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Novel Poly(propylene terephthalate-*co*-succinate) Random Copolymers: Synthesis, Solid Structure, and Enzymatic Degradation Study

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ABSTRACT: A series of aromatic/aliphatic poly(propylene terephthalate-*co*-succinate) (PPTSu) random copolyesters of high molecular weight were synthesized. Enzymatic hydrolysis study showed that copolymers with terephthalate content up to 60 mol % could be hydrolyzed. CocrySTALLIZATION, thermal behavior, and spherulitic morphology were investigated. Melting points of the copolymers were depressed and followed a rather sigmoid curve, without exhibiting a eutectic behavior. Wide-angle X-ray diffraction patterns indicated that the copolymers crystallized in PPT crystal, but the interplanar spacings varied linearly. These are probable indications of isomorphous cocrySTALLIZATION. A single T_g was found for the copolyesters. Interestingly, after crystallization of the PPTSu copolymers with up to 60 mol % terephthalate content, the remaining amorphous phase showed increased mobility, as proved by a reduction of the T_g compared to the amorphous samples. This indicates some kind of segregation of chain segments occurring during crystallization, with preferable incorporation of propylene terephthalate (PT) units into the crystals and enrichment of the amorphous phase in hydrolyzable propylene succinate (PSu) sequences. As for neat PPT, banded spherulites were observed for the copolyesters. Most mechanical properties decreased with increasing PSu content compared to neat PPT.

Introduction

Nowadays, there is an increasing interest for biodegradable polymers. This is due to the fact that there is a growing concern, from both the public and the scientific community, over the existing problem of synthetic plastic wastes accumulating in the environment. A much promising approach, and probably the only feasible, in coping with this problem, which originated in the 1980s and met with much enthusiasm by the “green” movement, involves the development of polymeric materials from nontoxic precursors that can fully degrade in the natural environment. Aliphatic polyesters comprise an important family of polymers exhibiting such “green” characteristics.¹

Poly(propylene succinate) (PPSu) is a relatively new biodegradable polymer that shows high biodegradation rates and is also produced using monomers from renewable resources.^{1–9} There were difficulties in its preparation since one of its monomers, 1,3-propanediol (PD), could not be produced up until recently in sufficient quantities and purity.^{10,11} PPSu has gained an increasing interest since it has a higher biodegradation rate compared to poly(ethylene succinate) (PESu) and poly(butylene succinate) (PBSu) and, also, degrades faster than poly(propylene adipate) (PPAd) and poly(propylene sebacate) (PPSe) and, probably, faster than most polymers due to its low crystallinity.^{12,13} In contrast to other biodegradable polyesters, a limited number of published works dealing with PPSu have been reported.^{1–9} Unfortunately, PPSu has low mechanical properties. Poly(propylene terephthalate), on the other hand, is a new engineering plastic, with excellent properties, which has already

gained a significant share in the polyester market, mainly in the form of fibers. It is expected to become one of the most important plastics in the future.¹⁴

Enzymatic degradation of polyesters is sensitive to their chemical structure, the hydrophilic/hydrophobic balance within the main chain, molecular weight, the specific solid-state morphology, crystallinity, and so forth. As for crystalline structure and morphology, spherulite size and lamellar structure can greatly influence the rate of biodegradation.^{1,15,16}

Aliphatic polyesters are biodegradable. However, in general, they have low mechanical properties.¹⁷ In contrast, aromatic polyesters such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and poly(propylene terephthalate) (PPT) show excellent thermal and mechanical performance.¹⁸ Consequently, introducing aromatic terephthalate units into the main chain of aliphatic polyesters is a way to produce aromatic/aliphatic copolyesters with better physical properties, while maintaining biodegradability. For this reason, copolyesters like poly(butylene adipate-*co*-terephthalate)s and, more recently, poly(propylene isophthalate-*co*-adipate), poly(butylene succinate-*co*-terephthalate)s, and poly(ethylene succinate-*co*-terephthalate)s have been studied.^{19–30} It has been reported that copolyesters with up to 60 mol % aromatic units are biodegradable, though the content in terephthalic acid greatly influences the degradation rates.³¹ Today, commercial products, like Ecoflex of BASF and Eastar Bio of Eastman Chemicals Co., which are poly(butylene terephthalate-*co*-adipate)s, and Biomax of DuPont, a copolyester based on PET and aliphatic monomers, are available.^{32,33} In fact, research on adipate copolymers has been recently focused on such commercial polyesters. Copolymers based on succinic and terephthalic acid have recently gained interest. Mainly poly(butylene succinate-*co*-terephthalate) copolymers have been studied up to now,

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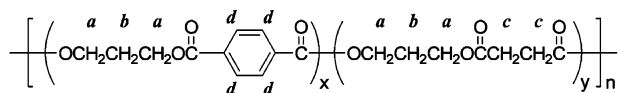


Figure 1. Chemical structure of poly(propylene terephthalate-*co*-succinate) copolymers.

though some works reported use of 1,2-ethylene glycol or 1,4-cyclohexanedimethanol.^{25–30,34}

The aim of this study was to synthesize a full series of aliphatic poly(propylene terephthalate-*co*-succinate) (PPT-Su) copolymers. Synthesis of such a series has not been reported before. In fact, for aliphatic copolymers based on 1,3-propanediol, only poly(propylene terephthalate-*co*-sebacate) and poly(propylene isophthalate-*co*-succinate) copolymers have been reported.^{35,36} An effort was made in this work to carry out detailed studies of the effect of the progressive variation in copolymer composition on both the enzymatic degradation and the solid structure. Thus, in the following paper synthesis of high molecular weight poly(propylene terephthalate-*co*-succinate)s, their enzymatic hydrolysis, and solid-state characteristics, such as cocrystallization and melting behavior, as well spherulitic morphology studies, are presented.

Experimental Section

Materials. The polyesters and copolymers were synthesized from dimethyl terephthalate (DMT), succinic acid (SA), and 1,3-propanediol (1,3-PDO). Dimethyl terephthalate was obtained from Fluka (purity 99%), and succinic acid (purity 99%) was purchased from Aldrich. 1,3-Propanediol (purity >99.7%) was kindly supplied by DuPont de Nemours, suitable for polyester synthesis. Tetraethyl titanate (TBT) catalyst of analytical grade and triphenyl phosphite (TPP) used as heat stabilizer were purchased from Aldrich. Zinc acetate was of industrial grade and used without further purification. All other materials and solvents used were of analytical grade.

The polyesters and copolymers were prepared by the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor. In the first step, dihydroxypropylene terephthalate and dihydroxypropylene succinate were prepared. For the preparation of dihydroxypropylene terephthalate, DMT and 1,3-PDO at a molar ratio of DMT/1,3-PDO = 1/2.2 and the transesterification catalyst zinc acetate [$\text{Zn}(\text{CH}_3\text{COO})_2$, 1×10^{-3} mol/mol DMT] were charged into the reaction tube of the polyesterification apparatus. The reaction mixture was heated to 190 °C for 1 h under an inert atmosphere and stirred at a constant speed (300 rpm). Then, the temperature was raised to 230 °C for a further 2 h, whereat the excess byproducts were distilled off. For the preparation of dihydroxypropylene succinate, succinic acid and 1,3-PDO at a molar ratio of succinic acid/1,3-PDO = 1/1.3 were charged in the reaction tube, and the flask was heated under nitrogen for 3 h at 200 °C and stirred at a constant speed (300 rpm), with water removed as the reaction byproduct of esterification.

