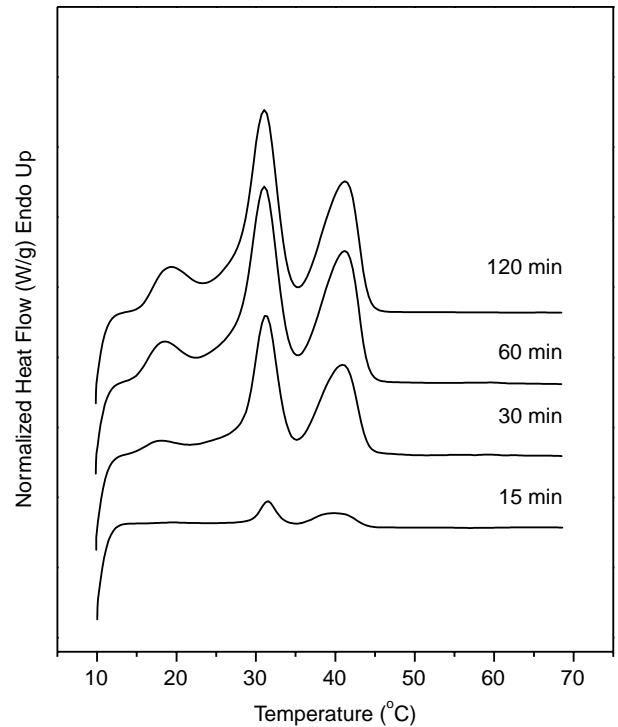

Fig. 10. Effect of crystallization time on melting of PPSu. All samples were crystallized at 15 °C. Heating rate 20 °C/min.

due to supplementary cold-crystallization. The same picture was obtained for PBSu samples crystallized at 90 °C. Besides, in Fig. 10 in which one can see the melting of PPSu samples after crystallization at 15 °C for different times, melting peak 1 is observable only after prolonged crystallization. It should be also noted that its temperature increased slightly with time. As it was also reported before, Schick et al. studied melting and reorganization of PET on fast heating and found no evidence for the formation of different populations of crystals with significantly different stability under isothermal conditions [45]. Thus, according to Schick et al., such a peak is associated with the re-crystallization processes, and its shape is determined by the balance of melting and re-crystallization.

In Fig. 11 the step scan MTDSC traces for a mean heating rate (heating-isothermal stages) 2.5 °C/min are shown for PESu samples crystallized at 60 and 70 °C and PBSu samples crystallized at 80 and 90 °C. What is important here is that melting in the reversing signal curves began at about 10 °C before the corresponding melting observed in the total curve. Furthermore, two well-distinguished re-crystallization exotherms were recorded in the non-reversing signal curves of the PESu and PBSu samples. In Fig. 11 the reversing part of the specific heat was enhanced after the second and third endotherm in the total heat flow curve. Also, this enhancement appeared at temperatures above the re-crystallization exotherm shown in the non-reversing curve. The observation of the increased reversing signal was probably because of a continuous partial melting and perfection of crystals at temperatures before their final melting. As it is well known polymer crystals formed at a temperature T_c melt at a relatively higher temperature. The conditions of the measurements as
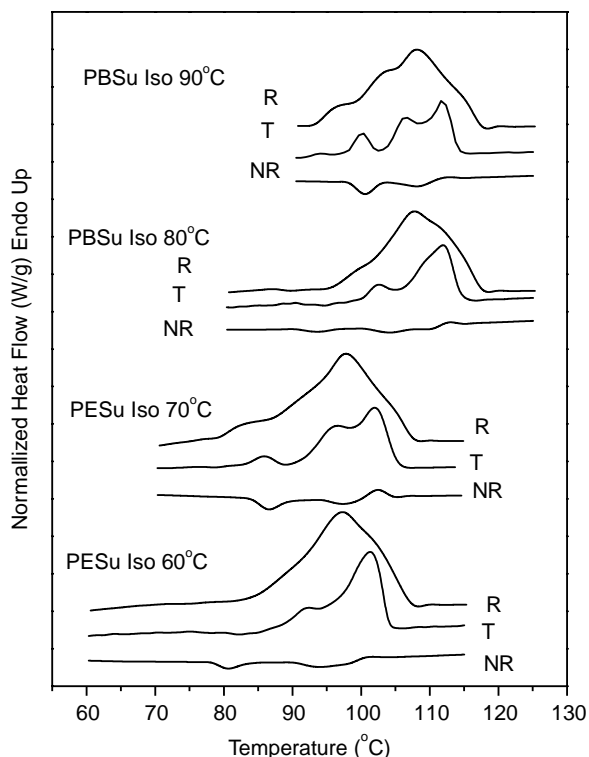
Fig. 11. Modulated temperature DSC traces for PESu and PBSu samples isothermally crystallized at various temperatures. Mean heating rate 2.5 °C/min.

