

Effect of Molecular Weight on Spherulitic Growth Rate of Poly(ϵ -caprolactone) and Poly(ϵ -caprolactone)-*b*-poly(ethylene glycol)

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ABSTRACT: The spherulitic growth rates of a series poly(ϵ -caprolactone) homopolymers and poly(ϵ -caprolactone)-*b*-poly(ethylene glycol) (PCL-*b*-PEG) block copolymers with different molecular weights but narrow polydispersity were studied. The results show that for both PCL homopolymers and PCL-*b*-PEG block copolymers, the spherulitic growth rate first increases with molecular weight and reaches a maximum, then decreases as molecular weight increases. Crystallization temperature has greater influence on the spherulitic growth rate of polymers with higher molecular

weight. Hoffman–Lauritzen theory was used to analyze spherulitic growth kinetics and the free energy of the folding surface (σ_e) was derived. It is found that the values of σ_e decrease with molecular weight at low molecular weight level and become constant for high molecular weight polymers. The chemically linked PEG block does not change the values of σ_e significantly. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2986–2991, 2007

Key words: spherulites; crystallization; diblock copolymers

INTRODUCTION

As a biocompatible and biodegradable material, poly(ϵ -caprolactone) (PCL) is of great importance in tissue engineering and controlled release. Since PCL is crystalline and the biodegradation rate of crystalline material is strongly dependent on the crystallinity and crystal structure,^{1–4} study on crystallization of PCL is of great importance. Crystallization behaviors of PCL, including morphology and crystallization kinetics, have been widely reported.^{5–11} However, in most literature the molecular weight distribution of the PCL samples used for study is not monodispersed. As is well known, molecular weight has an important influence on polymer crystallization.¹² Molecular weight can affect chain-folding, reorganization of polymer crystals, and crystallization kinetics due to end-groups and entanglement.^{13–23} Moreover, crystallization of poly(ϵ -caprolactone)-*b*-poly(ethylene glycol) (PCL-*b*-PEG) block copolymers has attracted many research interests,^{24–30} but the effect of molecular weight on spherulitic growth rate of PCL-*b*-PEG block copolymers has not been reported. In this paper, we prepared a series of PCL homopolymers and

PCL-*b*-PEG block copolymers with different molecular weights. The effects of molecular weight on spherulitic growth rate and the free energy of the folding surface were reported.

EXPERIMENTAL

Materials

Aniline, salicyl, and monomethoxy poly(ethylene glycol) were purchased from ACROS. Monomethoxy poly(ethylene glycol) was dissolved in toluene and distilled to remove water. Toluene was refluxed with Na-benzophenone under purified N₂ and distilled prior to use. ϵ -CL (from ACROS) was dried over CaH₂ and distilled under reduced pressure. AlEt₃ was purchased from Aldrich and solution in toluene (1.0M) was used. Polymerization was carried out under a dry Ar atmosphere with a Schlenk technique.

Preparation of the catalyst

The salicylaldehyde–aluminum catalyst was prepared according to literature.³¹ The solution of aniline (2.82 mL mmol) in dry ethanol (20 mL) was slowly added to the mixture of dry ethanol (40 mL), molecular sieve (3 Å), and salicyl (2.82 mL, 2.8 mmol). The mixture was stirred at room temperature overnight and filtrated, and the molecular sieve was washed with AcOEt twice (2 × 10 mL). The solvent was

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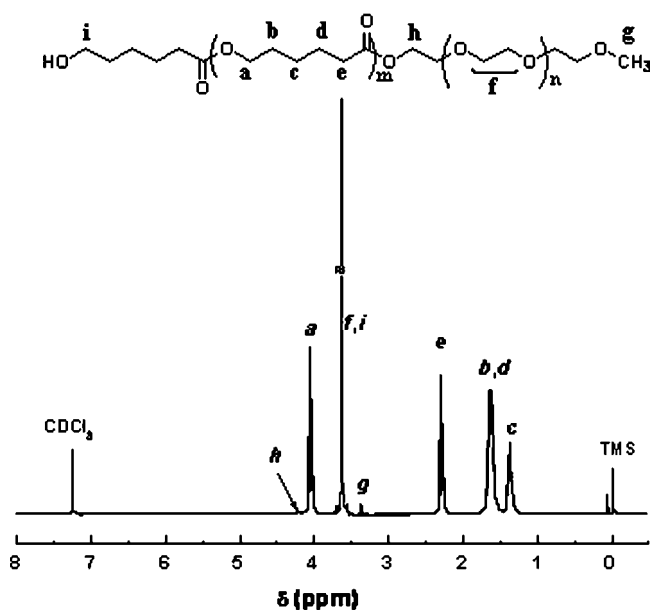


