Melting Behavior and Non-isothermal Crystallization Kinetics of Copolyamide 6/12

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Abstract

Polymer crystallization obeys the laws of thermodynamics. Studying dynamic crystallization from melt to solid state may extend the general understanding of the crystallization behavior of polymers. In this work, non-isothermal crystallization kinetics of copolyamide 6/12 (CoPA6/12) with different copolymerization ratios were investigated by differential scanning calorimetry (DSC). Jeziorny modified Avrami equation, Ozawa equation and Liu-Mo's method were applied to analyze the non-isothermal crystallization kinetics of CoPA6/12. The crystallization activation energy was evaluated using both Kissinger and Friedman methods. Results show that the incorporation of ω -lauro lactam (LL) into polyamide 6 (PA6) decreases crystallization rate and increases crystallization activation energy. The findings further indicate that

the crystallization of polyamide is inhibited because copolymerization hinders the formation of PA6 crystal nuclei.

Key words: Copolyamide; Non-isothermal crystallization; ω -laurolactam; Crystallization activation energy

1. Introduction

Polyamide (PA), commonly known as Nylon, was first synthesized by W. H. Carothers at Dupont in the 1930s.^[1] Since then, it has been widely applied as fibers and as engineering thermoplastics because of its beneficial properties, which include solvent resistance, corrosion resistance, toughness, relative high modulus, low creep, dimensional stability, and good processability.^[2] It also presents some drawbacks like high water absorption, low impact resistance, and limited transparency. Therefore, numerous modification methods have been applied to improve PA properties; among these methods, copolymerization has gained considerable attention for improving optical, thermal and mechanical properties, due to easy accessibility and high efficiency.^[3, 4] In particular, copolyamides have been synthesized by copolymerization of ϵ -caprolactam (CL) with a second monomer, for application in optical devices, motor parts, cosmetics, adhesive packing material, food packaging, films, monofilaments, and other fields.^[5, 6] Within copolyamides, copolyamide 6/12 (CoPA6/12) offers a low melting point and good transparency. It is commonly synthesized by random copolymerization, and it is used as hot melt adhesive to bond garments fabrics and nonwovens,^[7, 8] as flexible monofilaments in brushes, and as films in packaging.

Goodman and Kehayoglou^[9-11] synthesized CoPA6/12 by anionic

copolymerization of CL with ω -lauro lactam (LL) at 180 °C, using sodium caprolactamate-N-phenylcarbamoylecaprolactam as the initiator-activator system. They characterized the crystallization behavior of the copolymer by DSC, FTIR and NMR, and their melting temperature and density measurements indicated a minimum crystallinity with a CL proportion of 50-60 mol%. Moreover, mechanical properties, water absorption and rheological properties of CoPA6/12 in various compositions have been extensively discussed in literature. Rusu et al.^[12] studied thermal and dielectric behaviors of CoPA6/12, concluding that the copolyamide possesses a good thermal stability which is equivalent to that of PA6. Garner et al.^[13] discussed the effect of composition on the properties of CoPA6/12 and found that the glass transition temperature (T_g) is affected by the degree of crystallinity of the copolymer. Álvarez-Láinez et al.^[14] examined the correlation of thermal and tensile behavior with the friction coefficient of CoPA6/12. They concluded that using 60 wt% of LL, degree of crystallinity and elastic modulus of CoPA6/12 reach a minimum, while elongation and coefficient of friction reach a maximum.

The properties of polymers are not only determined by their chemical structure, chain conformation and molecular weight, but they are also affected by the condensed structure formed during processing, where crystallization plays a key role.^[15, 16] Therefore, the investigation of polymer crystallization kinetics is of great importance, both from a scientific and from a technical point of view. Many respective research studies on polyamides have been reported: isothermal crystallization kinetics of Nylon 66/6,^[17] Nylon 6/11,^[18] Nylon 6/6T and Nylon 66/6T,^[19] non-isothermal crystallization

kinetics of Nylon 12,^[16] Nylon 66/LCP blends,^[20] semi-aromatic polyamides,^[15] isothermal and non-isothermal crystallization of Nylon 11,^[21] Nylon 1011,^[22] Nylon 1111,^[23] Nylon 1212,^[1] Nylon 1012,^[24] Nylon 1313,^[25] Nylon 46.^[26] But as far as we know, there is still scarce literature about the non-isothermal crystallization of random copolyamides. In this work, we discuss the non-isothermal crystallization kinetics of CoPA6/12, as well as its crystallization and melting behavior according to differential scanning calorimetry (DSC) measurements.

