

Supplementary Information of

The crystallization kinetics of Poly (ϵ -caprolactone-co-trimethylene carbonate) (PCLTMC): effects of the molar ratio of CL and TMC

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Table S1 Molecular characteristics of the copolymers

Samples	CL/TMC composition	M_n^b (kg/mol)
PCLTMC-1	95/05	127
PCLTMC-2	90/10	144
PCLTMC-3	85/15	135
PCLTMC-4	80/20	131

^a Experimental composition in volume % as determined by ¹H NMR. $\rho_{\text{PCL}} = 1.15 \text{ g/cm}^3$ of a pure PCL homopolymer and $\rho_{\text{PTMC}} = 1.20 \text{ g/cm}^3$ of a pure PTMC homopolymer were used for the calculations.

^b Experimental M_n estimated by Ubbelohde viscometer for the copolymers using the viscometric methodology.

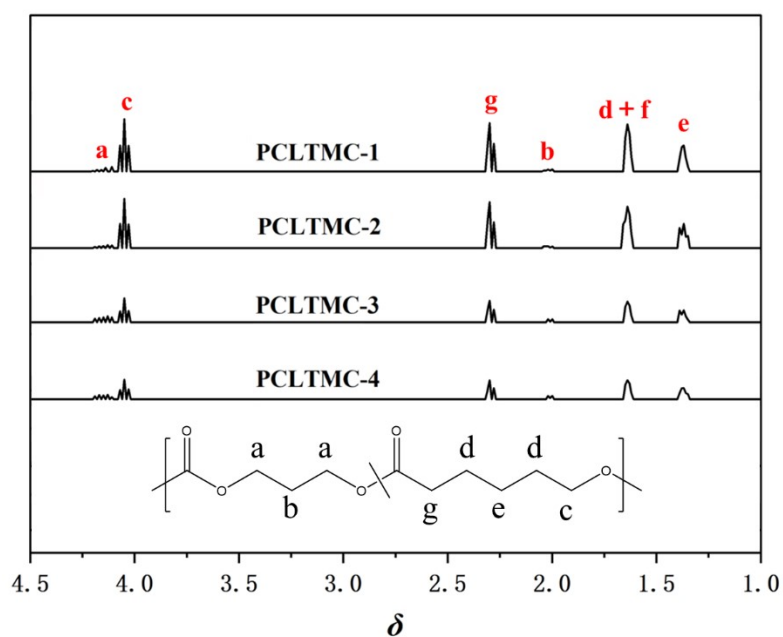


Figure S1 ¹H NMR spectra of polymers

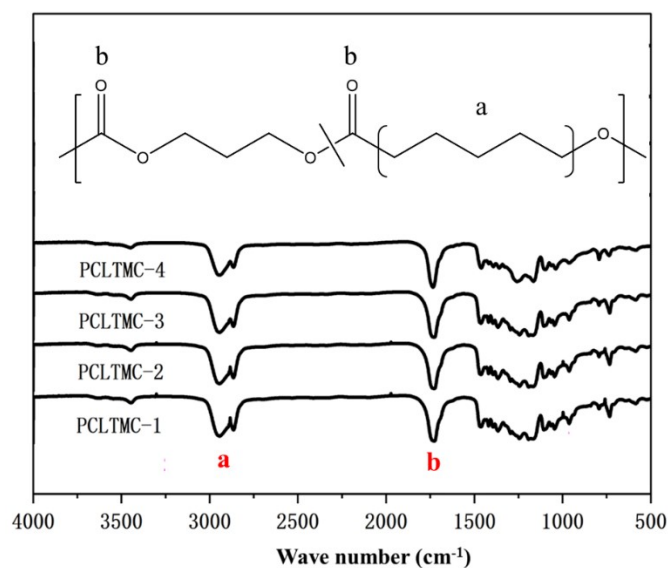


Figure S2 FT-IR spectra of polymers

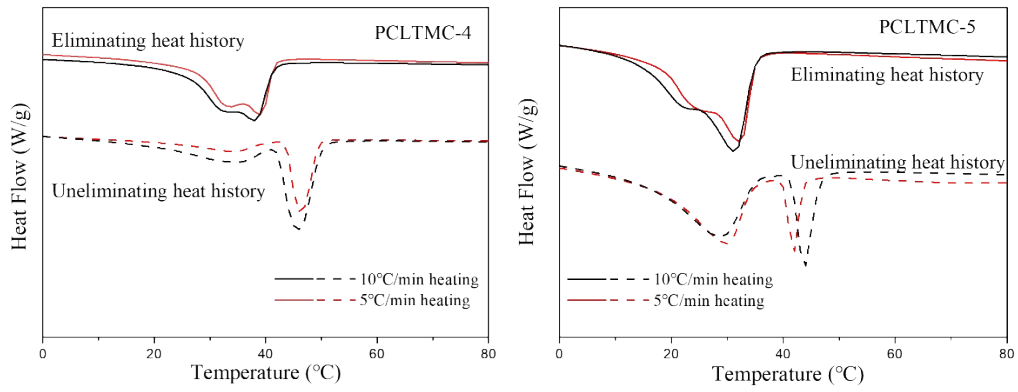


Figure S3 Double melting peak changes of PCLTMC-4 and PCLTMC-5

Table S2 The relationship between N and crystallization style

	homogeneous nucleation	heterogeneous nucleation
1D (acicular crystal)	1+1=2	1+0=1
2D (lamellar crystal)	2+1=3	2+0=2
3D (spherical crystal)	3+1=4	3+0=3

