

Poly(caprolactone) Thin Film Preparation, Morphology, and Surface Texture

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Received 23 August 2005; accepted 10 August 2006

DOI 10.1002/app.25228

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The properties and surface uniformity of poly(caprolactone) (PCL) thin films were measured. Thin films were prepared using a spin-coating technique. Film thickness and roughness were correlated with variation in solution concentration, spinning speed and spinning time. Differential scanning calorimetry (DSC) was used to investigate the crystallization and melting processes. The enthalpy of melting variation correlated with the film thickness, while melting temperature was independent of film thickness. In addition, surface roughness was found to be a function of PCL thickness. Film thickness and roughness showed a progressive

decrease when spinning speed was increased, while spinning time provided no significant influence on film thickness. PCL thickness and roughness significantly increased when PCL solution concentration increased. Hot stage optical microscopy showed that larger spherulitic crystals were present in thin films, and the smaller crystals present in thicker films had a coarser texture consistent with increased surface roughness. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1287–1294, 2007

Key words: polyesters; films; surfaces; morphology; crystallization

INTRODUCTION

Thin polymer films have attracted much interest in recent years. Crystallization is changed when a polymer is in a thin film on a substrate.¹ Adsorption on a surface will immobilize a polymer, restricting nucleation, diffusion, and segmental motions. Increase in molecular mobility decreases glass transition temperature.² Analytical techniques for thin polymer films and their various surface properties compared with bulk material are of increasing interest. Film structure can be controlled by melting, crystallization, and wetting.³ Crystallinity influences the mechanical properties of thin films.^{4,5} To obtain a typical thin film, many factors must be taken in account and these may have influence on the film thickness and properties. Some of these factors are the selection of solvent, concentration of the polymer, evaporation of the solvent, substrate surface nature, spin coating speed, and heating processes. The uniformity of the surface is also controlled by the crystallization process.³

Polymer melting temperature shows no significant changes in many processes,^{3,6} even in many blend compositions. Reversible melting phenomenon were found in the melting–recrystallization–remelting processes in the melting range.^{7,8} Larger and thicker

lamellae of polyethylene were formed during biaxial drawing of films. Uniform thin films can be deposited on a glass substrate.³ At high temperature, cracks and holes have been observed to occur during film formation.³ Rupture and holes have been found in polystyrene films at elevated temperatures.⁹

Polymers with less than 1 μm film thickness have been shown to have different properties than the bulk polymer.^{10,11} Some polymer crystallization is faster under ambient conditions when the polymer is in a thin film.¹² An amorphous polymer film may have an influence on neighboring crystallization.⁶ Crystallization and melting are modified in thin films, and they depend on substrate surface adsorption and nucleation. The glass transition temperature of a freely standing polystyrene film decreased with decreasing film thickness, compared with that of substrate-supported films.¹³ Crystallization was found to control many film properties on a substrate,³ and crystallization rate was influenced by polymer concentration with film formation from solution.¹⁴ A sufficient concentration and volume of solution is needed to provide full coverage and to form a continuous film of the polymer on a substrate. This was desired to peel the polymer film and obtain a free standing film for thermal testing.³ The film thickness, wetting, and dewetting of a polymer controlled many of the polymer parameters such as crystallization and the crystalline morphology.³ Crystal growth was found to depend on both substrate type and surface properties^{10,15,16} of the film. For very thin films ($<0.5 \mu\text{m}$), the morphology was composed of

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TABLE I
Thickness Versus Concentration for Different Spinning Speed

Concentration (g mL ⁻¹)	Spinning speed (rpm)			
	1,000	2,000	4,000	6,000
	Thickness (μm)			
0.2	0.2	0.1	0.09	0.07
0.4	0.9	1.7	0.3	0.1
0.6	1.7	1.1	0.7	0.5
1.0	3.3	2.3	1.6	1.5
1.6	7.2	6.3	3.7	3.3
2.0	16.3	9.6	6.6	4.1

aggregates on the edge of oriented lamellae instead of the flattened spherulites of thicker films.¹⁰

Poly(ε-caprolactone) (PCL) is used in this study. PCL has low melting temperature and it is soluble in many solvents.¹⁷ PCL is a thermoplastic with a high molecular weight that makes it possible to use it for casting very thin films. It is a highly crystalline polymer that crystallizes at room temperature. PCL has a high rate of crystallization and its crystals dominate and provide nucleation for other crystals when it is mixed with other polymers.¹⁸

