Electronic Supplementary Material (ESI) for Soft Matter.

Impact of Polymer Chain Packing and Crystallization on Emission Behavior of Curcumin-Embedded Poly(L-lactide)s

G. Virat[†, ‡], Kaustabh Kumar Maiti[ϒ, ‡], R.B. Amal Raj[†] and E. Bhoje Gowd*[, †, ‡]

[†]Materials Science and Technology Division
CSIR-National Institute for Interdisciplinary Science and Technology, Trivandrum 695 019, Kerala, India.

[ϒ]Chemical Sciences and Technology Division
CSIR-National Institute for Interdisciplinary Science and Technology, Trivandrum 695 019, Kerala, India.

[‡]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201 002, India.

Corresponding Author

*E-mail bhojegowd@niist.res.in; Tel +91-471-2515474; Fax +91-471-2491712 (E.B.G.).

Table of contents

Characterization and Measurements

The molecular weight and polydispersity (*Đ*) of the synthesized curcumin-PLLA were determined by gel permeation chromatography (GPC) using Agilent Technologies-1260 instrument with RI detector, which is equipped with a PL-gel 20 μm mixed bed column operated at 30 ºC with THF as solvent (flow rate of 1 mL/min). Narrow disperse polystyrene standards were used for the calibration. ^{1}H NMR spectra were recorded on a 500 MHz Bruker Advance DPX spectrometer using tetramethylsilane (TMS) as an internal reference. NMR samples were analyzed in d_6-DMSO. Differential scanning calorimetry (DSC) thermograms of Curcumin-PLLA were recorded using a thermal analyzer (TA instrument Q2000) at a heating and cooling rate of 10 °C/min under the N_2 atmosphere. Isothermally crystallized samples for UV and PL measurements were prepared using DSC. The thermal program used for the isothermal crystallization was given under the sample preparation. TGA thermograms were collected using a a thermogravimetric analyzer (TGA) TA Q50. The samples were heated from room temperature to 600 °C at a rate of 10 °C/min under nitrogen atmosphere. Circular dichroism (CD) spectra were recorded on a JASCO-J- 810 spectropolarimeter with a Peltier thermostatic controller using a quartz cell of 1.0 cm path length and the sample concentration was fixed at 1 mg/ml for Curcumin-PLLA in chloroform/hexane mixture. UV–vis absorption spectra were collected on a SHIMADZU UV-2600 spectrophotometer, and samples were analyzed at room temperature. Fluorescence emission spectra were recorded on SPEX-Flourolog-3 FL3-221 spectrofluorimeter at room temperature. Fluorescence quantum yield was measured with an integrating sphere method using a fluorescence spectrometer instrument, model-FL3C-KIT. Variable temperature fluorescence emission spectra were recorded on the Spex-Fluoromax FL22 spectrofluorimeter with a double grating 0.22 m Spex 1680 monochromator, a 450 W Xe lamp as the excitation source, and a Hamamatsu R928P photomultiplier tube detector. All these measurements were carried out using a 1 cm or 1 mm

quartz cuvette. The morphology of single crystals of curcumin-PLLA was investigated using JEOL 2010 transmission electron microscope (TEM) operating at 200 kV. For TEM measurements, the colloidal suspension of curcumin-PLLA in DMA was drop-casted on a carbon-coated copper grid and dried under dust free atmosphere. Leica DFC 490 Polarized optical microscope (POM) equipped with a Mettler Toledo FP82HT heating stage was used to observe the morphology of the spherulites at isothermal crystallization conditions.

Wide-angle X-ray diffraction (WAXD) patterns were measured using a XEUSS SAXS/WAXS system (from Xenocs) operated at 50 kV and 0.60 mA using Cu Kα radiation (wavelength, λ = 1.54 Å). The fiber diffraction patterns were recorded on a Mar 345 image plate system (detector) and the data was processed using the Fit2D program. Silver behenate was used as a calibration standard for the precise measurement of the sample-to-detector distance. The variable temperature measurements of curcumin-PLLA gels were carried out using a Linkam THMS 600 hot stage fitted to the X-ray system. Fourier transform infrared (FTIR) analysis was performed using a PerkinElmer Series FT-IR Spectrum Two machine at a resolution of 4 cm^{-1} and 32 scans in the wavenumber range of 4000-400 cm^{-1}. The variable temperature measurements of curcumin-PLLA were carried out using a Linkam THMS 600 hot stage fitted to the FTIR spectrometer.

