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Thermal analysis FTIR spectroscopy of poly (ϵ -caprolactone),

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Graphical abstract

Highlights

- Vibrational spectrum of PCL is complicated by changes on crystallization.
- TA-FTIR spectroscopy enables the absorption bands to be unambiguously assigned.
- Crystallinity can be determined from the ratio of crystalline and amorphous bands.

Abstract.

Vibrational spectra of poly (ϵ -caprolactone) have been measured as a function of temperature and time to assign the molecular origins of the absorption bands, to distinguish crystalline and amorphous bands and measure fractional crystallinity. While many changes occur within the spectrum on crystallization and melting those which occur to the carbonyl absorption band proved to be the most useful in determining the fractional crystallinity and following the development of crystallinity with time.

Two-dimensional IR correlation mapping applied to the carbonyl band clearly showed that the broad band at 1735 cm^{-1} was due to the stretching of the ester carbonyl group in the amorphous regions which decreased in intensity on isothermal crystallization. At the same time a narrower more intense band developed at 1725 cm^{-1} attributed to the absorption of the ester carbonyl group in the crystalline regions. Deconvoluting the band into these

components enabled the intensities of the two to be determined and the fractional crystallinity measured.

Keywords:

Poly (ϵ -caprolactone);

Two-dimensional Correlation Spectroscopy;

Synchronous and Asynchronous Mapping;

Phase transitions,

1. Introduction

Thermal analysis-FTIR spectroscopy has been widely used to follow the mechanism of polymer degradation [1-4] since it enables the intensities of functional groups to be followed as a function of temperature and time as well as recognizing the relative importance of competing side reactions by the build-up and disappearance of transient species. It has been used [5-8] to follow first and second order phase transitions in polymers from the change in intensity of absorption bands associated with changes in chain configuration or morphology. Recently the kinetics of crystallization of polyesters [9-11] have been measured by separating crystalline and amorphous components of the carbonyl absorption band which enabled the fractional crystallinity to be determined as a function of temperature and time.

This paper considers the value of TA-FTIR in measuring phase changes and fractional crystallinity of an important biodegradable polyester, poly (ϵ -caprolactone), PCL, which is widely used in biomedical applications as implants and drug delivery material, scaffolds for tissue repair, sutures and vehicle membranes. It is a partially crystalline polymer but because of its low melting point, 60 °C, and glass transition temperature, - 60 °C, it is prone to ageing at ambient temperatures. As a result of storing above the glass transition temperature the fractional crystallinity, mechanical and physical properties change with time [12]. In order to quantify these changes measurement of the fractional crystallinity becomes essential.

This paper considers the value of TA-FTIR to measure phase and molecular transitions in partially crystalline PCL and directly determine its crystallinity.

2.1 Experimental

Poly (ϵ -caprolactone), PCL, (CAPA 6800) was supplied in pellet form by Perstorp (Warrington, UK). The number and weight average molecular weights were 80 and 120 kg mol⁻¹ respectively, and the polydispersity 1.5. Films up to 500 μ m thick were cast from solution, concentration 3.3-6.6 gdm⁻³, by evaporation of the solvent, dichloromethane, at room temperature. Traces of solvent were removed by placing the films in a heated vacuum oven.

Potassium bromide powder, of IR grade, was supplied by Sigma Aldrich (Dorset, UK) and pre-dried in an air-oven at 120 °C before being pressed into discs for IR spectroscopic measurements. Dichloromethane, research grade, was used as a solvent for PCL. It was supplied by Sigma Aldrich (UK) and used as received.

Transmission FTIR spectra were measured on Nicolet spectrophotometers, models 1869 and 8700, with DTGS-KBR detector on thin films samples mounted between KBr discs and contained within the furnace of a Linkam hot stage. KBr powder was pressed at a pressure of 15 tons into 16 mm diameter discs, using a Specac, UK die-press. A disc of 300 mg. was used to measure the background spectrum. Two sample discs of 150 mg each were used to sandwich the polymer. Drops of polymer solution in dichloromethane were placed on the surface of one of the thin KBr discs and allowed to evaporate. They were subsequently heating in a vacuum oven. The thickness of the sample was adjusted to maintain absorbance values about 1.0.

Polymer film, sandwiched between two thin KBr discs, was mounted across the window of a Linkam THM600 (Surrey, UK) thermometric stage and placed vertically in the IR beam. The furnace temperature was controlled by a Unicam R600 thermal controller to an

accuracy of ± 0.1 °C. A Bibby Scientific Techne TE-10D (Stone, UK) water bath circulated water through the outer skin of the furnace and enabled faster cooling. Spectra were measured over the temperature range 30-70 °C, using variable heating and cooling rates up to 80 °C min^{-1} . Amorphous samples were prepared by heating to 70 °C and holding in the melt for 2 min. The sample was subsequently cooled and spectra recorded at a resolution of 4 cm^{-1} in sets of 100 scans and spectra recorded after every 2 min.. A background was subtracted from all spectra.

3. 2-D correlation spectroscopic analysis.

Two-dimensional infrared spectroscopy is used to simplify the interpretation of complex spectra consisting of many overlapped peaks, and enhance spectral resolution by spreading peaks over a second dimension. This helps to establish the assignment of peaks to certain groups within the molecule through correlation of the bands. The mathematical procedure involved in obtaining 2D correlation spectra from time or temperature dependent complex spectra has been explained by Noda and Ozaki [13] in some detail.

If $y(\nu, t)$ defines the perturbation-induced variations in intensities of spectra observed at fixed intervals of time or temperature (or an alternative external variable), t between t_{\min} and t_{\max} , then the dynamic spectrum of the system, $\tilde{y}(\nu, t)$ is defined as

$$\tilde{y}(\nu, t) = y(\nu, t) - \bar{y}(\nu) \quad \text{for } t_{\min} \leq t \leq t_{\max} \quad (1)$$

where $\bar{y}(\nu)$ is the initial or reference spectrum of the system.

The intensity of the 2D correlation spectrum $X(\nu_1, \nu_2)$ is then represented as

$$X(\nu_1, \nu_2) = \langle \tilde{y}(\nu_1, t) \cdot \tilde{y}(\nu_2, t') \rangle \quad (2)$$

where $X(\nu_1, \nu_2)$ is a quantitative measure of comparative similarities or differences in the intensities. $\tilde{y}(\nu, t)$ is measured at two separate variables; ν is the wavenumber and t is either time or temperature at fixed intervals. The symbol $\langle \rangle$ is the cross-correlation function and is designed to compare the two dependences of the spectra at t .

When the model of Noda and Ozaki is simplified, $X(v_1, v_2)$ becomes a complex number function, such that

$$\mathbf{X}(v_1, v_2) = \Phi(v_1, v_2) + \Psi(v_1, v_2) \quad (3)$$

This function includes both real and imaginary components, which are recognized as synchronous and asynchronous 2D correlation intensities.

The synchronous 2D correlation intensity, $\Phi(v_1, v_2)$, is a symmetrical spectrum with respect to a diagonal line of $v_1 = v_2$ and represents the overall similarity or coincidental trends between two separate intensity variations measured at different spectral variables as the value of t is scanned from t_{\min} to t_{\max} . This is the in-phase character of the system.

. The asynchronous 2D correlation intensity, $\Psi(v_1, v_2)$, is anti-symmetric with respect to the diagonal and is considered to measure out-of-phase character of the spectral intensity variations. The intensity of an asynchronous spectrum represents sequential or successive but not coincidental changes of spectral intensities measured separately at v_1 and v_2 .

