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Isothermal crystallization of random copolymers of ε-caprolactone with 2,2-dimethyltrimethylene carbonate

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Abstract

The isothermal crystallization of three random copolymers of ε-caprolactone with different contents of 2,2-dimethyltrimethylene carbonate (DTC) (DTC: 5, 9 and 18 mol%) and poly(ε-caprolactone) (PCL) was studied using DSC and PLM methods. The isothermal crystallization data were analyzed with the Avrami equation. The exponent *n*, from 3 of PCL to 2 of P(82%CL-ran-18%DTC), suggests a change of crystal form. The crystallization rate was lowered by the addition of DTC units, which interrupted the perfect crystallization of PCL.

Keywords: Isothermal crystallization; Random copolymer; 2,2-Dimethyltrimethylene carbonate (DTC)

1. Introduction

Poly(ε-caprolactone) (PCL) and poly(2,2-dimethyltrimethylene carbonate) (PDTC) attract much attention recently for their excellent properties of biodegradability, biocompatibility and low toxicity. Their homopolymers and copolymers are prepared via ring opening polymerization of ε-caprolactone (CL) and 2,2-dimethyltrimethylene carbonate (DTC) by many kinds of catalysts [1,2]. Only few reports concern the thermal behaviors of these copolymers, and no reports on their crystallization properties so far, except for a paper described the isothermal crystallization of PCL [3].

In our previous work [4–7], the copolymers of CL with DTC were synthesized using rare earth tris(2,6-di-tert-butyl-4-methylphenolate) initiators, which were characterized to be the random structure by ^{1}H NMR, GPC and DSC. The insertion of DTC units evenly into the PCL chain was also studied with Monte Carlo simulation [8]. In addition, the random copolymers P(CL-ran-DTC)s exhibit some quite different melt transitions according to their monomer composition. For crystalline polymer, the shift of the melting point indicates the variation of the crystallization or crystallinity. This article makes an overall study on the isothermal crystallization of the random copolymers of CL with DTC and homopolymer PCL by means of DSC and PLM methods in order to explore the influence of the DTC units in PCL chain.

2. Experimental section

The polymerizations of the homo- and copolymers of CL with DTC were initiated by lanthanum tris(2,6-di-tert-butyl-4-methylphenolate) following the details described in Ref. [4]. The molecular weights of the polymers were determined by GPC analyses and calibrated by polystyrene standards, which were carried out on a Waters 208 apparatus with Waters 2410 RI detector in THF (1.5 ml/min) at 30 °C. The monomer compositions in copolymer were determined by nuclear magnetic resonance spectra, which were recorded on a Bruker Avance DMX500 spectrometer in CDCl$_3$ with TMS as inner standard (Table 1). The kinetics of isothermal crystallization from the melt was studied using a Perkin Elmer Pyris 1 DSC instrument. A procedure was compiled as follows: samples were heated to an appointed temperature at which the samples melted completely, and kept at this temperature for 3 min in order to eliminate the heating history. After rapidly cooling to a selected crystallization temperature (T_c) at the rate of 100 °C/min, they were kept at T_c to the end of exothermic crystallization

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Table 1
Compositions and molecular weights of (co)polymers

CL:DTC	$M_n \times 10^{-3}$	M_w/M_n
100:0	35	1.87
95:5	46	1.98
91:9	54	1.88
82:18	58	2.23

peak. Finally, they were heated from T_c to the previous appointed temperature to ensure the sample melt at a scanning rate of 10 °C/min in order to determine the corresponding melting temperature (T_m).

The spherulite morphology and growth rate of the polymers were monitored with an LEICA DMLP polarized light microscope (PLM). Samples were heated on a Linkam TMS94 hot stage to an appointed temperature above T_m and kept for 1 min., followed by quickly cooling (100 °C/min) to the selected T_c. At that temperature the spherulite growth was monitored. Micrographs were taken at intervals of time for measuring the spherulite diameter (D). The growth rate was calculated from the change of spherulite diameter with time (dD/dt).