Figure 1 ^1H NMR spectrum of $\text{PCL}_{59}\text{PEG}_{44}$.

evaporated and the crude product was recrystallized in EtOH/AcOEt with a yield of 92%. Solution of AlEt_3 in toluene (1.0M) was added to a solution of *N*-(2-hydroxy-benzylidene) aniline in toluene under N_2 at room temperature, then heated to 70°C and held for 2 h. The obtained catalyst was used without further purification.

Polymerization

For homopolymerization of caprolactone, benzyl alcohol was added to the catalyst solution and the molar ratio of benzyl alcohol to the catalyst was 1 : 1. Prescribed amount of caprolactone was introduced. The polymerization lasted for 16 h at 50°C . For synthesis of PCL-*b*-PEG block copolymers, the solution of monomethoxy poly(ethylene glycol) ($M_n = 1960$, $M_w/M_n = 1.06$) in toluene was added to the catalyst solution at room temperature. The mixture was stirred at 75°C for 2 h, then ϵ -CL was added after it was cooled at room temperature. The reaction was lasted for 16 h at 50°C with stirring. The product was isolated by precipitation into diethyl ether. The polymer was redissolved in CHCl_3 and precipitated with 1-hexane, followed by drying in vacuum at room temperature for 24 h.

Measurements

The polydispersity index of the molecular weight of polymers was determined by GPC in a PL 220 GPC (Polymer Laboratories, Amherst, MA) instrument with tetrahydrofuran as the eluent at 40°C and polystyrene standards for column calibration. ^1H NMR spectra of the polymers in deuterated chloroform

solutions were recorded on a Bruker Avance-500 spectrometer (Rheinstetten, Germany) with tetramethylsilane as the internal standard. The PCL homopolymers and PCL-*b*-PEG block copolymers are also denoted as PCL_n and PCL_nPEG_m , where the subscripts n and m refer to the polymerization degree of the PCL and the PEG. Figure 1 shows the ^1H NMR spectrum of $\text{PCL}_{59}\text{PEG}_{44}$.

The number-average molecular weights of the PCL-*b*-PEG block copolymers can be calculated from the ^1H NMR spectra based on eqs. (1)–(3) (The molecular weights of the end-groups in the polymer chains are not included).³²

$$M_{n,\text{NMR}} = \text{DP}_{\text{PEG}} \times 44 + \text{DP}_{\text{PCL}} \times 114 \quad (1)$$

where

$$\text{DP}_{\text{PEG}} = 3(I_f + I_i)/4I_g \quad (2)$$

$$\text{DP}_{\text{PCL}} = 2\text{DP}_{\text{PEG}}[I_e/(I_f + I_i)] \quad (3)$$

In which $(I_f + I_i)$, I_g , and I_e are the integral intensities of proton resonances at 3.63, 3.37 and 2.30 ppm, respectively, (Fig. 1). The numbers 44 and 114 are the molar masses of the repeating units of the PEG and PCL blocks.

The molecular weight and molecular weight distribution of the PCL homopolymers and PCL-*b*-PEG block copolymers are given in Table I.