2. Experimental section

2.1. Materials

ϵ -caprolactam (CL) was purchased from Shanghai Macklin Biochemical Co. Ltd. ω -laurolactam (LL) was purchased from Shanghai Superplas Technology Co., Ltd. LL was vacuum dried at 105 °C prior to use. Phosphoric acid (H_3PO_4) was purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of random CoPA6/12

The synthesis of CoPA6/12 is as follows:^[27] A given amount of CL and LL (Table S1), 9.0 g H_3PO_4 , and 90 mL deionized water were added into a 10 L autoclave (GSH-10, Jinxin Petrochemical Equipment CO., LTD, China), which was previously purged with nitrogen for 10 min at 80 °C. The formulation was stirred at a rotational speed of 100 rpm, with the temperature rising to 280 °C in 3 hours, and the pressure reaching 1.0~1.2 MPa. After two hours at constant temperature and pressure, a depressurization

step down to atmospheric pressure was applied, and nitrogen gas was bubbled through a vessel for 2 hours to remove any trace of H₂O from the system. The polymeric material was extruded through a discharge slit by increasing the pressure with nitrogen gas. Finally, a cooling program was applied. After extraction and drying, the random copolyamide was obtained. Copolyamide in 100/0 (PA6), 90/10, 80/20, 70/30, 60/40, 50/50 compositions were prepared by changing the feeding ratio of CL/LL. In this work, the copolymer is named after its monomer content, e.g. CoPA6/12(90/10) means a copolymer synthesized with 90 mol% CL and 10 mol% LL. The relative viscosities of CoPA6/12 samples, measured by an Ubbelohde viscometer, are shown in Table S1.

2.3. Differential scanning calorimetry

The melting behavior and crystallization kinetics of samples were assessed by differential scanning calorimetry (DSC) using a Mettler DSC 3 (Mettler Toledo, Switzerland).

Melting behavior: A test sample was heated from room temperature up to 250 °C at a rate of 10 °C/min under nitrogen gas, with a flow rate of 40 mL/min. After 5 minutes at isothermal condition to eliminate the thermal history of the sample, a cooling ramp of 20 °C/min was conducted down to 20 °C, followed by a second heating ramp of 20 °C/min up to 250 °C.

Non-isothermal crystallization kinetics: A test sample was heated from room temperature up to (T_m+30) °C at a rate of 60 °C/min. After 5 minutes at isothermal condition to eliminate the thermal history of the sample, it was cooled down to 20 °C

at rates of 2, 5, 10, 20, 30 and 40 °C/min, respectively. Finally, the sample was heated up to 250 °C at 20 °C/min. Prior to the experiment, the instrument was calibrated using indium with a melting point of 156.6 °C and a fusion enthalpy of 28.5 J/g. To reduce discrepancies originating from variations in sample weight, all samples possessed a mass of 6.0 ± 0.2 mg.

3. Results and discussion

3.1. Non-isothermal crystallization behavior

The DSC cooling curves of PA6 and CoPA6/12 with varying copolymerization ratios can be seen for different cooling rates in Fig. 1 and Fig. S1, while their corresponding values are shown in Table 1.

For all samples, a single crystallization peak appears, indicating the completion of copolyamide polymerization from CL and LL. With increasing amounts of LL, the exothermic peak shifts to lower temperature as shown in Fig. 1(a), and it disappears when the ratio of LL reaches 40% and above. The random incorporation of LL into PA6 interrupts the polymer chain regularity, causing structure defects.^[28] The long alkyl chain in LL increases the proportion of $-\text{CH}_2-$, while the proportion of $-\text{CONH}-$ decreases. As a result, the hydrogen bond density of polyamide is reduced, which also accounts for the reduction of the degree of crystallinity.^[29]

With increasing cooling rate, the crystallization peak of CoPA6/12(90/10) shifts to lower temperatures and becomes broader (Fig. 1(b)). At a cooling rate of 2 °C/min, the onset temperature is about 168.78 °C and decreases to 141.00 °C at a cooling rate of

40 °C/min (Table 1). From the values of $t_{1/2}$ listed in Table 1, the time for crystallization is limited at high cooling rates. This might be explained by the fact that chain segments do not have enough time to arrange into perfect crystals at high cooling rates. The decrease of enthalpy (ΔH_c) also indicates that high cooling rates hinder the crystallization of copolyamide. It is also worth noting that the DSC curve of CoPA6/12(70/30) does not show any crystallization peak at 20 °C/min (Fig. S1, Table 1). As a result, we can conclude that both copolymerization and high cooling rates during processing can produce amorphous polyamides. Of course, the mechanical properties of the copolymer will differ from those of PA6 as well.