3. Results and discussion

We have found that the random copolymers of CL with DTC exhibit some quite different melt transitions according to the molar ratio of DTC in copolymers using DSC method [4]. As shown in Fig. 1, the melting peaks disappear in the second heating scan after rapid cooling as the DTC contents of the samples over 50%. Thus it is impossible to investigate the isothermal crystallization of high content DTC copolymers. Only the thermal and crystallization properties of the random copolymers of CL with DTC (DTC ≤ 18%) and PCL are studied.

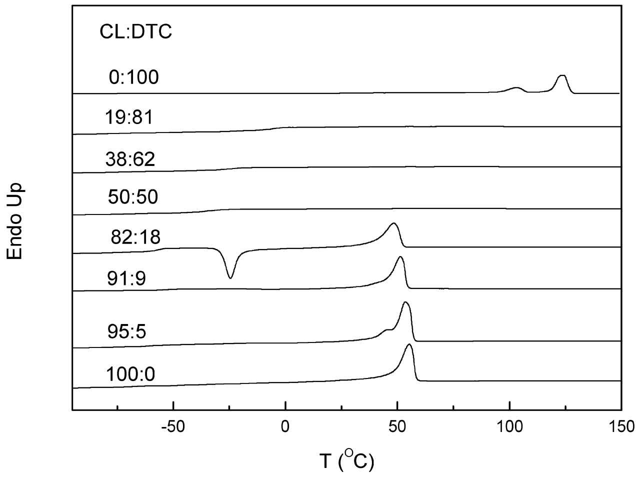


Fig. 1. DSC curves of P(CL-ran-DTC)s after rapid cooling from melt.

Table 2
The isothermal crystallization kinetics of (co)polymers

CL:DTC	ΔE (kJ/mol)	T_c (°C)	n	Z	$t_{1/2}$ (min)	$t_{\max}$ (min)[a]
100:0	36.4	42[b]	2.64	3.75	0.528	0.506
		44	3.36	0.520	1.09	1.09
		46	3.49	0.0388	2.28	2.30
		48	3.94	9.41×10^{-4}	5.34	5.44
		50	3.74	6.25×10^{-5}	12.1	12.2
95:5	9.56	26	1.99	2.65	0.510	0.432
		28	2.30	1.17	0.796	0.729
		30	2.39	0.431	1.22	1.13
		32	2.59	0.110	2.03	1.94
		34	2.48	0.0344	3.36	3.16
		36	2.26	0.0158	5.33	4.84
		38	2.14	0.00610	9.13	8.07
91:9	9.55	22	2.14	2.45	0.554	0.490
		24	2.69	1.46	0.758	0.731
		26	2.34	0.615	1.05	0.970
		28	2.37	0.253	1.53	1.42
		30	2.64	0.0692	2.39	2.30
		32	2.47	0.0259	3.79	3.56
		34	2.47	0.00779	6.16	5.79
		36	2.24	0.00390	10.1	9.14
82:18	3.29	14	1.84	0.604	1.08	0.859
		16	1.79	0.440	1.29	1.00
		18	1.77	0.293	1.63	1.25
		20	1.72	0.182	2.18	1.63
		22	1.68	0.127	2.74	1.99
		24	1.70	0.0837	3.47	2.55
		26	1.90	0.0411	4.42	3.62

[a] The peak time of the crystallization enthalpy.

[b] A partial crystallization begins reaching T_c when T_c is below 42 °C.

The isothermal crystallization kinetics is interpreted in terms of the Avrami equation (Eq. (1)):

$$1 - X(t) = \exp(-Zt^n) \tag{1}$$

$X(t)$ is the crystalline fraction or relative crystallinity at time t. Z is the kinetic rate constant. n is Avrami exponent, which can be 1, 2, 3 and 4 dependent on the nature of the nucleation and growth geometry. Different n values indicate one-, two- or three-dimensional forms of growth (rod, laminate or sphere) [9].