Polarized optical microscopy (POM)

An Olympus BX-5 polarized optical microscope (Tokyo, Japan) equipped with a hot-stage and a digital camera was used to study morphology of PCL homopolymers and PCL-*b*-PEG block copolymers under isothermal crystallization conditions. The samples were first melted at 90°C on the hot-

TABLE I
Molecular Weight and Polydispersity
of PCL and PCL-*b*-PEG

Samples	M_n of PEG ^a	M_n of PCL ^a	M_n of the samples ^a	PDI ^b
PCL ₂₄		2,730	2,730	1.08
PCL ₃₉		4,460	4,460	1.07
PCL ₅₇		6,530	6,530	1.05
PCL ₆₅		7,390	7,390	1.13
PCL ₉₃		10,600	10,600	1.13
PCL ₁₁₆		13,200	13,200	1.12
PCL ₂₄ PEG ₄₄	1,950	2,740	4,690	1.17
PCL ₄₀ PEG ₄₄	1,950	4,560	6,510	1.16
PCL ₅₉ PEG ₄₄	1,950	6,730	8,680	1.05
PCL ₆₈ PEG ₄₄	1,950	7,750	9,710	1.06
PCL ₉₀ PEG ₄₄	1,950	10,270	12,220	1.09
PCL ₁₄₂ PEG ₄₄	1,950	16,210	18,160	1.10

^a Determined by ^1H NMR.

^b Determined by GPC.

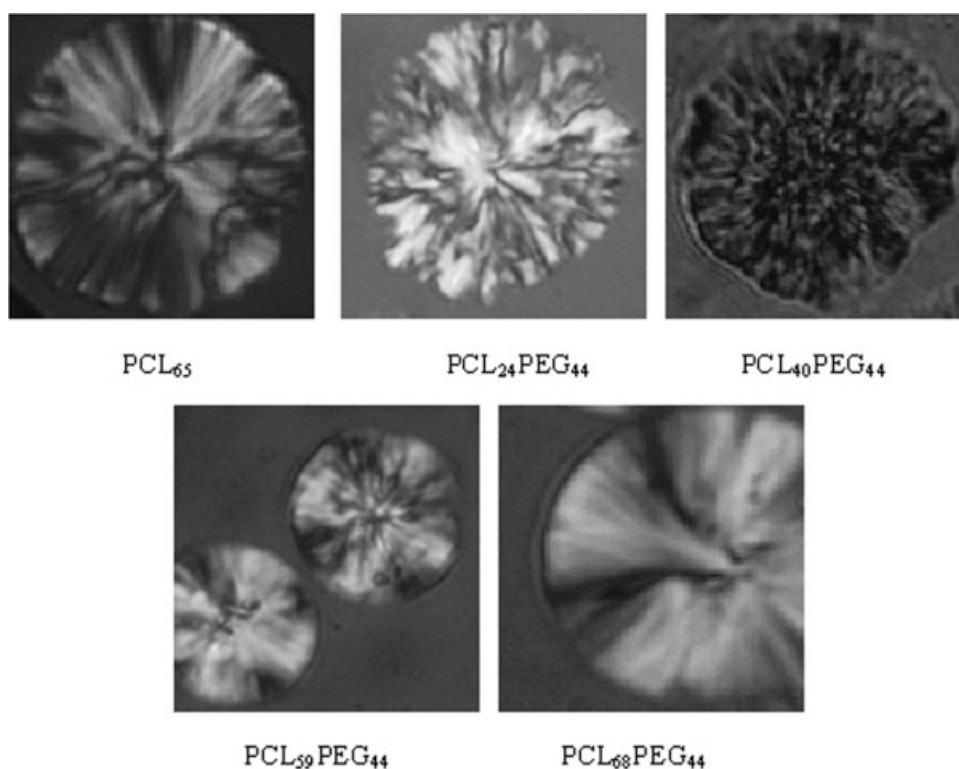


Figure 2 POM micrographs of spherulites of PCL₆₅ and PCL_nPEG₄₄.

stage, and then transferred to another hot-stage at the preset crystallization temperature, T_c , and allowed to crystallize isothermally. The hot-stage was calibrated with standard, sharp-melting substances. During crystallization, the growth of the spherulites was monitored as a function of time and the linear growth rate of spherulites (G) can be determined from the slope in the plot of spherulite radius versus time.