In the second stage of preparation, the polycondensation step, appropriate amounts of each ester, according to the desired dicarboxylate ratio in the final polyester, and TPP (0.03 wt % of the final polymer), which prevents side reactions, such as etherification and thermal decomposition, were added in the reaction tube. The flask, under a nitrogen atmosphere, was immersed in a thermostated bath at a temperature of 260 °C, for samples with terephthalate content down to 70 mol %, and 240 °C for the rest, to avoid extensive thermal degradation, under continuous stirring (500 rpm). A vacuum (5.0 Pa) was applied slowly over a period of 15 min to avoid excessive foaming and to minimize oligomer sublimation, which is a potential problem during the melt polycondensation. The reaction was carried out for 120 min for all prepared materials. After completion, the polyesters were cooled to room temperature with an ice bath and removed from the flask.

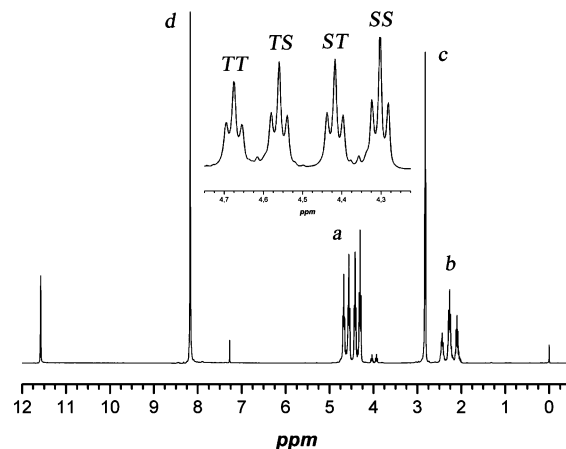


Figure 2. ^1H NMR spectrum of the poly(propylene terephthalate-*co*-propylene succinate) 50/50 copolymer.

Copolymers Characterization. Intrinsic Viscosity Measurement. Intrinsic viscosity $[\eta]$ measurements were performed using an Ubbelohde viscometer at 30 °C in a mixture of phenol/1,2,2-tetrachloroethane (60/40, w/w). The sample was maintained in the above mixture of solvents at 90 °C for some time to achieve a complete solution. The solution was then cooled to room temperature and filtered through a disposable membrane filter made from Teflon.

Gel Permeation Chromatography (GPC). Molecular weight determinations were performed by GPC using a Waters 150C GPC equipped with differential refractometer as detector and three ultrastaygel (103, 104, 105 Å) columns in series. A mixture of trifluoroacetic acid (TFA) and chloroform in a ratio 3/1 w/w was used as the eluent (1 mL/min), and measurements were performed at 50 °C. Calibration was performed using polystyrene standards with a narrow molecular weight distribution.

Nuclear Magnetic Resonance (NMR). ^1H NMR spectra of polyesters were obtained with a Bruker spectrometer operating at a frequency of 400 MHz for protons. A mixture of deuterated trifluoroacetic acid (DTFA) and chloroform in a ratio 3/1 w/w (DTFA/ CDCl_3) was used as solvent in order to prepare solutions of 5% w/v. The number of scans was 10, and the sweep width was 6 kHz.

Wide-Angle X-ray Diffraction Patterns (WAXD). X-ray diffraction measurements of the samples were performed using an automated powder diffractometer (PW 1050) with Bragg–Brentano geometry (θ – 2θ), using Cu K α radiation (λ = 0.154 nm) in the angle 2θ range from 5° to 60°.

Mechanical Properties. Measurements of tensile mechanical properties were performed on an Instron 3344 dynamometer in accordance with ASTM D638 using a crosshead speed of 50 mm/min. Relative thin films of about $350 \pm 25 \mu\text{m}$ were prepared using an Otto Weber, type PW 30 hydraulic press connected with an Omron E5AX temperature controller, at a temperature 30 °C higher than the melting temperature of each sample followed by rapid cooling with water at 20 °C. From these films dumbbell-shaped tensile-test specimens (central portions 5×0.5 mm thick, 22 mm gauge length) were cut in a Wallace cutting press and conditioned at 25 °C and 55–60% relative humidity for 48 h. The values of elongation at break and tensile strength were determined. At least five specimens were tested for each sample, and the average values along with the corresponding standard deviations are reported.

Thermal Analysis. A Perkin-Elmer, Pyris Diamond DSC differential scanning calorimeter, calibrated with pure indium and zinc standards, was used. The system also included an Intracooler 2P cooling accessory in order for the DSC apparatus to achieve function at subambient temperatures and high cooling rates. Samples of 10 ± 0.1 mg were used to test the thermal behavior of the quenched copolymers. In isothermal crystallization experiments samples of 5 ± 0.1 mg were used. The samples were sealed in aluminum pans. The samples were cooled to –50 °C (or –60 °C

Table 1. Propylene Terephthalate Content in Copolymers, Degree of Randomness (*R*), and Number-Average Sequence Length for Terephthalate (*L_{nT}*) and Succinate (*L_{nS}*) Units, Calculated from ¹H NMR Spectra

sample	PT (mol %)				
	feed	¹ H NMR	<i>R</i>	<i>L_{nT}</i>	<i>L_{nS}</i>
PPT	100	100			
PPTSu 95/5	95	95	1.00	16.11	1.07
PPTSu 90/10	90	90	1.00	8.51	1.14
PPTSu 80/20	80	79	1.00	4.63	1.27
PPTSu 70/30	70	68	1.01	3.17	1.45
PPTSu 60/40	60	58	0.98	2.44	1.74
PPTSu 50/50	50	47	1.00	1.93	2.09
PPTSu 40/60	40	36	0.99	1.65	2.65
PPTSu 30/70	30	28	1.00	1.43	3.35
PPTSu 20/80	20	18	1.00	1.24	5.17
PPTSu 10/90	10	9	1.01	1.11	9.66
PPSu	0	0			

in the case of PPSu) and then heated at a rate 20 °C/min to above the melting temperature. In order to obtain amorphous materials, samples were heated to 40 °C above the melting temperature and held there for 5 min, in order to erase any thermal history, before cooling in the DSC with the highest achievable rate. For isothermal crystallizations the same melting procedure as before was followed, and then the sample was cooled from the melt at 200 °C/min to 20 °C above the crystallization temperature (*T_c*) and finally cooled to the (*T_c*) at a rate of 50 °C/min, to achieve equilibration of the instrument. Heating rate was in most tests 20 °C/min. If some other procedure was followed, this will be discussed in the specific section.

Polarizing Light Microscopy (PLM). A polarizing light microscope (Nikon, Optiphot-2) equipped with a Linkam THMS 600 heating stage, a Linkam TP 91 control unit, and also a Jenoptic ProgRes C10Plus camera with the Capture Pro 2.1 software was used for PLM observations.