Figure 1

Figure 1. DSC heat flow of non-isothermal crystallization of (a) different CoPA6/12 samples at a cooling rate of 10 °C/min, and (b) CoPA6/12(90/10) at different cooling rates.

Table 1. Onset crystallization temperature ($T_{c \text{ onset}}$), crystallization peak (T_c) crystallization enthalpy (ΔH_c), and half time of crystallization ($t_{1/2}$) of PA6 and different CoPA6/12 samples at various cooling rates (Φ). (n.d.: not detected)

CoPA6/12 sample (CL/LL molar ratio)	Φ (°C/min)	$T_{c \text{ onset}}$ (°C)	T_c (°C)	ΔH_c (J/g)	$t_{1/2}$ (min)
100/0	2	196.60	193.53	66.23	3.95
	5	191.57	188.25	62.75	2.15
	10	187.11	183.50	58.88	0.95
	20	182.48	177.67	54.83	0.53
	30	178.69	173.50	52.22	0.40
	40	176.49	170.67	50.57	0.33
90/10	2	168.78	160.57	46.19	6.90
	5	162.89	152.58	41.67	2.97
	10	157.56	144.17	38.10	1.73
	20	150.78	133.00	34.69	1.12

	30	145.89	124.00	35.36	0.95
	40	141.00	117.67	34.11	0.82
80/20	2	149.61	141.40	41.53	7.60
	5	141.40	130.58	36.71	3.43
	10	132.81	119.17	32.15	2.00
	20	123.76	103.33	25.85	1.55
	30	118.44	96.00	11.61	0.98
	40	115.17	93.33	5.62	0.70
70/30	2	129.40	121.63	29.38	7.03
	5	117.92	107.92	26.57	3.87
	10	108.21	92.50	19.77	2.45
	20	n.d.	n.d.	n.d.	n.d.
	30	n.d.	n.d.	n.d.	n.d.
	40	n.d.	n.d.	n.d.	n.d.
60/40	2	n.d.	n.d.	n.d.	n.d.
	5	n.d.	n.d.	n.d.	n.d.
	10	n.d.	n.d.	n.d.	n.d.
	20	n.d.	n.d.	n.d.	n.d.
	30	n.d.	n.d.	n.d.	n.d.
	40	n.d.	n.d.	n.d.	n.d.
50/50	2	n.d.	n.d.	n.d.	n.d.
	5	n.d.	n.d.	n.d.	n.d.
	10	n.d.	n.d.	n.d.	n.d.
	20	n.d.	n.d.	n.d.	n.d.
	30	n.d.	n.d.	n.d.	n.d.
	40	n.d.	n.d.	n.d.	n.d.

3.2. Non-isothermal crystallization kinetics

3.2.1. Avrami analysis

To study the non-isothermal crystallization kinetics of random CoPA6/12, all samples that showed exothermal crystallization peaks at each selected cooling rate were assessed, namely PA6, CoPA6/12(90/10) and CoPA6/12(80/20). By evaluating the crystallinity as a function of time, the non-isothermal crystallization kinetics can be determined. The relative degree of crystallinity, X_c , is calculated by integrating the DSC exothermal peaks according to the following equation:

$$X_c(T) = \int_{T_0}^T \left(\frac{dH}{dT} \right) dT \Bigg/ \int_{T_0}^{T_\infty} \left(\frac{dH}{dT} \right) dT \quad (1)$$

where T_0 and T_∞ are the start and the end temperature of crystallization, respectively.

The numerator and denominator refer to the absolute crystallinity at temperature T , and at the end of the crystallization process, respectively. The plots of $X_c(T)$ of the selected samples at different temperatures are displayed in Fig. 2(a-c). The crystallization time, t (min), is calculated by applying the following equation:

$$t = \frac{|T_0 - T|}{\phi} \quad (2)$$

where Φ is the cooling rate ($^{\circ}\text{C}/\text{min}$). As a result, plots of $X_c(t)$ versus crystallization time (t) can be obtained (Fig. 2(d-f)).

Figure 2

Figure 2. Plots of relative crystallinity as a function of temperature (a-c) and time (d-f).