Fig. 12. Modulated temperature DSC traces for PPSu samples isothermally crystallized at various temperatures. Mean heating rate 2.5 °C/min.

well as the molecular weight of the polymers may also be important for the occurrence of reversible melting. The heating step in these measurements was 2 °C, the heating rate was 5 °C/min, while the time corresponding to the isothermal steps was 0.4 min. The gap between crystallization and final melting of the same crystals is usually larger than 2 °C, especially at large supercoolings like those observed in the specific experiments. Thus, melting during the short heating step is rather expected to be reversible. Also, the polymers used in this work had a molecular weight M_n of about 6900 g/mol. This molecular weight was rather low and this might have some influence in the multiple melting behavior, which is known to be enhanced for low molecular polymers, and also in reversing melting.

Reversible melting is under study last years. According to Wunderlich, fringed micellar melting (probably like for the first peak of Fig. 11) is a reversible melting. Short chain segments, which remain attached to the crystal surfaces, set up local equilibria after all, initial melting, re-crystallization and reorganization is completed [46]. Furthermore, Wunderlich et al. showed that reversible melting is more obvious for oligomers [47]. In general Wunderlich et al., interpreted reversible melting using the concept of molecular nucleation [48]. Strobl et al. studied reversible melting in PE, poly(-ethylene oxide) and other polymers like iPP, polycaprolactone and PET, and concluded that polymers with high longitudinal diffuse mobility within crystallites show a continuous, reversible surface melting and crystallization [49,50]. This also may be the explanation for the observations in the present
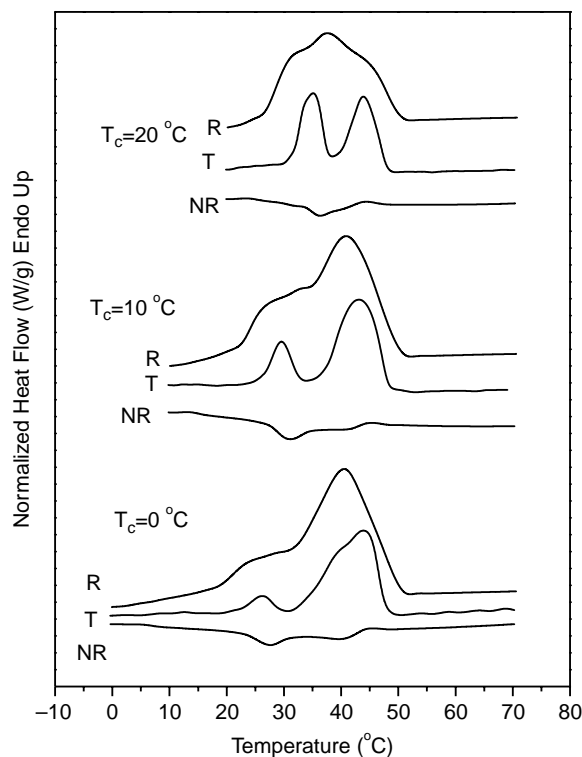
paper. Furthermore, Schick et al. observed an increase of complex heat capacity in TMDSC experiments above the annealing peak for polycarbonate and poly(hydroxy butyrate). They attributed that to the devitrification of the rigid amorphous fraction and also to the occurrence of reversible melting [51].