4. Results and discussion

4.1 Changes to the FTIR spectrum of PCL on crystallization

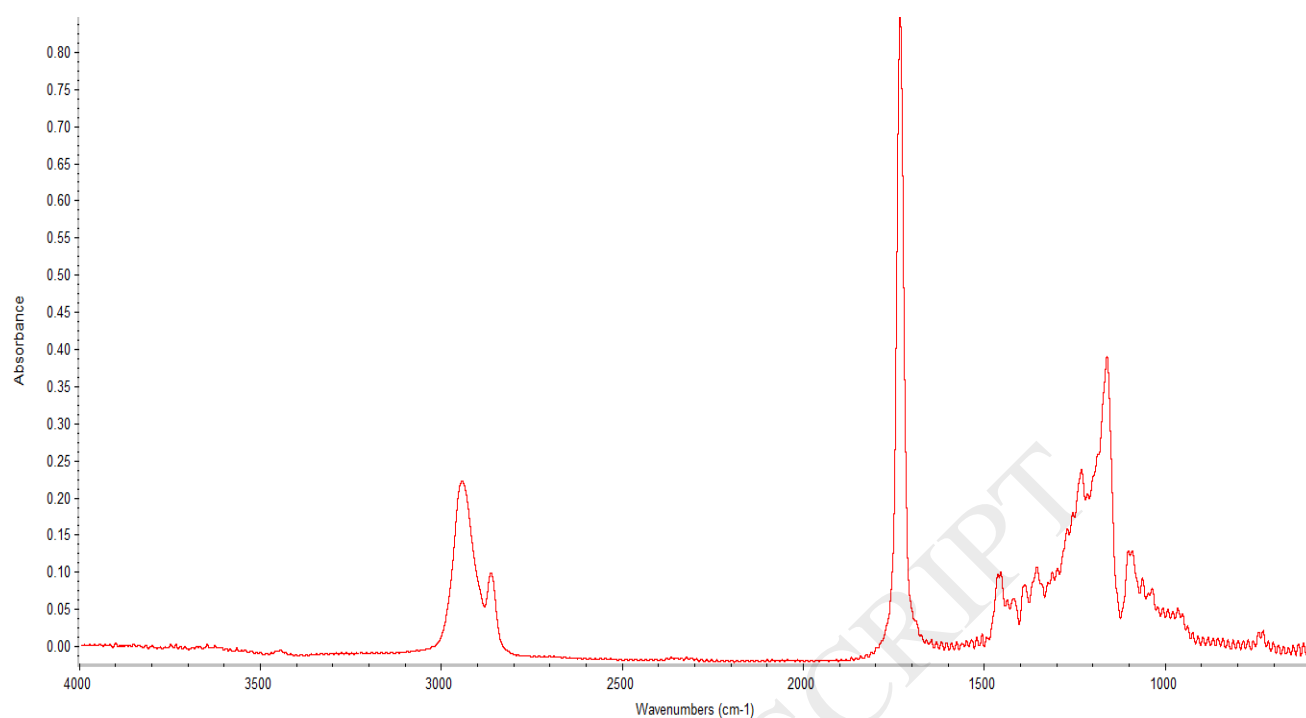


Fig. 2. Changes in IR Spectra on cooling from 70 to 30 °C.

The FTIR spectrum of partially crystalline PCL at room temperature exhibits the absorption bands of a linear aliphatic polyester, see Fig 1, consistent with its structure, i.e.



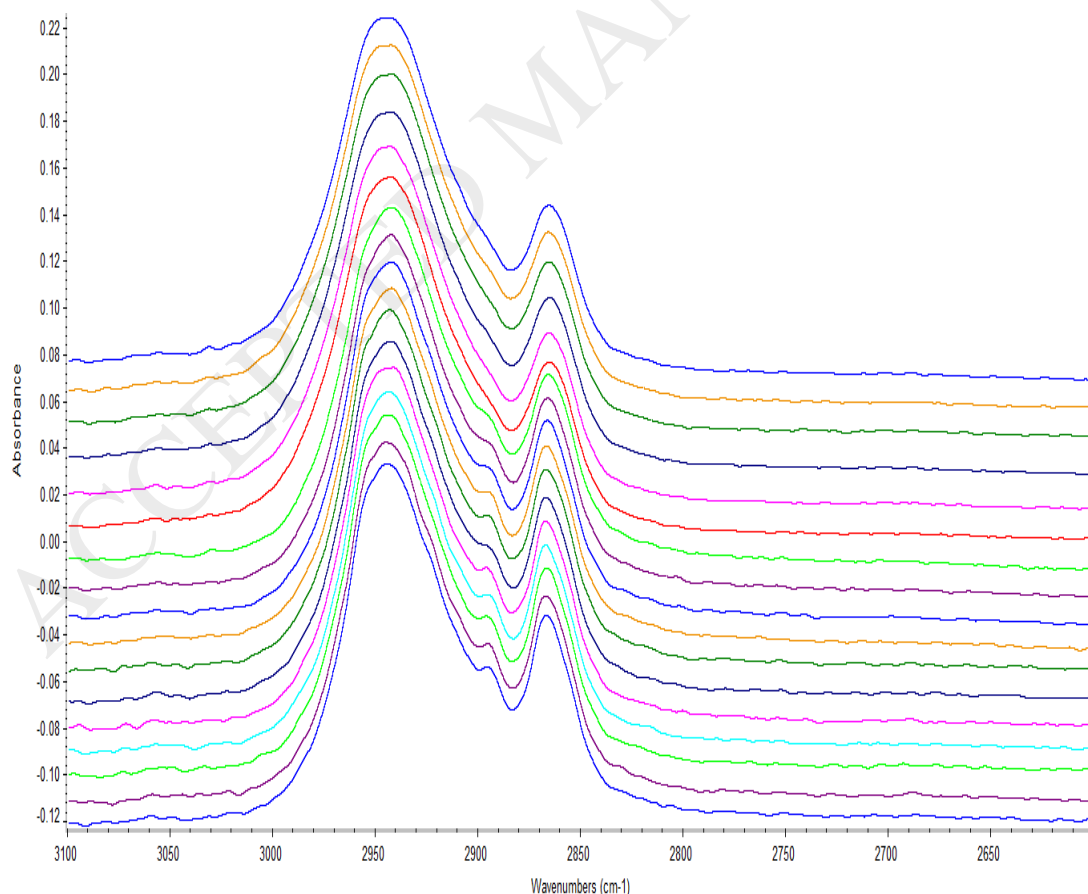
There is a doublet between 2800 and 3000 cm⁻¹ due to the stretching of the C-H bonds of the methylene groups and a singlet at 1720-30 cm⁻¹ characteristic of the carbonyl group. Further bands between 700-1600 cm⁻¹ are attributed to the skeletal structure of the polymer chain, bending, wagging and stretching of the methylene and gauche and trans isomerization of the ester groups, similar to those assigned for PET [6].

Several changes in the spectrum of PCL occurred which were reproducible on melting and crystallizing as can be seen by comparing the amorphous and partially crystalline spectra in Fig. 2 measured in the melt at 70 °C and on cooling to room temperature. Many of the

changes were minor due to differences in conformation of the chains in the amorphous and crystalline regions and also to the difference in the force fields in these two environments. In order to elucidate these changes the spectrum was divided into distinct regions and analyzed separately in greater detail.

4.2 Methylene region – 2600-3000 cm^{-1}

The change in the doublet on cooling from 70 to 30 °C can be seen in Fig. 3 and in particular on crystallizing in the region 40-45 °C. The bands are due to the asymmetric and symmetric stretching of the methylene $>\text{CH}_2$ bonds. On crystallization the asymmetric band sharpens and a minor band at 2900 develops along with a shoulder at 2960 cm^{-1} which we attribute to the symmetric and asymmetric stretching of the crystalline band, since they appear and disappear reversibly on crystallization and melting.