Enzymatic Hydrolysis. Polyesters in the form of films 2 × 3 cm in size and ~0.4 mm thickness, prepared by melt-pressing using a hydraulic press, were placed in Petries containing phosphate buffer solution (pH 7.2) with 0.09 mg/mL *Rhizopus delemar* lipase and 0.01 mg/mL *Pseudomonas Cepacia* lipase. The Petries were then incubated at 37 ± 1 °C in an oven for several days while the media was replaced every 3 days. After a specific period of incubation (every 72 h), the films were removed from the Petri, washed with distilled water, and weighted until constant weight. The degree of biodegradation was estimated from the mass loss.

Results and Discussion

Synthesis of PPTSu Copolymers. Copolyester synthesis was carried out following the two-step melt polycondensation method. In the first step dihydroxypropylene terephthalate and dihydroxypropylene succinate were prepared. In fact, dimers or trimers are also expected to be formed. Proper amounts of dihydroxypropylene terephthalate and dihydroxypropylene succinate were mixed and polycondensation followed. The use of dihydroxypropylene terephthalate and dihydroxypropylene succinate assures that the composition of the copolymers is almost the same with that in the reaction mixture, as only diol molecules are removed during polycondensation. Random chain scission due to ester bond cleavage and formation of new ester bonds occurs during this stage at elevated polycondensation reaction temperatures. The chemical structure of the copolymers is shown in Figure 1.

Molecular Characterization. The composition of the prepared polymers was determined by ¹H NMR spectroscopy. The ¹H NMR spectrum of poly(propylene terephthalate-co-succinate) 50/50 mol/mol, together with the corresponding chemical shift assignments, is presented in Figure 2. The spectra were consistent with the expected structures. Copolymers' composi-

tion was calculated using the relative areas of the d aromatic protons of the terephthalate units (T) located at 8.17 ppm and the c protons of the methylene groups of the succinic units (S) at 2.82 ppm. The actual molar composition in all cases was quite close to the corresponding used as feed.

Since the random, alternate, or block nature of a copolymer is a vital factor, significantly affecting its final properties, the degree of randomness (*R*) was calculated. This was accomplished by taking into consideration the resonance peaks of the propylene units' aliphatic protons (*a*). The degree of randomness is defined as³⁶

$$R = P_{TS} + P_{ST} \quad (1)$$

$$P_{TS} = \frac{\frac{f_{TS} + f_{ST}}{2}}{\frac{f_{TS} + f_{ST}}{2} + f_{TT}} = \frac{1}{L_{nT}} \quad (2)$$

$$P_{ST} = \frac{\frac{f_{TS} + f_{ST}}{2}}{\frac{f_{TS} + f_{ST}}{2} + f_{SS}} = \frac{1}{L_{nS}} \quad (3)$$

where *P_{TS}* and *P_{ST}* are the probability of finding a T unit next to a S unit and the probability of finding a S unit next to a T unit, respectively, while *f_{TT}*, *f_{TS}*, *f_{ST}*, and *f_{SS}* represent the dyads fraction, calculated from the integral intensities of the resonance signals TT, TS, ST, and SS, respectively.³⁶ *L_{nS}* and *L_{nT}* stand for the number-average sequence length, the so-called block length, of the S and T units, respectively. In the case of random copolymers *R* takes a value equal to 1, while for alternate copolymers equal to 2 and for block copolymers close to zero. In all cases, as seen in Table 1, the degree of randomness was equal or very close to 1, consolidating the random nature of the prepared copolymers.

According to Yamadera and Murano,³⁷ the number-average sequence length for terephthalate (*L_{nT}*) and succinate (*L_{nS}*) units, also known as the corresponding block length, can be calculated using eqs 2 and 3, respectively. The results are also presented in Table 1 for all prepared copolymers.

The measured intrinsic viscosity values were high, revealing high molecular weights of the polyesters (Table 2). For comparison, the intrinsic viscosity of commercial Shell's Corterra PPT resin is 0.92 dL/g at 25 °C, which is very close to the values of the produced polyesters in the present study.

Mechanical Properties. Tensile properties, such as tensile stress at the yield (*σ_{yield}*) and the break point (*σ_{break}*), elongation at break (*ε_{break}*), and Young's modulus (*E*), were determined for samples prepared from the melt and quenched in ice cold water. The results are listed in Table 2. Samples containing 50–80 wt % PSu are very brittle and brake before yielding. Also, PPTSu 10/90 is amorphous, and unfortunately tensile measurements could not be performed due to problems in specimen preparation. The stress–strain curves of the measured materials were similar to that of plain PPT, except for sample 60/40. They exhibited neck formation at the yield point and stress-at-break values fairly greater than at yield, showing behavior consistent with hard and tough materials. Young's modulus, as well as tensile stress at the yield and break point, gradually decreased with increasing PSu content. Elongation at break increased at small propylene succinate contents, up to 10 mol %, due to the presence of the more flexible PSu units in the copolymer's macromolecular chain, and decreased thereon since terephthalate

Table 2. Intrinsic Viscosity $[\eta]$ Values, Molecular Weight, and Mechanical Properties of Prepared PPTSu Copolyesters

polyester	$[\eta]$ (dL/g)	M_n (g/mol)	M_w (g/mol)	M_w/M_n	σ yield (MPa)	σ break (MPa)	E (MPa)	ϵ break (%)
PPT	1.01	58 900	88 400	1.50	32.4 \pm 1.5	32.7 \pm 1.0	1200 \pm 126	350 \pm 18
PPTSu 95/5	0.97	59 000	93 200	1.58	29.6 \pm 0.5	29.5 \pm 1.4	1034 \pm 52	431 \pm 26
PPTSu 90/10	0.92	51 600	84 500	1.64	25.2 \pm 0.3	27.2 \pm 0.4	793 \pm 108	520 \pm 16
PPTSu 80/20	1.04	60 300	102 200	1.70	21.4 \pm 1.1	24.2 \pm 1.5	527 \pm 26	446 \pm 40
PPTSu 70/30	1.14	68 200	104 900	1.54	16 \pm 0.8	20.7 \pm 0.7	307 \pm 37	323 \pm 16
PPTSu 60/40	0.84	47 800	78 300	1.64		4.7 \pm 0.5	129 \pm 17	8 \pm 1
PPTSu 50/50	0.47	26 100	48 300	1.85		3.2 \pm 0.3	110 \pm 10	7 \pm 2
PPTSu 40/60	0.53	24 600	49 200	2.00		3.4 \pm 0.5	93 \pm 12	6 \pm 3
PPTSu 30/70	0.80	36 900	58 600	1.59		3.2 \pm 0.3	72 \pm 13	6 \pm 2
PPTSu 20/80	0.78	32 200	58 200	1.81		2.1 \pm 0.2	74 \pm 9	7 \pm 1
PPTSu 10/90	0.73	31 500	58 800	1.77				
PPSu	0.63	29 500	54 300	1.84		1.8 \pm 0.3	80 \pm 17	6 \pm 2

Table 3. Glass Transition Temperature (T_g), C_p Increase at T_g (ΔC_p), Melting Temperature (T_m), Heat of Fusion (ΔH_m), Cold Crystallization Temperature (T_{cc}), and Heat of Cold Crystallization (ΔH_{cc}) for the Prepared PPTSu Copolyesters

polyester	T_g (°C)	ΔC_p (J/(g °C))	T_m (°C)	ΔH_m (J/g)	T_{cc} (°C)	ΔH_{cc} (J/g)
PPT	47.3	0.34	228.6	57.1	76.4	51.2
PPTSu 95/5	40.4	0.34	225	53.7	71	42.7
PPTSu 90/10	34.6	0.36	216	48.9	66.7	43.3
PPTSu 80/20	27.2	0.41	199.3	43.8	59.5	37.4
PPTSu 70/30	17.1	0.42	181.5	30.8	54.3	26.7
PPTSu 60/40	5.1	0.42	160.2	26.6	49.5	24.8
PPTSu 50/50	-13.4	0.47	136.7	22.7	32.6	19.2
PPTSu 40/60	-16.2	0.48	113.9	12.6	63.8	11.2
PPTSu 30/70	-22.4	0.54	78	6.3	29.1	5.6
PPTSu 20/80	-26.6	0.57	53.5	5.7		
PPTSu 10/90	-31.8	0.62				
PPSu	-33.2	0.61	46.7	42.4		

units, which are the main contributors to the material's durability, were significantly reduced. A ductile-to-brittle transition in the behavior under tension is observed for PPTSu 60/40, since this material exhibited only a low break point without yielding.