In contrast to what was reported for PESu and PBSu, for PPSu samples crystallized at equivalent supercoolings, usually one exotherm was recorded, or the second exotherm was not fully separated from the first one (see Fig. 12). In general for low T_c samples, and for all polyesters, multiple re-crystallizations occurred during heating. Also, re-crystallization took place even at temperatures a few degrees before final melting, (under very low supercoolings). For PBSu and PESu samples recrystallization was faster. Also, fast re-crystallization rates as proved by sharp re-crystallization exotherms, gave rise to increased number of melting peaks, for example in the case of PBSu crystallized at 90 °C or PESu crystallized at 70 °C.

3.4. Determination of equilibrium melting temperature

Equilibrium melting temperature (T_m^0) is a parameter, which must first be determined in order to analyze crystal growth kinetics. Equilibrium melting temperature is by definition the melting temperature of lamellar crystals with an infinite thickness. However, it is impossible to obtain such a lamella in practice, because of kinetic factors. Thus, extrapolative methods are used to estimate T_m^0. Thus, T_m^0 could be determined via four general methods including the Gibbs–Thomson and Flory–Vrij approaches, the Hoffman–Weeks procedure, and

the fitting of growth rate data at a sufficiently low supercooling with the classical theory of lamellar crystal growth [52]. Among them, the Hofmman–Weeks method has been commonly used and accepted to estimate T_m^0 [53]. However, there is criticism on the validity of the specific procedure. According to Heck et al. the Hoffmann–Weeks plots rather result in the temperature where the crystallization line vs the inverse of the crystal thickness meets the Gibbs–Thomson melting line vs the inverse of the crystal thickness, but this temperature may be lower than the equilibrium melting point [54]. Despite criticism, the Hoffmann–Weeks procedure is still in use because of its simplicity and straightforward experimental implementation. In this procedure, the measured T_ms of specimens crystallized at different T_cs are plotted against T_c and a linear extrapolation to the line $T_m = T_c$, and the intercept gives T_m^0. The Hoffman–Weeks extrapolation is based on an equation that was deduced from a combination of the Gibbs–Thomson equation and secondary nucleation theory [53]. In this equation

$$T_m = T_m^0 \left(1 - \frac{1}{r} \right) + \frac{T_c}{r} \qquad (2)$$

T_m is the observed melting temperature of a crystal formed at a temperature T_c, r is the thickening coefficient equal l_c/l_g^* where l_g^* is the initial thickness of a chain-folded lamellar crystal. The perquisite for the application of this theory is the isothermal thickening process of lamellar crystals at a specific crystallization temperature and the dependence of the thickening coefficient on the crystallization temperature. Lamellar thickening is a complicated kinetic process. It was suggested that this coefficient depends not only on the supercooling ΔT, but also on the polymer chemical structure and the crystalline and amorphous structure. For a more accurate estimation of T_m^0 the H–W approach should be applied for a wide T_c range.

The T_m^0s for the three poly(alkylene succinate)s were determined following the linear Hoffman–Weeks extrapolation. For PESu as was reported in the respective section it was found that the middle melting peak observed in DSC traces corresponds to primary crystals, formed during the isothermal stage. Thus, the respective melting temperatures T_{m2} were plotted against crystallization temperature as it is shown in Fig. 13. In the respective sections it was also reported that for PBSu and PPSu, like for PESu, the second peak was attributed to melting of primary crystals generated at the corresponding T_c. Thus, for these polymers plots of T_{m2} against T_c were constructed to arrive to the equilibrium melting points. Finally, the values obtained were $T_m^0 = 117$ °C for PESu, $T_m^0 = 133.5$ °C for PBSu and $T_m^0 = 58$ °C for PPSu. After that, since data for both heat of fusion and equilibrium melting temperatures were available, the entropy of fusion could be calculated. Since $\Delta G = \Delta H - T\Delta S$ for $\Delta G = 0$ for melting at T_m^0, ΔS_m^0 can be calculated as $\Delta S_m^0 = \Delta H_m^0/T_m^0$. Results are summarized in Table 2.

