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Isothermal Crystallization of Poly(ε-caprolactone−ethylene glycol) Block Copolymers

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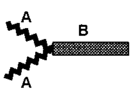
ABSTRACT: The isothermal crystallization of three different types of poly[ε-caprolactone-*co*-ethylene glycol] (PCL−PEG) incompatible block copolymers [A−B, $(A)_2$−B, and A−B−A] was investigated using DSC. The PEG weight fraction in the copolymers was slightly varied from 18 to 22 wt %. It was established that the kinetic parameters from the Avrami equation (the half time of crystallization, $\tau_{0.5}$, and the rate constant of overall crystallization, z) for the PCL constituent, which crystallizes first, are similar to the kinetic parameters of the corresponding homopolymer (PCL). The growth retardation of the constituent which crystallizes second (PEG block) is attributed to the mutual influence between the PEG constituent and the PCL crystal phase which fixes (hardened) the total copolymer structure.

1. Introduction

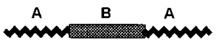
Poly(ε-caprolactone) (PCL) and poly(ethylene glycol) (PEG) are polymers that are known to be biocompatible.[1−6] The copolymers, which consist of both PCL and PEG segments (blocks), exhibit drug permeability and degradability and have been proposed for a wide range of medical applications.[2] Both drug permeability and biodegradability depend on the crystallinity.[7] Nevertheless, only a few studies have been published on the morphology and the crystallization (melting) properties of such block copolymers.[8−12] For example in the publications of Skoulius[9,10] detailed information is given about the crystallization and the lamellae structure of A−B−A type PCL−PEG−PCL block copolymers based on PEG with molecular weight MW=8600 and different length of PCL blocks. It was reported [9−12] that the crystallization properties of an A−B−A type poly(ε-caprolactone)−poly(ethylene glycol) triblock copolymer depend on the length of each block and the crystallization temperature. Gan et al.[13] studied the isothermal crystallization and melting behavior of the A−B type poly(ε-caprolactone)−poly(ethylene glycol) diblock copolymer. It was established that only the PCL block is crystallizable when the weight fraction of the PEG block is below 20%. Until now no comparative study of isothermal crystallization of different types of PCL−PEG copolymers was made.

Recently, we have reported the synthesis of three types of PCL−PEG copolymers with different architectures: (1) an A−B diblock copolymer; (2) an A_2−B star copolymer; (3) an A−B−A triblock copolymer.[14]

A-B



$(A)_2$-B



A-B-A

The molecular weight of the PEG blocks is 4000 or 5000 and the PCL weight fraction ranged from 68 to 85 wt %. It was established that the thermal properties and the morphology are significantly effected by the sequence of the different blocks (type of copolymers). In all three types of copolymers the PCL block crystallizes first at cooling from the molten state. This results in a significant undercooling and imperfect crystallization of the PEG block.

To obtain more detailed information about the mutual influence between the PCL and the PEG constituents (blocks), the isothermal crystallization of different types of PCL−PEG copolymers [A−B, $(A)_2$−B, and A−B−A] is performed. The results are presented and discussed in this paper.

2. Experimental Section

2.1. Materials. Poly(ethylene glycol) with molecular weight 4000 (PEG-4000) and monomethoxy−poly(ethylene glycol) with molecular weight 5000 (PEG-5000) were obtained from Fluka. They were dried by azeotropic distillation in toluene.

The synthesis of the PCL−PEG copolymers is described in detail in our previous paper.[14] The reaction mixtures were prepared by introducing, under a nitrogen atmosphere, a known amount of caprolactone monomer into a silanised flask containing a preweighed amount of PEG and 50 μL of stannous octoate. The flask was connected to a vacuum line, evacuated, sealed off and placed at 130 °C. After 24 h the resulting block copolymers were dissolved in methylene chloride and precipitated in an excess of cold hexane. Polymers were dried at 40 °C under vacuum.

2.2. Characterization. The copolymers were characterized by gel permeation chromatography (GPC) (Millipore-Waters GPC instrument) with chloroform as an eluent and a PL gel 5μ Mixed-D column; PEG standards were used for calibration.