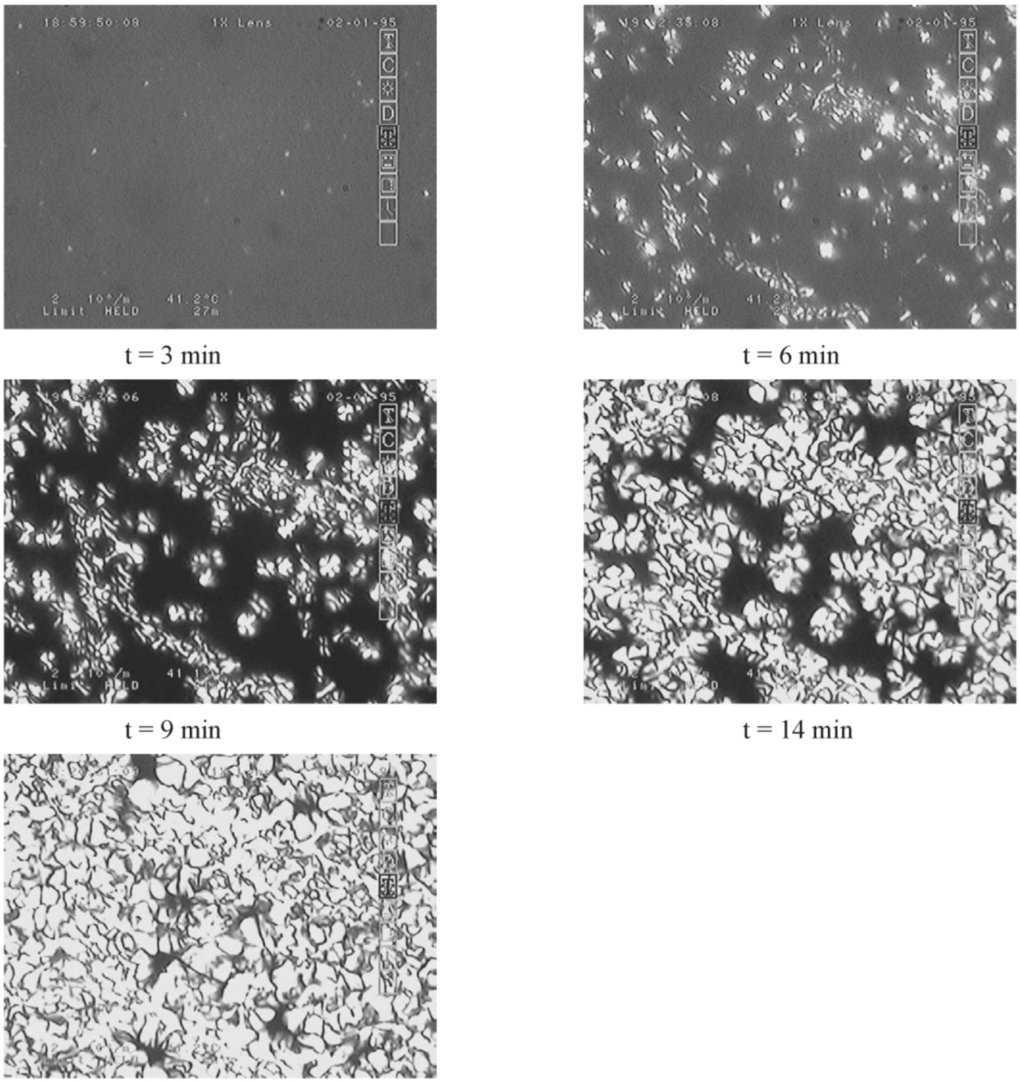
The reciprocal of $t_{1/2}$ can be used as the crystallization rate G, shown in Eq. (2). $t_{1/2}$ is the time when the relative crystallinity equals 0.5, and it can be determined by Eq. (3).

$$G = \tau_{0.5} = \frac{1}{t_{1/2}} \tag{2}$$

$$t_{1/2} = \left(\frac{\ln 2}{Z}\right)^{1/n} \tag{3}$$

The values of Avrami exponent (n), the half time of crystallization ($t_{1/2}$), and the kinetic rate constant (Z) of the polymers are summarized in Table 2. When increasing T_c and DTC contents in the copolymers, $t_{1/2}$ increases, i.e. the rate of crystallization decreases.

