

MOLECULAR WEIGHT DEPENDENCE OF THE MELTING BEHAVIOR OF POLY(ϵ -CAPROLACTONE)

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Abstract Poly(ϵ -caprolactone) (PCL) with different molecular weights was synthesized and characterized by a gel permeation chromatograph equipped with multiple detector. The melting behavior of PCL was also studied. It was found that the equilibrium melting points (T_m^0) of PCL samples depend on their molecular weights. Wide angle X-ray diffraction measurements (WAXD) and DSC measurements showed that the crystals of the high molecular weight PCLs were more perfect than those of the low molecular weight ones. These results demonstrate that the concentration of the end groups of PCL chains is the main factor that influences the melting behavior. The fusion enthalpy per repeating unit (ΔH_u) was determined to be 11.3 kJ/mol for PCL.

Keywords Poly(ϵ -caprolactone), Equilibrium melting point, Fusion enthalpy

INTRODUCTION

Poly(ϵ -caprolactone) (PCL) is a semicrystalline aliphatic polyester widely used in polymer blends and block copolymers, especially segmented copolymers. Polyurethanes (PUs) with PCL as the soft segment are thermoplastic elastomers possessing good mechanical properties and resistance to hydrolysis^[1-4]. In order to obtain good elastomeric character, the soft segment in PU should have a lower glass transition temperature and can not crystallize in any case. Besides the chemical composition of the chain structure, the molecular weight (MW) of the soft segments is the main factor determining the crystallizability^[2-4]. For PCL soft segments of lower MW the urethane elastomer exhibits good compatibility between its soft and hard segments, and there is a single glass transition temperature (T_g) for these samples. Generally, the segmented polyurethane exhibits a certain degree of microphase separation^[1]. The higher the MW of the soft segments, the more complete the phase separation. It indicates that the soft segment of high MW may crystallize more easily. So as a soft segment of the urethane elastomer, the PCL segments usually have a lower MW.

Our previous work indicates that some PCL-based polyurethanes evidently exhibit a thermally stimulated shape-memory effect^[5-10]. According to the mechanism of this effect, the soft segments must have appropriate crystallization ability and the hard segments can form stable domains acting as the physical crosslinks at temperatures above the melting temperature of the soft segment crystals. When the MW of PCL segments in the segmented PU increases, the movement of the soft segments becomes easier, and the crystallinity, the crystallization rate and the melting temperature of PCL increase accordingly^[2-10]. In addition, the length of the soft segment in PUs can obviously affect the strain recovery speed and the final shape recovery rate of the shape-memory materials and lead to the formation of stable hard-segment domains. So, as the soft segment of shape-memory materials, the PCL segments should have a relatively higher MW.

On the other hand, PCL can be miscible (or compatible) with many polymers as a crystallizable component^[11-15]. The miscibility (or compatibility) is related to the interaction species existing between PCL and

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the second component^[15–19]. The differences in compatibility and interaction influence the crystallization morphology of PCL in the blends. It can be presumed that the MW of PCL in the blends may affect the interaction between PCL and the second component. In other words, the MW of PCL influences the crystallization and melting behavior of PCL in the blends.

Obviously, it is important to study the dependence of crystallization and melting behavior of PCL on its MW. However only a few studies on the crystalline structure and the properties of PCL in various solvents have been reported^[20–23]. Crescenzi *et al.* investigated the melting behavior of a PCL sample and obtained the equilibrium melting point T_m^0 and the enthalpy of fusion per repeating unit ΔH_u ^[24]. Phillips studied the morphology and crystallization kinetics of three PCL samples^[25, 26]. It is acknowledged that these studies are not enough to reflect comprehensively the crystallization and the melting behavior of PCL. So in the present work, PCL samples with MW ranging from 1000 to 40000 were synthesized and characterized. The dependence of the melting behavior on the MW of PCL was studied. The equilibrium melting temperature of a perfect PCL crystal formed by chains of infinite MW has also been obtained by extrapolation.

EXPERIMENTAL

PCL samples used in this research were synthesized by bulk polymerization, and characterized by using a gel permeation chromatograph (GPC)/SEC (Viscotek Co.), with tetrahydrofuran as eluant at 25°C. The M_w , the M_n and the ratio α ($\alpha = M_w/M_n$) of the samples are listed in Table 1. These samples are more or less polydisperse, and their α values are in the range of 1.15 to 2.00.

Table 1. The results of characterization of PCL by GPC

Notation	M_n	M_w	$\alpha = M_w/M_n$
PCL1	578	1040	1.80
PCL2	1750	3500	2.00
PCL3	3950	4540	1.15
PCL4	6760	8410	1.24
PCL5	6590	9340	1.42
PCL6	8860	12600	1.42
PCL7	9290	15800	1.70
PCL8	16600	27000	1.63
PCL9	15700	30000	1.91
PCL10*		40000	

* Supplied by Scientific Polymer Products Inc.