^{1}H NMR spectra of the copolymers in deuterated chloroform solutions were recorded using a Brucker 360 MHz spectrometer with tetramethylsilane as an internal standard.

2.3. Differential Scanning Calorimetry. The kinetics of isothermal crystallization from the melt has been studied using a Perkin-Elmer DSC-7 differential scanning calorimeter operating under a helium atmosphere (20 mL/min). The following procedure was used: the samples were first melted at 80 °C for 5 min and then rapidly (60 °C/min) cooled to a selected crystallization temperature, T_c, and kept at this temperature to the end of the exothermic crystallization peak. The heat evolved during the isothermal crystallization was recorded as a function of time.

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Table 1. Composition and Molecular Weights of PCL−PEO Block Copolymers (A = PCL; B = PEG)

copolymer	total mol wt (GPC) M_n	M_w	M_n of PCL and PEG blocks calcd from NMR	PCL/PEG, wt % ratio (from NMR)
A−B	25 550	39 100	MeO−PEG$_{5000}$−PCL$_{20500}$	80/20
(A)$_2$−B	23 350	34 320	MeO−PEG$_{5000}$−N(CH$_2$CH$_2$−PCL$_{9000}$)$_2$	78/22
A−B−A	22 150	30 790	PCL$_{9000}$−PEG$_{4000}$−PCL$_{9000}$	82/18

After the isothermal crystallization, the melting temperature of the samples was measured as follow: the samples were heated from the crystallization temperature to a temperature above the melting point at a heating rate of 10 °C/min without any previous cooling of the samples.

3. Results and Discussion

The molecular weight and the PCL/PEG ratios of the three different types of copolymers prepared starting from PEG of known molecular weight are determined by ^{1}H NMR. The molecular weight values were compared with those obtained by gel permeation chromatography. The PEG weight fraction in the copolymers varies from 18 to 22 wt % (Table 1).

The phase structure of the block copolymers was analyzed by small-angle X-ray scattering (SAXS) at different temperatures ranging from 0 to 70 °C (results not presented). The type of the domain lattice was determined by comparing the observed sequence at d spacing—calculated for example from the Bragg equation ($n\lambda = 2d(\sin\theta)$, where the Bragg angle θ is half the scattering angle at witch the diffraction peak is observed)—with the characteristic sequences of the model latttices.[15] Generally for the PCL−PEG block copolymers referred to in this work the sequence of the spacing indicated that above the melting temperature of the PEG constituent (51−58 °C) spherical domains are packed in face-centered cubic forms. At higher temperature the intensity of the SAXS diffraction patterns decreases dramatically and any peaks in SAXS diagrams are indicated above 60 °C. These results suggest that a homogeneous phase structure appears in the PCL−PEG block copolymer melts.

The kinetics of isothermal crystallization of the three different types of PCL−PEG copolymers, A−B, (A)$_2$−B, and A−B−A, with approximately the same total molecular weight and length of the PEG block, are performed. For comparison the PEG and PCL homopolymers are included as well.

3.1. Poly(ethylene oxide) and Poly(ϵ-caprolactone) Homopolymers. The crystallization exotherms for PEG-4000 and PCL with a molecular weight which is close to that of the PCL blocks in the copolymers (PCL-8500 and PCL-20600), show that in the crystallization temperature range, selected in this study, a single crystallization peak for both PEG and PCL is obtained.

It was further observed that a partial crystallization before T_c occurs when the PEG and PCL polymers are undercooled below a certain temperature. This was observed for the PEG-4000 homopolymer below 45 °C and for the PCL-8500 and PCL- 20600 homopolymers below 40 °C. This makes it difficult to apply some of the known kinetic models to evaluate the overall rate of crystallization below a certain temperature. In such cases the peak time of the crystallization exotherm, τ_{max}, which represents reciprocally the overall rate of crystallization, can be used for comparative measurements. The τ_{max} values at different crystallization temperatures for the PEG and PCL homopolymers are shown in Table 2. One can see that the τ_{max} increases, i.e., the rate of crystallization decreases, with increasing temperature of isothermal crystallization, T_c.