For all samples, crystallinity vs. temperature curves present reverse S-like shapes, while crystallinity vs. time curves show S-like shape, which is consistent with previous results on the crystallization of polyamide and its copolymers.^[21, 24]

In earlier isothermal crystallization studies of polymers,^[30, 31] the Avrami equation is the most prominent. The equation can be expressed as follows:

$$1 - X_c = \exp(-Z_t t^n) \quad (3)$$

$$\log[-\ln(1 - X_c)] = n \log t + \log Z_t \quad (4)$$

where X_c is the relative degree of crystallinity as calculated above (Eq. 1). Z_t is the rate

constant (min^{-n}) and t is the time (min). n is the Avrami exponent, which depends on the nucleation mechanism and the crystal growth mode.^[32] Its value is the sum of space dimension of spherulitic growth mode, and time dimension of nucleation. The values for n and Z_t can be attained from slope and intercept of the plots of $\log[-\ln(1-X_c)]$ versus $\log t$, respectively. As shown in Fig. 3, the curves are not overall linear lines, especially not at lower cooling rates, indicating an interplay of different crystallization processes. The slopes decrease at the end of the crystallization process, which corresponds to spherulitic impingement and secondary crystallization.^[33] However, they show linearity at the primary stage, i.e. where $\log[-\ln(1-X_c)] < 0$, hence the values of the Avrami equation were calculated from this region. Respective results are listed in Table 2.

Table 2. Avrami exponent (n), rate constant (Z_t), coefficient of determination R^2 , modified rate constant (Z_c), and normalized rate constant (K_a) of PA6, CoPA612(90/10) and CoPA6/12(80/20) at various cooling rates (Φ).

CoPA6/12 (CL/LL ratio)	Φ (°C/min)	n	Z_t (min^{-n})	R^2	Z_c (min^{-n})	K_a (min^{-1})
100/0	2	4.71	1.94×10^{-3}	0.9937	0.04	0.23
	5	4.48	6.56×10^{-3}	0.9959	0.37	0.43
	10	4.20	8.54×10^{-1}	0.9975	0.98	0.97
	20	3.95	8.18×10^0	0.9951	1.11	1.70
	30	3.77	2.06×10^1	0.9937	1.11	2.23
	40	3.47	3.09×10^1	0.9939	1.09	2.68
90/10	2	3.94	3.43×10^{-4}	0.9998	0.02	0.13
	5	3.40	1.70×10^{-2}	0.9996	0.44	0.30
	10	3.20	1.15×10^{-1}	0.9990	0.81	0.51
	20	3.12	4.63×10^{-1}	0.9987	0.96	0.78
	30	3.15	7.50×10^{-1}	0.9971	0.99	0.91
	40	3.06	1.19×10^0	0.9954	1.00	1.06
80/20	2	4.06	1.87×10^{-4}	0.9980	0.01	0.12
	5	3.72	7.06×10^{-3}	0.9995	0.37	0.26
	10	3.25	7.24×10^{-2}	0.9998	0.77	0.45
	20	3.21	1.70×10^{-1}	0.9991	0.92	0.58

30	2.56	6.79×10^{-1}	0.9940	0.99	0.86
40	2.13	1.28×10^0	0.9866	1.01	1.12

Figure 3

Figure 3. Plots of $\log[-\ln(1-X_c)]$ as a function of $\log t$ for (a) PA6, (b) CoPA6/12(90/10) and (c) CoPA6/12 at different cooling rates.

Though the parameters Z_t and n have a different meaning in non-isothermal and in isothermal crystallization kinetics, we can still use them to discuss the mechanisms of non-isothermal crystallization.^[34] Jeziorny^[35] considered the influence of cooling rate (Φ), proposing a corrected rate parameter to characterize the kinetics of non-isothermal crystallization, expressed as follows:

$$\log Z_c = \frac{\log Z_t}{\phi} \quad (5)$$

Both Z_t and Z_c increase with increasing cooling rate, which can be explained considering that the temperature drops rapidly at high cooling rates, and that the free energy barrier of nucleation decreases with temperature, thus resulting in an increase of the overall bulk crystallization rate. In contrast, the values of Z_t and Z_c of CoPA6/12s are lower than those of PA6, indicating that the introduction of the second monomer hinders the growth of polyamide crystallites under non-isothermal condition which is in accordance with the result of $t_{1/2}$ (Table 1). The copolymerization disrupts the structural symmetry and regularity of the molecular chains, so that chain segments of CoPA6/12 need more time to crystallize compared to the situation of ordered structures present in PA6. Anormalized rate constant (K_a)^[36] can be calculated from $K_a = Z_t^{1/n}$; it

shows the same trend as Z_c (Table 2).