In biaxial drawing of PCL, it was found that crystallinity has no effect on the melting temperature.³ It has been found that the PCL crystallinity was enhanced in poly(4-vinylphenol) blends.¹⁹ Crystallization started at the surface of the film maintaining the same bulk properties.²⁰ It was found that crystallization of PCL was influenced by the composition and crystallization temperature.²¹

The sensitivity of differential scanning calorimetry (DSC) allows study of the variation of crystallinity.^{7,15,16} Hot-stage microscopy is a suitable technique to observe and measure the radial growth rate of spherulites.⁶ PCL of low molecular weight often have high crystallinity. Crystallinity often controls the biodegradation rate of polymers rather than molecular weight.^{17,8} Many researchers have investigated the properties changes due to the crystallinity of PCL. A systematic study of film formation, morphology, and surface roughness is performed in this work.

The aim is to prepare thin films with controlled thickness, of PCL, a semicrystalline thermoplastic, from solution using spin coating on glass and silicon substrates. Solution concentration, spinning speed, and spinning time are variables used to control film thickness and consequently film roughness. A further aim is to investigate dependence of crystallinity, spherulite size, melting temperature, and melting enthalpy on film thickness and substrate type. The objectives of this research include investigations of the preparation of thin films using spin-coating technique, study of the property variations of PCL thin films corresponding to film thickness variations.

EXPERIMENTAL

Materials

Poly(ε-caprolactone) [PCL] H(OCH₂(CH₂)₃CH₂CO)_nOH, $M_w = 80\,000\text{ g mol}^{-1}$, Aldrich] [$T_m = 60^\circ\text{C}$] was used to prepare thin films of 0.07–16.0 μm thickness. Solutions of poly(ε-caprolactone) (0.2 and 2 g mL⁻¹) were prepared by dissolving PCL in tetrachloroethane [Cl₂CHCHCl₂], obtained from Aldrich, [$T_b = 144\text{--}148^\circ\text{C}$] at room temperature.

Solution preparation

The characteristics of PCL have attracted researchers to use the polymer in many applications.¹⁷ PCL solutions in tetrachloroethane were diluted to provide a series of concentrations shown in Table I. The solutions were filtered through a 0.2 μm syringe filter. Before the experiments, glass slides were cleaned with acetone and rinsed with deionized water. Finally, they were dried under a nitrogen purge and stored in a clean room before use in the spinning process.

Spin coating process and thickness measurements

The spin coating process was used to spin-coat a solution of PCL at different speeds for a constant spinning time. PCL was spin coated at different speeds to obtain thin films on glass substrates in a clean room at ambient temperature. Drops of the solution were deposited on the glass substrate using a pipette after setting the spin-coating machine to a specific speed in the range of 1000–6000 rpm. Excess solution spilled instantly from the substrate surface while spinning, leaving a thin film covering the glass. After the spinning process, the coated specimens were kept in fume cupboard in a clean room while allowing the solvent to evaporate. The films were dried in a vacuum oven at 40°C for 24 h to remove any residual solvent. Finally, the films were cooled to room temperature in the clean room.

The films were scratched using a sharp blade and the thickness was measured using a stylus XP-2 AMBIOS profilometer to scan across the cut. The surface roughness was measured using the same instrument (Table II).

TABLE II
Surface Roughness Versus Spinning Speed for Different Concentration

Spinning speed (rpm)	Concentration (g mL ⁻¹)			
	0.2	0.6	1	1.6
	Roughness (μm)			
1,000	0.004	0.031	0.043	0.130
2,000	0.005	0.017	0.036	0.083
4,000	0.002	0.030	0.023	0.053
6,000	0.003	0.010	0.022	0.053

TABLE III
Melting Properties and Spherulite Size Versus Thickness

Film thickness (μm)	Melting temperature ($^{\circ}\text{C}$)	Enthalpy ΔH (J g^{-1})	Crystal size (μm)
0.1	59.5	81.2	89
0.7	59	69.3	
1.1	60.2	72.3	
1.6	58.8	66.1	
1.7	60.2	70.4	
2.3	58.8	66.3	
3.3	59.1	65.2	62
4.1	59.7	59.7	60
6.6	59.7	59	50
9.6	59.0	59.2	48
16.3	59.2	59.6	

Hot stage with optical microscopy

A hot stage was used to precisely control the temperature while visualizing crystallization in the polymer films. Heating the films above their melting temperature and cooling them to room temperature was used to create a thermal history.² Optical microscope was used to view the crystallization and surface morphology using glass substrates.²² A Mettler FP82HT Hot-stage with Mettler FP90 central processor was used. PCL films on glass substrates were inserted in the hot stage chamber. For the heating stage, the film was heated from 20°C to 80°C at a rate $10^{\circ}\text{C min}^{-1}$, and then held for 3 min at 80°C . For the cooling stage, the film was cooled from 80°C to 20°C at rate $10^{\circ}\text{C min}^{-1}$. A Nikon Labophot 2 optical microscope was used for observing the PCL film crystals with and without a polarizer. Images were captured using a Nikon digital camera (Coolpix 5000). These images were employed to measure crystal size and investigate surface morphology using the same magnification with all images and a standard graticule for calibration.