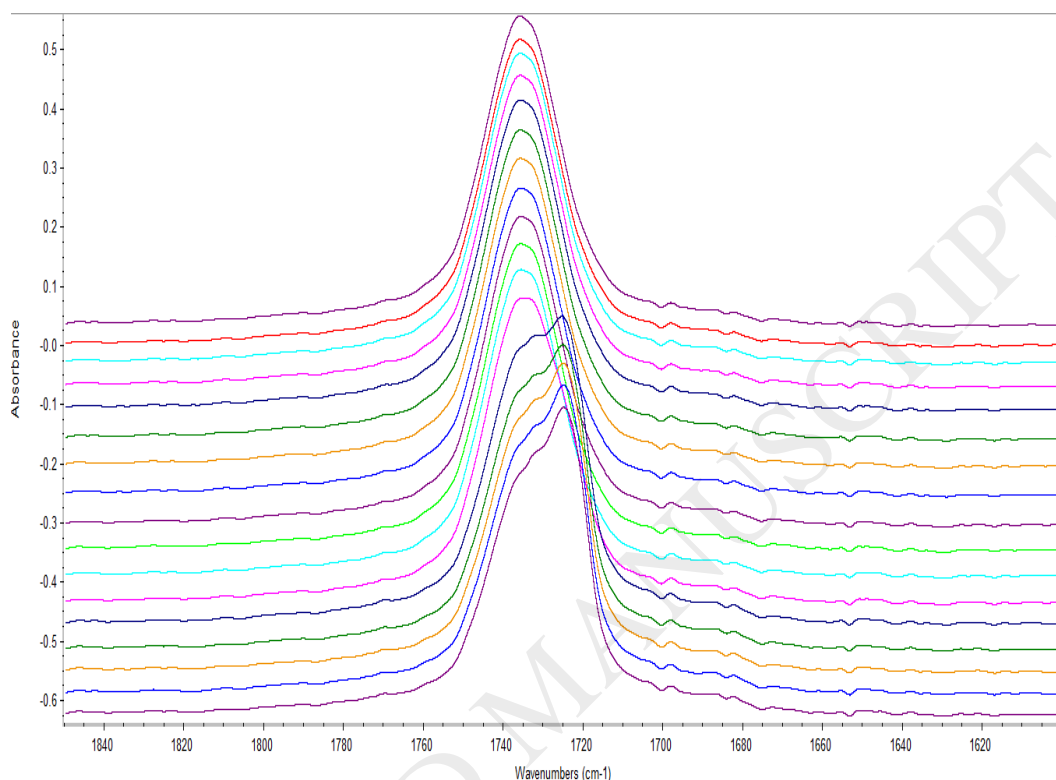


70 °C

30 °C

Fig. 3. Changes in the FTIR Spectrum of PCL -2750-3000 cm⁻¹. on cooling from 70 to 30 °C.

4.3. Carbonyl region – 1700-1750 cm⁻¹.



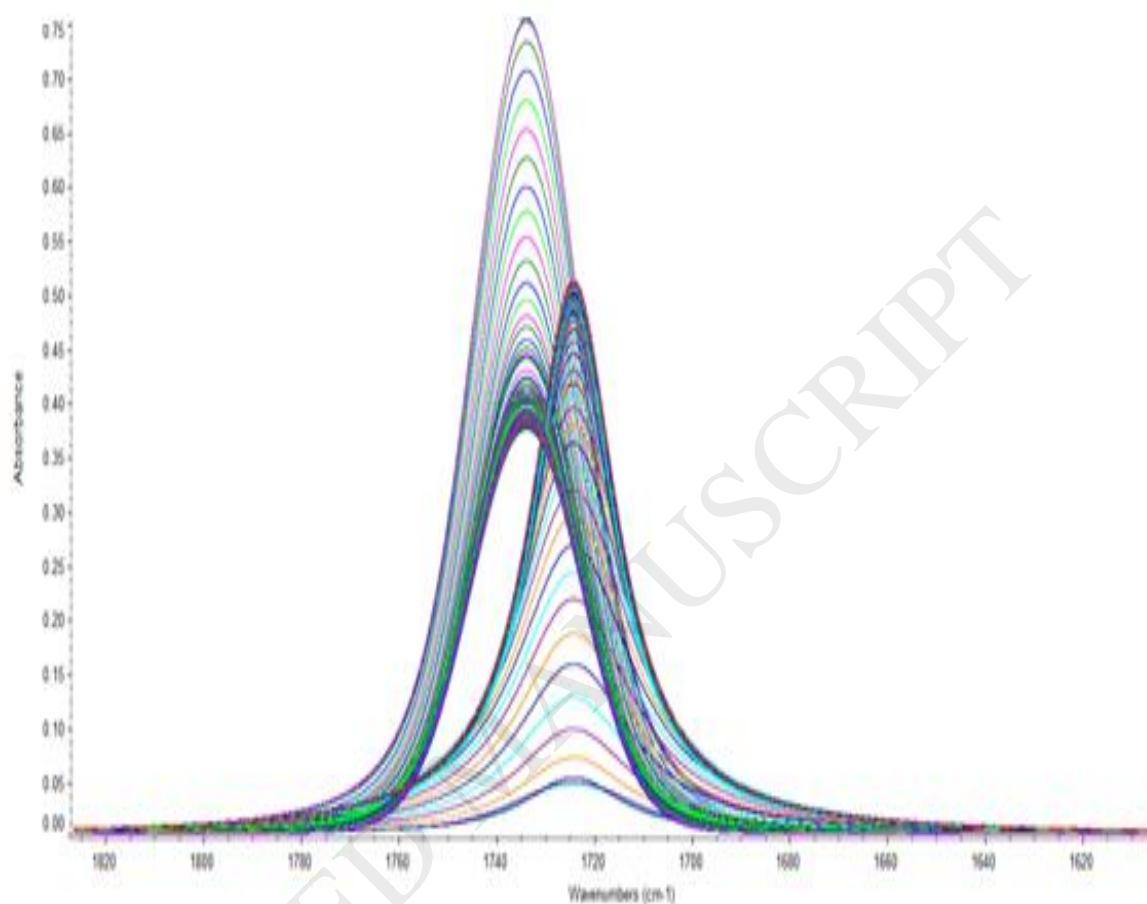
70 °C

30 °C

Fig. 4. Change in carbonyl absorption band on cooling from 70 to 30 °C.

Marked changes occurred to the amorphous carbonyl band centred at 1735 cm⁻¹ on cooling from 70 °C and in particular corresponded with the onset of crystallization between 45 and 40 °C, see Fig. 4. A narrower band with a maximum developed progressively with time at 1724 cm⁻¹. These bands were attributed to amorphous and crystalline regions of PCL since the changes were reversible on heating and their absorbances used to measure the crystallinity of PCL by resolving the overlapping carbonyl bands. Baseline corrections were

applied at two fixed wavenumbers and the absorption band auto-smoothed repeatedly with Omnic software into two absorption bands until a best fit was achieved. The analysis was carried out on the basis of two Lorentzian shaped absorption bands with maximum



absorbances at 1735 and 1725 cm^{-1} as shown in Fig. 3

Fig. 5. Separation of the carbonyl absorption band into two components at 1725 and 1735 cm^{-1} .

The resulting separation of the carbonyl enabled the intensities of the two bands to be determined separately and as the amorphous band decreased so the crystalline increased, see Fig.6 where the crystalline and amorphous intensities are compared with one another. To confirm that the intensity of the carbonyl absorption bands can be used quantitatively to measure the

fractional crystallinity samples were crystallized isothermally to eliminate any differences due to the temperature dependence of the intensities. Samples were heated at 70 °C for 3 min. in order to remove any trace of crystallinity and subsequently rapidly cooled to a constant temperature, in the region 40 to 47 °C. The crystalline and amorphous absorbances were followed with time and an increase in the crystalline was followed by a decrease in the amorphous intensity.

If both bands obey Beer-Lambert law then the intensity of the bands is proportional to the weight fractions present in the sample and defining the weight fraction amorphous content, X_a , from Beers-Lamberts Law then

$$X_a = A_a/A_{a, o} \quad (4)$$

where A_a and $A_{a,o}$ are the absorbances of the amorphous band and initially before any crystallinity has developed.

