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Temperature dependent IR-Transition Moment Orientational Analysis — Supplementary Materials

Temperature dependent IR-Transition Moment Orientational Analysis applied to thin supported films of Poly- ϵ -caprolactone — Supplementary Materials

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I. SUPPORTING INFORMATION

A. Kinetics of isothermal crystallization

Kinetics of crystallization is traced based on the absorption coefficient of IR absorption bands originating from vibrational transition moments related to crystalline polymer strands. Poly- ϵ -Caprolactone (PCL) films are molten and equilibrated at 90° C, before quenching to the desired crystallization temperature T_X (with about 60 K/min), where we measure IR-spectra depending on time (fig. 1a). After baseline-correction the band at about 1296 cm^{-1} is fitted as a pseudo-Voigt peak and the resulting integrated absorbance (area of the peak) is plotted with respect to time (fig. 1b). This area is proportional to crystallinity, and therefore the extracted characteristic times reflect net crystallinity resulting from nucleation and lamellar growth. For $T_x \leq 40^\circ$ C crystallization finishes in less than 8 minutes, which is in agreement with literature data.^{1,2} The resulting spherulites exhibit a diameter of $0-60 \ \mu m$.

Based on these time dependencies assignment of bands referring to the crystalline or amorphous state can be achieved. The band at around 1245 cm⁻¹ originates from several transition dipole moments within the amorphous or crystalline parts (fig. 1a). Difference spectra, with respect to the amorphous state at the same temperature, reveal furthermore that there are two peaks corresponding to crystalline regions with this absorption band.



FIG. 1. a) Temporal evoluation of IR-spectra upon isothermal crystallization at 23° C, 32° C, 35° C, 37° C (measured twice), 40° C and 45° C. The lowest set of dashed lines are difference spectra for $T = 40^{\circ}$ C (spectra of amorphous state subtracted). b) Integrated area of the band at about 1296 cm⁻¹ depending on time. The color code agrees with panel a). Spectra are shifted vertically, to compensate the delay before crystallization starts.

²È. Zhuravlev, J. W. P. Schmelzer, B. Wunderlich, and C. Schick, "Kinetics of nucleation and crystallization in poly(ε-caprolactone) (PCL)," Polymer **52**, 1983–1997 (2011).

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¹P. J. Phillips, G. J. Rensch, and K. D. Taylor, "Crystallization studies of poly(ε -caprolactone).I. Morphology and kinetics," Journal of Polymer Science Part B: Polymer Physics **25**, 1725–1740 (1987).



FIG. 2. Integrated absorbance, $A^{\rm c}$ and $A^{\rm a}$, of the absorptions bands respectively related to crystalline ($\nu^{\rm c}$) and amorphous ($\nu^{\rm a}$) carbonyl units; Dotted and solid lines depict linear excluding and including the point at $A^{\rm a} = 4.8$ measured for $T = 59^{\circ}$ C. The mean value of the fit parameters of these fits are used to determine the molecular attenuation coefficients ϵ .



FIG. 3. Exploded view of the device to perform temperature dependent Infrared-Transition Moment Orientational Analysis (a), cf. fig. 1 in the manuscript. The whole setup (b) is sealed within a double walled housing with ZnSe windows (b). c) The sample holder is screwed onto a movable support and surrounded by two hollow frames for gas-supply. d,f) Holder and frame are mounted to revolving wheels (blue) which are connected to a stepper-motor (right, f) and a micrometer-screw (left, d) for moving the sample holder.