Crystallization and melting analysis

DSC was used to characterize the crystallization and melting process of the PCL films. A thermal history was created for all films by heating the films to 80°C for 3 min and cooling at $10^{\circ}\text{C min}^{-1}$. A PerkinElmer Pyris1 DSC with Intracooler 2P was used after calibration using indium and zinc standards for temperature and indium for enthalpy. Films made from a mass of 1–3 mg were accurately weighed after peeling them from the glass substrate and hermetically sealing in $10 \mu\text{L}$ aluminum pans. It was difficult to peel films that had a thickness less than $0.5 \mu\text{m}$ from the glass substrate although other reports describe that PCL does not show strong nucleation on a glass surface with thickness less than $0.5 \mu\text{m}$.^{23,24} The melting parameters were measured from a second heating scan at $10^{\circ}\text{C min}^{-1}$. After completion of the

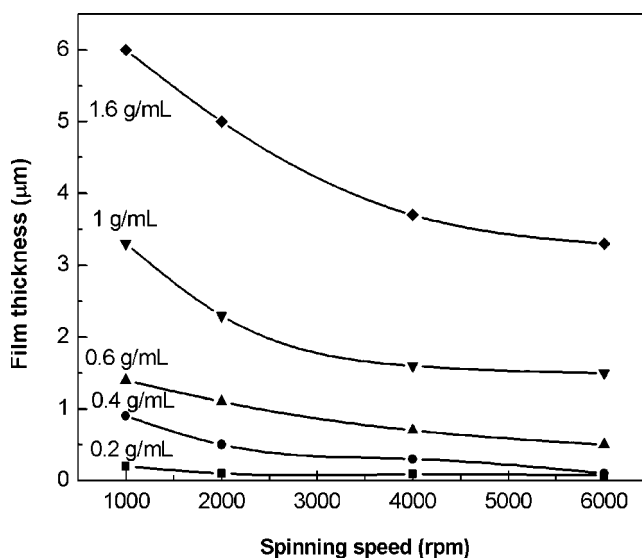


Figure 1 Correlation between film thickness and spinning speed at various concentrations.

DSC measurements the lid was removed from the DSC pan and the thickness of each film was confirmed using the stylus profilometer (Table III).

RESULTS AND DISCUSSION

The polymer concentration in the solution used for spinning, spinning speed and the resulting film thickness control the film properties. In this investigation, the spinning time had no significant influence on the thin film thickness. Concentration and spinning speed were used to obtain thin films of varying thickness. The data for film thickness corresponding to spinning speed are plotted in Figure 1 as a correlation between

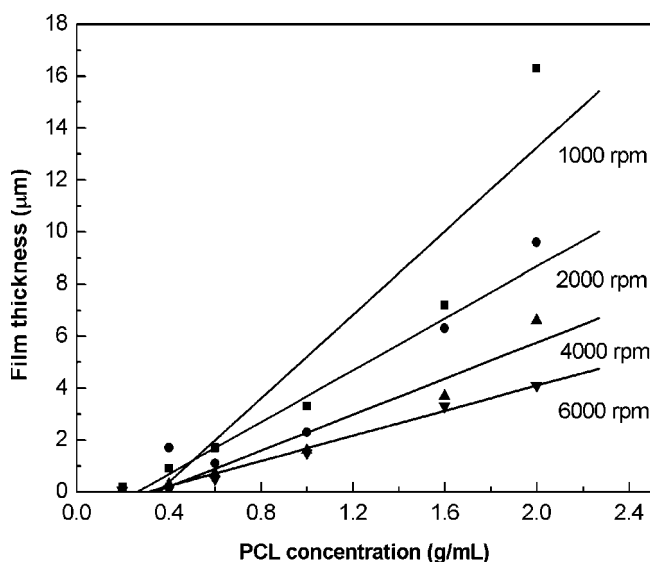


Figure 2 Correlation between film thickness and concentration of polycaprolactone at different spinning speeds.