DSC Study. Thermal behavior study of the copolyesters was carried out using DSC. The first heating scan of the samples showed that the homopolyesters and almost all copolyesters were semicrystalline. Only the copolymer PPTSu 10/90 was purely amorphous. The melting points and heat of fusion decreased with increasing propylene succinate (PSu) unit content. The respective values are summarized in Table 3. However, since the samples bear the thermal history created during the preparation and purification procedures, the first heating scans may not be indicative of the thermal behavior of the materials, and thus, the copolymers were further tested.

Figures 5a,b show the DSC heating traces for the copolymer samples after melt quenching. In these heating traces a clear single glass transition can be seen for all of the copolymers, further proving that the prepared copolymers were random. For the neat PPT and all the copolymers having up to a 70 mol % (PSu) units a cold crystallization was recorded after the glass transition. The cold crystallization peak, however, is sharp for those samples with as high as 50 mol % PSu unit content. For PPTSu 40/60 and 30/70 copolymers, broad peaks with less heat of crystallization were observed. Finally, PPTSu 20/80 and 10/90 copolymers, as well as neat PPSu, did not show any cold crystallization. Characteristic temperatures and values for heat of fusion or heat of crystallization for the copolymers and homopolymers are presented in Table 3.

Figure 4 shows the variation of the melting points of the copolymers with comonomer's units content. The melting points rather follow a sigmoid curve with an inflection point at about 70% PSu content. It is important that the usual pseudo-eutectic behavior for random copolymers is not observed. The melting point of the PPTSu 10/90 copolymer could not be determined since it did not crystallize at all.

The glass transition temperatures (T_g) of quenched samples decreased monotonically with PSu content, between the two values of the neat polymers, which were 47.3 °C for PPT and -33.2 °C for PPSu. In amorphous random copolymers T_g is usually a monotonic function of composition. The applicability of the Couchman–Karasz equation was tested in the case of the PPTSu copolymers. The Couchman–Karasz equation is given by³⁸

$$\ln T_g = \frac{w_I \Delta C_{pI} \ln T_{gI} + w_{II} \Delta C_{pII} \ln T_{gII}}{w_I \Delta C_{pI} + w_{II} \Delta C_{pII}} \quad (4)$$

where w_I and w_{II} are the weight fractions of the comonomers and T_{gI} and T_{gII} the glass transition temperatures of the respective homopolymers. ΔC_{pI} and ΔC_{pII} are the values of the increase in heat capacity associated with the glass transition of the two homopolymers, respectively. ΔC_p values were experimentally measured at the glass transition temperatures of the polymers, and they were found equal to 0.61 J/(g °C) and 0.34 J/(g °C) for neat PPSu (ΔC_{pI}) and neat PPT (ΔC_{pII}), respectively. The Couchman–Karasz prediction seems to fit the glass transition temperature of the PPTSu copolymers, as seen in Figure 4.

PPT and also those copolyesters with up to 50 mol % PSu units have fast crystallization rates, as one can conclude from the sharp cold crystallization peaks just above the T_g for quenched samples (Figure 3). However, the crystallization rates of neat PPT were slower than those observed in previous studies because of the high molecular weight of the sample synthesized in this work.³⁹ Also, isothermal experiments showed a continuous decrease in the crystallization rates with increasing comonomer content for a given supercooling ($\Delta T = T_m - T_c$), as is evidenced by the increase in the crystallization half-time plot vs temperature of Figure 5a. The temperature window for crystallization shifts to lower temperatures and becomes narrower.

The copolymers as well as neat PPT showed multiple melting behaviors after isothermal crystallization from the melt. Figure

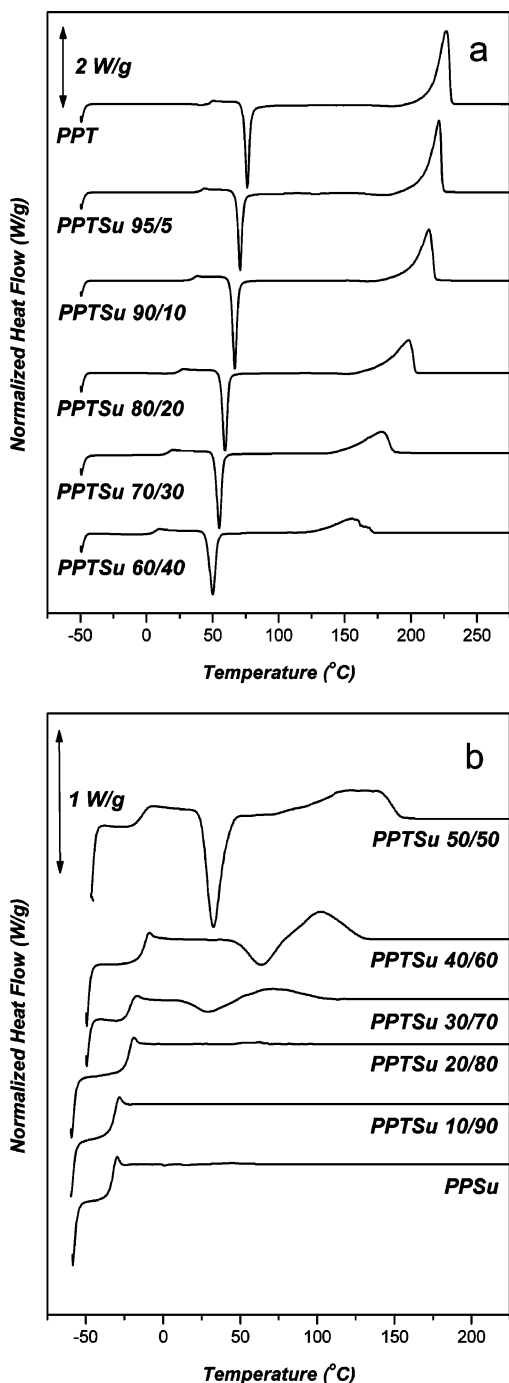


Figure 3. DSC heating scans for the quenched samples: (a) PPT and PPTSu copolymers with more than 50 mol % propylene terephthalate units and (b) PPSu and PPTSu copolymers with 50 mol % or less propylene terephthalate units content.

