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Effect of transesterification reactions on the crystallization behaviour and morphology of poly(butylene/diethylene succinate) block copolymers

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ABSTRACT

The melting behaviour, the crystallization kinetics and the morphology of block poly(butylene/diethylene succinate) copolymers (PBSPDGS) were investigated by means of differential scanning calorimetry and hot stage optical microscopy. Multiple endotherms were evidenced in the PBSPDGS samples, due to melting and recrystallization processes, similarly to PBS. By applying the Hoffman–Weeks' method, the T_m^0 of both the homopolymer and the copolymers was derived. The isothermal crystallization kinetics was analyzed according to the Avrami's treatment. The copolymers with long PBS blocks are characterized by a very similar behaviour with respect to pure poly(butilene succinate), indicating that PBS macromolecular folding is not affected by the presence of non-crystallizable diethylene succinate blocks. On the contrary, the copolymers characterized by very short PBS block length were found to crystallize at a slower rate than the homopolymer. As a matter of fact, a higher value of the work of chain folding was also derived on the basis of Hoffman–Lauritzen nucleation theory. Anyway, in all cases the crystallization mechanism (heterogeneous nucleation and three-dimensional growth) was found to be the same.

1. Introduction

In the last two decades much attention has been devoted to the biodegradable polymers because of their potential applications in the fields related to environmental protection and the maintenance of its physical health. Biodegradable polymers can be classified into two groups on the basis of the preparation method. One class is represented by the biosynthetic polymers, such as bacterial polyhydroxyalkanoates; the other one is formed by the chemiosynthetic polymers, among which the linear aliphatic polyesters play an important role. Poly(butylene succinate) (PBS) is just one of them. It can be found in packaging film, bags, flushable hygienic products and garden mulch. PBS has a melting point similar to that of the low density polyethylene, so that it can be processed with conventional equipments commonly used for polyolefins. However, its full-scale commercialization is precluded by its poor mechanical properties and higher cost compared with other universal plastics. Copolymerization and polymer blending have been used to improve the final properties and extend the fields of application [1–12]. In this view, recently, we synthesized a series of block poly(butylene/diethylene succinate) copolymers (PBSPDGS) by reactive blending and investigated the effect of BS block length on the thermal properties and miscibility [13].

It is well known that the physical properties and biodegradability of biodegradable polymers are greatly influenced by the morphology, crystal structure and degree of crystallinity. Consequently, a great attention has to be paid to the crystallization kinetics, which affects not only the crystallization rate, the crystal structure and the morphology, but also the physical properties and the biodegradability of a material. In front of the relevant academic and industrial importance of the studies of the isothermal crystallization of polymers, and taking also into account that at present no data have been yet reported in the literature on PBSPDGS block copolymers, it appeared very interesting to complete our previous work by investigating

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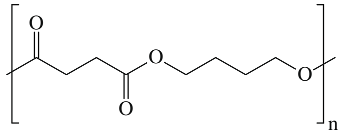
the crystallization process and the crystal morphology under isothermal conditions by means of both differential scanning calorimetry and optical microscopy. The melting phenomenon of samples isothermally crystallized from the molten state has been also explored. Aim of the work is to correlate the kinetics parameter, the melting behaviour and the morphology of the copolymers with butylene succinate block length.

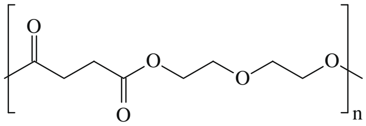
2. Experimental

2.1. Materials

Poly(butylene/diethylene succinate) block copolymers were obtained by reactive blending of PBS and poly(diethylene succinate) (PDGS), as previously reported [13]. The chemical structures of the two parent homopolymers are the following:



PBS



PDGS

The chemical structure, composition and block length were evaluated by means of ^{1}H NMR spectroscopy, and the molecular weights were determined by GPC. The main molecular characterization data are reported in Table 1, along with the results of the thermal characterization previously carried out [13]. The copolyesters obtained and analyzed in this work will be indicated with PBSPDGSX, where X is the mixing time in minutes.

2.2. DSC measurements

The isothermal crystallization kinetics and the melting behaviour were investigated using a Perkin–Elmer DSC7 calorimeter. The external block temperature control was set at −60 °C. All the measurements were carried out under a nitrogen atmosphere to minimize oxidative degradation. The instrument was calibrated using high-purity standards (indium and cyclohexane) for melting temperature and heat of fusion. A relatively small sample size, ca. 5 mg, was used to minimize the effect of the thermal conductivity of the polymers. A fresh specimen was used for each run. The following standard procedure was employed: the samples were heated to about 30 °C above fusion temperature, held there for 3 min, then quickly cooled by liquid nitrogen to the crystallization temperature T_c. Such brief annealing did not lead to any significant thermal degradation of the copolymers. The T_c range was chosen in order to avoid crystallization during the cooling step. The heat flow evolving during the isothermal crystallization was recorded as a function of time and the completion of the crystallization process was detected by the leveling of the DSC trace. For a better definition of the starting time, for each isothermal scan a blank run was also performed with the same sample, at a temperature above the melting point where no phase change occurred [14]. The blank run was subtracted from the isothermal crystallization scan and the start of the process was taken as the intersection of the extrapolated baseline and the resulting exothermal curve. The isothermally crystallized samples were then heated directly from T_c up to melting at 10 °C/min.

2.3. Optical crystallization measurements

The isothermal rate of crystallization was measured through the observation of the spherulitic radial growth, using a Zeiss Axioscop 2 optical polarizing microscope, equipped with a Linkam TMS94 hot stage. Isothermal crystallization measurements were performed on small fragment of polymer, inserted between two microscope cover glasses, and subjected to the following thermal program: the samples were heated to about 30 °C above fusion temperature, at 20 °C/min, kept at this temperature for 3 min (where the melt was squeezed into a film through a small pressure applied to the upper glass), then quenched by means of N_2 gas flow (cooling rate > 250 °C/min) to the selected crystallization temperature T_c, where isothermal crystallization was carried out. The whole procedure was

Table 1
Molecular and thermal characterization data [13].

					1st scan		2nd scan*					
Polymers	M_n	PDGS (mol%) (^{1}H NMR)	L_{BS}	B	T_m (°C)	ΔH_m (J/g)	T_g (°C)	Δc_p (J/°C·g)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)
PBS	38,300	0			113	70	−34	0.104	–	–	113	63
PDGS	28,200	100			–	–	−23	0.804	–	–	–	–
PBSPDGS5	22,800	50	–	0.00	110	32.4	−24	0.405	–	–	110	30.4
PBSPDGS15	21,500	50	25	0.079	110	33.4	−24	0.533	–	–	111	30.1
PBSPDGS30	20,200	50	11	0.181	105	31.7	−25	0.481	5.0	3.3	105	30.5
PBSPDGS45	21,500	50	4.2	0.460	96	33	−28	0.666	15	33.1	95	36.5
PBSPDGS60	23,600	50	3.7	0.534	82	32	−30	0.683	24	31.2	82	31.2
PBSPDGS90	26,200	50	2.5	0.803	65	32.2	−29	0.698	–	–	–	–
PBSPDGS120	25,200	50	2	0.985	47	23.3	−29	0.622	–	–	–	–

* After melt quenching.