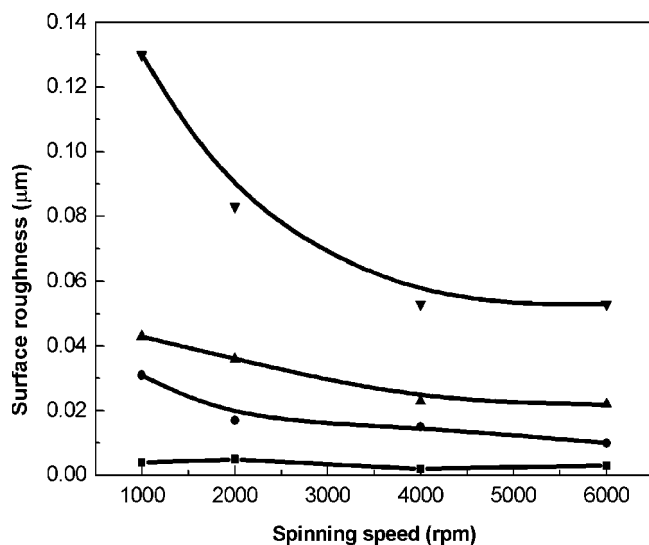


Figure 3 Correlation between surface roughness and spinning speed at four concentrations.

film thicknesses and spinning speed for different concentrations and this was a foundation for this study. Figure 2 shows the PCL films that were prepared from solutions of different concentration; their thicknesses have shown dependency on the concentration of PCL. Films that were made from solutions of higher concentration have greater thickness. The film thickness was less sensitive to concentration at low concentration. This was due to the viscosity of polymer solution changing with concentration and entanglement concentration controlling film thickness.²⁵

The surface uniformity has been studied in correlation with spinning speed. Figure 3 shows the relation between the surface uniformity (surface roughness)

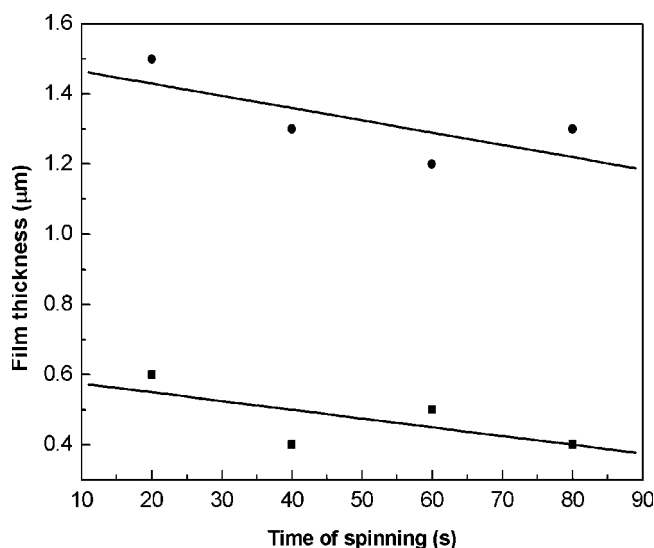


Figure 4 Correlation between film thickness and spinning time at two concentrations.

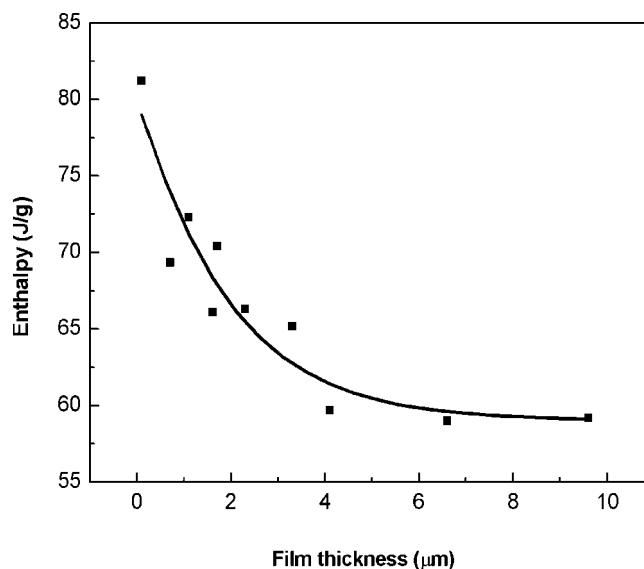


Figure 5 DSC melting endotherms for PCL for different film thickness.