DSC measurements were conducted on a Perkin-Elmer DSC-2C apparatus equipped with a TADS microcomputer and an intracooler II. The DSC was calibrated with ultrapure indium. In the DSC apparatus, the samples were first heated at a rate of 40 K/min to 370 K and maintained at that temperature for 3 min. The samples were then quenched to 210 K at a rate of 160 K/min. The samples were heated again to 370 K at a rate of 10 K/min and then cooled to 210 K at the same rate. In order to obtain the T_m^0 , the samples were quenched from melt to the selected isothermal crystallization temperatures and crystallized at these temperatures for a sufficiently long period of time. Afterwards, the DSC heating scan was carried out at a rate of 10 K/min.

Wide angle X-ray diffraction measurements (WAXD) were carried out with a MXP18AHF diffractometer (Mac. Science Co.), using a Cu K_α radiation ($\lambda = 0.15406$ nm; 45.0 kV; 80.0 mA). Before the WAXD measurements, the samples were melted at 75°C for 10 min, then cooled gradually and maintained at room temperature for 72h in a vacuum oven.

RESULTS AND DISCUSSIONS

The Equilibrium Melting Point

The equilibrium melting point (T_m^0) is one of the most important thermodynamic parameters for crystallizable polymers. In order to obtain the equilibrium melting points of PCLs, the isothermal crystallization of PCL with

different MW at different crystallization temperatures was studied. Figure 1 shows the curves of the isothermal crystallization process for PCL8. With the rise of crystallization temperature (T_c), the crystallization peak becomes broader and the time of crystallization lengthens. The corresponding melting curves of PCL8 after isothermally crystallized at different temperatures are shown in Fig. 2. As expected the melting temperature (T_m) increases with T_c . The Hoffman-Weeks plots^[27] of T_m versus T_c corresponding to some PCL samples are

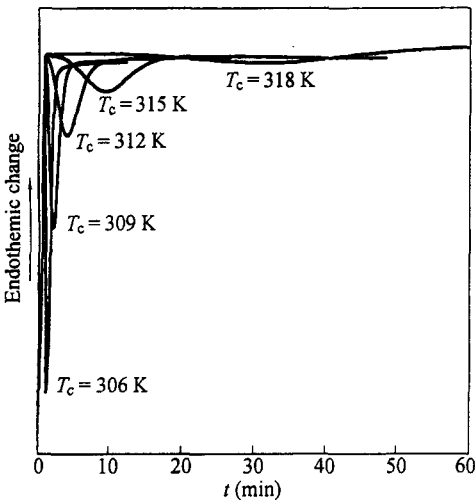


Fig. 1 The isothermal crystallization curves for PCL8 at different crystallization temperatures