The Avrami exponent, n , of PA6 ranges between 3 and 5. For copolyamides, n values range between 2 and 4. When the cooling rate is set at 2 °C/min, the Avrami exponent of PA6, CoPA6/12(90/10) and CoPA6/12(80/20) is close to 4. This corresponds to three-dimensional growth and homogeneous nucleation.^[28, 37] However, at a cooling rate of 40 °C/min, n decreases from 3.47 for PA6 to 2.13 for CoPA6/12(80/20), which is related to a plane growth with sporadic nucleation^[38]. Thus, the crystallization mechanisms deviate at high cooling rate and the change of CoPA6/12 is more apparent, indicating that the crystallization of CoPA is more sensitive to the cooling rate.

3.2.2. Ozawa analysis

Ozawa considered the nucleation and growth of polymer crystallization based on Evans' theory, and proposed a crystallization kinetics equation at constant cooling rate conditions.^[39] The respective relationship between temperature and corresponding relative degree of crystallinity can be expressed as follows:

$$\ln(1 - X_c(T)) = -K(T)/\phi^m \quad (6)$$

$$\log[-\ln(1 - X_c(T))] = \log K(T) - m \log \phi \quad (7)$$

where Φ is the cooling rate (°C/min), $K(T)$ is the Ozawa crystallization rate, and m is the Ozawa exponent. The values of m and $K(T)$ can be calculated from slope and intercept of the plots of $\log[-\ln(1 - X_c(T))]$ versus $\log \Phi$, respectively.

Fig. 4 shows plots of $\log(-\ln(1 - X_c))$ as a function of $\log \Phi$. As can be seen, these

curves are also not straight, and transitions happen at different points. This has also been observed in other systems,^[21, 36, 40] and it is usually attributed to the secondary crystallization. As the crystallization rate in the dynamic non-isothermal crystallization process is inconstant, but a function of time and cooling rate,^[32, 34] the Ozawa equation is not suitable to describe the non-isothermal crystallization kinetics of random CoPA6/12.

Figure 4

Figure 4. Plots of $\log[-\ln(1-X_c)]$ as a function of $\log \Phi$ for (a) PA6, (b) CoPA6/12(90/10) and CoPA6/12(80/20) at selected temperatures.

3.2.3. Analysis combining Avrami and Ozawa equations

To find an appropriate model to describe the entire process of polymeric non-isothermal crystallization, Liu and Mo et al.^[21, 41] proposed a new equation by combining the Avrami and the Ozawa equations as follows:

$$\log Z_t + n \log t = \log K(T) + m \log \phi \quad (8)$$

where n and m represent the Avrami and the Ozawa exponents, respectively. Assuming $a=n/m$ and $F(T)=[K(T)/Z_t]^{1/m}$, the final form of the new equation can be represented as follows:

$$\log \phi = \log F(T) - a \log t \quad (9)$$

where a is the ratio between Avrami and Ozawa exponents. $F(T)=[K(T)/Z_t]^{1/m}$ is the crystallization rate signifying the required cooling rate for a polymer system to reach a

defined degree of crystallinity at the unit crystallization time. Higher $F(T)$ values mean that more time is required to reach a certain degree of crystallinity at a given cooling rate, thus reducing the crystallization rate.^[33] This analysis has been employed to derive the non-isothermal crystallization kinetics of e.g. PA12,^[16] PA1111,^[23] PA1011,^[22] and multiwalled carbon nanotubes/PA6 composites.^[32]

The plots of $\log \Phi$ as a function of $\log t$ at various relative degrees of crystallinity are presented in Fig. 5. The high correlation (coefficient of determination $R^2 > 0.97$) verifies the applicability of the combined method to this copolymer system. The values of $F(T)$ and a derived from intercepts and slopes of the fitted lines are listed in Table 3. The values of $F(T)$ increase with the relative degree of crystallinity X_c for all considered samples, implying that the crystallization process slows down as it proceeds. Comparing PA6 with CoPA6/12, the $F(T)$ of the copolyamides is higher, indicating that the random copolymerization decreases the crystallization rate of polyamide under non-isothermal conditions.