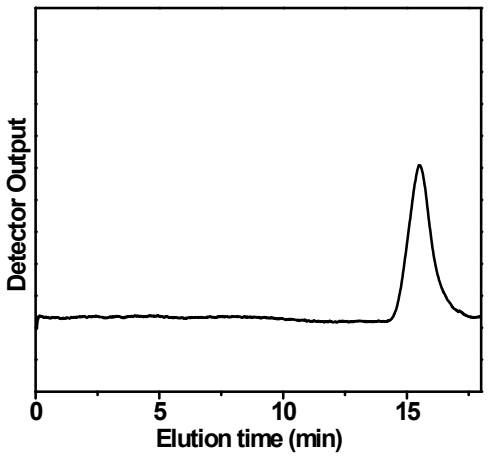

Figure S1. GPC trace of curcumin-PLLA in THF.

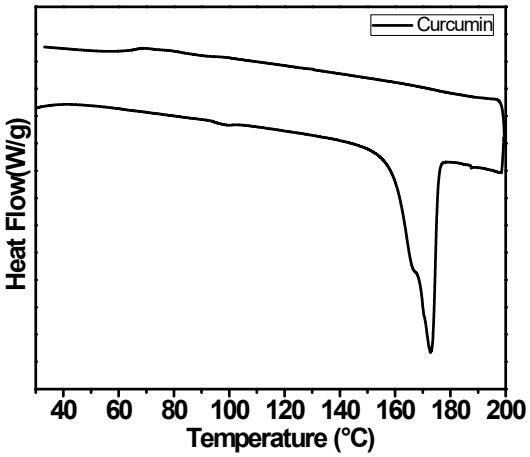

Figure S2. DSC thermograms of pristine curcumin during heating and cooling process at a rate of 10 °C/min.

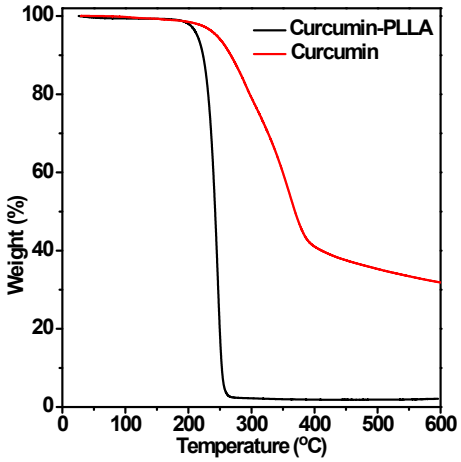

Figure S3. TGA thermograms of pristine curcumin and curcumin-PLLA during heating at a rate of 10 °C/min under nitrogen atmosphere.

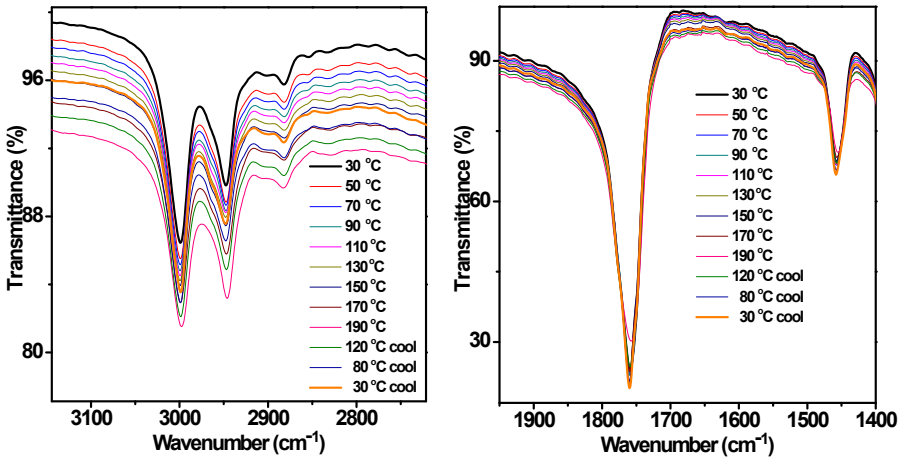

Figure S4. Temperature-dependant FTIR spectra of curcumin-PLLA during heating and cooling in two wavenumber regions.

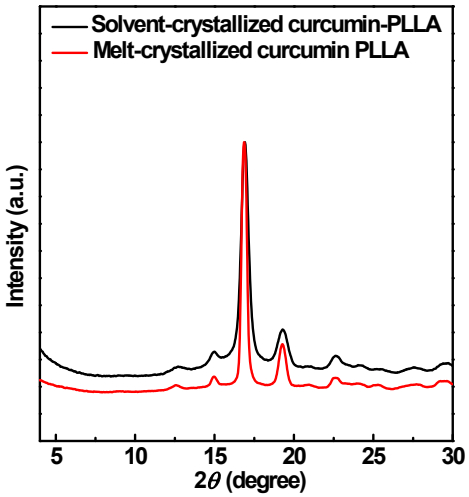

Figure S5. WAXD patterns of solvent-crystallized and melt-crystallized curcumin-PLLA.

