11th BROADBAND DIELECTRIC SPECTROSCOPY AND ITS APPLICATIONS
DONOSTIA - SAN SEBASTIAN – SPAIN – SEPTEMBER, 2022

T.A. Ezquerra

Is the sub-glass temperature relaxation of furan-based polymers related to their high gas barrier properties?

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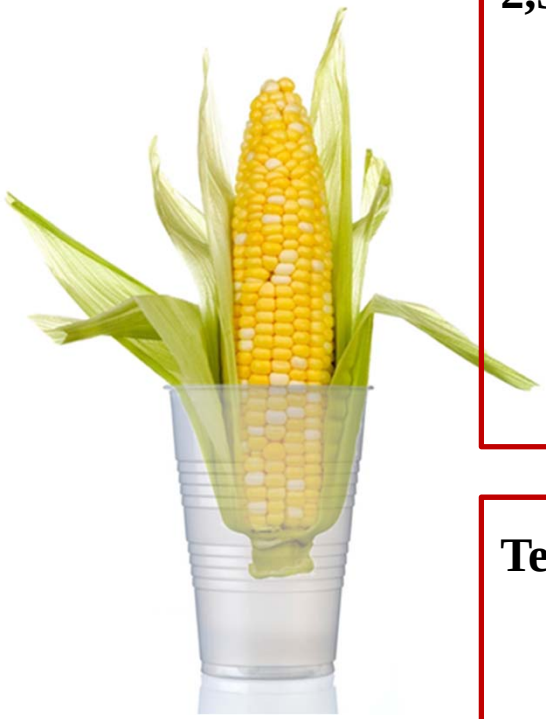
CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

Outline

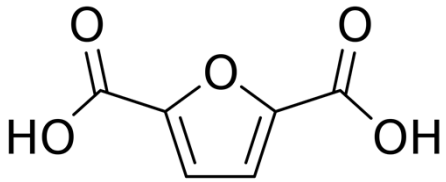
- Introduction to polyfuranoates : Outstanding gas barrier properties
- Broadband Dielectric Spectroscopy (BDS) of Poly(trimethylene 2,5-furanoate) (PTF)
  Poly(trimethylene terephthalate) (PTT)
- Fourier transform Infrared Spectroscopy (FTIR) of Poly(trimethylene 2,5-furanoate) PTF
  Poly(trimethylene terephthalate) (PTT)
- BDS versus FTIR

Motivation

- **Interest in Polymers based on renewable raw materials** for potential applications in pharmacy, medicine, agriculture, tissue engineering, textile industry, packaging etc.

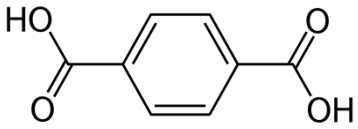


2,5-furanedicarboxylic acid (FDCA)



One of the 12 most promising compounds of plant origin for the synthesis of polymeric materials