The plots of the other peak temperatures against T_c were also studied. In the estimation of the first peak temperature from the DSC traces there was uncertainty due to the very
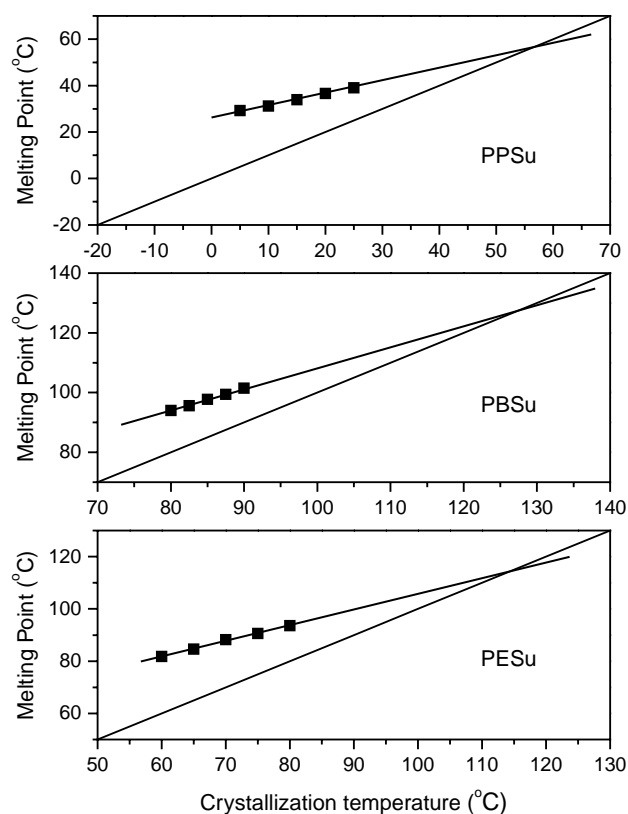

Fig. 13. Hoffman–Weeks plots for PESu, PBSu and PPSu. T_{m2} values were used for the construction of the plots.

small peak intensity and spreading. However, the respective plots had slopes close to unity. At least for PBSu, the estimated T_m^0 was very close to that obtained by plotting the second peak temperature. The use of T_{m3} values gave lower T_m^0 values, while the ultimate peak temperature was constant.

3.5. Analysis of spherulitic growth rates

Large spherulites were observed with polarized optical microscope during isothermal crystallization of PESu and PBSu. Linear increase in spherulite radius with time was observed for these two polyesters, and thus the spherulitic growth rates were measured. On the other hand only very small spherulites of PPSu were observed. This difference in morphology is supposed to be strongly related with enhanced biodegradation rates of PPSu, since enzymatic hydrolysis is faster in the amorphous phase between spherulites than inside them. From the plots of spherulite radius against time, the

Table 2
Glass transition temperature, melting temperature, equilibrium melting temperature, enthalpy of fusion and entropy of fusion for pure crystalline poly(alkylene succinate)s

Polymer	T_g (°C)	T_m (°C)	T_m^0 (°C)	ΔH_m^0 (kJ/mol)	ΔS_m^0[kJ/(mol K)]
PESu	−11.5	104	114	26	78.8
PPSu	−35	46	58	22	56.7
PBSu	−43.9	112	133.5	36	88.2

Table 3
Parameters used and results of secondary nucleation analysis for PESu and PBSu

Quantity	PESu	PBSu
ΔH_m^0 (J/m^3)	252×10^6	281.4×10^6
T_m^0 (°C)	114	133.5
d_{110} (m)	6.2×10^{-10}	4.5×10^{-10}
T_g (°C)	-11.5	-43.9
U^* (J/mol)	17,570	17,570
K_g^{III} (K^2)	1.85×10^5	1.88×10^5
$\sigma\sigma_e$ (J^2/m^4)	6.7×10^{-4}	4.9×10^{-4}
σ (J/m^2)	173×10^{-4}	136×10^{-4}
σ_e (J/m^2)	387×10^{-4}	360×10^{-4}
q (kJ/mol)	15.3	10.25

growth rates at various temperatures were calculated for PESu and PBSu. Crystallization was performed at temperatures in the range between 50 and 90 °C for PESu, because crystallization was very rapid and thus valid measurements could not be achieved below 50 °C. Also, in the case of PBSu crystallizations were carried out at temperatures between 80 and 106 °C.