5b shows the melting behavior of PPTSu 90/10 sample isothermally crystallized from the melt at different temperatures. Up to four melting peaks marked as P I, P II, P III, and P IV can be observed in the heating traces of the copolymer in Figure 5b, including the annealing peak. The multiple melting behavior is associated with partial melting and recrystallization and, in general, crystal perfection process during the heating scan. P I is the so-called annealing peak, observed in general for polymers about 10–15 °C above the crystallization temperature, and is due to melting of secondary crystals. Tests showed that peaks II and III are associated with primary crystals since they increased in heat of fusion with increasing heating rate. The peak temperature of peaks II and III increased with crystalliza-

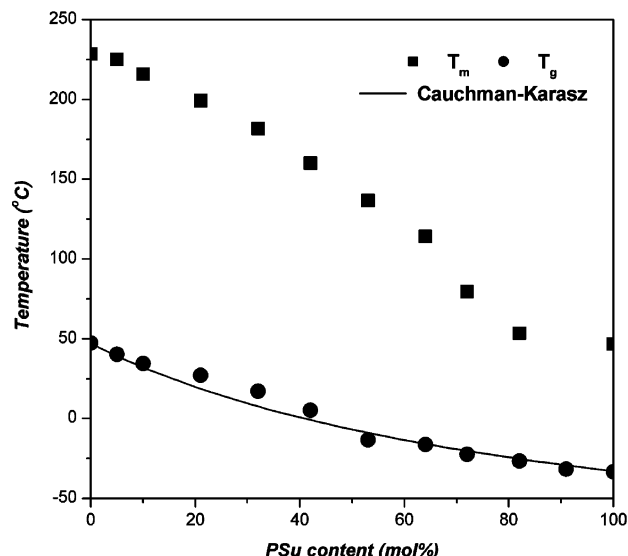


Figure 4. Melting points (T_m) and glass transition temperatures (T_g) for the neat PPT and PPSu and the PPTSu copolymers. Also plotted is the Couchman-Karasz prediction for the T_g of the copolymers.

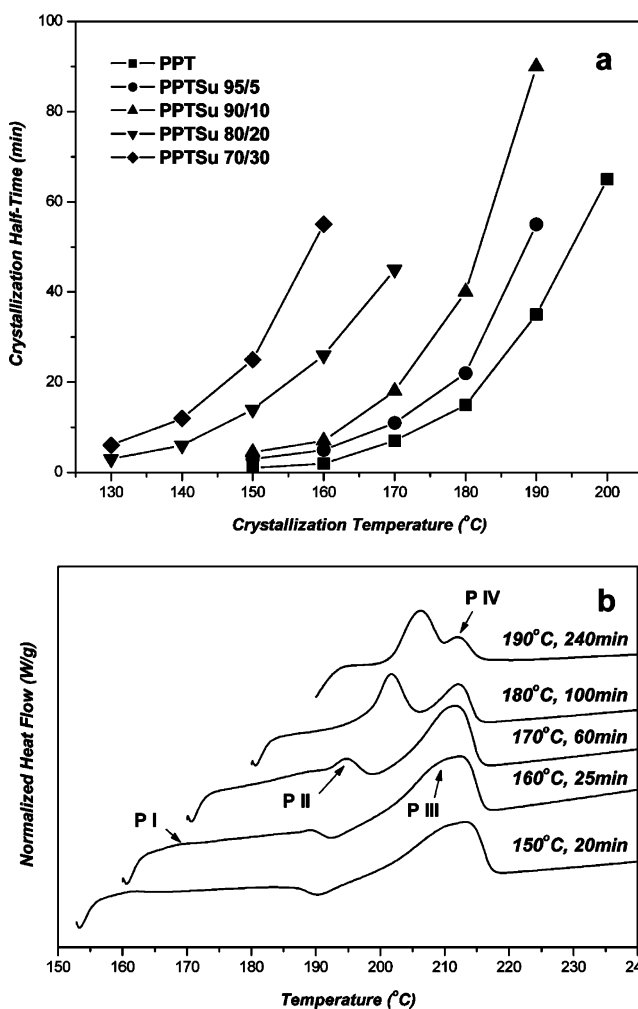


Figure 5. (a) Half-times of isothermal crystallization for PPT and copolymers with high propylene terephthalate content and (b) DSC heating scans for PPTSu 90/10 copolymer samples after isothermal crystallization at the indicated temperatures.

tion temperature. Finally, the temperature of the ultimate peak IV was constant, not depending on the crystallization temperature. The results of the experiments showed it is associated with melting of crystals after perfection or recrystallization

during the heating scan. The recrystallization, however, was not so fast for the specific PPT and PPTSu copolymers compared to what was observed in our previous study for PPT due to their high molecular weight.¹⁷ Furthermore, copolymers cannot show significant recrystallization compared to the neat homopolymer.

Cocrystallization Behavior. In copolyesters where both components are crystallizable, incompatibility in crystal lattices of the two components results in a reduction of the degree of crystallinity as the minor component content increases. If the two crystallizable units are compatible in each crystal lattice, cocrystallization can take place. Two cases of cocrystallization behavior have been reported.⁴⁰ Isomorphism is observed when the two components have similar chemical structure, occupying about the same volume. Only one crystalline phase is present at all compositions, containing both comonomer units. Isomorphism is associated with a clear melting temperature or with some crystallinity over the entire copolymer composition. In isodimorphism, two crystalline phases are observed, and the increase of minor comonomer concentration in each crystalline phase results in lowering of the melting temperature and the crystallinity of copolymer, resulting in pseudo-eutectic behavior.⁴⁰

The monomeric units of PPT and PPSu have one difference, the presence of a benzene ring in the case of PPT, instead of the two methylene units in the case of PPSu in the moiety of the diacid. The monomeric unit of PPSu is a little shorter. For PPT it is known that the α -crystal modification is triclinic with unit cell dimensions $a = 0.453$ nm, $b = 0.62$ nm, $c = 1.87$ nm, $\alpha = 97.6^\circ$, $\beta = 93.2^\circ$, and $\gamma = 110.1^\circ$.⁴¹ The crystal lattice parameters of PPSu have not been reported up to now. WAXD was used to investigate the nature of the crystalline phase of the PPTSu copolymers. Figure 6a shows the WAXD patterns of the PPTSu copolymers. Except for the PPTSu 10/90, which was completely amorphous (its pattern is not shown in the figure), in the WAXD patterns of the copolymers crystalline reflection peaks can be observed. The reflections show that exclusively PPT crystals are formed, even for a 80 mol % PSu content. A systematic decrease in the crystallinity is obvious in the patterns due to the reduction in length of crystallizable homopolymer sequences and occurrence of defects. The intensity of the peaks decreases and a peak broadening is observed for high comonomer content in the copolymer. There are also some continuous shifts in the peak positions with increasing content of PSu units. This is most probably an effect of comonomer cocrystallization. In the patterns the peaks are indexed according to the data of Ho et al.⁴¹ The peak positions for the low angle peaks which are the (010), (012), and (012) shift steadily to higher 2θ diffraction angles. In contrast, the positions of the (102) and (113) diffractions show a very slight shift to lower angles. The interplanar d -spacings of the (010), (012), and (012) planes seem to decrease linearly with comonomer content (Figure 6b). Also, a very slight but linear variation is observed for the d -spacing of the other planes.