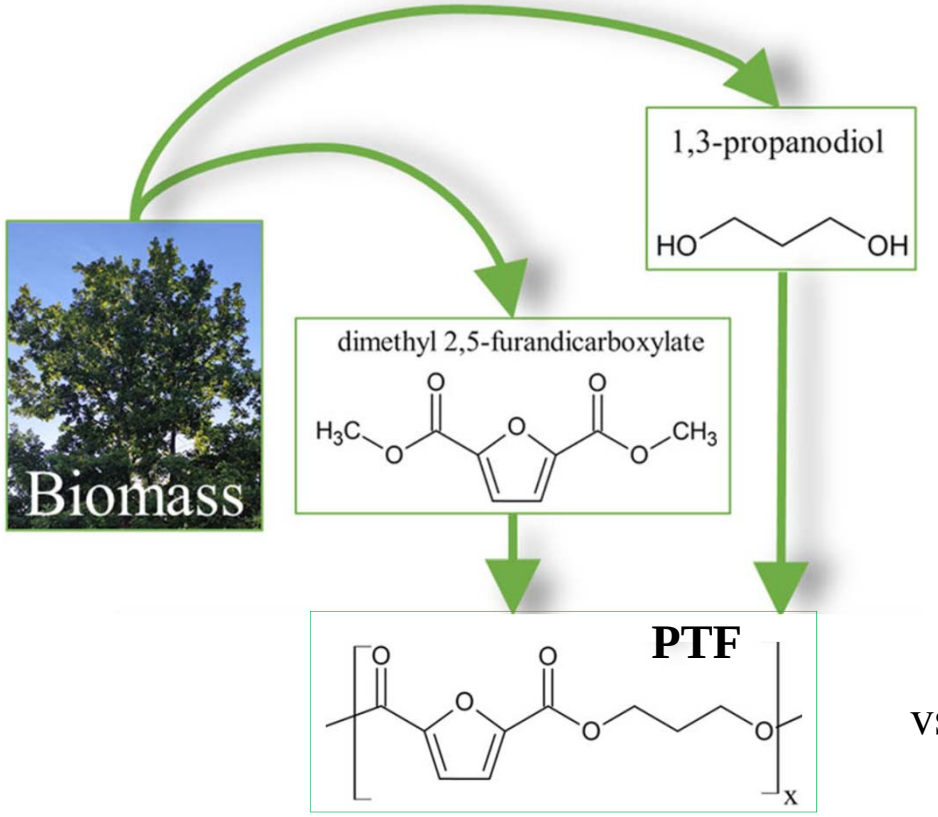
Terephthalic acid (TPA)



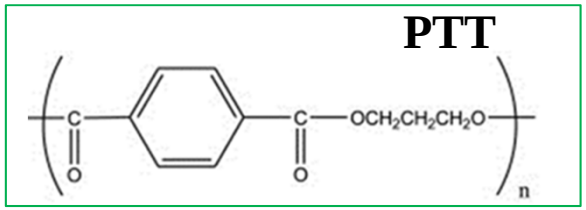
- Werpy T, Petersen G (2004) Top Value Added Chemicals from Biomass: Volume I – Results of Screening for Potential Candidates from Sugars and Synthesis Gas. Golden, CO (United States).

Motivation

- The use of FDCA allows obtaining polymers with better properties than their counterparts based on TPA.



VS



- Poly(ethylene 2,5-furanoate) (PEF), exhibit much better barrier properties (11 times lower O_2 permeability, 19 times lower CO_2 permeability) than polyethylene terephthalate (PET).

- Poly(trimethylene 2,5-furanoate) PTF presents as well superior gas barrier properties than PET. (16-times for O_2, 48-times for CO_2, and 2 times for H_2O).

- S.K. Burgess, R.M. Kriegel,W.J. Koros, Macromolecules 2015, 48, 2184−2193.
- L. Genovese, M. Soccio, N. Lotti, A. Munari, A. Szymczyk, S. Paszkiewicz, A. Linares, A. Nogales, T.A. Ezquerra, Physical Chemistry Chemical Physics 2018, 20 (23), 15696-15706.
- G. Guidotti, M. Soccio, M.C. García-Gutiérrez, T.A. Ezquerra, V. Siracusa, E. Gutiérrez-Fernández, A. Munari and N. Lotti ACS Sustain. Chem. Eng., 2020, 8, 9558–9568.

BDS

- Complex dielectric permittivity (ε∗) measurements (ε∗ = ε′ − ιε′′) were performed over a frequency range of $10^{-1} < F/Hz < 10^{6}$ starting at T= 123 K up to room temperature by using a Novocontrol system integrating an ALPHA dielectric interface and QUATRO temperature control system (Novocontrol).