The spherulite growth rates can be treated according to the secondary nucleation theory of Lauritzen and Hoffman [55]. At this point, it should be reported that though in this work the Lauritzen–Hoffmann treatment was elaborated, there are new theories on polymer crystallization, which disagree with the concept of secondary nucleation [56].

According to the secondary nucleation theory of Lauritzen and Hoffman [55] the spherulitic growth rates can be expressed as

$$G = G_0 \exp\left[\frac{-U^*}{R(T_c - T_\infty)}\right] \exp\left[\frac{-K_g}{T_c(\Delta T)f}\right] \quad (3)$$

where G_0 is a pre-exponetial factor independent of temperature. The first exponential term in the above equation contains the contribution of diffusion process to the growth rate, where U^* is the activation energy of the molecular transferring through the melt-crystal interface, T_∞ is the temperature below which diffusion stops and R is the gas constant. The second exponential term is the contribution of nucleation process, where K_g is the activation energy for nucleation for a crystal with a critical size and strongly depends on the degree of supercooling ($\Delta T = T_m^0 - T_c$). The factor f is a correction factor for the temperature dependence of enthalpy of fusion, which is close to unity at high temperature ($f = 2T_c/(T_m + T_c)$). In order to obtain best fit for the secondary nucleation theory two parameters should be predefined, i.e. the equilibrium melting temperature $T_m^0 = 114$ °C for PESu and $T_m^0 = 133.5$ °C for PBSu and the equilibrium melting enthalpy $\Delta H = 252 \times 10^6$ J/m^3 and $\Delta H = 281.4 \times 10^6$ J/m^3 for PESu and PBSu respectively, according to our calculations presented in the previous sections (Table 3).

The parameter K_g contains the variable n reflecting the regime behavior.

K_g is given by

$$K_g = \frac{nb_0\sigma\sigma_e T_m^0}{\Delta H_m^0 k} \quad (4)$$

where n is a constant equal to 4 for regime I and III and 2 for regime II, b_0 is the molecular thickness σ is the lateral surface free energy, σ_e is the fold surface free energy, and k is the Boltzmann constant.

Generally Eq. (3) is rewritten in a logarithmic form as follows

$$\log G + \left[\frac{-U^*}{2.303R(T_c - T_\infty)}\right] = \log G_0 - \frac{K_g}{2.303T_c(\Delta T)f} \quad (5)$$

There exist two alternative sets of values for U^* and T_∞, the first being the empirical values $U^* = 1500$ cal/mol and $T_\infty = T_g - 30$ K and the second are the set of Williams–Landel–Ferry (WLF) values of $U^* = 4200$ cal/mol and $T_\infty = T_g - 51.6$ K [57]. In many cases of polymers, selection of one of the above sets can fit well the crystallization kinetic data of polymers. However, in some other cases different U^* values were used for best fit of data.