RESULTS AND DISCUSSION

Since in PCL-*b*-PEG block copolymers both PEG and PCL blocks may crystallize, the crystallization temperatures in the present work were chosen for crystallization of PCL block, and PEG block cannot crystallize at these temperatures. The measured spherulitic growth rate is only for the PCL block. The POM micrographs of one PCL homopolymer (PCL₆₅) and four PCL-*b*-PEG block copolymers during isothermal crystallization are shown in Figure 2. It is found that all samples form spherulites. The PCL-*b*-PEG block copolymers with shorter PCL block exhibit less perfect spherulite morphology, as compared with the PCL homopolymer and the PCL-*b*-PEG block copolymers with longer PCL block. It is observed that the spherulites grow linearly as crystallization time increases for all the PCL homopolymer and PCL-*b*-PEG block copolymers, showing that the chemically linked PEG block does not alter the

growth mode of the PCL spherulites. The changes of spherulitic growth rate with crystallization temperature are shown in Figures 3 and 4 for PCL homopolymers and PCL-*b*-PEG block copolymers, respectively. One can see that the spherulitic growth rate decreases as crystallization temperature increases. Especially, the spherulitic growth rate of the polymers

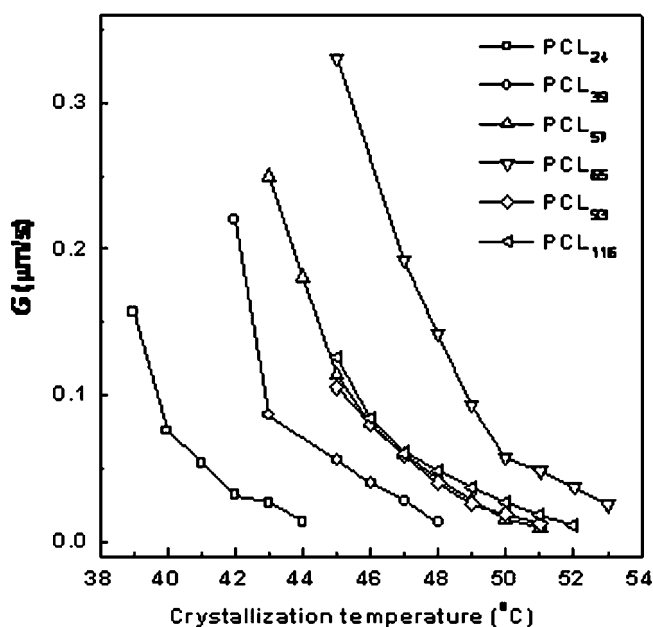


Figure 3 Plots of G versus crystallization temperature for PCL_n.

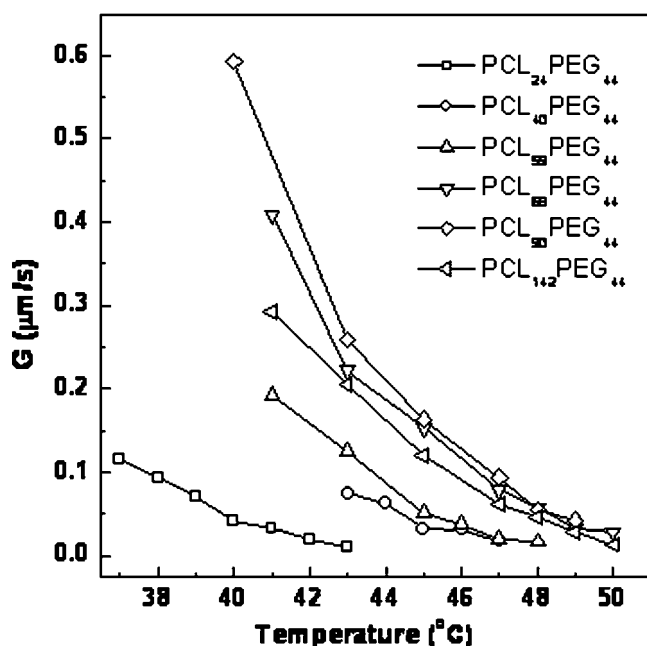


Figure 4 Plots of G versus crystallization temperature for PCL_nPEG_{44} .