As was reported above, the copolymers form PPT crystals, with the interplanar spacing varying linearly. Furthermore, no eutectic behavior was indicated by the plot of the melting points with composition, and despite the broad melting peaks, a rather linear drop in the melting temperature occurred. These facts are consistent with isomorphic cocrystallization of the PPTSu copolymers. However, isomorphic cocrystallization is a very rare phenomenon, and to our knowledge, for polyesters it has been reported only for the poly(hexamethylene naphthalate-co-1,4-cyclohexylene naphthalate) copolymers.⁴² On the other hand,

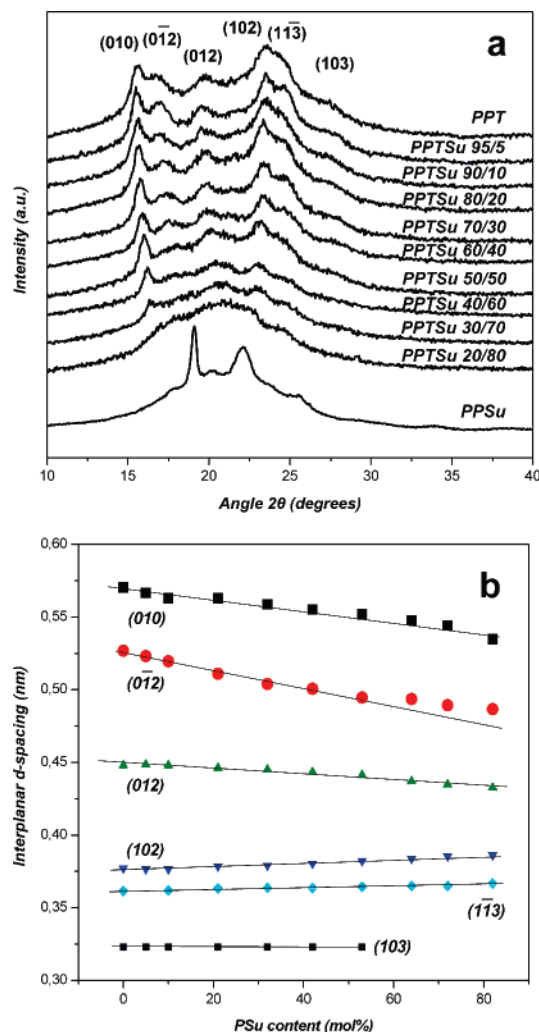


Figure 6. (a) WAXD patterns of the PPTSu copolymers and (b) variation of the interplanar spacings of PPT crystal with propylene succinate units content in the copolymers.

for the two series of copolymers based on propylene succinate which have been examined in past, isodimorphic cocrystallization was proven by eutectic behavior and WAXD observations.^{36,43}

Melting Point Depression. The melting point depression of the PPTSu copolymers was analyzed using the equations of Flory,⁴⁴ Sanchez-Eby,⁴⁵ Baur,⁴⁶ and the model of Wendling-Suter⁴⁷ for cocrystallization of copolymers of A and B comonomers.

Flory proposed an equation for the calculation of the upper bound of the copolymer melting temperature assuming comonomer exclusion.⁴⁴ This is given as follows:

$$\frac{1}{T_m^\circ} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^\circ} \ln(1 - X_B) \quad (5)$$

where X_B is the concentration of the minor comonomer B units in the polymer and $\ln(1 - X_B)$ equals the collective activities of A sequences in the limit of the upper bound of the melting temperature. T_m° and ΔH_m° are the homopolymer equilibrium melting temperature and heat of fusion, and R is the gas constant.

Sanchez-Eby assumed that B comonomer units are included into the crystals of A where they act as defects.⁴⁵ The related equation is

$$\frac{1}{T_m^\circ} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^\circ} \ln(1 - X_B + X_B e^{-\epsilon/RT}) \quad (6)$$

Here, $X_B e^{-\epsilon/RT}$ is the equilibrium fraction of repeat units B that are able to crystallize, and ϵ is the excess free energy of a defect created by the incorporation of one B unit into the crystal.

Also, a “pseudo-eutectic” system was supposed by Baur for copolymers where the homopolymer sequences of length ξ may be included into crystals of lamellar thickness corresponding to that length.⁴⁶ The melting point is calculated as follows:

$$\frac{1}{T_m^\circ} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^\circ} [\ln(1 - X_B) - \langle \xi \rangle^{-1}] \quad (7)$$

where $\langle \xi \rangle = [2X_B(1 - X_B)]^{-1}$ is the average length of homopolymer sequences in the melt.

Apart from the above equations, the melting point depression of the PPTSu copolymers was also analyzed using the model of Wendling–Suter,⁴⁷ which combines both inclusion and exclusion models and is given by

$$\frac{1}{T_m^\circ} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^\circ} \left[\frac{\epsilon X_{CB}}{RT} + (1 - X_{CB}) \ln \frac{1 - X_{CB}}{1 - X_B} + X_{CB} \ln \frac{X_{CB}}{X_B} + \langle \xi \rangle^{-1} \right] \quad (8)$$

where X_{CB} is the concentration of the B units in the crystal. In the equilibrium comonomer inclusion, the concentration of B units in the crystal is given by

$$X_{CB}^{eq} = \frac{X_B e^{-\epsilon/RT}}{1 - X_B + X_B e^{-\epsilon/RT}} \quad (9)$$

Substitution of X_{CB} in eq 8 by eq 9 results in simplification of eq 8 to the following equilibrium inclusion model:

$$\frac{1}{T_m^\circ} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^\circ} \{ \ln(1 - X_B + X_B e^{-\epsilon/RT}) - \langle \xi \rangle^{-1} \} \quad (10)$$

where

$$\langle \xi \rangle^{-1} = 2(X_B - X_B e^{-\epsilon/RT})(1 - X_B + X_B e^{-\epsilon/RT}) \quad (11)$$

when $X_{CB} = X_B$ and $X_{CB} = 0$, eq 8 is reduced to the uniform inclusion model and the exclusion model, respectively.

For the PPTSu copolymers it is very difficult to estimate the equilibrium melting temperature using peak temperatures and an extrapolative method like the popular Hoffman–Weeks method, since they show only broad and multiple melting peaks. Also, for the PPT homopolymer, like other polymers which undergo recrystallization on heating of their isothermally crystallized samples, values with significant differences have been reported in the literature for its equilibrium melting point.^{36,48,49} Thus, in this work the temperature corresponding to the end of the melting peak was used, as an approach of the equilibrium melting temperature. Such a value indeed corresponds to an upper melting temperature and is also directly measured and, thus, more reliable. In fact, the temperature of 237 °C, which corresponds to the end of melting of PPT, was also among those values reported for the equilibrium melting