Table 2. Peak Time of the Crystallization Exotherm (τ_{max}) and the Avrami Parameters for Isothermal Crystallization of PEG-4000, PCL-8500, and PCL-20600

T_c (°C)	τ_{max} (s)	Avrami parameters n	z	$\tau_{0.5}$ (s)
1. PEG-4000				
35[a]	19			
40[a]	29			
45	187	2.5	1.9×10^{-6}	200
47	310	3.3	1.0×10^{-9}	450
2. PCL-8500				
35[a]	20			
40	46	2.0	1.2×10^{-4}	56
42	85	2.3	1.9×10^{-5}	100
45	282	3.2	5.6×10^{-9}	320
3. PCL-20600				
35[a]	24			
40	84	2.0	4.8×10^{-5}	114
42	162	3.1	5.4×10^{-8}	201
45	547	3.3	6.9×10^{-10}	559

[a] A partial crystallization begins before reaching T_c.

At the same crystallization temperature (e.g. from 35 to 45 °C), the τ_{max} for the PEG-4000 homopolymer is lower than the τ_{max} for the PCL-8500 and PCL-20600 homopolymers; i.e., the overall rate of crystallization of the PEG-4000 homopolymer is higher than those for the PCL homopolymers.

The melting behavior of the PEG-4000, PCL-8500, and PCL-20600 homopolymers, after isothermal crystallization at different temperatures, is studied. A heating rate of 10 °C/min has been used, starting from the crystallization temperature.

When the crystallization temperatures are ranging from 35 to 47 °C, there are multiple melting peaks for PEG-4000. This can be attributed to crystals of different thickness due to varying number of folds in the polymer chain.[16] At lower temperature of crystallization (below 40 °C) a partial crystallization already occurs before reaching T_c. Three distinct melting peaks in the DSC heating curve are observed. The small melting peak at 53 °C probably corresponds to thin crystals (twice folded chains), and the melting peak about 60 °C, to the once folded crystals. The melting peak of the extended chain crystals appears at 62 °C. At higher crystallization temperature (47 °C) the fully extended chain crystals have a melting temperature of 63 °C.

Generally, the PCL-8600 and PCL 20600 homopolymers show a single melting endotherm at high crystallization temperatures (30 °C and above). Only at lower temperature of crystallization (25 °C and below) does the melting endotherm show a second melting peak or shoulder at 54 °C. The multiple peak endotherms of PCL arise usually from recrystallization during the DSC measurement; i.e., imperfect crystals melt and recrystallize into crystals with a higher order.

The melting temperatures of PEG-4000, PCL-8500, and PCL-20600 have been measured by DSC as a function of the crystallization temperature T_c. The

Table 3. Crystalline Phases in the PCL−PEG Block Copolymers for Isothermal Crystallization at Different Crystallization Temperatures (A = PCL; B = PEG)

copolymer	mol wt (M_n) of PCL and PEG blocks	T_c (°C)	crystalline phases
A−B	$MeO{-}PEG_{5000}{-}PCL_{20500}$	15−25	PCL and PEG
		30−42	PCL
$(A)_2{-}B$	$MeO{-}PEG_{5000}{-}N(CH_2CH_2{-}PCL_{9000})_2$	10−20	PCL and PEG
		25−42	PCL
A−B−A	$PCL_{9000}{-}PEG_{4000}{-}PCL_{9000}$	−14 to 0	PCL and PEG
		30−45	PCL

equilibrium melting temperature, $T_m°$, was determined by the Hoffman−Weeks extrapolation method[17]

$$T_m = (1 - 1/\gamma)T_m° + T_c/\gamma \tag{1}$$

where γ is the ratio of the lamellae thickness to the thickness of the initial nucleus at crystallization temperature T_c.