Figure 5

Figure 5. Plots of $\log \Phi$ as a function of $\log t$ for (a) PA6, (b) CoPA6/12(90/10) and (c) CoPA6/12(80/20) at different relative degrees of crystallinity.

Table 3. Values of $F(T)$ and a , derived from a combination of the Avrami and the Ozawa equations for PA6, CoPA6/12(90/10) and CoPA6/12(80/20). X_c = relative degree of crystallinity, R^2 = coefficient of determination.

CoPA6/12	X_c	$\log F(T)$	$F(T)$	$a (= n/m)$	R^2
100/0	10%	0.81	6.52	1.05	0.9861
	30%	0.93	8.56	1.12	0.9884
	50%	1.02	10.40	1.16	0.9909
	70%	1.13	13.61	1.17	0.9918
	90%	1.41	25.82	1.02	0.9965
90/10	10%	1.08	12.00	1.34	0.9720
	30%	1.30	19.82	1.39	0.9756
	50%	1.41	25.65	1.39	0.9795
	70%	1.50	31.61	1.39	0.9827
	90%	1.59	38.82	1.31	0.9764
80/20	10%	1.10	12.64	1.18	0.9755
	30%	1.32	20.75	1.28	0.9822
	50%	1.44	27.85	1.31	0.9815
	70%	1.56	36.34	1.32	0.9822
	90%	1.65	44.54	1.16	0.9767

3.3. Crystallization activation energy

Considering the influence of the cooling rate on the crystallization temperature, the crystallization activation energy of the polymer, ΔE , can be calculated using the equation proposed by Kissinger:^[42]

$$\frac{d[\ln(\Phi/T_p^2)]}{d(1/T_p)} = -\frac{\Delta E}{R} \quad (10)$$

where R is the universal gas constant, Φ is the cooling rate, T_p is the peak temperature of the cooling thermogram, and ΔE is the crystallization activation energy. The Kissinger plots of $\ln(\Phi/T_p^2)$ versus $1/T_p$ are shown in Fig. 6(a), with the linear correlation of the experimental data clearly visible ($R^2 > 0.98$). The values of ΔE can directly be obtained from the slopes of the fitted lines. Hence, the crystallization activation energies of PA6, CoPA6/12(90/10) and CoPA6/12(80/20) are -228.96 kJ/mol, -101.51 kJ/mol, and -79.32 kJ/mol, respectively. In other words, ΔE increases with increasing LL content in CoPA6/12.

Figure 6

Figure 6. (a) Kissinger plots of $\ln(\Phi/T_p^2)$ versus $1/T_p$, (b) Friedman plots for 50% conversion, and (c) Friedman activation energy of PA6, CoPA6/12(90/10) and CoPA6/12(80/20), respectively.

However, Vyazovkin^[43] comments that the Kissinger equation is not appropriate to estimate the crystallization activation energy of non-isothermal kinetics. The reason is that the activation energy calculated from a narrow temperature region, and the use of a cooling rate with positive values, may lead to erroneous values of the activation energy. A more recommendable method developed by Friedman^[44] is represented as follows:

$$\ln\left(\frac{dX}{dt}\right)_X = A - \frac{\Delta E_X}{RT_X} \quad (11)$$

where $(dX/dt)_X$ is the crystallization rate at a conversion X (relative crystallization), ΔE_X is the corresponding activation energy, T_X is the temperature at the relative crystallization X , and A is a pre-exponential factor. The activation energy ΔE_X of a particular relative crystallinity X can be calculated from the slope of the plots of $\ln(dX/dt)_X$ versus $1/T_X$ at different cooling rates. As can be seen in Fig. 6(b), the curves of $\ln(dX/dt)_X$ versus $1/T_X$ are not linear. Thus, the activation energy has to be calculated from the initial linear part; the respective values of ΔE_X are plotted in Fig. 6(c). ΔE_X first increases to a maximum and then decreases with increasing relative crystallinity. The change in ΔE_X of CoPA6/12 is smaller than that of PA6, which indicates that the crystallization process of CoPA6/12 becomes simpler. Moreover, the value of ΔE_X

increases with increasing LL content for each relative crystallinity, corroborating the results obtained from the Kissinger method.