with higher molecular weight decreases more rapidly, indicating a stronger dependence on T_c . The spherulitic growth rate is also plotted against molecular weight, as shown in Figures 5 and 6. It is observed that, for both PCL homopolymers and PCL-*b*-PEG block copolymers, the spherulitic growth rate does not change monotonically with molecular weight. The spherulitic growth rate firstly increases with molecular weight and reaches a maximum, then decreases with molecular weight. Similar phenomenon

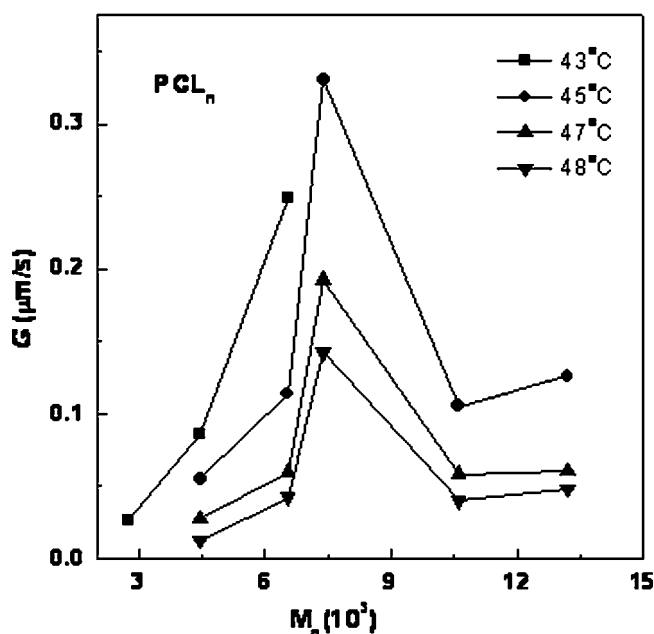


Figure 5 Plots of G versus M_n for PCL_n .

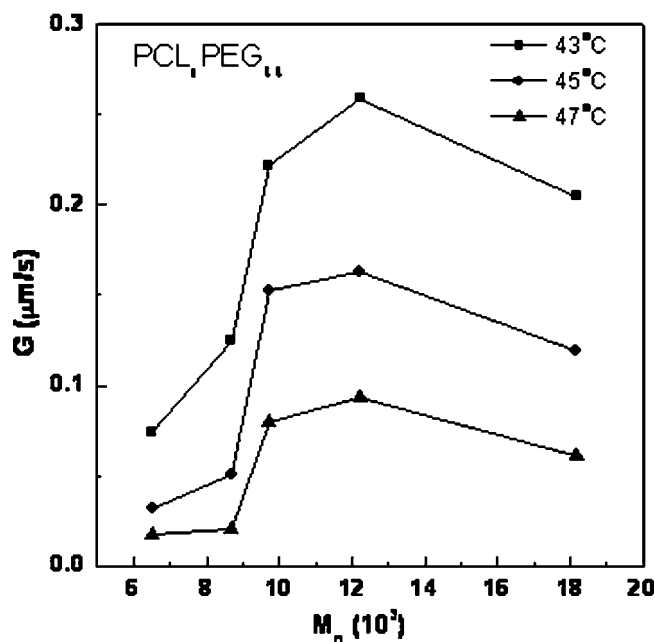


Figure 6 Plots of G versus M_n for PCL_nPEG_{44} .

has been reported for PCL homopolymers in literature,³³ but the molecular weight corresponding to the maximal G is slightly larger than that in our work. When comparing the spherulitic growth rates of PCL homopolymers and PCL-*b*-PEG block copolymers with similar molecular weights at the same crystallization temperature, for example, 45 and 47°C, the spherulitic growth rate of the PCL-*b*-PEG block copolymer is smaller than that of the PCL homopolymer with similar molecular weight. Obviously, the chemically linked PEG block reduces the spherulitic growth rate of the PCL.