A reasonable straight line can be drawn in the Hoffman−Weeks plots for each polymer in the temperature range of crystallization above 35 °C (for PCL) and above 40 °C (for PEG). It is normal to expect that the melting temperature, T_m, increases with increasing crystallization temperature, T_c. The equilibrium melting temperature, $T_m°$, is obtained by extrapolation of T_m data by a least-squares analysis to the reference line $T_m = T_c$.

The equilibrium melting temperature, $T_m°$, for pure PEG-4000 as determined from this plot is 70 °C, and for PCL-8500 and PCL-20600 it is 64 °C. They are in good agreement with the values reported before by Wunderlich ($T_m°$ of PEG = 68.8 °C and $T_m°$ of PCL = 63.8 °C).[18]

The isothermal crystallization kinetics of the PEG and PCL homopolymers and their copolymers is interpreted in terms of the Avrami equation[19,20]

$$\alpha(t) = 1 - \exp(-zt^n) \tag{2}$$

where $\alpha(t)$ is a mass fraction of polymer transformed from melt to solid at time t, n is an exponent which contains contributions related to the crystal growth geometry and the time dependency of the nucleation rate, and z is an overall crystallization rate constant including contributions from crystal growth and nucleation.

The half time of crystallization, $\tau_{0.5}$, the rate constant of crystallization, z, and the Avrami parameter, n, are calculated and summarized in Table 2. The half time of crystallization $\tau_{0.5}$ is related to the rate constant and can be determined from the Avrami expression as follows:

$$\tau_{0.5} = (\ln(2/z))^{1/n} \tag{3}$$

Application of the Avrami equation on the isothermal DSC data for PEG-4000 at 45° and 47 °C gives n values of 2.5 and 3.3, respectively. For PCL-8500 and PCL-20600 at 45 °C, the n values are 3.2 and 3.3, respectively, which indicates the formation of spherulites in the PEG and PCL homopolymers[16] (Table 2).

The overall crystallization rate constant z for PEG-4000 is several orders of magnitude higher than for the PCL homopolymers at the same temperature of crystallization (T_c = 45 °C). This clearly indicates that the PEG homopolymer crystallizes much faster than the PCL polymers (PCL-8500 and PCL-20600) under the same conditions.

3.2. PEG−PCL Copolymers. The isothermal crystallization of three types of copolymers A−B, $(A)_2$−B and A−B−A with similar total molecular weights and identical lengths of the PEG block (the PEG weight fraction in the copolymers varies from 18 to 22 wt %) was carried out at different temperatures.

Our recent results from continuously crystallization during cooling of the same PEG−PCL copolymers show that the PCL constituent crystallizes first (above 25 °C). The second exotherm, below 25 °C, corresponds to the crystallization of the PEG block.[14]

Consequently, if an isothermal crystallization is performed above a certain crystallization temperature, it is reasonable to expect that only the PCL constituent crystallizes during this isothermal step. The crystallization temperatures of the PCL blocks, which are used in this study, vary for the different types of copolymers between 25 and 45 °C (Table 3). The PEG constituent is undercooled or is in the partially molten state in this temperature range and is not able to crystallize during the time of the isothermal crystallization of the PCL constituent.

Below a certain temperature, which is presented as well in Table 3, both PCL and PEG blocks are able to crystallize. Since the PCL constituent crystallizes first, it is possible to register the succeeding isothermal crystallization of the PEG constituent in the DSC curves as a function of time.

3.2.1. A−B and $(A)_2$−B Type Copolymers. It is reasonable to expect a similar behavior at isothermal crystallization for the A−B and the $(A)_2$−B type copolymers since they both consist of terminal PCL and PEG blocks.

In the temperature range from 15 to 25 °C for the A−B block copolymer and from 10 to 20 °C for the $(A)_2$−B star copolymer, both PCL and PEG constituents crystallize. The PCL constituent crystallizes first, before reaching the temperature of crystallization, T_c, or at the onset of the isothermal step. Next the PEG constituent crystallizes isothermally. For example the isothermal DSC traces of PEG blocks at T_c = 20 °C are shown in Figure 1.