The calculation of the activation energy can be derived from the Arrhenius equation:^[42]

$$k_T = Ae^{\frac{\Delta E}{RT}} \quad (12)$$

where k_T is the rate constant at a temperature T , and the constant A is the so-called frequency factor. k_T decreases with increasing activation energy ΔE . In consequence, the crystallization rate of CoPA6/12 decreases with increasing LL content, which is in accordance with the discussed results from both Avrami and Liu-Mo's analyses. The activation energy consists of the transport activation energy ΔE^* and the nucleation activation energy ΔF^* .^[45] In polymer crystallization, ΔE^* is the activation energy required to transport molecular segments to the crystallization surface. The introduction of LL co-monomers decreases the sum of $-\text{CONH}-$, and in consequence lowers the hydrogen bond density. Thus, the molecular segment is more flexible, which is to the benefit of crystal growth. In other word, transport activation energy ΔE^* should be decreased, but crystallization activation energy, sum of transport activation energy ΔE^* and nucleation activation energy ΔF^* , are increased. Thus, we can conclude that copolymerization hinders the formation of crystal nuclei, increases the crystallization activation energy, and in consequence decreases the overall crystallization rate of polyamide. Therefore, nucleation is the governing step in the non-isothermal crystallization of CoPA6/12.

3.4. Melting behavior

Fig. 7 and Fig. S2 show the second heating curves of PA6 and CoPA6/12 with different CL/LL ratios, after cooling at various rates. The corresponding values are listed in Table 4. The melting enthalpy decreases with cooling rate for all samples, which is consistent with the trend observed for the crystallization enthalpy. Actually, the crystallization time is not enough to produce a complete recrystallization of the crystalline structure, which is responsible for a lower ΔH_m . However, the melting peaks are almost the same as depicted in Table 4, which can be attributed to cold crystallization. During heating, the previously obtained amorphous fraction rearranges into crystal particles and micro-crystallites, whose growth perfection depends on the time given by Φ .^[1, 22] As heating proceeds, micro-crystallites melt at lower temperature, and reorganized crystalline structures melt at the same peak temperature.

Table 4 also shows that both enthalpy and melting temperature decrease as the amount of LL increases. The endothermic melting peak disappears with an LL content of 40% (Fig 7(b)). Melting enthalpy, or enthalpy of fusion, is the amount of heat which is required to melt only the crystalline portion of a polymer. Therefore, the decrease of enthalpy of fusion by adding LL to the system, is as a result of the lower degree of crystallinity that the copolymer possesses.^[29] At 50/50 composition, the peak appears once again, due to the cold crystallization that happens during heating. It is important to mention that the melting peak becomes broader with increasing LL content (compare $T_{m \text{ onset}}$ with $T_{m \text{ end}}$ in Table 4). This may result from the larger size distribution of lamellae and/or crystals, which becomes broader with increasing co-monomer

content.^[46, 47] From the results we can conclude that CoPA6/12(60/40) is an amorphous polymer, where cold crystallization does not occur when reheating at 10 °C/min.

Table 4. Enthalpy (ΔH_m), peak temperature (T_m), Onset temperature ($T_{m \text{ onset}}$) and end temperature ($T_{m \text{ end}}$) of PA6 and CoPA6/12 in different CL/LL compositions. (n.d.: not detected)

CoPA6/12	Φ (°C/min)	ΔH_m (J/g)	T_m (°C)	$T_{m \text{ onset}}$ (°C)	$T_{m \text{ end}}$ (°C)
100/0	2	-67.44	217.00	204.48	223.79
	5	-62.64	216.33	205.58	223.30
	10	-58.91	217.00	202.28	223.79
	20	-55.17	217.33	201.79	223.79
	30	-52.68	217.67	199.59	223.79
90/10	2	-47.16	194.00	176.00	204.97
	5	-44.75	195.67	173.92	205.58
	10	-39.52	197.00	171.23	206.07
	20	-37.09	196.67	173.92	205.58
	30	-31.40	190.33	174.90	204.97
80/20	2	-35.42	177.67	158.56	191.78
	5	-35.82	174.67	154.67	192.22
	10	-26.54	181.00	150.22	192.22
	20	-24.92	180.33	149.22	191.78
	30	-32.41	179.00	149.78	192.22
70/30	2	-28.05	159.00	140.19	171.73
	5	-26.60	154.00	133.56	176.23
	10	-23.47	165.00	128.71	176.68
	20	-17.06	157.00	131.51	177.05
	30	-14.92	156.33	136.83	176.21
60/40	2	n.d.	n.d.	n.d.	n.d.
	5	n.d.	n.d.	n.d.	n.d.
	10	n.d.	n.d.	n.d.	n.d.
	20	n.d.	n.d.	n.d.	n.d.
	30	n.d.	n.d.	n.d.	n.d.
50/50	2	-18.37	128.00	115.20	135.28
	5	-16.19	127.67	114.88	134.16
	10	-15.58	127.33	114.48	134.16
	20	-12.89	127.00	115.52	134.16
	30	-12.75	126.67	115.52	133.84

Figure 7

Figure 7. DSC thermograms of (a) the second heating curves of CoPA6/12(90/10) crystallized at different heating rates, and (b) the second heating curves of CoPA6/12 in different CL/LL compositions, crystallized at 10 °C/min.