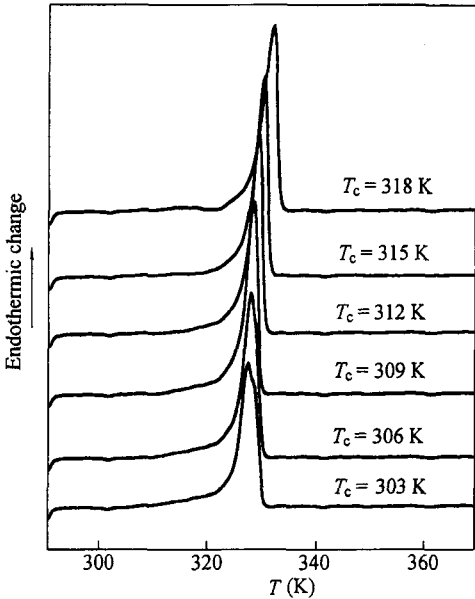


Fig. 2 The DSC heating curves of PCL8 after isothermal crystallization

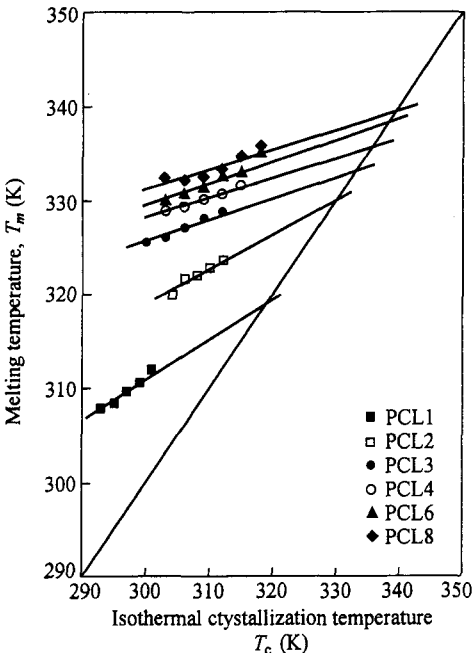


Fig. 3 Hoffman-Weeks plots for some PCL samples with different MW

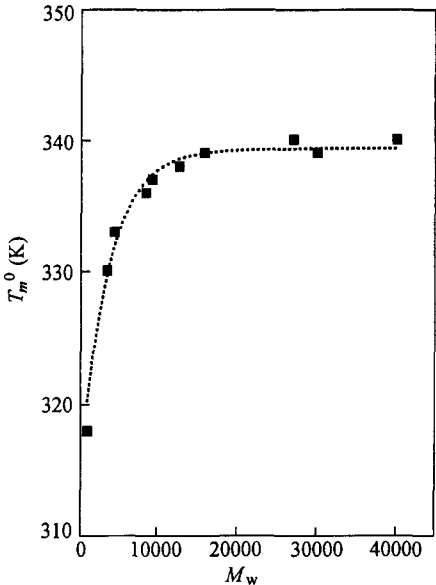


Fig. 4 The equilibrium melting points (T_m^0) as a function of MW of PCL

presented in Fig. 3. The equilibrium melting points (T_m^0) of PCL samples are listed in Table 2 and they increase rapidly with the MW of PCL until about 8000. Beyond this MW, a further slight increase in the T_m^0 is noted, as shown in Fig. 4.

Table 2. DSC results of PCL with different MW

Notation	T_m^0 (K)	ΔH_f (J/g)
PCL1	318	829.
PCL2	330	82.9
PCL3	333	84.2
PCL4	336	86.3
PCL5	337	85.8
PCL6	338	86.3
PCL7	339	87.9
PCL8	340	87.5
PCL9	339	89.2
PCL10	340	89.6

The Crystal Perfectness of PCL with Different MW

In order to verify the relationship between the T_m^0 and the MW of PCL, the WAXD curves for some PCL samples in the 2θ range of 0° – 45° are measured and illustrated in Fig. 5. Although all the diffraction peaks for PCL samples with different MW appear at the same position, the shape and the intensity of diffraction peaks for higher MW are evidently sharper and stronger than those for low MW ones. It indicates that the crystal of the higher MW PCL samples is more perfect. It is interesting to note that the heating and cooling curves of DSC for some PCL samples display similar results, as shown in Fig. 6. The curves for the lower MW samples exhibit two melting peaks, signifying that these samples can not crystallize completely when they are quenched from the melt. They crystallize again in the heating process and two melting peaks appear at lower temperatures, indicating that the crystallization process is difficult and the crystal is not perfect. On the contrary, for higher MW samples, there is only one fusion peak on the heating curve, indicating that these samples can crystallize completely and give perfect crystals when they are quenched from the melt. The MW dependence of the crystal perfectness is consistent with the MW dependence of the T_m^0 of PCL.