When the crystallization temperature is varied from 30 to 42 °C for the A−B block copolymer and from 25 to 42 °C for the $(A)_2$−B star copolymer, only the PCL constituent crystallizes during the isothermal step (Figure 1, curves 1, 2). No distinct melting peak for the PEG constituent is observed in the heating DSC curves.

At the same temperature of isothermal crystallization, the peak time of the crystallization exotherm, τ_{max}, for the PCL constituent in the A−B copolymer has an identical value which is close to the value of τ_{max} for the PCL-20600 homopolymer, i.e., the PCL blocks in the copolymers and the PCL-20600 homopolymer have approximately the same overall rate of crystallization (Table 4). The τ_{max} values for the crystallization of the PCL blocks in the $(A)_2$−B type copolymer suggests that

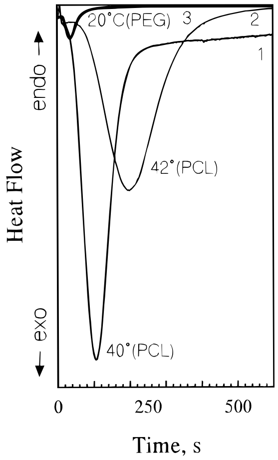


Figure 1. DSC curves for the isothermal crystallization of the A−B PCL−PEG block copolymer. The temperatures of crystallization are indicated in the DSC curves.The type of the polymer constituent that crystallizes isothermally is noted at the crystallization temperature.

the PCL constituent crystallizes slower than the corresponding PCL-8500 homopolymer.

The τ_{max} of the PEG constituent has a higher value in the $(A)_2$−B star copolymer in comparison with the τ_{max} in the A−B diblock copolymer at the same temperature of crystallization, 20 °C (Table 4). This indicates that the PEG block in the A−B copolymer crystallizes slightly faster than the PEG block in the $(A)_2$−B star copolymer. As was mentioned above, at a crystallization temperature below 35 °C the PEG-4000 homopolymer crystallizes extremely rapidly during cooling before reaching T_c. For example, the value of τ_{max} for the PEG homopolymer is 19 s at $T_c = 35$ °C (Table 2) which is identical to the value of τ_{max} for the A−B block copolymer at significantly lower crystallization temperature $T_c = 18$ °C and with τ_{max} for the $(A)_2$−B star copolymer at $T_c = 15$ °C (Table 4).

The half-time of crystallization, $\tau_{0.5}$, and the reciprocal value of the rate constant of crystallization z from the Avrami equation for the PEG and the PCL constituents change in the same way as the τ_{max}. Hence, the kinetic parameters of isothermal crystallization for the constituent which crystallizes first (PCL block) in the A−B type block copolymer are similar to the kinetic parameters of isothermal crystallization for the corresponding homopolymer (PCL-20600). The kinetic parameters (z and $\tau_{0.5}$) for the PCL blocks in the $(A)_2$−B type copolymer indicated a slower crystallization rate in comparison with corresponding PCL-8500 homopolymer. The growth retardation of the constituent which crystallizes next (PEG block) is attributable to the PCL block(s) which is (are) covalently attached to the PEG block and restricts (restrict) the mobility of the total copolymer structure at crystallization.

The melting endotherms after isothermal crystallization for the A−B and $(A)_2$−B type copolymers are shown in Figure 2. The samples which crystallized at low T_c (below 25 °C) show multiple melting peaks (Figure 2, curves 1). The lower melting peak (about 46 °C) is attributed to the melting of the PEG crystals. The higher temperature melting peaks at 53 and 56 °C are due to the melting of the PCL crystals with a different perfection. At higher heating rate (more than 40 °C/min), a single melting peak for the PCL block can be seen in the DSC curves (results not shown).

The samples which are crystallized above 30 °C show only one melting endotherm for the PCL crystals at about 58 °C (Figure 2, curves 2).

The same melting behavior is registered for the $(A)_2$−B type copolymer.

The Hoffman−Weeks plot in Figure 3 represents, for example, the dependence of the melting temperature, T_m, on the temperature of crystallization, T_c, for the PCL and the PEG constituents in the A−B type copolymer. The equilibrium melting temperature, $T_m°$, for the PCL block in both the A−B and the $(A)_2$−B copolymer is 61 °C. This is slightly lower than the $T_m°$ of the PCL homopolymer ($T_m° = 64$ °C) due to the influence of the PEG block that is covalently linked to the PCL blocks.