The homopolymer of PCL gives an n value about 3, indicating the formation of spherulites. With the increase of DTC contents in the P(CL-ran-DTC)s, n is lowered even to



t = 3 min

t = 6 min

t = 9 min

t = 14 min

t = 24 min

Fig. 2. The morphologies of P(95%CL-ran-5%DTC) crystallized isothermally at $T_c = 41$ °C.

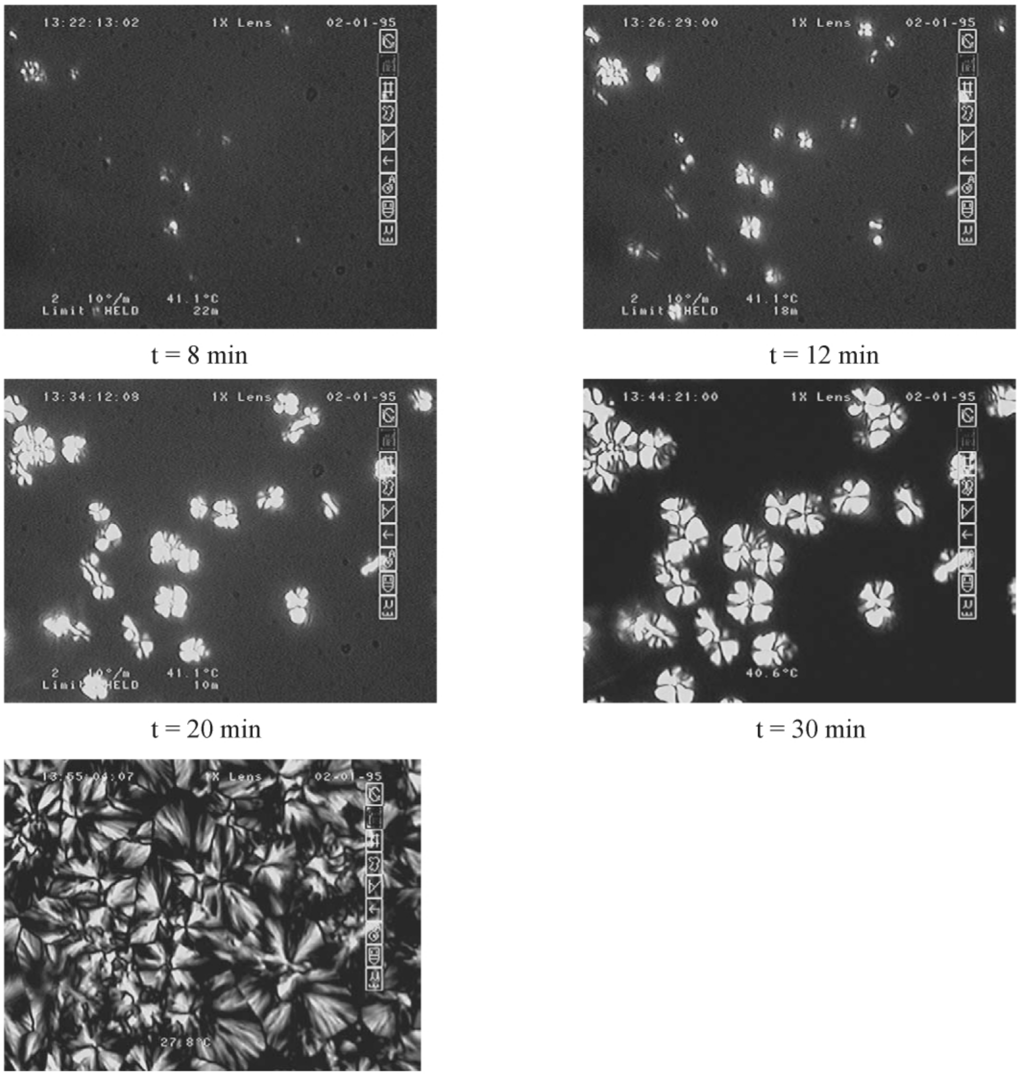
less than 2 (DTC = 18% in the copolymer). The different n values mean their different nucleation and crystal growth forms.