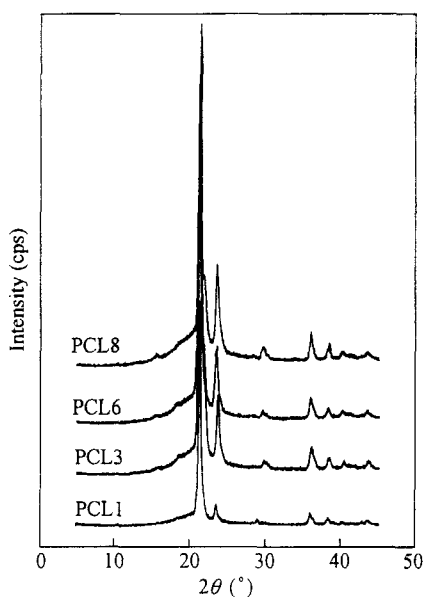


Fig. 5 Wide angle X-ray diffraction patterns for some PCLs

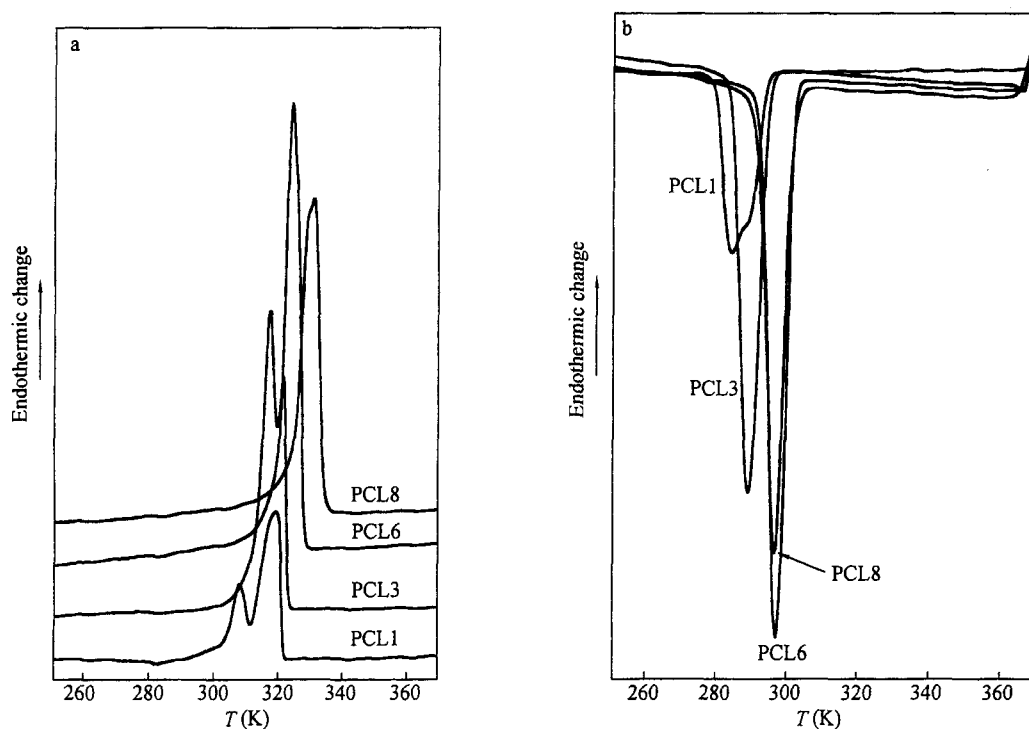


Fig. 6 The DSC curves for some PCL samples
a) The heating curves obtained at a rate of 10 K/min
b) The cooling curves obtained at a rate of 10 K/min

The Effect of Concentration of the End Groups on the T_m^0

According to the explanation proposed by Flory^[28] and Mandelkern^[29], the influence of MW on the equilibrium fusion process results from the concentration of end groups in the polymer. It is evident that the influence of the concentration of end groups for the low MW PCL samples is more prominent than that for the high MW ones. The higher concentration of the end groups will produce more dislocations in the lamellar thickening process^[25]. The higher the concentration of the end groups, the lower is the perfectness of the T_m^0 of PCL. Moreover, Flory pointed out that the relationship between the T_m^0 and the MW of polymers can be expressed as^[28, 30]

$$1/T_m^0 - 1/T_m^* = 2R/\Delta H_u X$$

where T_m^* is the equilibrium melting point for crystals of infinite MW chains, ΔH_u is the enthalpy of fusion per repeating unit and X is the average polymerization degree. According to this equation, as X is increased, the influence of MW on T_m^0 will be strongly diminished. This is proved likewise by our experimental results. Figure 7 shows a plot of $1/T_m^0$ versus $1/X$, and a good linear relationship was obtained, from which T_m^* and ΔH_u were calculated to be 340.2 K and 11.3 kJ/mol, respectively. Phillips *et al.* have studied the crystallization and melting behavior of three commercial PCL samples and the value of T_m^0 was found to be 343.5 K (PCL-700, $M_w = 40000$), 342.5 K (PCL-300, $M_w = 15000$) and 341 K (PCL-150, $M_w = 7000$), respectively^[25]. Before that, Crescenzi *et al.* had obtained a value of 336 K for T_m^0 of PCL-700. These values are close our findings in the corresponding MW range. As the MW of their samples is comparatively higher, only a slight increasing T_m^0 with increasing MW can be observed. The experimental results obtained for the present PCL samples covering a wide range of MW may permit a understanding of the dependence of melting behavior of PCL on their MW.

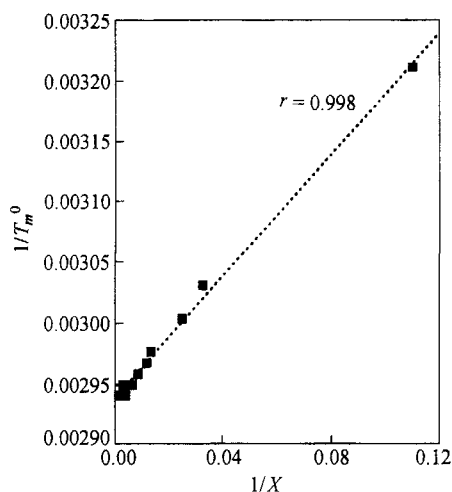


Fig. 7 The reciprocal of the equilibrium melting points ($1/T_m^0$) as a function of the reciprocal of the average polymerization degree ($1/X$)

Moreover, the value of ΔH_u obtained in this work is far below 15.9 kJ/mol as reported by Crescenzi^[24]. It is interesting to note that the value of ΔH_u for poly(ethylene oxide) obtained by our method is also far below the value obtained on the basis of the solvent effect on the melting point^[31]. Possibly, this difference is caused by using different measuring methods, and it should be confirmed by more experimental results.

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