The equilibrium melting temperatures, $T_m°$, for the PEG block in both the A−B and the $(A)_2$−B copolymers are dramatically lower ($T_m° = 52$ and 56 °C respectively) than $T_m°$ of the PEG homopolymer ($T_m° = 70$ °C).

It is known that the equilibrium melting temperature, $T_m°$ is influenced by the molecular weight of the polymer and decreases with decreasing molecular weight.[21] In the PCL−PEG copolymers, which consist of thermodynamically noncompatible constituents, the segments of each block near to the covalent bonding point between them, practically can be sorted away from the growth faces of the crystals. This results in a decrease of the crystallizable length of the constituent blocks as well as a lowering of the equilibrium melting temperature $T_m°$. The crystallization of the PCL block rigidifies the total structure of the copolymers and additionally reduces the crystallizable length of the PEG constituent. This leads to a significant decrease of the $T_m°$ and nonperfect crystallization of the PEG block.

The Avrami exponent n for the PCL constituent in both the A−B and the $(A)_2$−B copolymers is around 3 (Table 4) which is approximately the same as for the PCL homopolymer (Table 2). This indicates the growth of spherulites.

The Avrami exponent n for the PEG block is about 2 for both the A−B block copolymer and the $(A)_2$−B star-copolymer (Table 4), while the PEG homopolymer has a value of n of 2.5−3.3 (Table 2). This result indicates that while the PEG homopolymer crystallizes in a spherulitic morphology, the PEG blocks in the copolymers can be supposed to form a two-dimensional lamellar growth corresponding to athermal (simultaneously) formed nuclei, suggesting that the PEG crystals grow on the growth faces of the PCL crystals which have already formed a spherulite structure. This is illustrated schematically in Figure 4.

3.2.2. A−B−A Triblock Copolymer. In the triblock copolymer, which is used in this study, the length of the terminal PCL blocks is approximately twice as long as the length of the central PEG block. As reported before,[14] the results from WAXD analysis at room temperature show only crystal patterns typical for the PCL crystal phase. According to the DSC cooling and heating curves, the PEG constituent is in the molten state at room temperature. The crystallization at cooling, of the PEG constituent in this type of copolymer is suppressed more significantly in comparison with the PEG block in the A−B or $(A)_2$−B copolymers or A−B−A triblock copolymer with comparable length of the central PEG block and the terminal PCL blocks. A very small exothermal peak is registered in the cooling DSC curve at −14 °C which is attributed to the crystallization of the PEG constituent.[14]

Table 4. Peak Time of the Crystallization Exotherm (τ_{max}) and the Avrami Parameters for Isothermal Crystallization of A−B (MeO−PEG$_{5000}$−PCL$_{20500}$) and A$_2$−B [(MeO−PEG$_{5000}$−N(CH$_2$CH$_2$−PCL$_{9000}$)$_2$] Block Copolymers

T_c (°C)	τ_{max} for the PEG block (s)	Avrami parameters for the PEG block			τ_{max} for the PCL block (s)	Avrami parameters for the PCL block		
		n	z	$\tau_{0.5}$ (s)		n	z	$\tau_{0.5}$ (s)
1. A−B Block Copolymer								
18[a]	19	2.0	8×10^{-4}	27				
20	35	2.2	2×10^{-4}	42				
23	85	2.3	4.6×10^{-5}	62				
35[a]					25			
40					106	2.9	6.1×10^{-7}	112
42					201	3.1	3.2×10^{-8}	213
2. A$_2$−B Block Copolymer								
10[a]	7							
15[a]	17							
20	50	2.2	1.3×10^{-4}	49				
30[a]					12			
35[a]					29			
40					107	2.7	1.4×10^{-6}	124
42					203	2.9	1.9×10^{-7}	190

[a] A partial crystallization begins before reaching T_c.