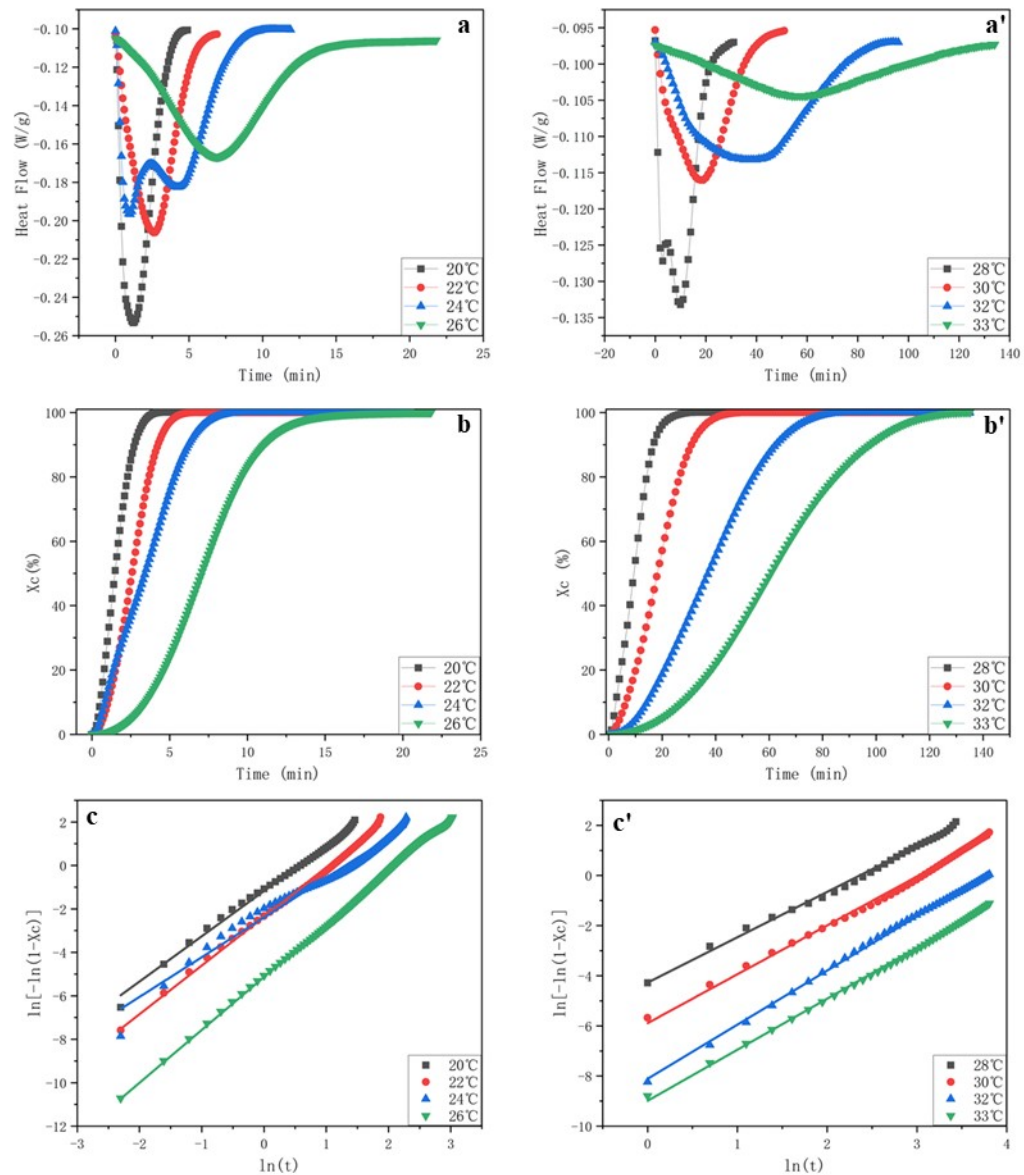


Figure S4 The Avrami isothermal crystallization kinetics of PCLTMC-2 (a, a' DSC isothermal crystallization curves at different T_c ; b, b' relationship between relative crystallinity and isothermal crystallization time; c, c' in isothermal crystallization process of $\ln[-\ln(1-X_c)]$ and $\ln(t)$ relation).