Figs. 2–4 display the morphologies of random copolymers [P(CL-ran-DTC)s] taken from PLM at different crystallizing time. The increasing DTC contents in copolymers enlarge the imperfectness of crystals and decrease the crystallinity and crystal growth rate. There are more spaces and longer time to allow the crystals grow up. Therefore, the spherulite radius becomes larger and the difference of the size dwindles, even hard to distinguish in the copolymer with 18% DTC. The influence of temperature on nucleation decreases. Nucleation mode exhibits the trend from thermal to athermal one. This result is in good agreement with the values of the crystallization activation energies shown in Table 2. As DTC contents increase in the copolymer, the crystallization activation energy decreases, indicating the smaller influence of temperature on nucleation. Moreover, their morphologies have been changed, demonstrating that the extent of interfibrillar segregation increases and the lobes of the spherulites become sparse due to the decreasing of crystal density.

Table 3
Diameter growth rate of spherulites with various DTC content copolymers

CL:DTC (molar ratio)	d*D*/d*t* (μm/min)		
	$T = 40$ °C	$T = 41$ °C	$T = 43$ °C
95:5	–	1.36	–
91:9	–	0.90	0.50
82:18	0.60	0.42	–

The growth rates of the spherulite diameter have been determined. Fig. 5 shows the spherulites diameter growth for the samples with different DTC contents. Table 3 lists the corresponding values of growth rate, which dwindles with increasing DTC content and crystallization temperature. The



t = 8 min

t = 12 min

t = 20 min

t = 30 min

T = 27 °C (cooling to 27 °C after isothermal crystallized for 30 min at 41 °C)

Fig. 3. The morphologies of P(91%CL-ran-9%DTC) crystallized isothermally at $T_c = 41$ °C.