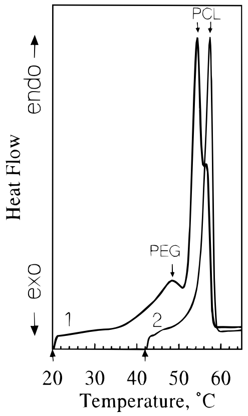


Figure 2. DSC heating curves (10 °C/min) for the A−B PCL−PEG block copolymer after isothermal crystallization at 20 °C (curve 1) and 42 °C (curve 2). Melting peaks are attributed to PEG and PCL constituents.The arrows in the temperature axis indicate the crystallization temperatures.

For this reason only the isothermal kinetics of crystallization of the PCL constituent for this type of A−B−A copolymer is investigated in this study.

The exotherms of crystallization at different temperatures and the corresponding melting endotherms for the A−B−A block show that, in the crystallization range studied, there are single crystallization and melting peaks for the PCL blocks. At the same temperature of isothermal crystallization, the peak time of the crystallization exotherm τ_{max}, the half time of crystallization $\tau_{0.5}$, and the overall crystallization rate z, for the PCL constituent in the A−B−A copolymer (Table 5) are comparable to the same parameters of isothermal crystallization of the PCL constituent in the (A)$_2$−B copolymer. The overal crystallization rate of the PCL blocks is slightly lower than that for the corresponding PCL-8500 homopolymer.

The equilibrium melting temperature, $T_m°$, determined from a Hoffman−Weeks plot for the PCL block in the A−B−A copolymer, is 61.2 °C which is comparable with the equilibrium melting temperatures of the PCL blocks in the A−B and the (A)$_2$−B copolymers. In all three types of copolymers, $T_m°$ of the PCL constituent is slightly lower than the $T_m°$ of the PCL homopolymer ($T_m° = 64$ °C) due to the influence of the PEG block that is covalently linked to the PCL blocks.

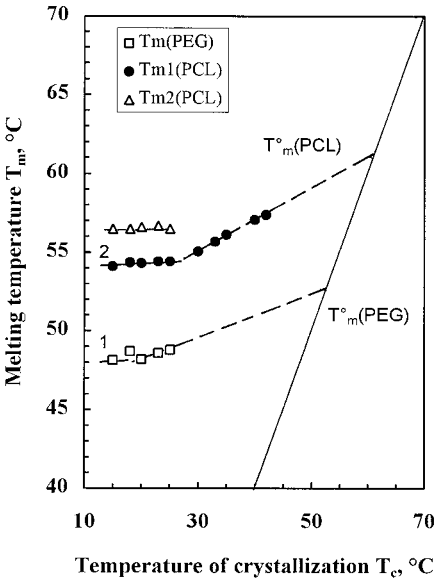


Figure 3. Dependence of the melting temperature (T_m) of the isothermally crystallized A−B PCL−PEG block copolymer on crystallization temperature (T_c). The equilibrium temperature for PEG constituent in the A−B block copolymer is $T_m° = 52$ °C (curve 1). The equilibrium temperature for the PCL constituent is $T_m° = 61$ °C (curve 2).

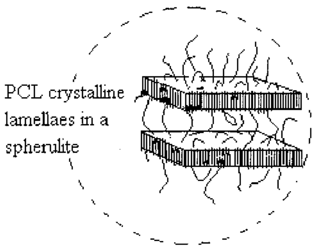
The Avrami exponent n for the PCL constituent has a value ranging from 2.5 to 2.7, which indicates spherulitic morphology.

4. Conclusions

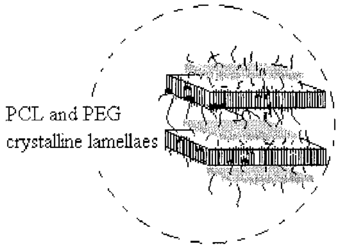
This study compares the kinetics of isothermal crystallization of three different types of PCL−PEG copolymers [A−B, (A)$_2$−B, and A−B−A] with comparable total molecular weights and identical lengths of the PEG block. The PEG weight fractions in the copolymers varied from 18 to 22 wt %. The PEG-4000 and PCL-8500 and PCL-20600 homopolymers are included for comparison.