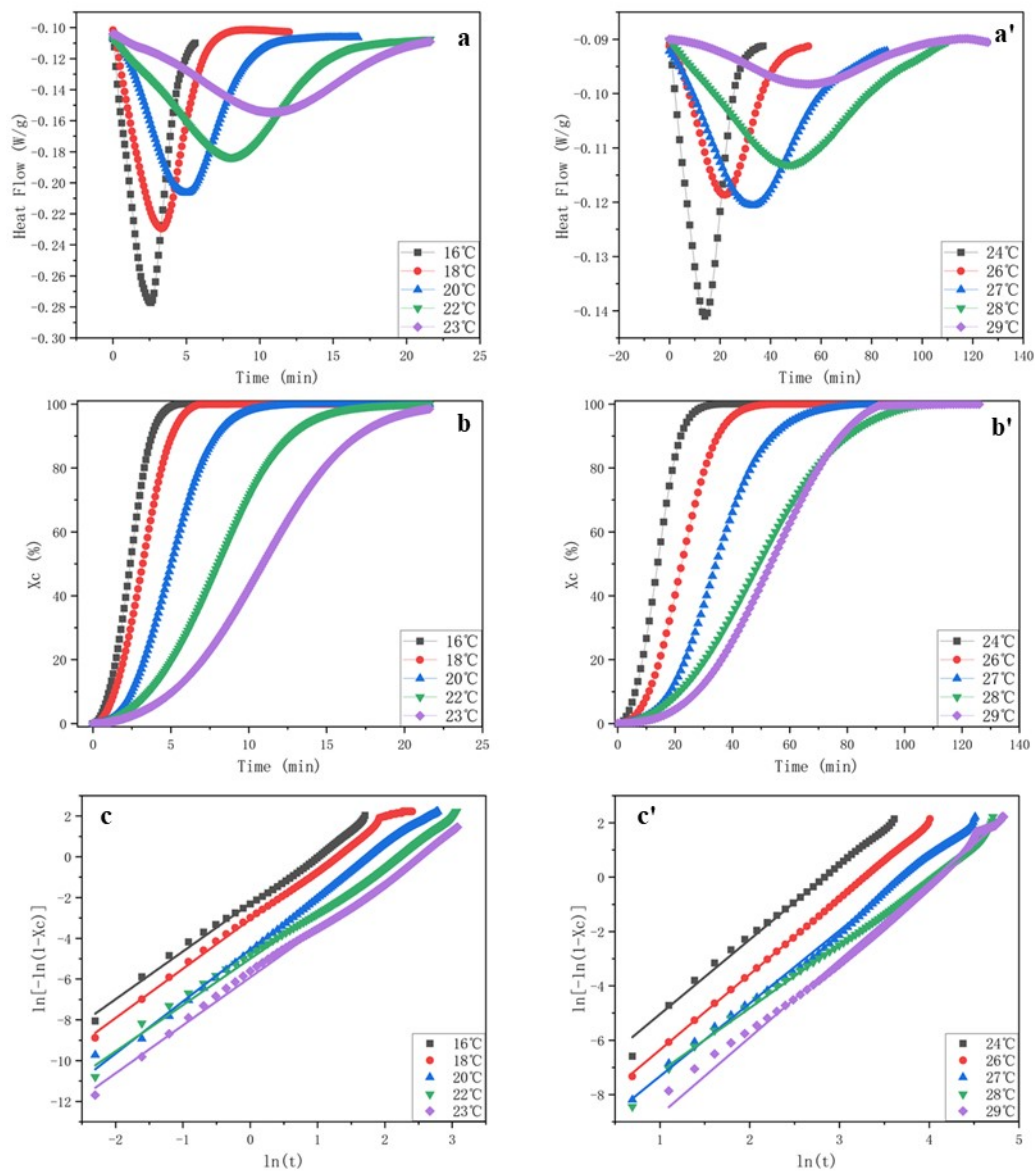


Figure S5 The Avrami isothermal crystallization kinetics of PCLTMC-3 (a, a' DSC isothermal crystallization curves at different T_c ; b, b' relationship between relative crystallinity and isothermal crystallization time; c, c' in isothermal crystallization process of $\ln[-\ln(1-X_c)]$ and $\ln(t)$ relation).