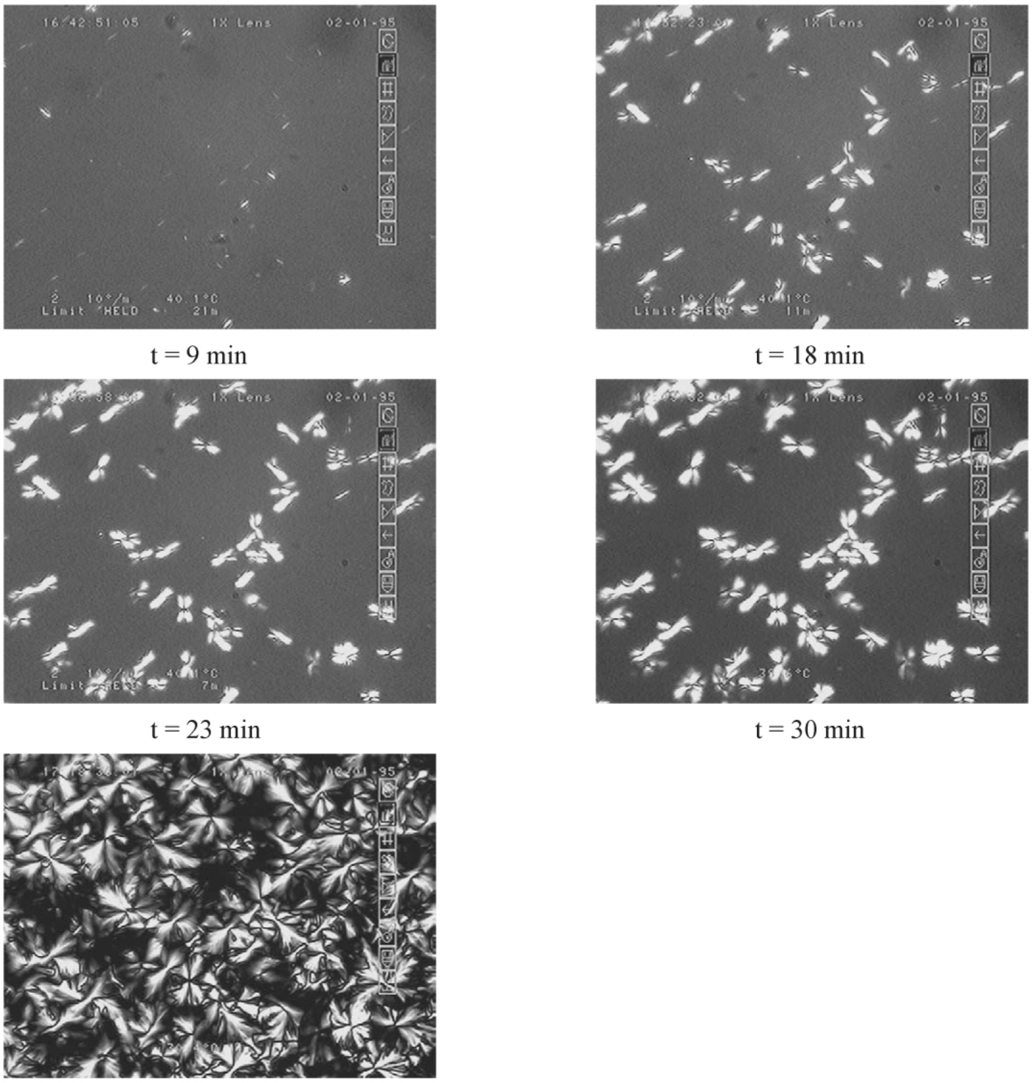
facts shown above support the viewpoint that irregular polymer chain and the defect of the polymer chain will interfere crystal growth, leading to slow down the crystal growth rate.

After isothermal crystallization by DSC, the polymer samples were heated to melt in order to investigate their melting transition. Two melting peaks appear in each copolymer sample's DSC curve when the crystallization temperature is below certain temperature, which separate from each other clearly with increasing DTC content or lowering the crystallization temperature (as shown in Figs. 6–8). This can be attributed to imperfect crystals in crystallization by a few DTC units inserting into the CL linkage randomly, and partly destroying the regular structure of PCL chains, resulting in the decrease of the melting temperature. This imperfectness of crystals was intensified at lower temperature. After a long period of storage at room temperature, crystal models of higher temperature had been formed, thus only one melting peak was detected (as shown in Fig. 9).

The melting temperatures have been measured by DSC as a function of the crystallization temperature (T_c). The equilibrium melting temperature (T_m^0) was determined by the Hoffman–Weeks extrapolation method. β in Eq. (4) is morphology factor, which is equal to the ratio of the lamellae thickness to the initial thickness of the nucleus at crystallization temperature T_c [10].

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

A plot can be drawn in the Hoffman–Weeks equation for each polymer at different crystallization temperature T_c, giving a straight line and extrapolating to the reference line $T_m = T_c$. Thus, the T_m^0 is obtained from the point of intersection. The pursuant theory comes from that the perfectness of the polymeric crystal is relevant to the



t = 9 min

t = 18 min

t = 23 min

t = 30 min

T = 30 °C (cooling to 30 °C after isothermal crystallized for 30 min at 40 °C)

Fig. 4. The morphologies of P(82%CL-ran-18%DTC) crystallized isothermally at $T_c = 40$ °C.