and the spinning speed. In Figure 3, the surface roughness of the thinner films of PCL (low concentration of PCL) had the lowest roughness at ambient conditions. The PCL films were prepared under ambient conditions and after evaporation of solvent at room temperature; they were placed in a vacuum oven set to a temperature lower than the melting temperature. The surface uniformity (roughness variations) for different thicknesses depended on the ambient conditions, substrate nature, such as nucleation, and the nature of the solvent, such as boiling temperature or evaporation rate. Solvent evaporation and its evaporation rate, the nature of the substrate and its relation with the polymer and polymer concentration are factors involved

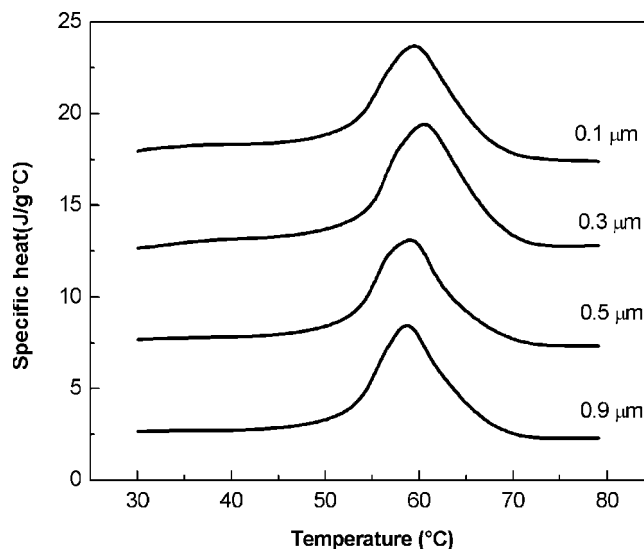


Figure 6 Correlation between PCL melting enthalpy and film thickness.

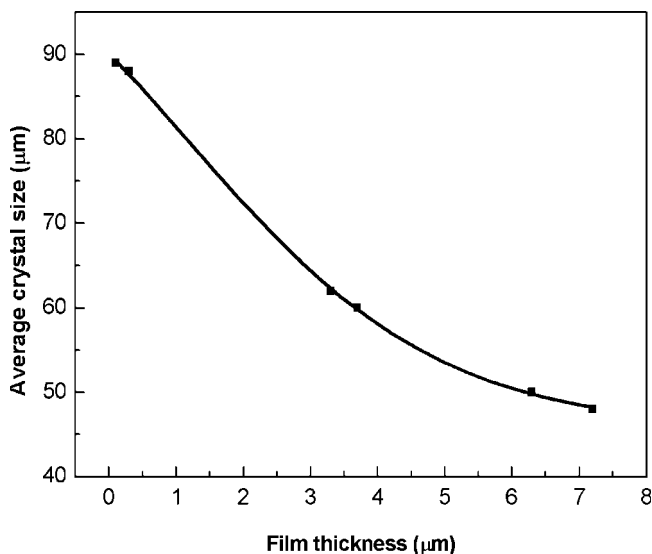


Figure 7 Correlation between average PCL crystal size and film thickness.

in shaping the surface uniformity without any further treatment to the surface just under ambient conditions. A correlation between film thickness and spinning time was made in this study to show the influence of time. The relation is shown in Figure 4. No significant changes to the film thickness are observed in correlation with spinning time.

DSC was used to measure crystallization and melting, as a function of film thickness. Some DSC melting curves, calibrated to specific heat, are shown in Figure 5 for four thicknesses of PCL films. The DSC melting endotherms were used to measure enthalpy of melting corresponding to film thickness. A correlation of melting enthalpy variation is shown in Figure 6. Figure 6 shows that enthalpy, and hence crystallinity, increases as the film thickness decreases.²⁶

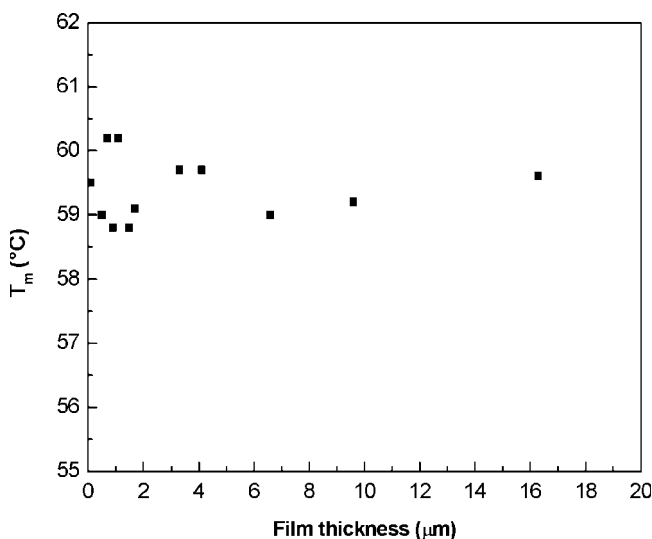


Figure 8 PCL melting temperature and film thickness.