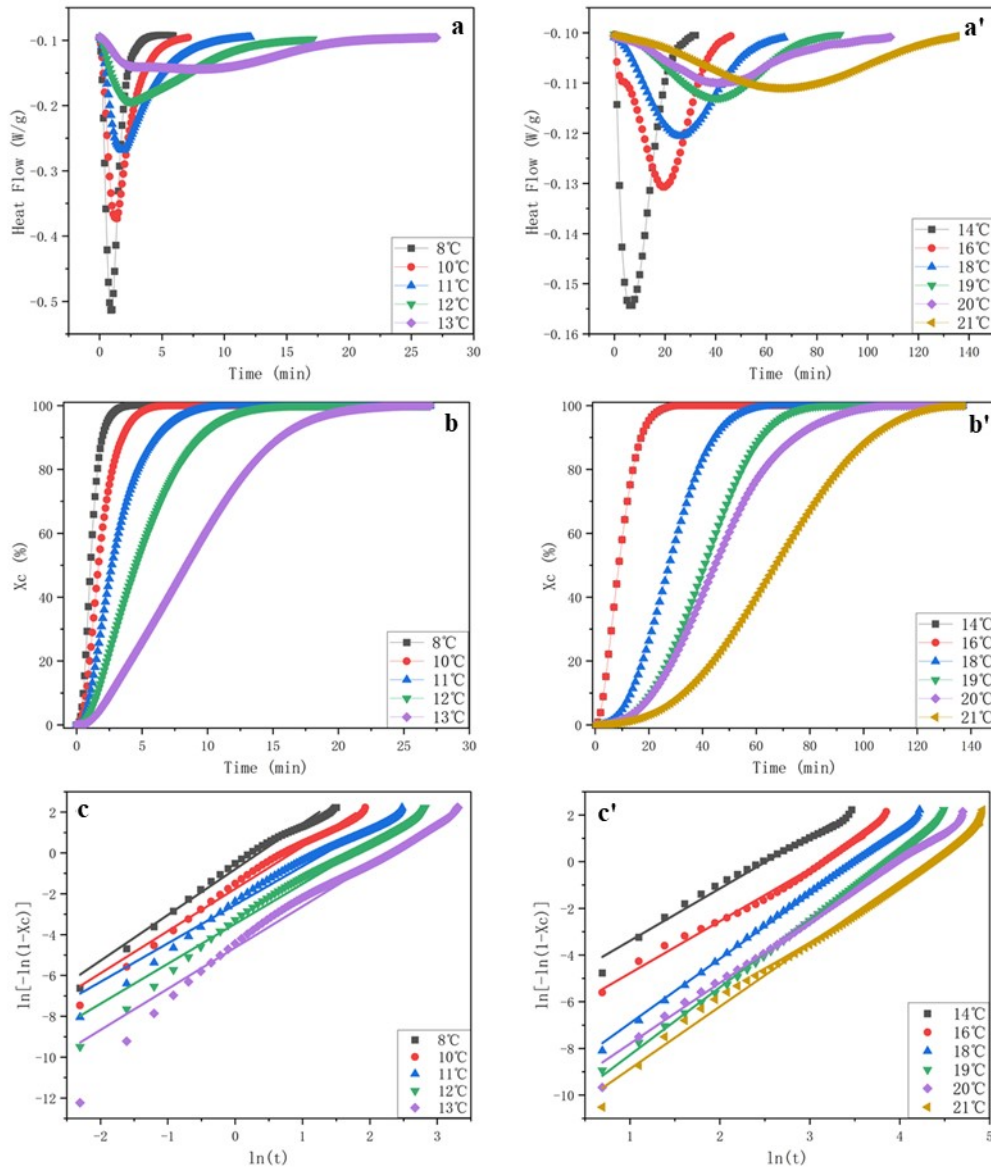


Figure S6 The Avrami isothermal crystallization kinetics of PCLTMC-4 (a, a' DSC isothermal crystallization curves at different T_c ; b, b' relationship between relative crystallinity and isothermal crystallization time; c, c' in isothermal crystallization process of $\ln[-\ln(1-X_c)]$ and $\ln(t)$ relation).

Lauritzen-Hoffman theory

Lauritzen-Hoffman theory, also known as surface nucleation theory, is one of the classical theories of crystal dynamics. This theory is the most widely used crystallization theory, which can explain the formation of wafer morphology and chain folding conformation. According to Lauritzen-Hoffman theory, polymer crystallization requires the stacking of a chain segment on the substrate (i.e., a