- Polymer films were sandwiched between the two metallic electrodes of the spectrometer. The dielectric relaxations were empirically described in terms of the Havriliak-Negami (HN) equation

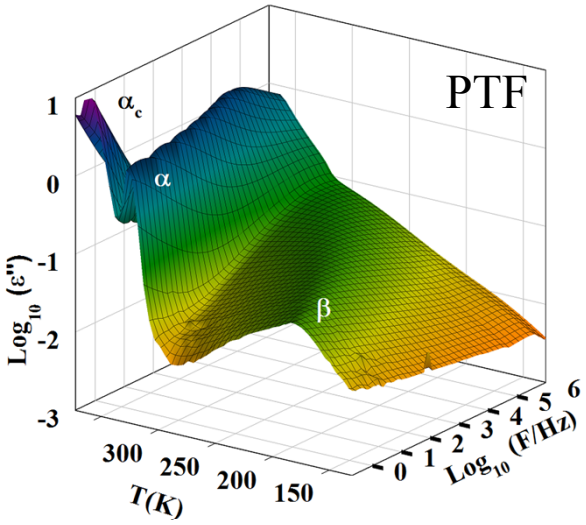
- Broadband Dielectric Spectroscopy; Kremer, F.; Schönhals, A., Eds.; Springer-Verlag: Berlin Heidelberg, 2003.

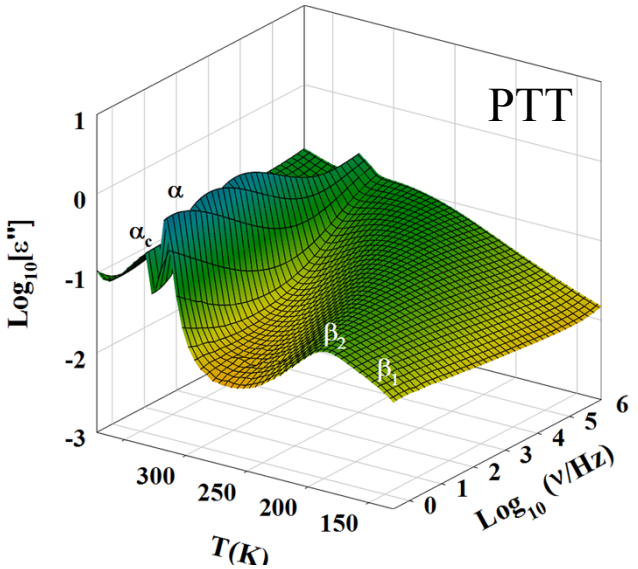
FTIR

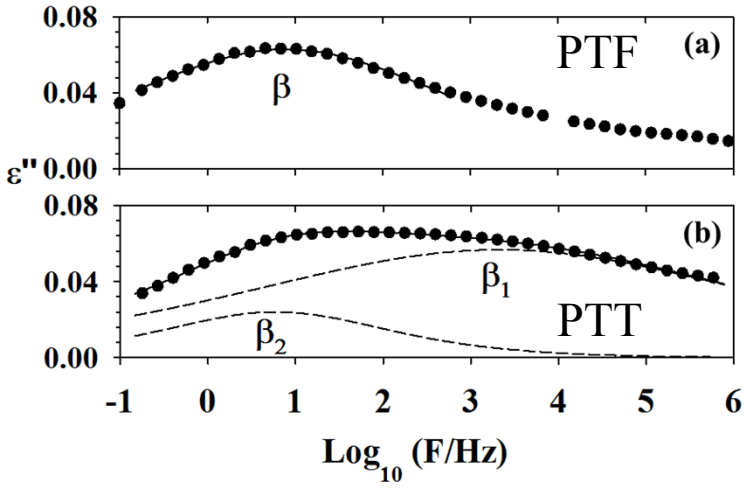
- Fourier Transform IR (FTIR) spectra were acquired in vacuum (background pressure of 10^{-6} mbar) with a Perkin Elmer, Frontier spectrometer in a 4500-500 cm^{-1} range with a resolution in the wavenumber of 2 and 4 cm^{-1}.
- The temperature range was varied between 20 K and 330 K by using a closed cycle He cryostat (CTI cryogenics).
- A spectrum for the background was taken at every temperature.
- The FTIR spectroscopy experiments were performed in polymer thin films prepared by spin-coating on special IR transparent silicon substrates (Si FZ 25.4mm Ø x 1mm polished window).