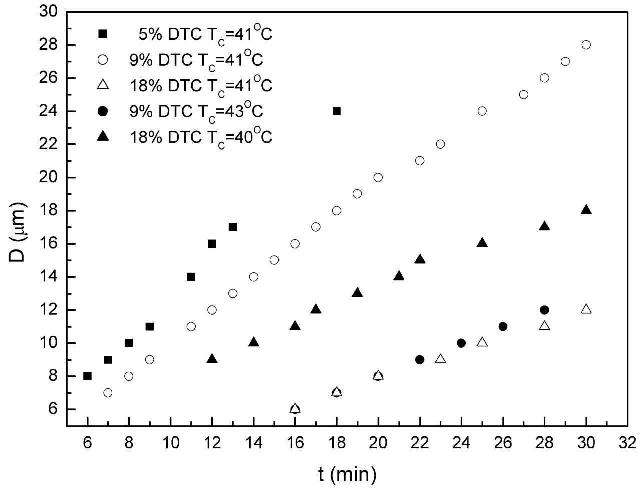


Fig. 5. The spherulite diameter growth for P(CL-ran-DTC)s crystallized isothermally at T_c.

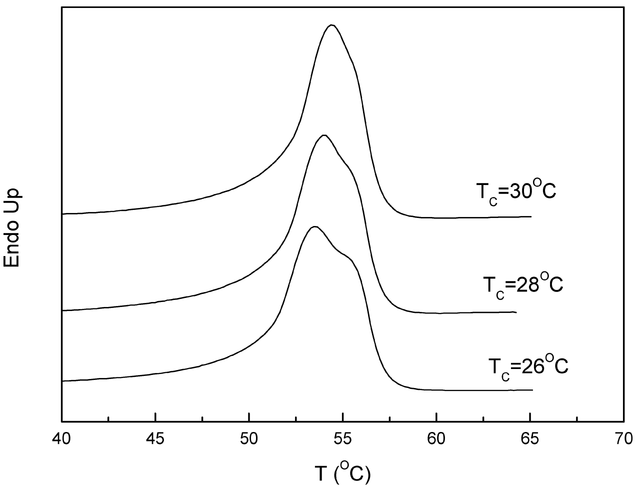


Fig. 6. DSC curves of P(95%CL-ran-5%DTC) after the isothermal crystallization at T_c of 26,28,30 °C.

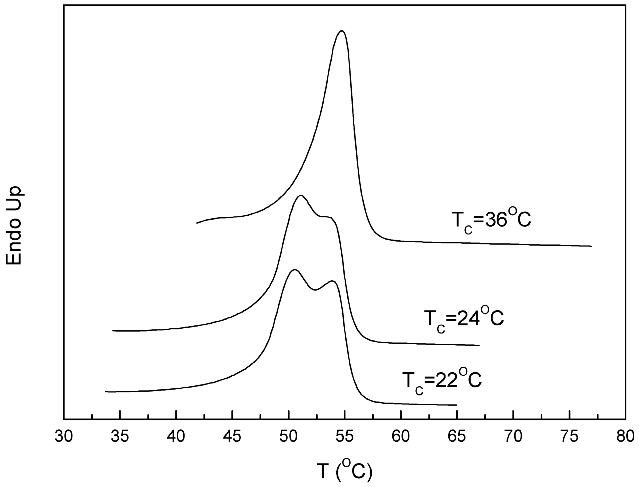


Fig. 7. DSC curves of P(91%CL-ran-9%DTC) after the isothermal crystallization at T_c of 22,24,36 °C.