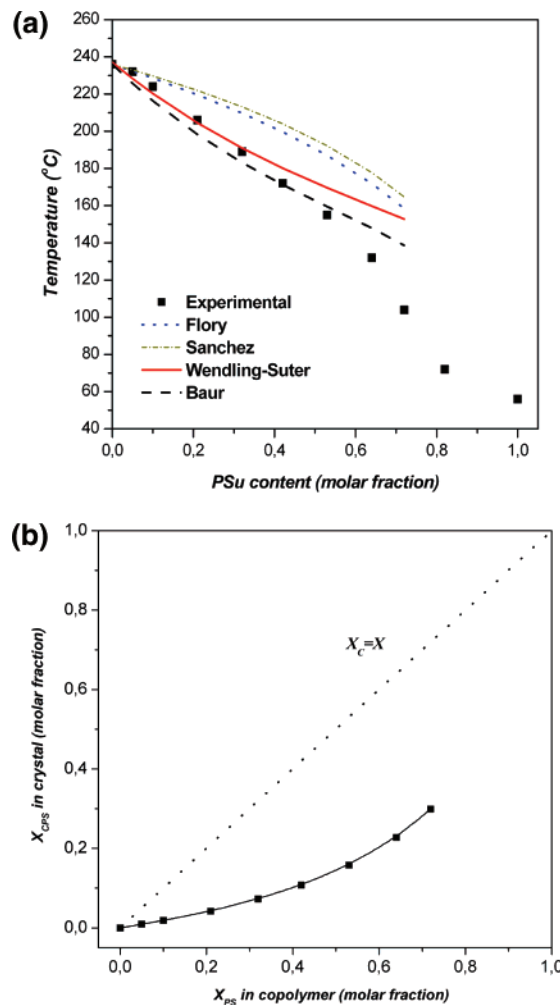


Figure 7. (a) Comparison of the theoretical melting temperatures and experimental values and (b) equilibrium concentrations of propylene succinate units incorporated in PPT crystal as a function of copolymer composition.

temperature of PPT.¹⁸ Also, in calculations, the equilibrium melting enthalpy of PPT was taken to be 30 kJ/mol.¹⁸

In Figure 7a, the equilibrium melting temperatures calculated using the Flory, Baur, Sanchez–Eby, and Wendling–Suter equations are shown in comparison to the experimental values. It is obvious that the Flory and the Sanchez–Eby models lead to overestimation of the equilibrium melting points. On the other hand, Baur’s prediction seems to be realistic. However, for comonomer content lower than 30 mol % in copolymers, the predicted values were lower than the experimental. The Wendling–Suter model fits better to the experimental data for lower comonomer content. The value of the function ϵ/RT is determined as an adjustable parameter. The model gives the constant ϵ/RT value regardless of the comonomer composition. Best fit to the experimental data was for $\epsilon/RT = 1.8$ for PPT. When the average defect free energy in the case of incorporation of PSu unit into the PPT crystal was calculated from the value of ϵ/RT for PPT ($X_{PSu} = 0$), it was found that $\epsilon = 7.63$ kJ/mol.

If comonomer exclusion alone is assumed, the length of crystallizing sequences is supposed to decrease steadily as the comonomer content increases in copolymers, resulting in a decrease of the lamellar thickness, which in turn results in melting point depression. However, the WAXD patterns showed that the PPT crystal structure was preferred by the copolymers when they crystallized, but they also showed an almost linear variation in the interplanar spacings of PPT crystal with

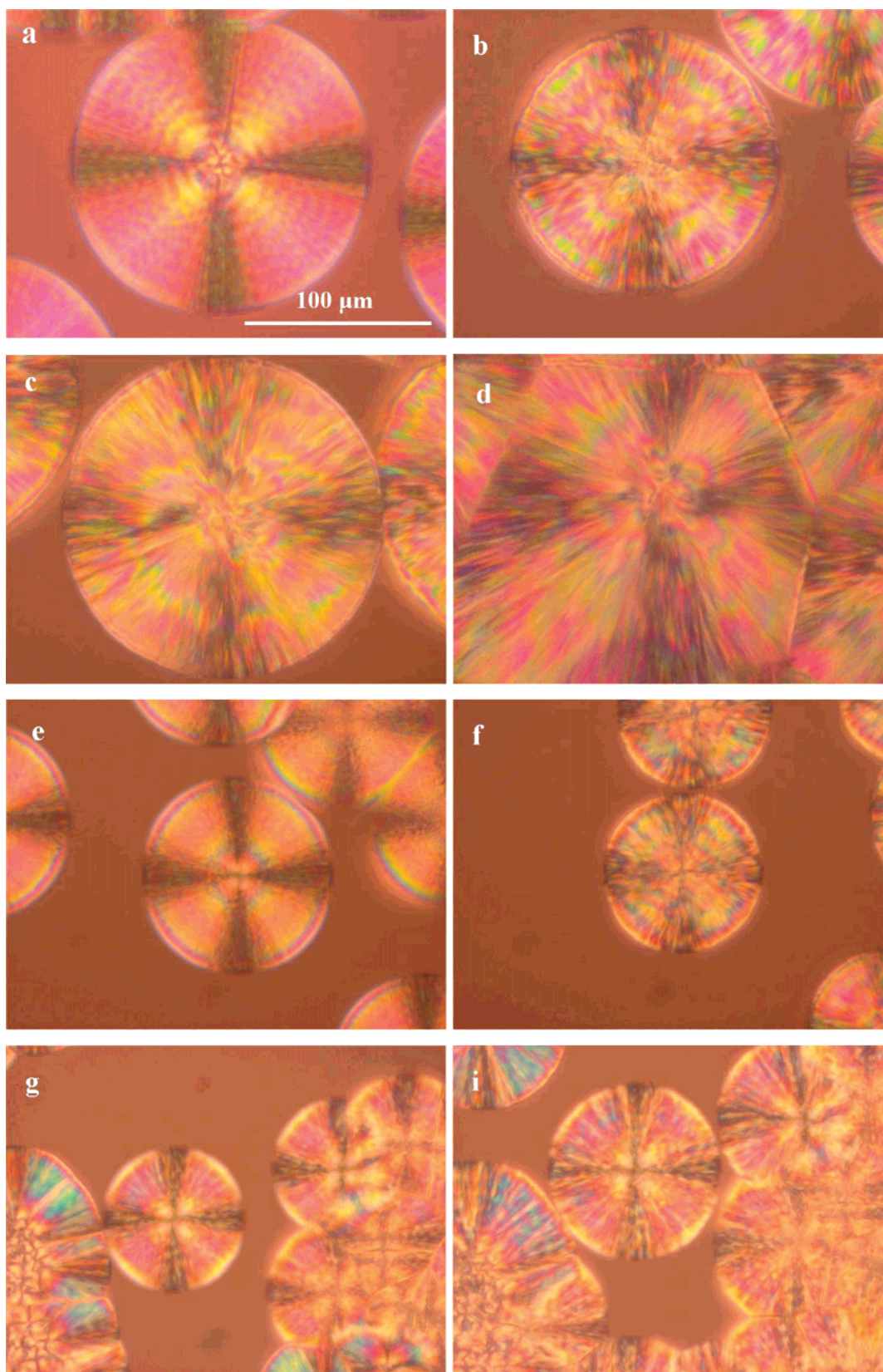


Figure 8. Spherulitic morphology for the PPTSu copolymers (a) PPTSu 90/10 at 160 °C, (b) PPTSu 90/10 at 175 °C, (c) PPTSu 90/10 at 180 °C, (d) PPTSu 90/10 at 190 °C, (e) PPTSu 80/20 at 135 °C, (f) PPTSu 80/20 at 145 °C, (g) PPTSu 70/30 at 125 °C, and (i) PPTSu 70/30 at 135 °C. The same scale in all photos.