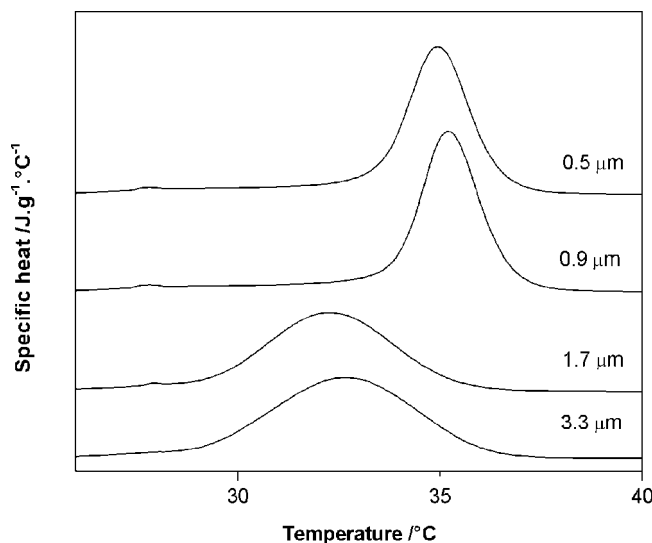


Figure 9 Crystallization exotherms for PCL films of four different thicknesses.

Crystals size measurements performed on PCL films of different thickness have shown significant variation in spherulite size corresponding to the film thickness as shown in Figure 7. This variation provided a correlation for the thinner films on a substrate surface that causes nucleation due to adsorption of molecules on the surface; and this caused slower growth of crystals with less nuclei density allowing crystals to grow to bigger size. The correlation of spherulite size with film thickness was consistent with the increase in enthalpy of melting shown in Figure 6.

A graph showing melting temperature variations with film thickness is shown in Figure 8. Figure 8 shows that there was no change in melting temperature.

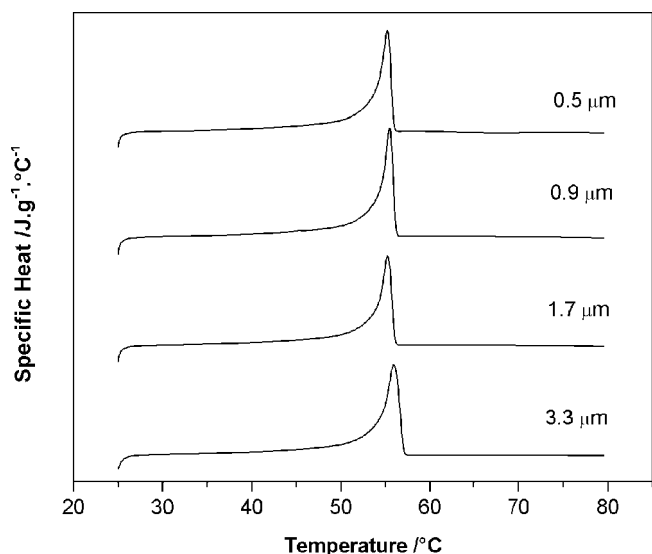


Figure 10 Melting endotherms for PCL films of four different thicknesses.