In Fig. 14 the plots of $\ln G + U^*/R(T_c - T_\infty)$ against $1/T_c(\Delta T)f$ are shown for PESu and PBSu. In calculations of the data presented in this figure the WLF values were used for both polymers. By the use of WLF values regime II to regime III
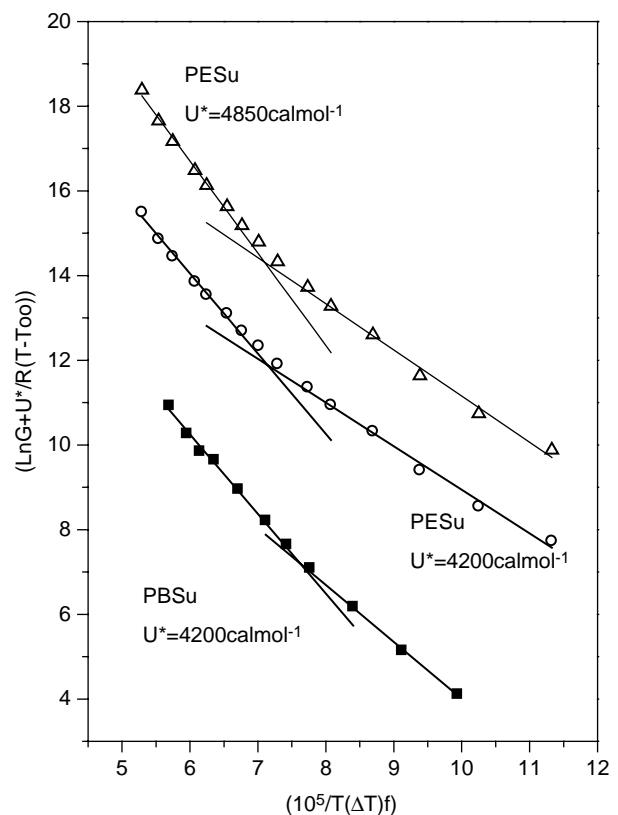

Fig. 14. Plots of $\ln G + U^*/R(T_c - T_\infty)$ against $1/T_c(\Delta T)f$ for PESu and PBSu. Open triangles correspond to data for PESu calculated using $U^* = 4850$ cal/mol. Open circles correspond to data for PESu calculated using $U^* = 4200$ cal/mol. Solid squares correspond to data for PBSu calculated using $U^* = 4200$ cal/mol.

transition is observable for PESu at about 70 °C, in agreement with findings of Doi et al. [11]. The ratio of K_g^{III}/K_g^{II} is 1.8, close to the expected value 2.0 according to the secondary nucleation theory. To achieve a ratio $K_g^{III}/K_g^{II} = 2.0$, a $U^* = 4850$ cal/mol should be assumed. For PBSu analysis by using the WLF values showed that a regime II to regime III transition may occur at about 96 °C but the K_g^{III}/K_g^{II} ratio was only 1.4. In fact to obtain a ratio of 2 a $U^* = 11500$ cal/mol should be assumed. These findings are also similar to those reported by Doi et al. [5].

For $K_g^{III} = 1.85 \times 10^5$ K^2 (assuming the WLF values) for PBSu and from Eq. (4), the $\sigma\sigma_e$ product was estimated to be 4.9×10^{-4} J^2/m^4. Miyata and Masuko [4] found $\sigma\sigma_e = 5.6 \times 10^{-4}$ J^2/m^4, while Park et al. reported a $\sigma\sigma_e$ product equal to 7.45×10^{-4} J^2/m^4 [58]. The reason for their larger values is that they supposed that no transition occurs in the temperature range of crystallization. Also, for $K_g^{III} = 1.85 \times 10^5$ K^2 for PESu the $\sigma\sigma_e$ product was estimated to be 6.7×10^{-4} J^2/m^4. For the above calculations it was assumed that the growth front was the (110) plane for both PESu and PBSu, as in the case of high-density polyethylene. For PBSu this was assumed in the previous studies [4,5,58].

The lateral surface free energy σ can be estimated by the empirical treatment proposed by Thomas and Stavely [59]

$$\sigma = \alpha(\Delta H_f)(a_0 b_0)^{1/2} \tag{6}$$

The a_0 and b_0 factors are the molecular width and molecular layer thickness respectively. Generally, the Thomas–Stavely constant a ranges between 0.1 and 0.3. The value $a = 0.1$ is widely applied in polyethylene and other flexible polymers. Roitman and Marand found that the a value was ca. 0.25 for polypivalolactone. The a value is not at all universal and strongly depends on the chemical structure of the polymer, and it is related to entropy differences between the crystal and the melt interface. Also, the work of chain folding can be obtained from the fold surface free energy as

$$q = 2\sigma_e a_0 b_0 \tag{7}$$

The q value is defined as the work for chain folding by bending the polymer chain back upon itself in the appropriate configuration. q has been found to be a parameter closely related with molecular structure, the inherent stiffness of the chain itself.