While the PEG-4000 homopolymer crystallizes faster than PCL-8500 and PCL-20600 homopolymers, the PEG constituent overall crystallization rate is reduced dramatically in all three types of copolymers, resulting in a faster crystallization of the PCL constituent than the PEG block.

When the crystallization temperature is varied above 25−30 °C only the PCL constituent crystallizes; the PEG



(a) Tc > Tm(PEG)



(b) Tc = Tc(PEG)

Figure 4. Mechanism of crystallization of the PCL and PEG constituent in the A−B and $(A)_2$−B block copolymers at different crystallization temperature: (a) $T_c > T_m$(PEG); (b) $T_c = T_c$(PEG). Spherulitic crystallization of the PCL blocks is shown in part a. A sequence lamellar crystallization of the PEG block at decreasing crystallization temperature is shown in part b.

Table 5. Peak Time of the Crystallization Exotherm (τ_{max}) and the Avrami Parameters for Isothermal Crystallization for the PCL Constituent in A−B−A PCL_{9000}−PEG_{4000}−PCL_{9000} Triblock Copolymer

		Avrami parameters for the PCL block		
T_c (°C)	τ_{max} for the PCL block (s)	n	z	$t_{0.5}$ (s)
30[a]	11			
37	44	2.5	4.8×10^{-5}	45
40	102	2.5	5.3×10^{-6}	115
42	158	2.7	8.7×10^{-7}	158

[a] A partial crystallization begins before reaching T_c.

constituent is undercooled or is in the partially molten state above this temperatures. Below 25−30 °C, both the PCL and the PEG blocks are able to crystallize (the PCL constituent crystallizes first).

The isothermal kinetics of the PCL−PEG copolymers and the PCL and PEG homopolymers is interpreted in terms of the Avrami equation.

It was established that the kinetic parameters from the Avrami equation (the half time of crystallization, $\tau_{0.5}$, and the rate constant of overall crystallization, z) for the PCL constituent in A−B type copolymer, which crystallizes first, are similar to the kinetic parameters of isothermal crystallization for the corresponding homopolymer (PCL-20600). A somewhat slower crystallization rate of the PCL blocks in the $(A)_2$−B and A−B−A copolymers in comparison with the coresponding PCL homopolymers is observed.

The significant growth retardation of the PEG constituent which crystallizes second is established. The PEG constituent in the A−B−A triblock copolymer with longer terminal PCL blocks than the central PEG block did even not crystallize above −14 °C.

The dramatically lower overall crystallization rate of the PEG constituent is attributed to the mutual influence between the PEG constituent and the PCL crystal phase which fixes (hardened) the total copolymer structure.

The Avrami exponent n for the PCL constituent in the A−B, the $(A)_2$−B, and the A−B−A copolymers is around 3 and this is approximately the same as the n value for the PCL homopolymer which indicates that spherulites grow.

The Avrami exponent n for the PEG block is about 2 for both the A−B block copolymer and the $(A)_2$−B star-copolymer. This suggests a two-dimensional lamellar growth of the PEG crystals on the growth faces of the PCL crystals which have already formed a spherulite structure.

The equilibrium melting temperature, $T_m°$, for the PCL constituent in the PCL−PEG copolymers is 61 °C which is comparable, but slightly lower than the $T_m°$ of the PCL homopolymer ($T_m° = 64$ °C). The equilibrium melting temperature, $T_m°$, for the PEG block in both the A−B and $(A)_2$−B copolymers is dramatically lower ($T_m° = 52$ and 56 °C respectively) than the $T_m°$ of the PEG homopolymer ($T_m° = 70$ °C).

It is proposed that the lowering of $T_m°$ of each noncompatible constituent is due to the mutual influence between the PEG and PCL blocks that are covalently bonded. This leads to a decrease of the crystallizable length of the constituent blocks as well as to a reduction of the equilibrium melting temperature $T_m°$.

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