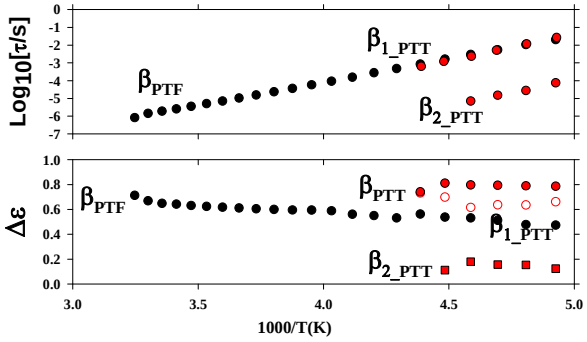
Poly(trimethylene 2,5-furanoate) (PTF) versus Poly(trimethylene terephthalate) (PTT)

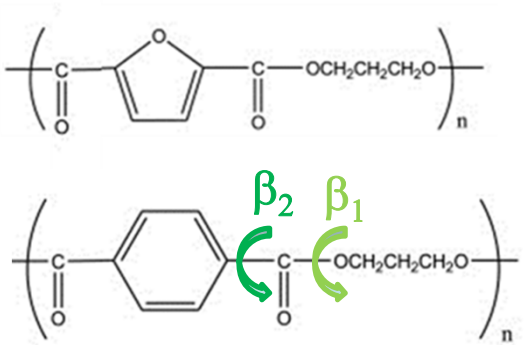
BDS









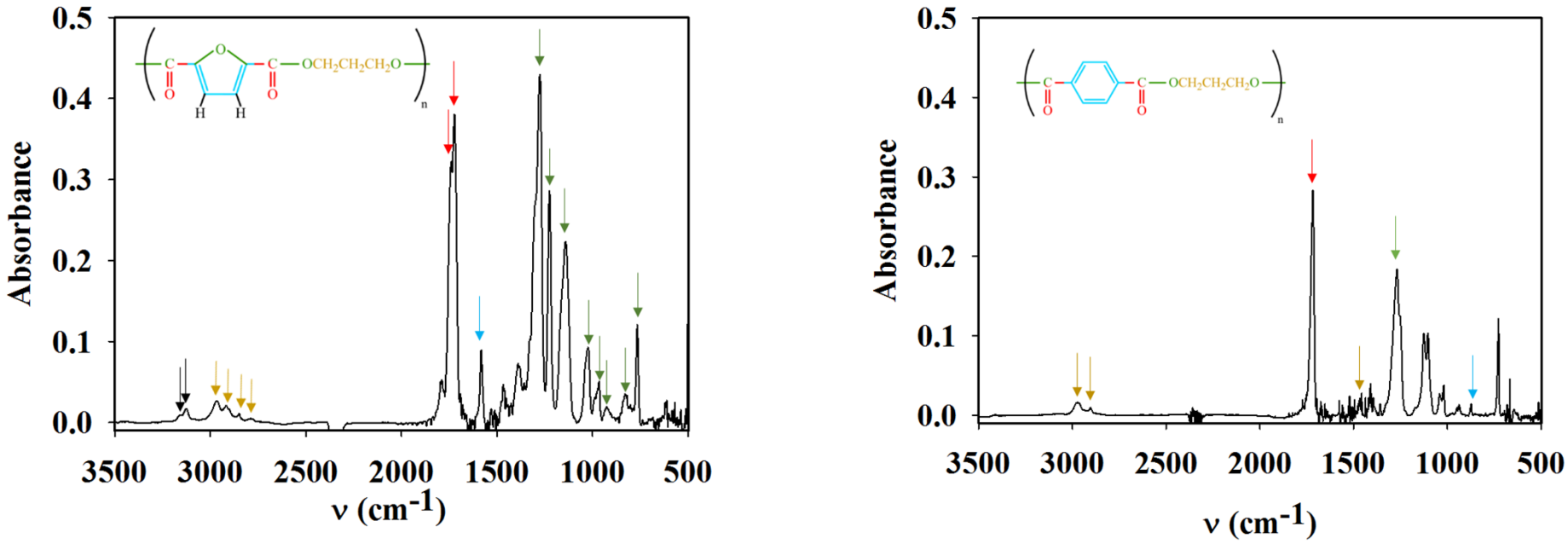


- Genovese, L.; Soccio, M.; Lotti, N.; Munari, A.; Szymczyk, A.; Paszkiewicz, S.; Linares, A.; Nogales, A.; Ezquerra, T. A. Physical Chemistry Chemical Physics 2018, 20 (23), 15696-15706.
- Soccio, M.; Nogales, A.; Ezquerra, T. A.; Lotti, N.; Munari, A. Macromolecules 2012, 45 (1), 180-188
- Papadopoulos, P.; Kossack, W.; Kremer, F.; Soft Matter, 2013, 9, 1600–1603