Similarly for the crystalline weight fraction,

$$X_c = A_c/A_{c, o} \quad (5).$$

For a two phase model of a partially crystalline polymer, the amorphous weight fraction, X_a is related to the crystalline weight fraction, X_c , and

$$X_a + X_c = 1.0 \quad (6)$$

Accordingly $A_a/A_{a, o} + A_c/A_{c, o} = 1$,

and $A_c = A_{c, o} - A_a (A_{c, o}/A_{a, o}) \quad (7).$

Plots of A_c against A_a were linear, see Fig. 6, with degree of fit greater than 0.99, see table 2. These values varied with temperature and sample thickness but were used to calculate the fractional crystallinity at each temperature from the ratio of $A_c/A_{c, o}$, see Table 1. The final crystallinity achieved was in the range 35-55% over 1000 min.

At each temperature prior to the onset of crystallization $A_c = 0$ and increased linearly as A_a decreased, see Fig. 6 indicating that it was not due to changes in chain conformation but to crystallinity.

The crystalline absorbance at 100% crystallinity, $A_{c,o}$, varied according to the thickness of the sample but was greater than the corresponding value for the amorphous band, $A_{a,o}$, by about 20-50%.

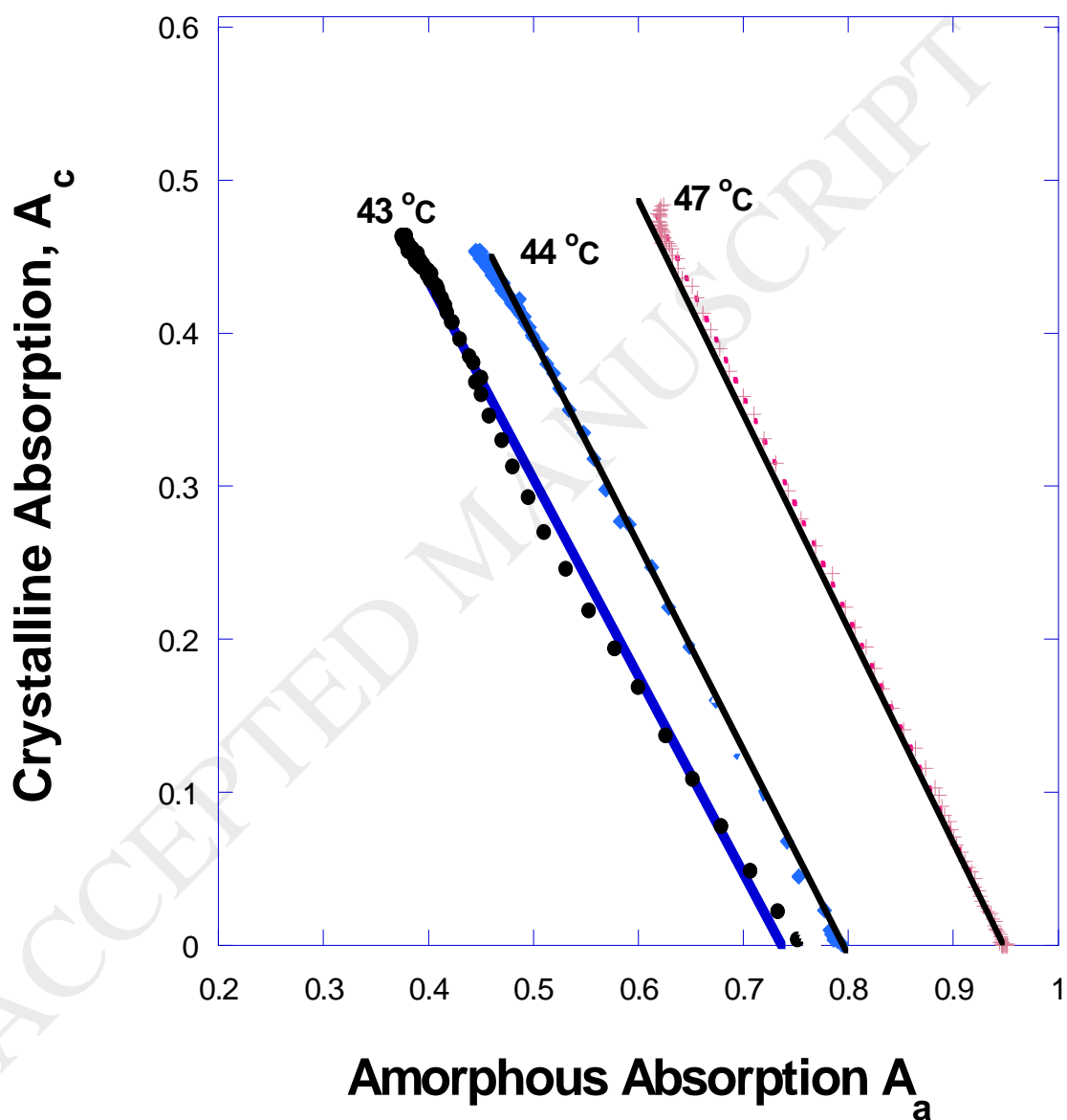


Fig. 6. Dependence of crystalline on amorphous absorption on crystallizing at various temperatures.

4.4 The region – 1600-900 cm⁻¹

This region of the spectrum is sensitive to chain configuration and to the vibration of the methylene and ester groups. The bands at 1458, 1390 and 1163 cm⁻¹ are attributed to the methylene groups in the amorphous regions and are associated with the gauche isomer. These bands are reduced in intensity on crystallization while the bands at 1470, 1395 and 1193 cm⁻¹ increase. We associated them with the trans isomer which is present in the crystal but also in an equilibrium amount in the melt. In a similar manner molecular assignments were made to the other absorption bands, as listed in Table 2, to the gauche or trans isomers according to whether they were both present in the melt and increased or decreased in intensity on crystallization or melting..

The bands at 1235 and 1275 cm⁻¹ are attributed to the stretching of the ester group contained within the chain in the amorphous regions which shift to higher wavenumbers, 1245 and 1295 cm⁻¹ as well as develop in intensity on crystallization.

The ratio of intensities of the crystalline and amorphous bands changed on crystallization, but the intensities were too weak and the baseline too complex by the presence of adjacent absorption bands to be useful in measuring the degree of crystallinity.

Similar changes occur to the >CH₂ deformation band at 1163 cm⁻¹ in that it decreases in intensity on crystallization while a narrower band develops at 1193 cm⁻¹, This is also present as a very weak shoulder in the amorphous sample and is attributed to the trans isomer and the original to the cis. Assignment of the bands to the isomeric form of the configuration was made according to how the intensity of the bands changed on crystallization, see Table 2.

A minor but broad band at 960 cm⁻¹ in the amorphous sample sharpened and increased in intensity with the development of crystallinity and at the same time split into

two, at 960 and 940 cm^{-1} . This was attributed to the bending of ester $-\text{C}-\text{O}-\text{C}$ band from the cis to trans configuration on crystallization. Its intensity was too weak for accurate measurement of intensities and determination of the fractional crystallinity.