previously grown crystal) and then spreading growth to the sides. So, the first chain segment is the most difficult to stack on the substrate surface and has the largest barrier to overcome. Therefore, Lauritzen-Hoffman theory divides three nucleation modes of polymer chains on the substrate surface: Regime I, Regime II, and Regime III, according to the different degrees of undercooling during melt crystallization (Figure S7).

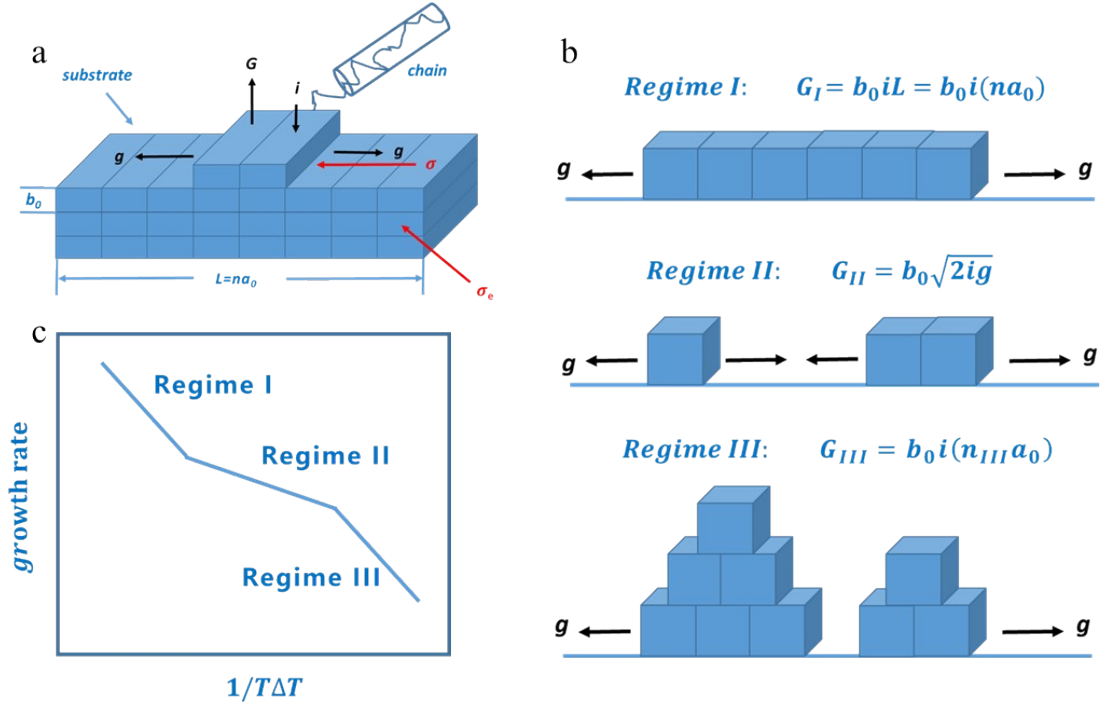


Figure S7 Lauritzen-Hoffman theoretical model. a) Lauritzen-Hoffman theoretical model; b) Three types of surface nucleation in Lauritzen-Hoffman theoretical model; c) The relationship between crystallization rate and undercooling for 3 surface nucleation modes in Lauritzen-Hoffman theoretical model.