Poly(trimethylene 2,5-furanoate) (PTF) versus Poly(trimethylene terephthalate) (PTT)

FTIR

PTF T =300 K PTT

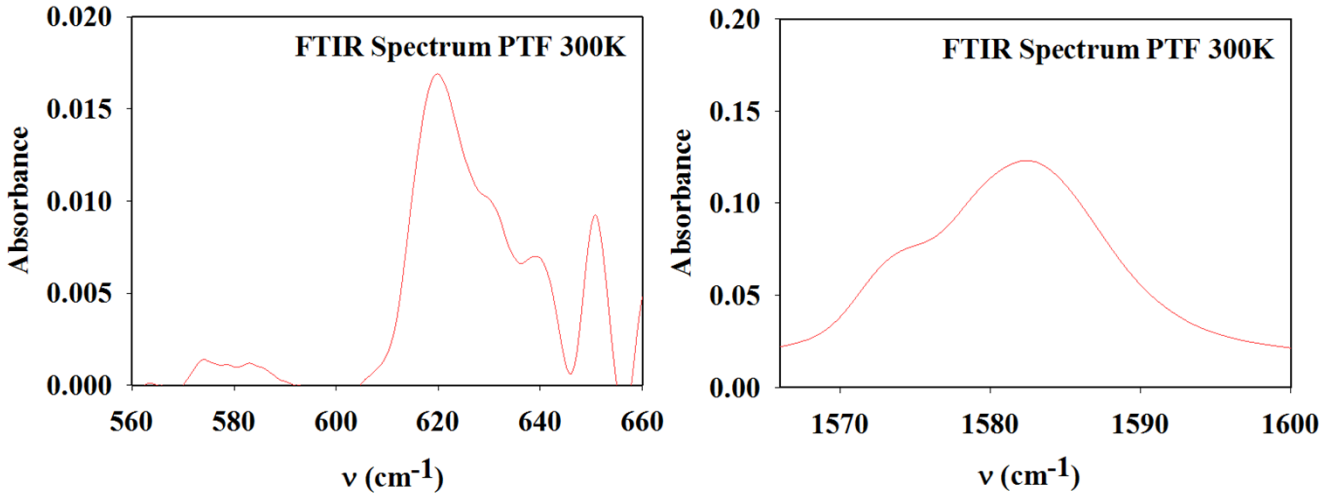


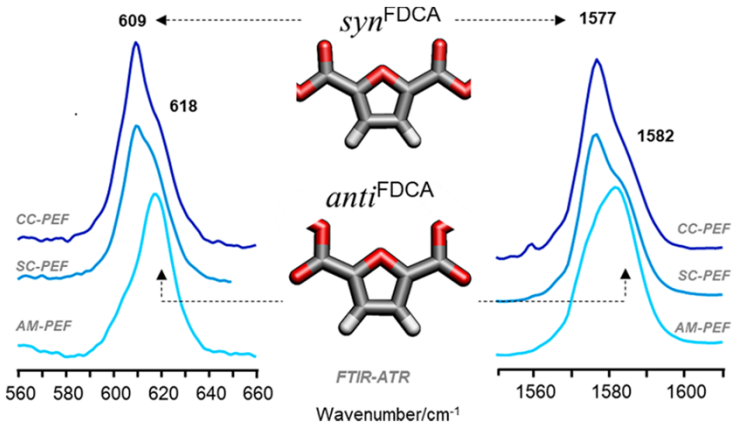
- Araujo, C. F.; Nolasco, M. M.; Ribeiro-Claro, P. J. A.; Rudic, S.; Silvestre, A. J. D.; Vaz, P. D.; Sousa, A. F. Macromolecules 2018, 51 (9), 3515-3526
- Papamokos,G.; Dimitriadis,T; Bikiaris,D.N.; Papageorgiou,G.Z.; Floudas G.: Macromolecules 2019, 52, 6533−6546
- Irska, I.; Paszkiewicz, S.; Pawlikowska, D.; Dryzek, J.; Linares, A.; Nogales, A.; Ezquerra, T. A.; Piesowicz, E. Polymer 2021, 229,