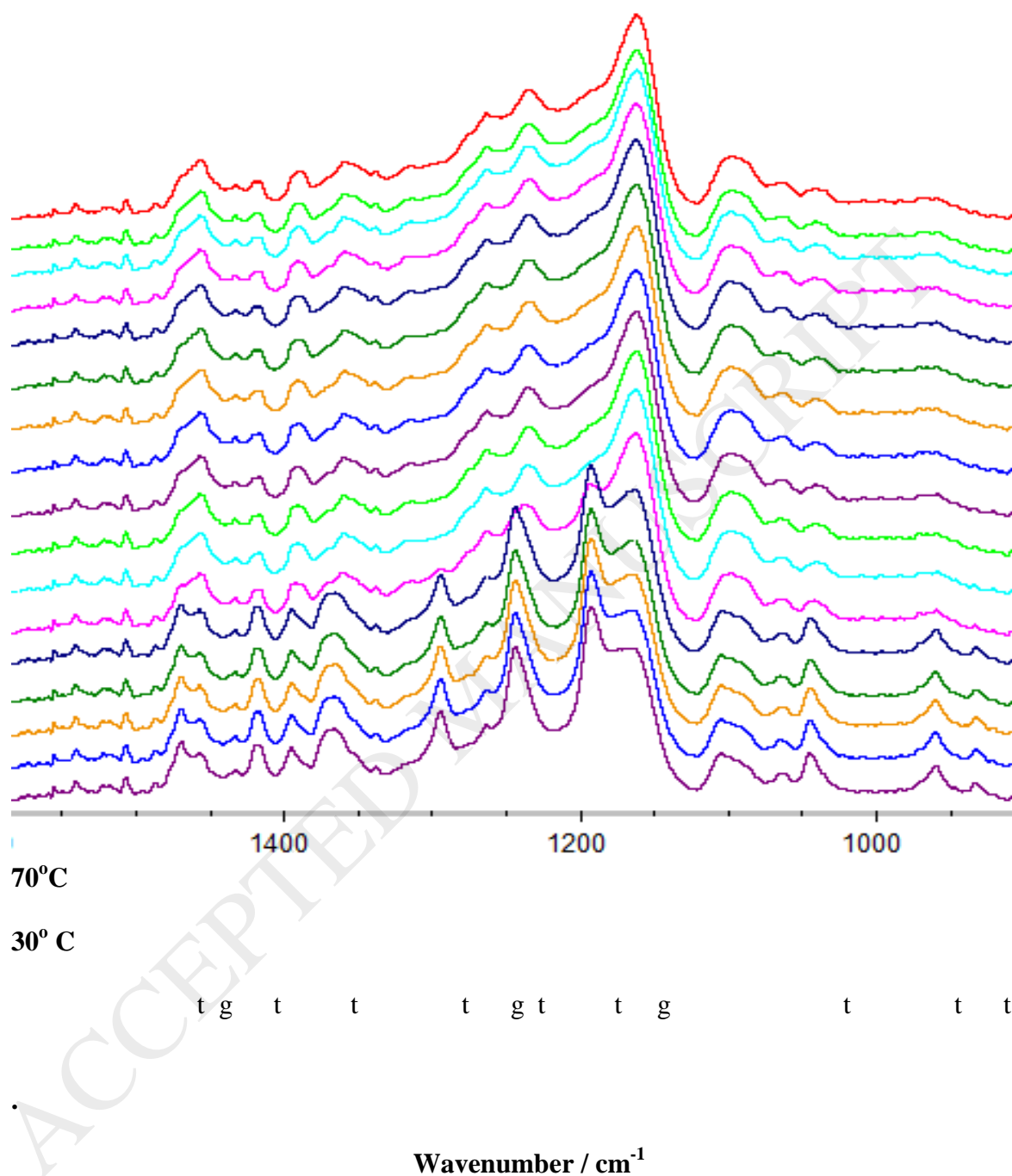


Fig. 7. Changes in FTIR spectrum on cooling from 70 to 30 °C – 900 to 1500 cm^{-1} .

Assignments to t trans and g gauche isomers.

s: strong, m: medium, w: weak and vw: very weak intensity sh shoulder.

4.5 2-D correlation infrared spectroscopy.

In order to confirm that the changes to the carbonyl band were due to the development of crystallinity 2D- correlations mapping was applied to peak shifts and changes in intensity with time at constant temperature on crystallizing from the melt. Generalized 2D-IR correlation spectra based on the partially crystallized, v_2 , and totally amorphous PCL samples, v_1 , in the range 1800-1650 cm^{-1} were the dominant changes observed are shown in Figs. 8 and 9

The symmetric and asymmetric correlation maps of the carbonyl absorption band in 2-dimensions are clearly coupled. The 2-dimensional map in Fig. 8 has the characteristic angel pattern of a single absorption band which shifts from higher to lower wavenumber with the two having different intensities. The lower symmetry of the angel pattern arises from the difference in breadth of the two bands – the amorphous is broad and the crystalline comparatively sharp and the different relative intensities [13]. The maximum intensity of the two autopeaks can be used to define the wavenumber of the initial and final peak, at 1735 and 1725 cm^{-1} respectively, They comprise two positive autopeaks and two negative cross peaks with long tails spreading out to 1800 and 1600 cm^{-1} reflecting the breadth of the carbonyl absorbances.

The asynchronous spectra, Fig. 9, show a double positive (1725, 1735 cm^{-1}) and a double negative cross peak (1735,1725 cm^{-1}) and 4 to 5 smaller peaks as a two way pattern reflecting the decrease in intensity of the higher wavelength band as the lower wavelength band intensity increases. The smaller peaks reflect changes in the breadth of the peak with crystallinity. The angel pattern and the two way pattern are all characteristic of a two component band, amorphous and crystalline, both changing intensities in opposite directions.

This is in complete agreement with the changes observed in the TA-FTIR study of the changes to the carbonyl band on crystallization and melting of PCL.

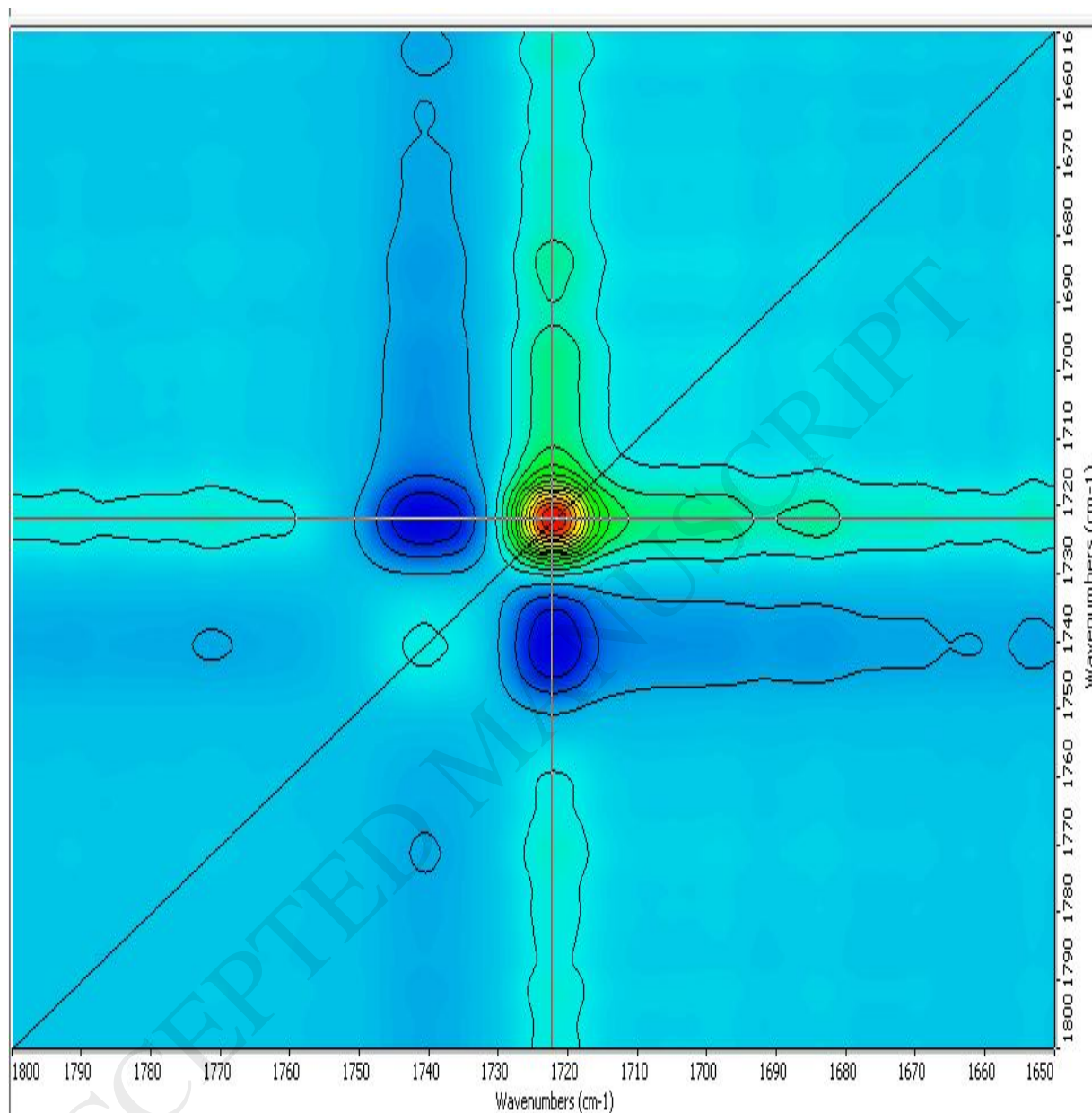


Fig. 8. Two- Dimensional Synchronous Correlation Intensity Contour Map of the Carbonyl Absorption Band in Region 1800-1650 cm⁻¹ on crystallization at 47 °C