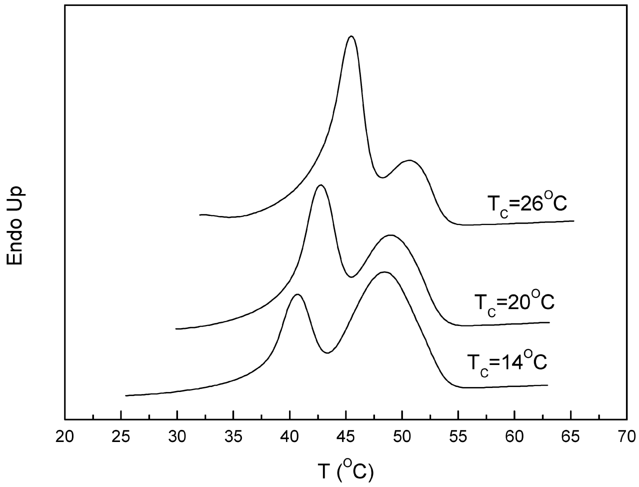


Fig. 8. DSC curves of P(82%CL-ran-18%DTC) after the isothermal crystallization at T_c of 14,20,26 °C.

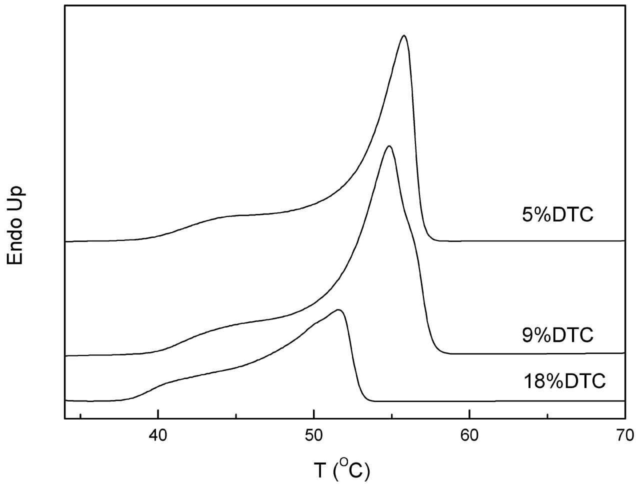


Fig. 9. DSC curves of P(CL-ran-DTC)s stored at room temperature for 5 months after rapid cooling from the melt.

Table 4
The thermal properties of the (co)polymer samples

CL:DTC	T_{m0} (°C)[a]	T_{c0} (°C)[a]	ΔT_{c0} ($= T_{m0} - T_{c0}$)	ΔH (J/g)	T_m^0(°C)
100:0	64.0	28.4	35.6	98.1	65.1
95:5	61.6	20.1	41.5	67.4	63.1
91:9	60.3	16.9	43.4	58.6	63.3
82:18	53.1	−2.0	55.1	51.9	59.4

[a] The values of the melting temperature and crystallization temperature comes from the first heating and cooling scan of DSC at a rate of 10 °C/min.

crystallization temperature, i.e. the higher the T_c is, the more perfect the crystal becomes and the higher its corresponding melting temperature is. Table 4 lists the T_m^0 values of the polymers. T_m^0 is 65.1 °C for PCL, which is in good agreement with the values reported ($T_m^0 = 64$ °C) [11]. A few DTC units in PCL chain decrease the corresponding value of T_m^0 of copolymers, indicating the regular chain structure has been deducted. Meanwhile, the corresponding crystallinity also decreases based on the fact that the melting enthalpies were smaller, which is proportional to the crystallinity.

The larger values of supercooling ($\Delta T_c = T_{m0} - T_{c0}$) with increasing DTC content in Table 4 mean the decrease of the capability of crystallization, for it is well known that the smaller ΔT_{c0} value possesses higher capability of crystallization.

4. Conclusion

This study compares the kinetics of isothermal crystallization of homopolymer PCL and random copolymer P(CL-ran-DTC)s in which DTC contents are 5, 9 and 18% (molar ratio), respectively. The increasing DTC content results in irregular polymer chain, decreased crystallinity and reduced crystallization rate. The isothermal kinetics is interpreted in terms of the Avrami equation. The equilibrium melting temperature (T_m^0) for the copolymer is lowered to 59.4 °C of P(82%CL-ran-18%DTC) from 65.1 °C of PCL.

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