Poly(trimethylene 2,5-furanoate) (PTF)

FTIR

PTF amorphous



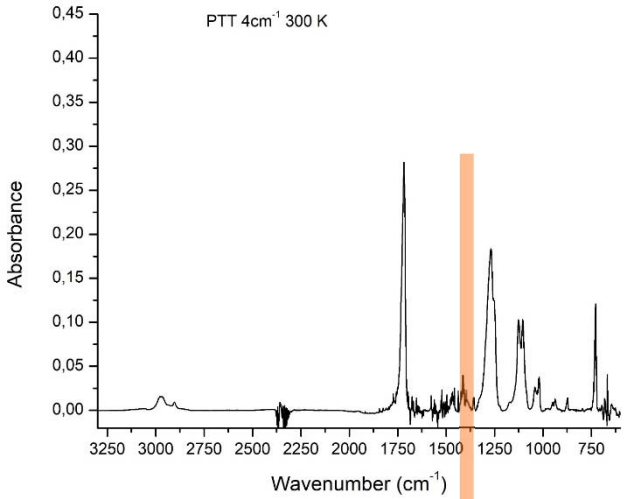


PEF*

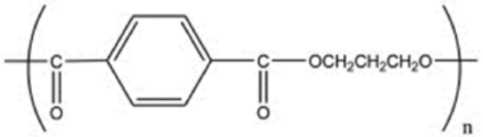
*Araujo, C. F.; Nolasco, M. M.; Ribeiro-Claro, P. J. A.; Rudic, S.; Silvestre, A. J. D.; Vaz, P. D.; Sousa, A. F. Macromolecules 2018, 51 (9), 3515-3526

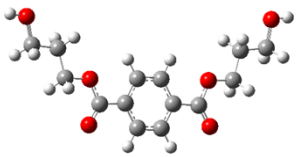
Poly(trimethylene 2,5-furanoate) (PTF) versus Poly(trimethylene terephthalate) (PTT)

FTIR

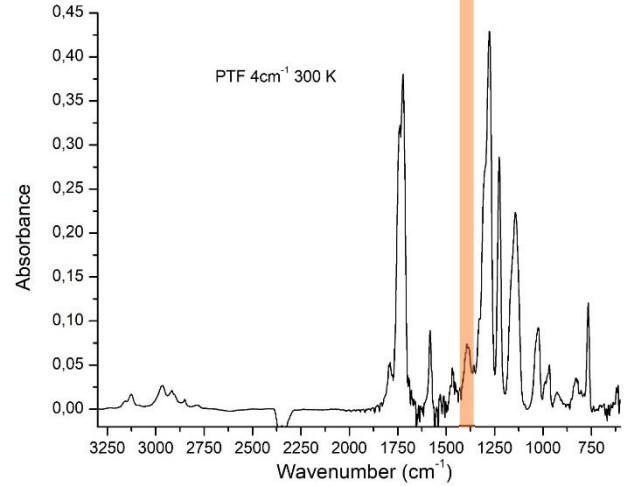


PTT

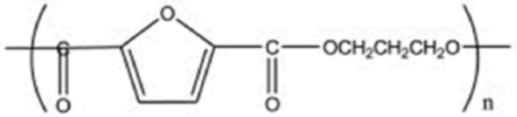




1410 cm^{-1} (**PTT CH_2 wagging**)
$(C\text{-}C)_{ring}$ stretching, $(CH)_{ring}$ in-plane deformation)



PTF



1391 cm^{-1} (**PTF CH_2 wagging**)