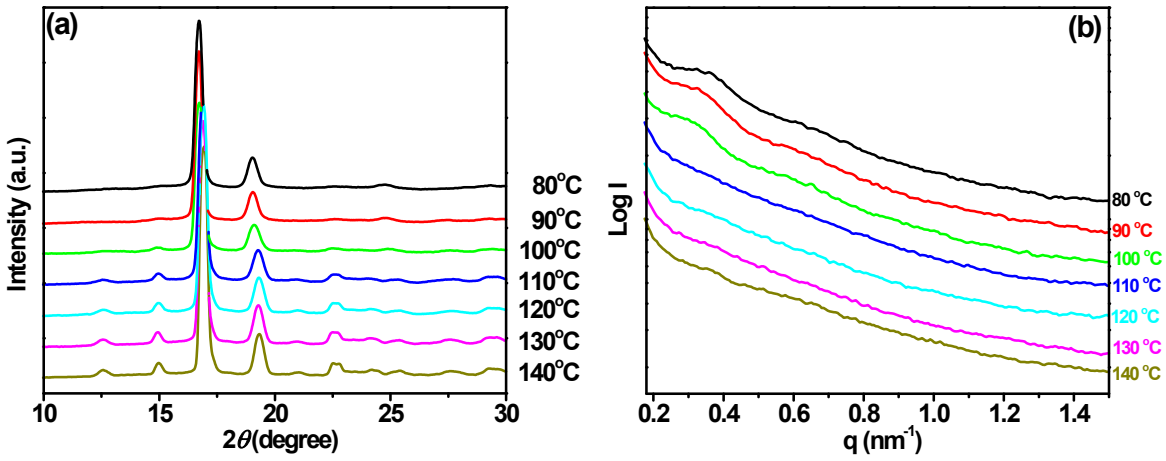

Figure S6. (a) WAXD patterns and (b) SAXS patterns of curcumin-PLLA crystallized at various isothermal crystallization temperatures.

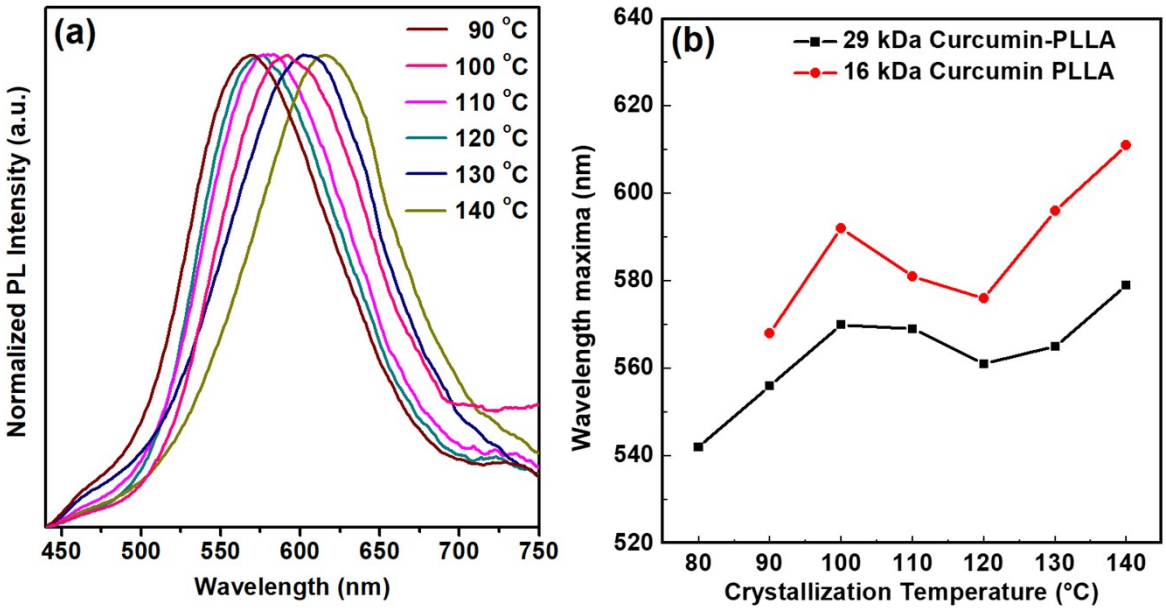

Figure S7. (a) PL spectra of curcumin-PLLA (16 kDa) crystallized at various isothermal crystallization temperatures and (b) comparison of the temperature dependence of PL wavelength maxima of curcumin-PLLA (29 kDa and 16 kDa) crystallized at various isothermal crystallization temperatures.