Based on the crystallization regime theory of Lauritzen and Hoffman,³⁴ the linear growth rate (G) of polymer spherulites can be expressed as the following:

$$G = G_0 \exp[-U^*/R(T_c - T_0)] \exp[-K_g/T_c(T_m^0 - T_c)f] \quad (4)$$

where G_0 is a constant and is independent of temperature, U^* is the activation energy related with the short distance diffusion of the crystalline unit across the phase boundary, T_c is crystallization temperature, T_0 is the temperature below which there is no chain motion (usually $T_0 = T_g - 30$ K), f is the correction factor and is equal to $2T_c/(T_m^0 + T_c)$.

The nucleation constant, K_g , is expressed as:

$$K_g = j b_0 \sigma \sigma_e T_m^0 / k (\Delta h_f) \quad (5)$$

where $j = 4$ for crystallization regimes I and III, and $j = 2$ for crystallization regime II, b_0 is the layer thick-

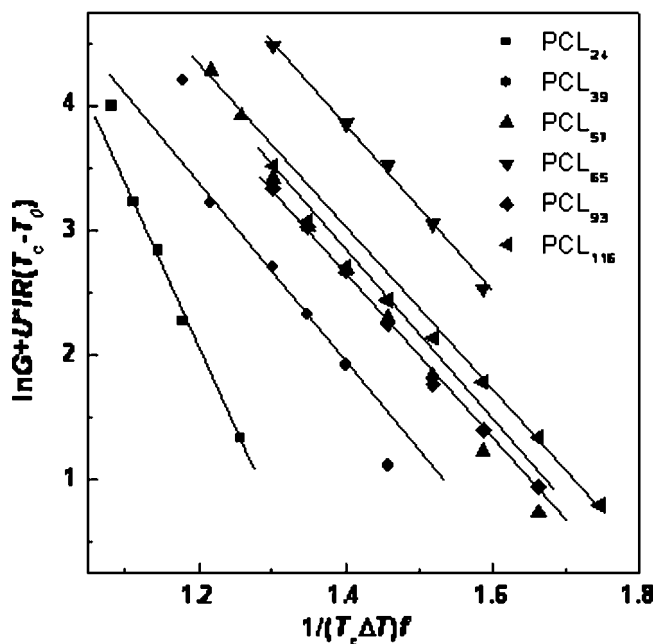


Figure 7 Plots of $\ln G + U^*/R(T_c - T_0)$ versus $1/T_c(\Delta T)f$ for PCL_n .

ness, σ is the lateral surface free energy, σ_e is the free energy of the folding surface, Δh_f is fusion enthalpy, and k is Boltzmann's constant. The values of U^* , T_m^0 , T_g , T_0 , Δh_f , b_0 , and σ are 6.28 kJ/mol, 343.3 K, 213 K, 183 K, 1.63×10^8 J/m³, 4.12 Å, and 6.7 erg/cm², respectively.⁵ The value of T_m^0 may vary with molecular weight and also is different for the PCL homopolymer and PCL-*b*-PEG block copolymer. For simplicity, the value of 343.3 K is used as T_m^0 for all samples in the present work. We have tested different values of T_m^0 around this value, no significant differences are observed, as reported by literature.⁵

Figures 7 and 8 shows the plots of $\ln G + U^*/R(T_c - T_0)$ versus $1/T_c(\Delta T)f$ for PCL_n and PCL-*b*-PEG, respectively. Linear relationship is observed for all samples. Assuming that crystallization takes place in regime II, the free energy of the folding surface (σ_e) can be calculated. The change of σ_e with molecular weight was shown in Figure 9 for PCL and PCL-*b*-PEG. It is found that the values of σ_e for both PCL homopolymers and PCL-*b*-PEG block copolymers show similar dependence on molecular weight. When the molecular weight is low, the value of σ_e is larger and decreases rapidly as molecular weight increases. For high molecular weight polymers, σ_e does not change with molecular weight. The larger σ_e for the low molecular weight polymers may be due to higher portion of end-groups enriched at the folding surface. The values of σ_e for higher molecular weight PCL homopolymers and PCL-*b*-PEG block copolymers range from 80 to 90 erg/cm², which are similar to the values reported in literature.^{5,33} One can also see from Figure 9 that, when the molecular