4. Conclusions

The non-isothermal crystallization kinetics of PA6 and CoPA6/12 were studied by DSC and analyzed by Avrami, Ozawa and Liu-Mo's methods. The incorporation of LL as a co-monomer hinders the crystallization of polyamide under non-isothermal conditions. Actually, when the LL content reaches 40% and above, crystallization is not visible at the cooling rates investigated in this work. The Avrami analysis indicates that the spherulitic growth mode of polyamide is varying in the overall crystallization process. CoPA6/12 presents lower crystallization rates compared to PA6. The Ozawa model was only valid for a small range of selected temperatures, while Liu-Mo's model was applicable over a wide conversion range, providing a high correlation factor for the respective plots. The crystallization activation energies calculated by Kissinger and Friedman methods indicated that CoPA6/12 has the higher crystallization activation energy compared to PA6. Both lower crystallization rate and higher activation energy of CoPA6/12 are a result of the disordered array of monomers.

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Figure Captions:

Figure 1. DSC heat flow of non-isothermal crystallization of (a) different CoPA6/12 samples at a cooling rate of 10 °C/min, and (b) CoPA6/12(90/10) at different cooling rates.

Figure 2. Plots of relative crystallinity as a function of temperature (a-c) and time (d-f).

Figure 3. Plots of $\log[-\ln(1-X_c)]$ as a function of $\log t$ for (a) PA6, (b) CoPA6/12(90/10) and (c) CoPA6/12 at different cooling rates.

Figure 4. Plots of $\log[-\ln(1-X_c)]$ as a function of $\log \Phi$ for (a) PA6, (b) CoPA6/12(90/10) and CoPA6/12(80/20) at selected temperatures.

Figure 5. Plots of $\log \Phi$ as a function of $\log t$ for (a) PA6, (b) CoPA6/12(90/10) and (c) CoPA6/12(80/20) at different relative degrees of crystallinity.

Figure 6. (a) Kissinger plots of $\ln(\Phi/T_p^2)$ versus $1/T_p$, (b) Friedman plots for 50% conversion, and (c) Friedman activation energy of PA6, CoPA6/12(90/10) and CoPA6/12(80/20), respectively.

Figure 7. DSC thermograms of (a) the second heating curves of CoPA6/12(90/10) crystallized at different heating rates, and (b) the second heating curves of CoPA6/12 in different CL/LL compositions, crystallized at 10 °C/min.

Graphical Abstract Text and Image

Title:

Melting Behavior and Non-isothermal Crystallization Kinetics of Copolyamide 6/12

Graphical Abstract Text:

- Different methods were applied to study the non-isothermal crystallization kinetics of copolyamide 6/12.
- The incorporation of ω -laurolactam decreases the crystallization rate of copolyamide 6/12 in comparison to that of polyamide 6.
- Copolymerization hinders the formation of crystal nuclei and thus can produce amorphous polyamides.

Graphical Abstract Image:

Polymer Crystallization

Supplementary Data

Melting Behavior and Non-isothermal Crystallization Kinetics of Copolyamide 6/12

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Table S1 Reaction components and relative viscosity of samples.

Sample	Caprolactam/kg	Lauro lactam/kg	H ₃ PO ₄ /g	H ₂ O/mL	Relative viscosity
PA6	3.000	0	9	90	2.987
CoPA612-90/10	2.513	0.487	9	90	3.068
CoPA612-80/20	2.098	0.911	9	90	2.999
CoPA612-70/30	1.717	1.283	9	90	2.967
CoPA612-60/40	1.387	1.613	9	90	3.120
CoPA612-50/50	1.093	1.907	9	90	2.990

Figure S1. DSC heat flow of non-isothermal crystallization of CoPA6/12 in different CL/LL compositions at different cooling rates.

Figure S2. DSC thermograms of second heating curves of CoPA6/12 in different CL/LL compositions, crystallized at different heating rates.