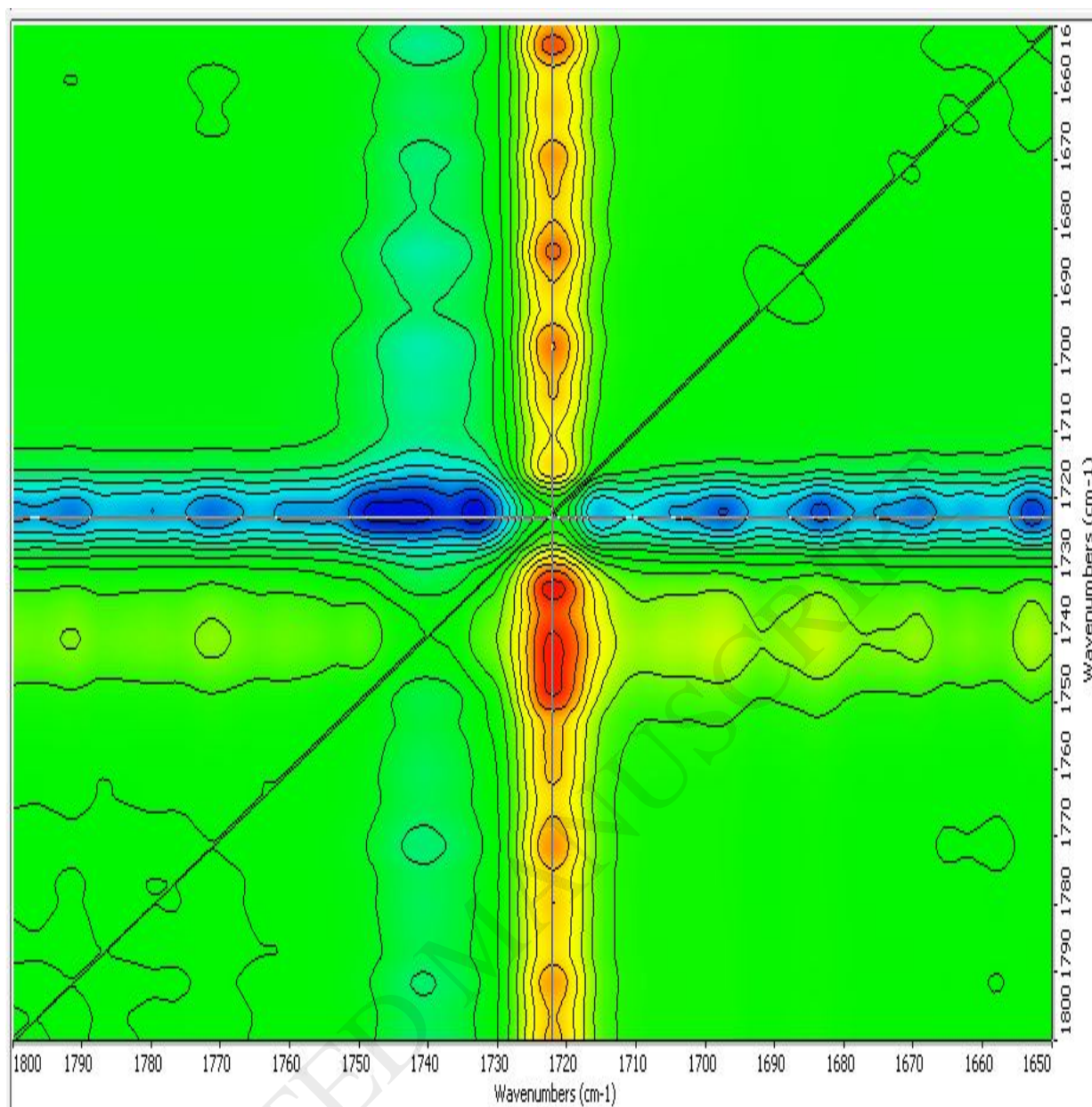


Fig. 9. Two Dimensional Asynchronous Correlation Map of the Carbonyl Absorption Band in Region 1800-1650 cm^{-1} on crystallizing at 47 °C.

5. Conclusions.

The carbonyl absorption band has a maximum absorption in the amorphous regions at 1735 cm^{-1} and at 1724 cm^{-1} in crystalline material, such that on crystallization the intensity of the higher wavenumber band decreases and is progressively shifted to lower wavenumber. These changes makes the ratio of the two carbonyl absorption bands a

convenient method of measuring the fractional crystallinity of PCL but is dependent on the temperature of measurement..

Acknowledgement

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6.

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Figure captions

Fig. 1 The IR Spectrum of partially crystalline PCL at room temperature.gr1

Fig. 2 Changes in IR Spectra on cooling from 70 to 30 °C.gr2

Fig. 3 Changes in the FTIR Spectrum of PCL -2750–3000 cm^{-1} . on cooling from 70 to 30 °C.gr3

Fig. 4 Change in carbonyl absorption band on cooling from 70 to 30 °C.gr4

Fig. 5 Separation of the carbonyl absorption band into two components at 1725 and 1735 cm^{-1} .gr5

Fig. 6 Dependence of crystalline on amorphous absorption on crystallizing at various temperatures.gr6

Fig. 7 Changes in FTIR spectrum on cooling from 70 to 30 °C–900 to 1500 cm^{-1} .gr7

Fig. 8 Two- Dimensional Synchronous Correlation Intensity Contour Map of the Carbonyl Absorption Band in Region 1800–1650 cm^{-1} on crystallization at 47 °C.gr8

Fig. 9 Two Dimensional Asynchronous Correlation Map of the Carbonyl Absorption Band in Region 1800–1650 cm^{-1} on crystallizing at 47 °C.gr9

Table 1. Absorbance of Crystalline and Amorphous Band.