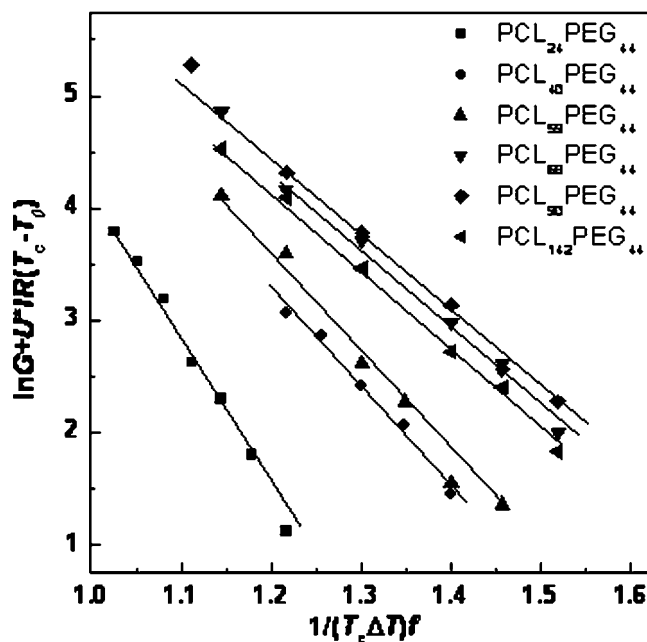


Figure 8 Plots of $\ln G + U^*/R(T_c - T_0)$ versus $1/T_c(\Delta T)f$ for $PCL_n\text{-PEG}_{44}$.

weight of PEG block is subtracted from that of PCL-*b*-PEG block copolymer, the σ_e of PCL homopolymers is similar to that of the PCL-*b*-PEG block copolymers with the same PCL length, showing that the PEG block does not change the free energy of the folding surface significantly.

CONCLUSIONS

The effect of molecular weight on spherulitic growth of PCL homopolymers and PCL-*b*-PEG block copoly-

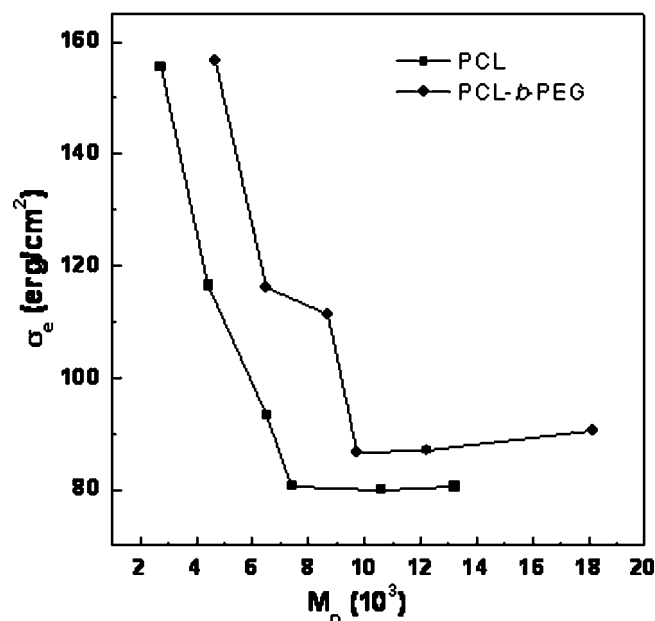


Figure 9 Change of free energy of the folding surface with molecular weight.

mers were examined for the first time and a maximal spherulitic growth rate is reached at a certain molecular weight. The spherulitic growth rate of polymers with a higher molecular weight is more dependent on crystallization temperature. Analysis with Hoffman–Lauritzen theory shows that the low molecular weight polymers have much higher free energy of the folding surface (σ_e), while for high molecular weight polymers, σ_e does not change.

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