comonomer content. This indicates that comonomer units are not completely excluded from the crystallizing chain segments in copolymers, prior to forming PPT crystals. Especially, for those random copolymers with terephthalate content less than 50 mol %, the probability for homopolymer sequences to occur

along the macromolecular chains is significantly reduced, as was proved by ^1H NMR spectra. It is reminded here that even PPTSu 30/70 formed PPT crystals, though in the particular copolymer propylene terephthalate was the minor comonomer. It seems that for PPTSu copolymers sequences of a minimum

length and terephthalate content and also some tacticity and similarity between them can crystallize. Such assumptions are common for most theories for copolymer crystallization^{50,51} It has also been reported for copolymers containing aromatic moieties that chain segments with random but similar sequences can crystallize by parallel alignment.⁵²

Furthermore, it must be noted that some kind of segregation of chain segments occurs during crystallization, resulting in rejection of noncrystallizing chain segments with long propylene succinate sequences to the amorphous phase. This was evidenced by the fact that in contrast to what was expected, for the copolymers with more than 50 mol % propylene succinate units, a reduction of about 4–5 °C was observed in the glass transition temperature after crystallization, compared to amorphous samples. Obviously, after crystallization the amorphous phase was enriched in flexible aliphatic PSu sequences. This is a significant factor as far as degradation of the polymer is concerned, since it is known that the amorphous content and the mobility of the amorphous phase determine the rate of the hydrolytic degradation of polyesters.^{1,3}

In an attempt to estimate the percentage of PSu units which was practically incorporated in the crystals, the results from the Wendling–Suter model were further analyzed. Using eq 9 the equilibrium concentrations X_{CPSu} of comonomer units in the crystals were calculated. The plot of the equilibrium concentration of PSu units in PPT crystal (X_{CPSu}) vs the concentration of PSu units in the copolymer (X_{PSu}) is shown in Figure 7b. It is revealed that the comonomer concentration in crystals increases with increasing the comonomer composition in bulk. Although the comonomer concentration in crystal is not so small, it is much lower than the copolymer concentration corresponding to uniform inclusion, i.e., $X_{\text{CPSu}} = X_{\text{PSu}}$. The plot of X_{CPSu} vs X_{PSu} shows curvature, and it has an increasing slope, which means that it is easier to create the excess volume necessary for a comonomer unit in an already imperfect crystal lattice.⁵³

Finally, it is important that PPSu crystals were not observed in the copolymers. As it is known, neat PPSu shows low crystallinity and crystallizes very slowly due to lack of symmetry in its chemical structure.³ Incorporation of comonomer units in PPSu chains further reduces symmetry. Thus, the case of incorporation of propylene terephthalate comonomer units into the PPSu crystals should be excluded, since propylene terephthalate units are bulkier, and the incorporation of the bulkier comonomer units in the crystal of the homopolymer corresponding to the other monomer is, in general, sterically hindered.

Spherulitic Morphology. The spherulitic morphologies of PPTSu copolymers with high terephthalate content (more than 70 mol % terephthalate) were observed after isothermal or nonisothermal crystallization from the melt. The size of the spherulites increased with crystallization temperature due to reduced nucleation density. Banded spherulites were observed for the copolyesters, like in neat PPT homopolymer. The spacing of the bands increased with increasing crystallization temperature. Figure 8 shows photographs taken with PLM. An interesting feature was that the magnitude of the spherulites decreased drastically for PPTSu 70/30. Also, because of the high molecular weight of the studied polymers, the growth rates were slow even for neat PPT compared to samples of lower molecular weight studied in past.⁵⁴

Enzymatic Hydrolysis Study. It is well-known that the enzymatic degradation rates of polyesters depend on many factors, such as the chemical structure, the degree of crystallinity, and molecular mobility of the amorphous phase.¹ PPSu, as was found in our previous study, shows fast biodegradation rates.¹²

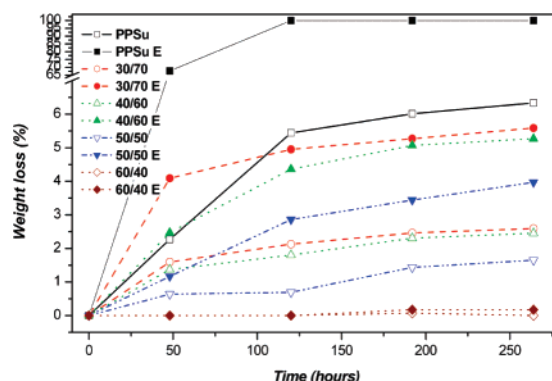


Figure 9. Weight loss against time of hydrolysis of the PPTSu copolymers. Open symbols represent data for hydrolysis in the absence of enzymes, while solid symbols represent data for enzymatic hydrolysis.

Tests however showed that the introduction of terephthalate units in the macromolecular chains of the aliphatic polyester PPSu resulted in a decrease of the biodegradation rates of the resulting PPTSu copolymers. Similar findings have been reported by Müller and co-workers for other aromatic/aliphatic biodegradable copolymers.^{55,56} The weight losses of the neat polyesters and the PPTSu copolymers during enzymatic hydrolysis for several days using *Rhizopus delemar* and *Pseudomonas Cepacia* lipases are presented in Figure 9. As was expected, the biodegradation rates of the copolymers decreased with terephthalate content. The copolymers with up to 60 mol % terephthalate content showed significant biodegradation rates. For example, PPTSu 50/50 showed a 4% weight loss after only 5 days of enzymatic hydrolysis (Figure 9). Finally, PPT and copolymers with more than 70 mol % terephthalate units practically did not hydrolyze. It is also obvious in Figure 9 that hydrolysis rates increased using enzymes. However, because of the presence of the benzene rings, the attack onto the ester groups by the enzymes is sterically hindered. Terephthalate dyads or longer sequences present nonhydrolyzable segments of the copolymers. The probability for the appearance of terephthalate sequences increases with increasing terephthalate content of copolymers and becomes significant, especially above 60 mol % terephthalate content. Also, the melting point increases with terephthalate content, while the amorphous fraction and mobility of the amorphous phase decrease. These factors drastically restricted enzymatic hydrolysis. Furthermore, biodegradation rates were reduced with time due to the increasing crystallinity of the sample, since the amorphous phase of the polymer is hydrolyzed much faster than the crystalline phase.

Ultimately, the copolymers such as PPTSu 50/50 show significant biodegradation rates and at the same time sufficient thermal properties, such as a melting point of 137 °C.

Conclusions

Aromatic/aliphatic poly(propylene terephthalate-*co*-succinate) copolyesters of high molecular weight were synthesized. Thermal and mechanical properties of the copolyesters increased with increasing aromatic content. Moreover, copolymers with 60 mol % terephthalate content were found to be biodegradable. The biodegradation rates of the copolyesters were composition dependent. Increase of the terephthalate content limited the hydrolytic degradation rates, with or without use of enzymes. This is due to increase of melting points and the expected propylene terephthalate average sequence length with increasing aromatic content and also due to the decrease of the amorphous portion as well as the mobility reduction of the amorphous phase.

Some extent of comonomer cocrystallization was evidenced in the copolymers by the WAXD observations and the monotonic variation of the melting points. Finally, copolymers with high terephthalate content (more than 70 mol %) formed large spherulites with banded textures, similar to neat PPT. The spherulites' size and growth rates decreased dramatically with increasing propylene succinate content in the copolymer.

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