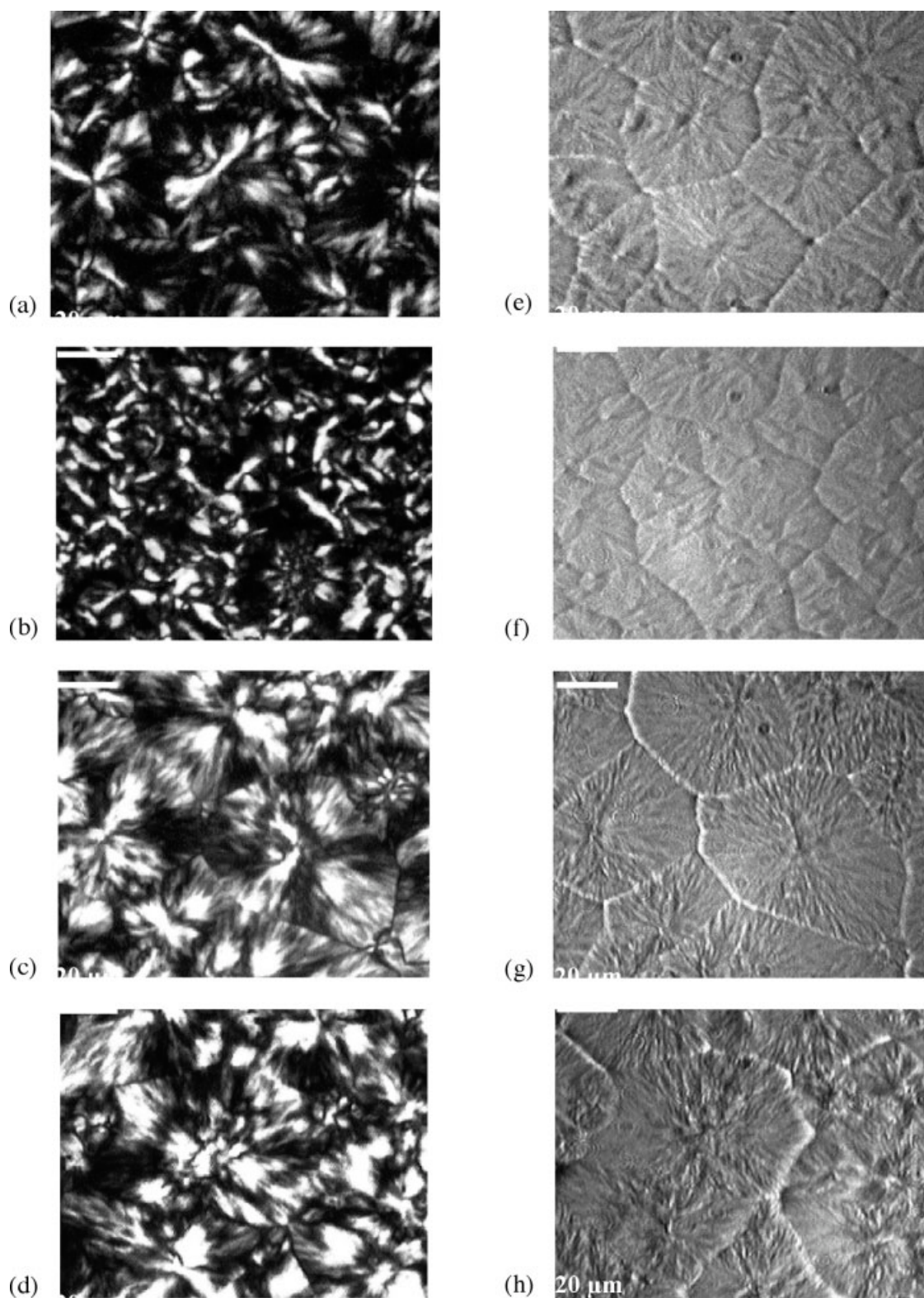


Figure 11 Optical microscope images of PCL thin films, polarized (left) and unpolarised (right); (a) and (e) 0.10 μm , (b) and (f) 0.30 μm , (c) and (g) 0.50 μm , (d) and (h) 0.90 μm .

ture with film thickness or crystallinity. The data at low film thickness are scattered due to the uncertainty in measuring peak melting temperature from the low intensity endotherms.

Figure 9 shows some representative crystallization exotherms, expressed in specific heat convention, for PCL films of varying thickness on cooling. Figure 9 shows that the thicker PCL films had a lower peak

temperature with a wider exothermic transition. The wider transition is indicative of slower crystallization rate. Figure 10 shows the corresponding melting endotherms of the same films after the crystallization shown in Figure 9.

Optical microscopy images of PCL thin films of different thickness and showing different spherulites patterns are shown in Figure 11. The average film thickness that was used in imaging the polymer film was between 0.90 and 0.10 μm . The film structure was formed after melting and then crystallization on the microscope hot stage. The images of the PCL films of different thicknesses show that the spherulites of the thinner films have larger size. The correlation of spherulite size with film thickness measured from microscopy images shown Figure 7 confirms the qualitative observation of the images.