Assuming that $a = 0.1$ for both polymers, substitution of the proper values gave for PBSu $\sigma = 136 \times 10^{-4}$ J/m^2 and for PESu $\sigma = 173 \times 10^{-4}$ J/m^2. Then, a $\sigma_e = 360 \times 10^{-4}$ J/m^2 and a $q = 2.45$ kcal/mol (10.25 kJ/mol) was calculated for PBSu. For PESu $\sigma_e = 387 \times 10^{-4}$ J/m^2 and $q = 3.65$ kcal/mol (15.3 J/mol). These results are reasonable, since they prove that PBSu chains can fold easier than PESu chains do. This was anticipated because of the fact that butylene groups are more flexible than ethylene ones.

4. Conclusions

PPSu, which exhibits faster biodegradation rates comparing to PESu and PBSu, has slower crystallization than the others.

Crystallization half-times are much larger for PPSu especially when they are compared to those of PBSu. Also, only small spherulites of PPSu were observed in contrast to the other succinates, which form large spherulites. This fact should be related to faster biodegradation of PPSu. For the three polyesters multiple melting was observed and it was associated with partial melting, re-crystallization and re-melting. PPSu always exhibits lower crystallinity, lower melting temperature and heat of fusion. PBSu on the other hand is characterized by high values for melting parameters and increased crystallinity. The spherulitic growth rates of PESu and PBSu were analyzed. For PESu clear regime transition was observed at about 70 °C. For PBSu regime transition probably occurs at 96 °C.

References

[1] Ihn JJ, Yoo ES, Im SS. Macromolecules 1995;28:2460.
[2] Ichicawa Y, Kondo H, Igarashi Y, Noguchi K, Okuyama K, Washiyama J. Polymer 2000;41:4719.
[3] Ichikawa Y, Suzuki J, Washiyama J, Moteki Y, Noguchi K, Okuyama K. Polymer 1994;35:3338.
[4] Miyata T, Masuko T. Polymer 1998;39:1399.
[5] Gan Z, Abe H, Kurokawa H, Doi Y. Biomacromolecules 2001;2:605.
[6] Qiu Z, Komura M, Ikehara T, Nishi T. Polymer 2003;44:7781.
[7] Yasuniwa M, Satou T. J Polym Sci, Polym Phys 2002;40:2411.
[8] Yoo ES, Im SS. J Polym Sci, Polym Phys 1999;37:1357.
[9] Qiu Z, Ikehara T, Nishi T. Polymer 2003;44:2799.
[10] Ichikawa Y, Nogushi K, Okuyama K, Washiyama J. Polymer 2001;42:3703.
[11] Gan Z, Abe H, Doi Y. Biomacromolecules 2000;1:704.
[12] Caminiti R, Isopo A, Orru MA, Albertini VR. Chem Mater 2000;12:369.
[13] Qiu Z, Ikehara T, Nishi T. Polymer 2003;44:5429.
[14] Qiu Z, Fujinami S, Komura M, Nakajima K, Ikehara T, Nishi T. Polymer 2004;45:4515.
[15] Ranucci E, Liu Y, Soderqvist-Lindblad M, Albertson AC. Macromol Rapid Commun 2000;21:680.
[16] Liu Y, Ranucci E, Soderqvist-Lindblad M, Albertson AC. J Polym Sci, Polym Chem 2001;39:2508.
[17] Bikiaris D, Papageorgiou G, Achilias D. Polym Degrad Stab 2006;91:31.
[18] Fields RD, Rodriguez F, Finn RK. J Appl Polym Sci 1974;18:3571.
[19] Montaudo G, Rizzarelli P. Polym Degrad Stab 2000;70:305.
[20] Rizzarelli P, Impallomeni G, Montaudo G. Biomacromolecules 2004;5:433.
[21] Seretoudi G, Bikiaris D, Panayiotou C. Polymer 2002;43:5405.
[22] Nagata M, Machida T, Sakai W, Tsutsumi N. Macromolecules 1998;31:6450.
[23] Lyoo WS, Kim JH, Yoon WS, Ji BC, Choi JH, Cho J, et al. Polymer 2000;41:9055.
[24] Kumagai Y, Kanesawa Y, Doi Y. Makromol Chem 1992;193:53.
[25] Medellin-Rodriguez FJ, Phillips PJ, Lin JS. Macromolecules 1996;29:7491.
[26] Nichols ME, Robertson RE. J Polym Sci, Polym Phys 1992;30:755.
[27] Denchev Z, Nogales A, Ezquerra A, Fernandes-Nascimento J, Balta-Calleja FJ. J Polym Sci, Polym Phys 2000;38:116.
[28] Sauer BB, Kampert WG, Neal Blanchard E, Threefoot SA, Hsiao BS. Polymer 2000;41:1099.
[29] Papageorgiou GZ, Karayannidis GP. Polymer 1999;40:5325.
[30] Ju M-Y, Chang F-C. Polymer 2001;42:5037.
[31] Wang Z-G, Wang X-H, Hsiao BS, Philips RA, Medellin-Rodriguez FJ, Srinivas S, et al. J Polym Sci, Polym Phys 2001;39:2982.
[32] Sun YS, Woo EM. Macromolecules 1999;32:7836.
[33] Marand H, Alizadeh A, Farmer R, Desai R, Velikov V. Macromolecules 2000;33:3392.
[34] Hsiao BS, Gardner KH, Wu DQ, Chu B. Polymer 1993;34:3986.
[35] Blundell DJ, Osborn BN. Polymer 1983;24:953.