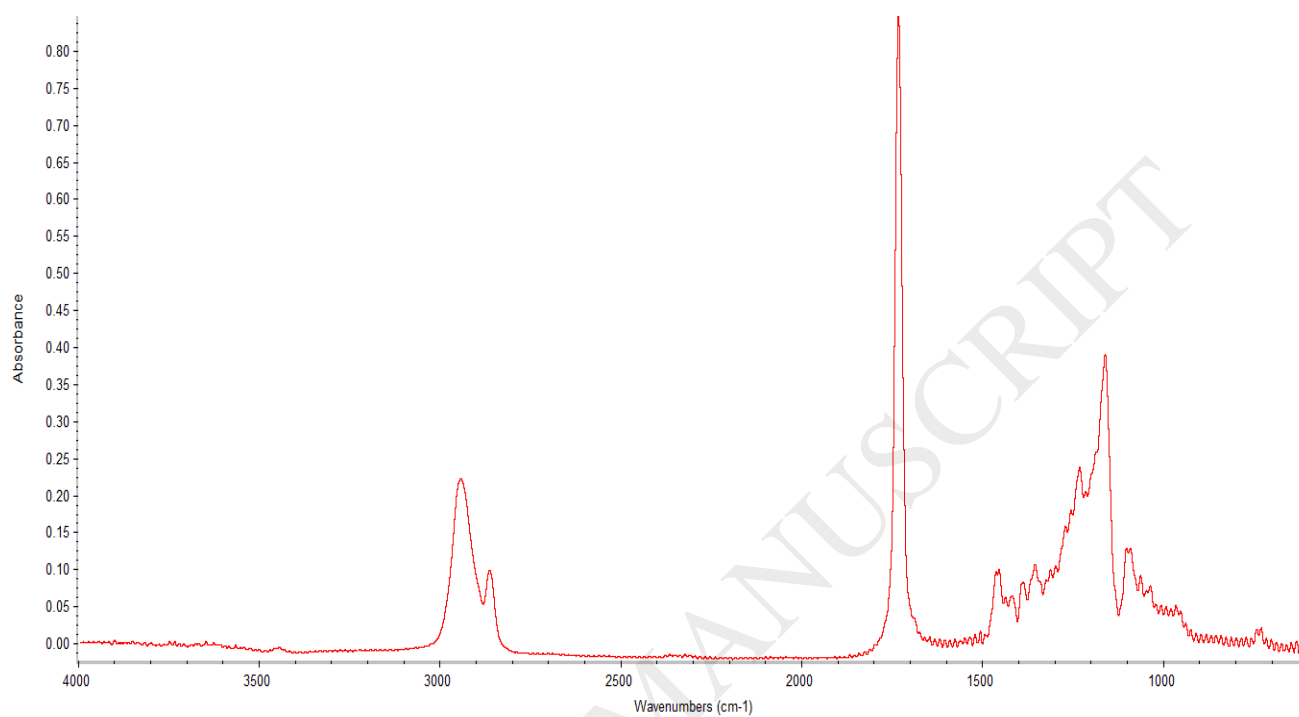
Crystallization Temperature °C	Crystalline Absorbance $A_{c,o}$	Amorphous Absorbance $A_{a,o}$	Degree of Fit R^2	Fractional Crystallinity Range
43.0	0.948	0.737	0.996	0 - 0.49
44.0	1.057	0.765	0.998	0 - 0.43
45.0	0.968	0.508	0.997	0 - 0.55
46.0	1.472	0.784	0.996	0 - 0.40
47.0	1.366	0.949	1.00	0 - 0.35

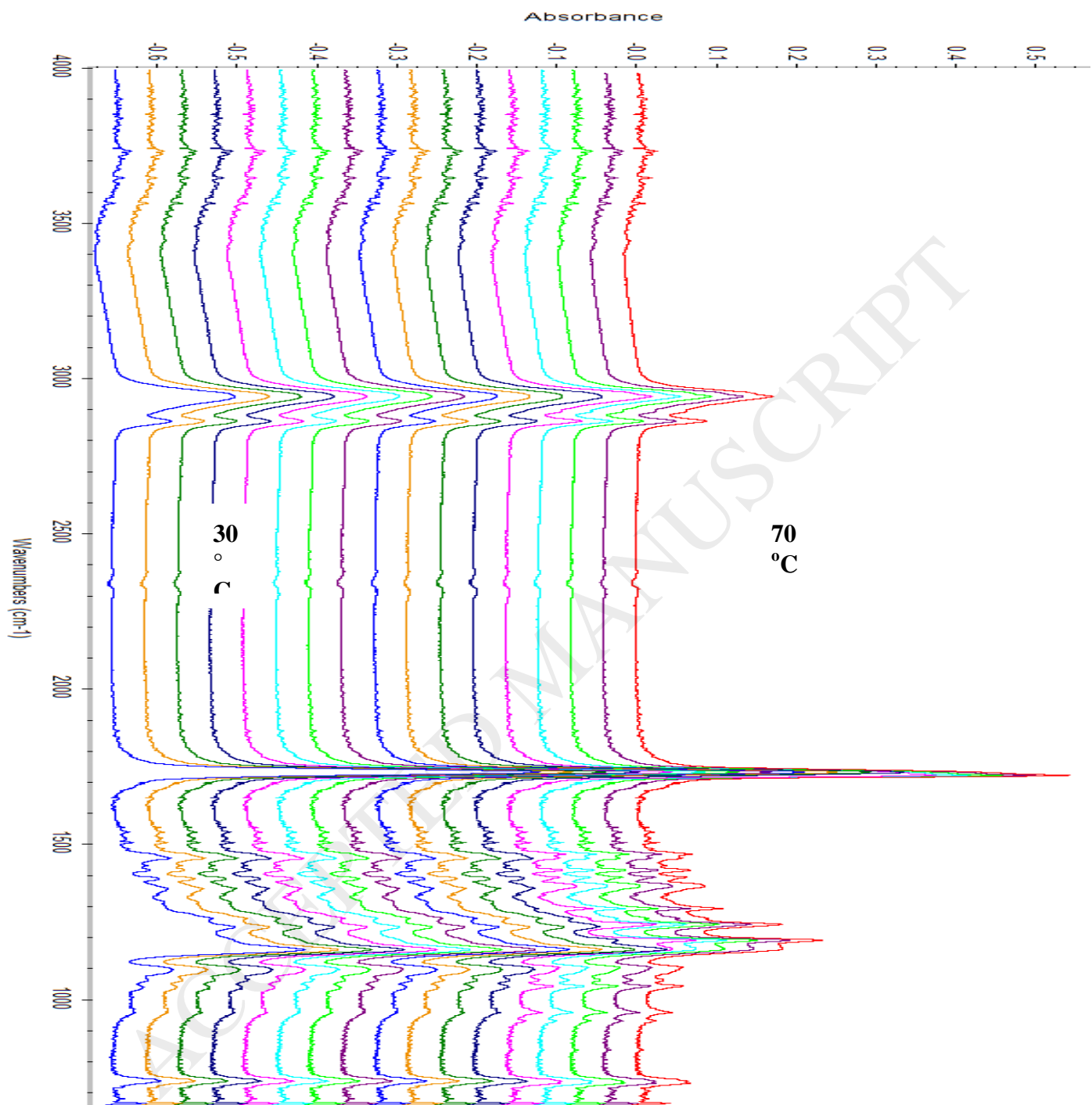
Table 2. – Molecular assignment of the characteristic IR bands of PCL.[14]