- Araujo, C. F.; Nolasco, M. M.; Ribeiro-Claro, P. J. A.; Rudic, S.; Silvestre, A. J. D.; Vaz, P. D.; Sousa, A. F. Macromolecules 2018, 51 (9), 3515-3526
- Papamokos,G.; Dimitriadis,T; Bikiaris,D.N.; Papageorgiou,G.Z.; Floudas G.: Macromolecules 2019, 52, 6533−6546
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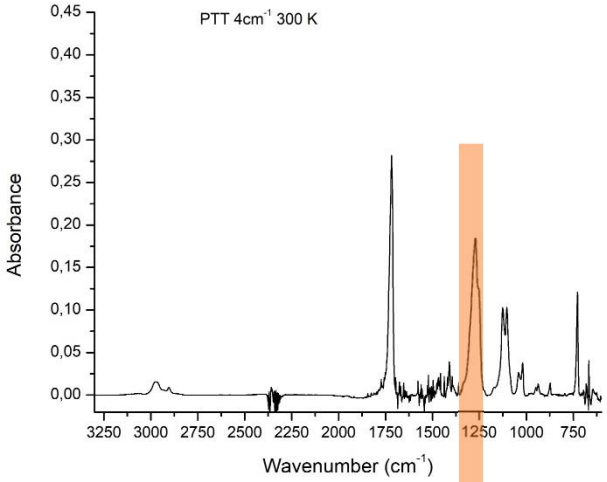
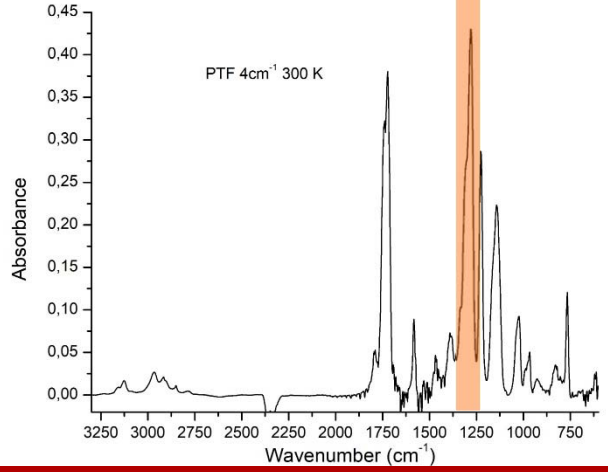
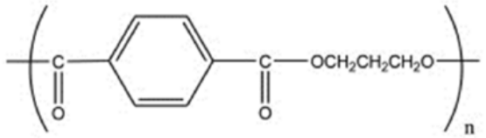
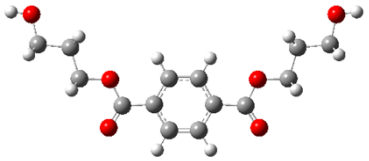
FTIR





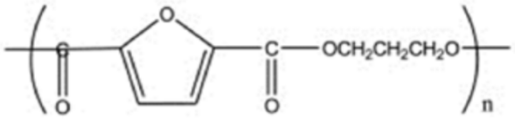
PTT

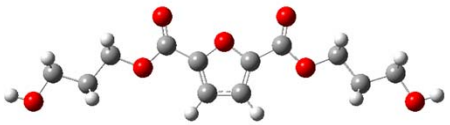




1268 cm^{-1} (**PTT C-O asymmetric stretching**, $CH)_{ring}$ rocking).

PTF





1276 cm^{-1} (**PTF C-O asymmetric stretching**)