PCL spherulites viewed under polarized light are shown in Figure 11(a–d) for four different thickness and the spherulite images without polarized light are shown in Figure 11(e–h). The images show that the PCL spherulites completely filled the area and they are composed of lamellae spreading from nuclei. It can be seen from these images that the lamellae of thinner films are more spherical than thicker films and they have a higher nucleation rate with less sharp boundaries and they are in general less ordered. The dark boundaries or dark areas indicate inconsistency in surface uniformity. It is important to allow enough time for solvent evaporation at ambient condition, which leads to low roughness or a more uniform surface. A low rate of evaporation of the solvent near ambient or at low temperature is best to minimize deformation of macroscopic defects in the films, such as microcircular holes, to minimize any instability at the center of the film and to avoid irregular shaped cells.

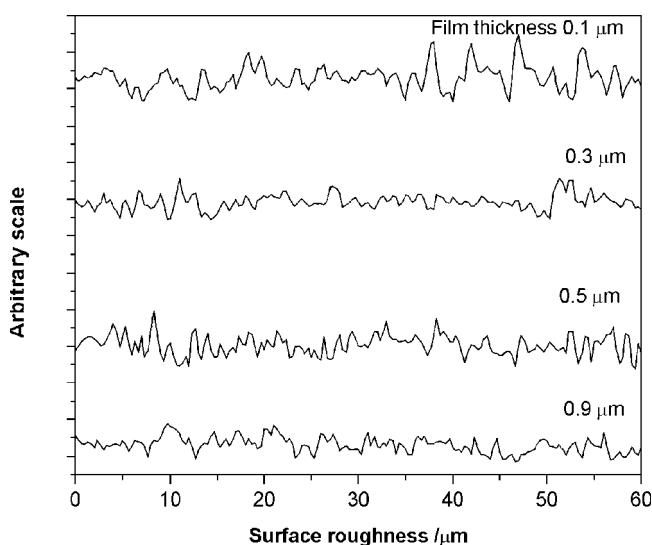


Figure 12 Surface roughnesses of PCL films of four different thickness.

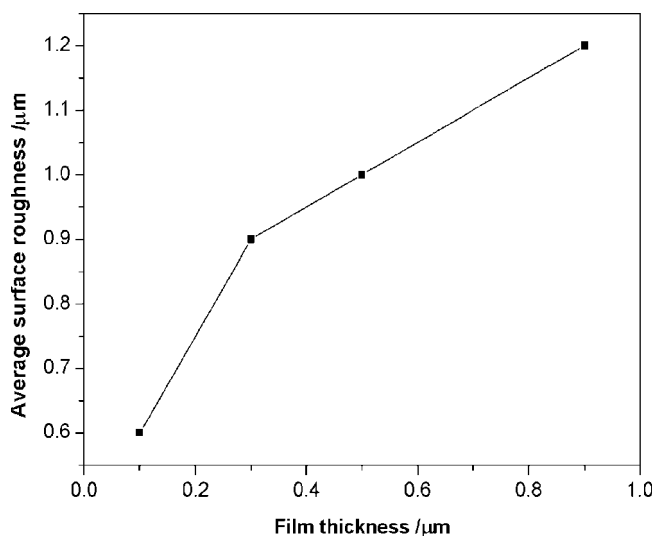


Figure 13 Average surface roughness of PCL film using films from a solution of concentration of 0.4 g mL^{-1} .

Changing the vacuum oven pressure was useful in avoiding films with holes. It can be seen that thicker films had spherulites of smaller size, dark texture, higher nucleation density, and less intense radial patterns.

The surface textures of four film thicknesses were calculated using the microscope images of lamella by graphing the intensity across each image as shown in Figure 12. The variation in intensity across each image qualitatively correlated with surface roughness measured using the profilometer demonstrating that the roughness was a consequence of spherulite texture, rather than a surface wetting phenomena or surface tension skin effect. Figure 13 shows the correlation between the average surface roughness, measured using the profilometer, and the film thickness using four different thicknesses showing significant variation of roughness increasing as the film thickness increased.

CONCLUSIONS

Solution concentration, spinning speed, and evaporation rate were the variables used to control film thickness and roughness. Selection of speed was used to spin PCL solutions to prepare films of different thicknesses. Film thickness and roughness showed a progressive decrease when the spinning speed was increased. DSC measurements showed melting enthalpy, and hence crystallinity, decreased with film thickness. Melting temperature had no significant variation with film thickness. Spherulite size decreased with film thickness since nucleation and crystallization were slower in thin films due to decreased molecular mobility. The optical microscopy PCL film images of different thicknesses demonstrated that the spherulites

of the thinner films were larger with well-defined geometric shapes. A comparison of the average film roughness with film thickness showed increasing roughness as the film thickness increases, due to the increased size of the spherulites.

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