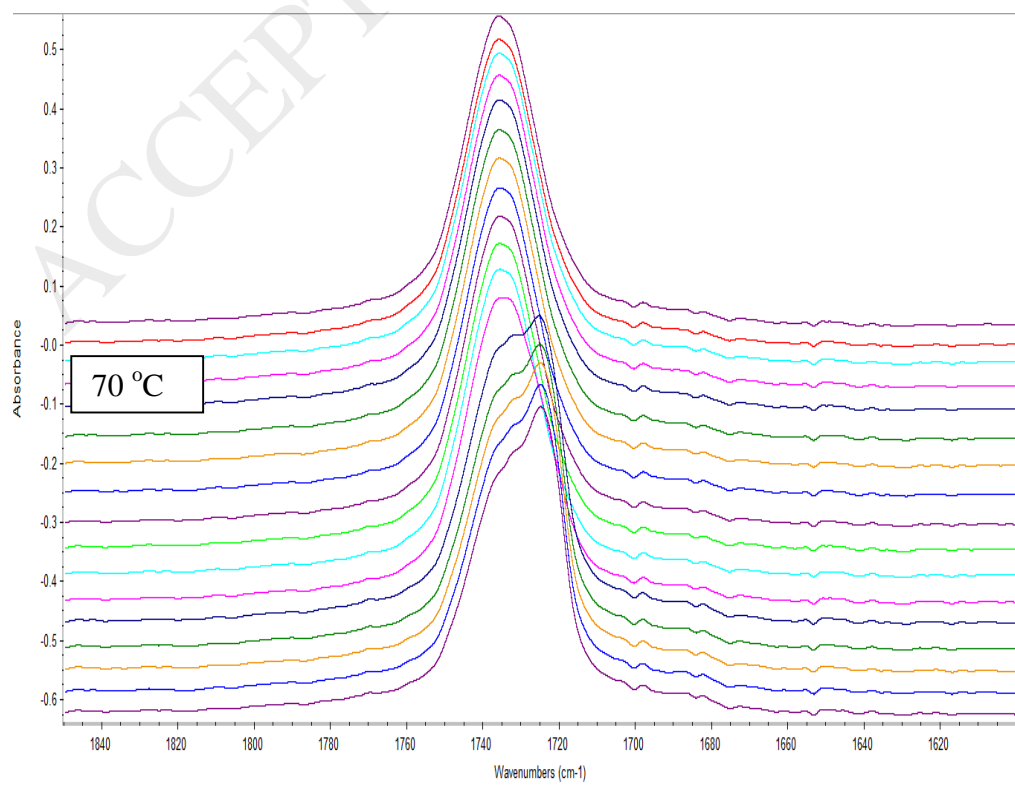
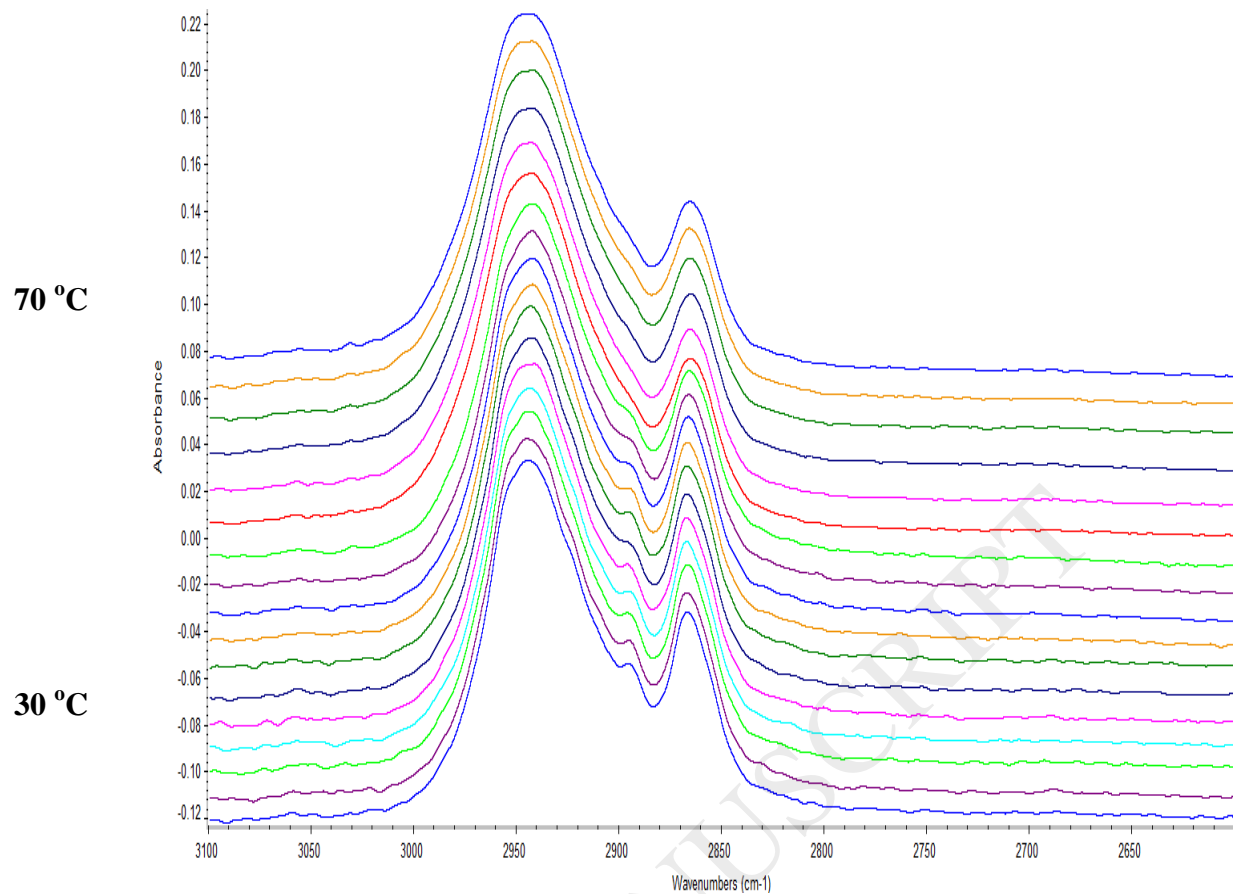
Wavenumber /cm ⁻¹	Vibrational Assignment	Intensity	Comments
2960 2945 2900 2865	Asymmetric Stretching of >CH ₂ Symmetric Stretching of >CH ₂	w sh m w m	Crystalline Amorphous Crystalline Amorphous
1735 1725	>C=O Stretching	S s	Amorphous Crystalline
1470 1458	>CH ₂ Bending	Vw vw	Gauche Trans
1415,1395,1370 1385	>CH ₂ Wagging	W w	Trans Gauche
1295 1275 1245 1235	Asymmetric Stretching of OC-O-Symmetric Stretching of C-O-C Symmetric Stretching of C-O-C	w m w w	Gauche Trans Gauche Trans
1193 1163 1107 1066 1047	>CH ₂ Deformation >CH ₂ Deformation	w w w	Crystalline, trans GaucheNo change No changeNo change

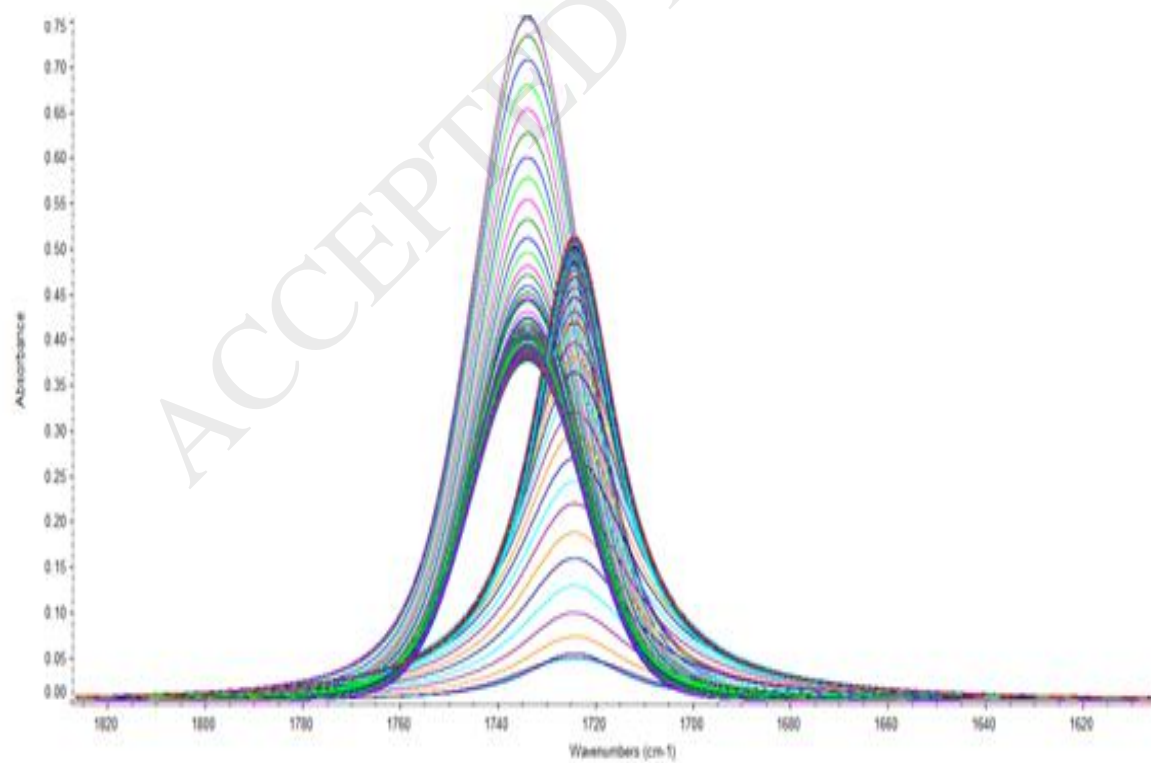
960 960	940	C-O-C	w w w	TransTransGauche
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Fig. 1









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