A nucleation event causes lateral growth of crystals of length L and thickness b_0 . The line growth rate of Regime I is

$$G_I = b_0 i L = b_0 i (na_0) \quad (1)$$

Regime II occurs at low T_c and nucleation rate is fast. And multiple nucleation events can occur. The line growth rate of Regime II is

$$G_{II} = b_0 \sqrt{2ig} \quad (2)$$

Regime III occurs at extremely low T_c , where the rate of nucleation is so fast that the average distance between each nucleation event approaches the chain width. Therefore, crystal lateral growth actually replaced by surface nucleation events ($G_{III} \propto i$).

$$G_{III} = b_0 i (n_{III} a_0), \quad n_{III} \text{为} 2.0 \sim 2.5 \quad (3)$$

Hoffman-Weeks extrapolation method and Crystallization rate growth fitting method

Hoffman-Weeks extrapolation method is derived by substituting the wafer expression obtained by Lauritzen-Hoffman theory into Gibbs-Thomson equation, and its basic equation is as follows:

$$T_m = T_m^0 \left(1 - \frac{1}{r}\right) + \frac{T_c}{r} \quad (4)$$

T_c is crystallization temperature; T_m is melting point in T_c ; r is the thickening coefficient. When r is constant, with T_m to T_c drawing a straight line can be obtained. The straight line and $T_m = T_c$ (free energy for 0) intersection, the equilibrium melting point $T_m^0(\infty)$ can be obtained.

Crystallization rate growth fitting method is a method to get equilibrium melting point by

fitting the crystallization rate of polymer according to Lauritzen-Hoffman theory. Its basic expression is

$$\ln G_i + \frac{U^*}{R(T_c - T_\infty)} = \ln G_i^0 - \frac{K_{g(i)}}{T_c \Delta T f(T_c)} \quad (5)$$

Where, the growth rate subscript i is three different kinetic intervals in Lauritzen-Hoffman theory: Regime I, Regime II and Regime III. ΔT is the condensate depression; $K_{g(i)}$ is the nucleation constant. The expressions is

$$K_{g(i)} = \frac{2j_i b_0 \sigma \sigma_e T_m^0}{k \Delta H_f} \quad (6)$$

The equation on the left as a whole, for $\frac{1}{T_c \Delta T f(T_c)}$ drawing a straight line can be obtained. The best linear fitting relationship represents is the equilibrium melting point $T_m^0(\infty)$.

Inference details for Table 1

As shown in Figure 7, the slope $K_{g(i)}$ of PCLTMC-1 and PCLTMC-2 are 131×10^3 and 176×10^3 respectively, and the intercept G_i^0 is 44.3×10^3 and 50×10^3 respectively. $K_{g(i)}$ represents the crystal growth rate, and G_i^0 represents the crystal nucleation rate. According to Thomas-Stavely relationship:

$$\sigma = b_0 \Delta H_f \alpha \quad (7)$$

ΔH_f is the melting heat (163 J/cm^3) of a unit volume PCL perfect crystal; k is Boltzmann constant ($1.38 \times 10^{-23} \text{ J/K}$); b_0 is the thickness of (110) crystal plane, which is 0.412 nm. For polyethylene and other hydrocarbon crystals, alpha is equal to 0.1.

Due to its low undercooling, j_i is relative to Regime III. Eq (3) can be used to calculate the value of σ_e ; q is the energy of Adjacent Re-entry folding,

$$\sigma_e = \frac{q}{2A_0} + \sigma_{e0} \quad (8)$$

A_0 can be calculated from crystallographic data as $18.6 \times 10^{-20} \text{ m}^2$. As with polyethylene, σ_{e0} is tricky to determine. The crudest approximation makes it equal to zero, while another approach might make it equal to $\sigma = 6.72 \text{ erg/cm}^2$. In PCLTMC-1 and PCLTMC-2, $\sigma_{e0} = 0$ and the q value is $3.0 \times 10^{-13} \text{ erg}$, while $\sigma_{e0} = \sigma = 6.72 \text{ erg/cm}^2$ yields a q value of $2.7 \times 10^{-13} \text{ erg}$. Either way, the differences are not very large and are within the acceptable range of known values. But in fact, the addition of oxygen in the main chain may produce a lower folding free energy, and the calculation of the actual folding energy is complicated and may lead to the opposite result. Therefore, the experimentally determined correspondence between the folding energies of the two polymers cannot be used as evidence of identical folding.