[36] Samuels RJ. J Polym Sci, Part B: Polym Phys 1975;13:1417.

[37] Cebe P, Hong SD. Polymer 1986;27:1183.

[38] Blundell DJ. Polymer 1987;28:2248.

[39] Wang Z-G, Hsiao BS, Sauer BB, Kampert WG. Polymer 1999;40:4615.

[40] Kruger KN, Zachmann HG. Macromolecules 1993;26:5202.

[41] Cheng SZD, Wunderlich B. Macromolecules 1988;21:789.

[42] Pijpers TFJ, Mathot VBF, Goderis B, Scherrenberg RL, van der Vegte EW. Macromolecules 2002;35:3601.

[43] Hay JN, Langford JI, Lloyd JR. Polymer 1989;30:489.

[44] Yoo ES, Im SS. J Polym Sci, Part B: Polym Phys 1999;17:1357.

[45] Minakov AA, Mordvintsev DA, Schick C. Polymer 2004;45:3755.

[46] Pyda M, Wunderlich B. J Polym Sci, Polym Phys 2000;38:622.

[47] Pak J, Wunderlich B. Macromolecules 2001;34:4492.

[48] Okazaki I, Wunderlich B. Macromolecules 1997;30:1758.

[49] Hu W, Albrect T, Strobl G. Macromolecules 1999;32:7548.

[50] Albrecht T, Armbruster S, Keller S, Strobl G. Macromolecules 2001;34: 8456.

[51] Schick C, Wurm A, Mohamed A. Thermochim Acta 2002;392:303.

[52] Xu J, Srivatsan S, Marand H, Agarwal P. Macromolecules 1998;31: 8230.

[53] Hoffman JD, Weeks JJ. J Res Natl Bur Stand 1962;661:13.

[54] Heck B, Hugel T, Iijima M, Sadiku E, Strobl G. NJ Phys 1999;1:17.1.

[55] Hoffman JD, Davis GT, Lauritzen JI. In: Hannay NB, editor. Treaties on solid state chemistry, vol. 3. New York: Plenum; 1976.

[56] Strobl G. Eur Phys J E 2000;3:165.

[57] Williams ML, Landel RF, Ferry JD. J Am Chem Soc 1955;77:3701.

[58] Park JW, Kim DK, Im SS. Polym Int 2002;51:239.

[59] Thomas DG, Stavely LAK. J Chem Soc 1952;4569.