- Araujo, C. F.; Nolasco, M. M.; Ribeiro-Claro, P. J. A.; Rudic, S.; Silvestre, A. J. D.; Vaz, P. D.; Sousa, A. F. Macromolecules 2018, 51 (9), 3515-3526
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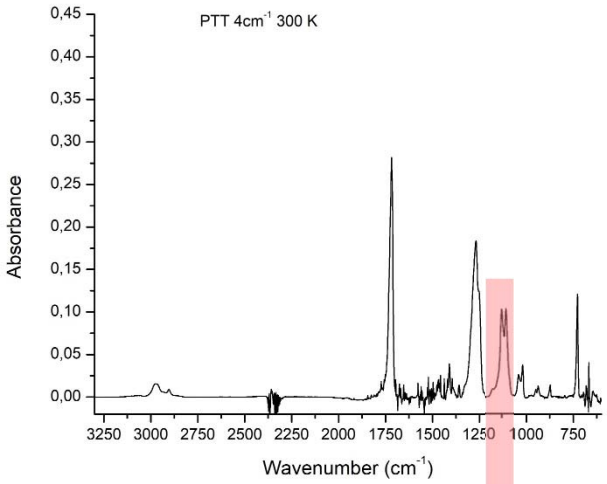
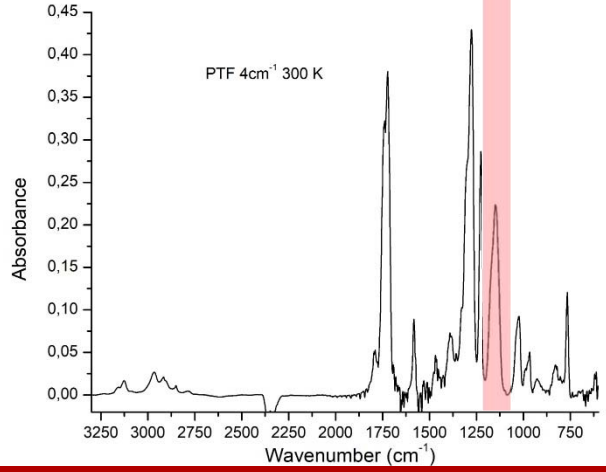
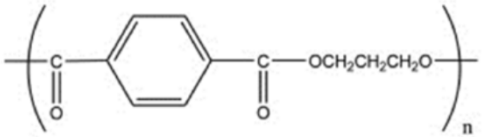
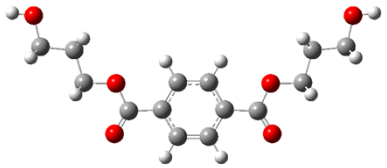
FTIR





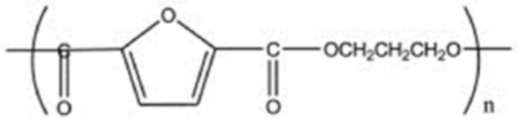
PTT

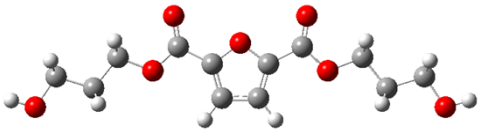




1126 cm^{-1} (**PTT $(CH)_{ring}$ rocking**, C-O asymmetric stretching).

PTF





1143 cm^{-1} (**PTF $(C\text{-}H)_{ring}$ rocking**, $(C\text{-}O)_{ring}$ stretching, C-O stretching),

- Araujo, C. F.; Nolasco, M. M.; Ribeiro-Claro, P. J. A.; Rudic, S.; Silvestre, A. J. D.; Vaz, P. D.; Sousa, A. F. Macromolecules 2018, 51 (9), 3515-3526
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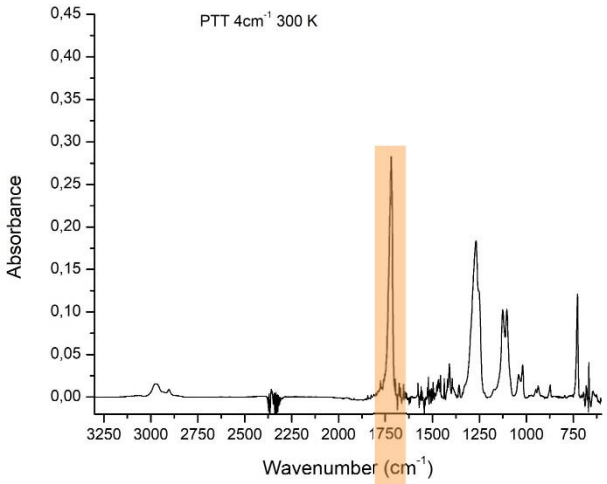
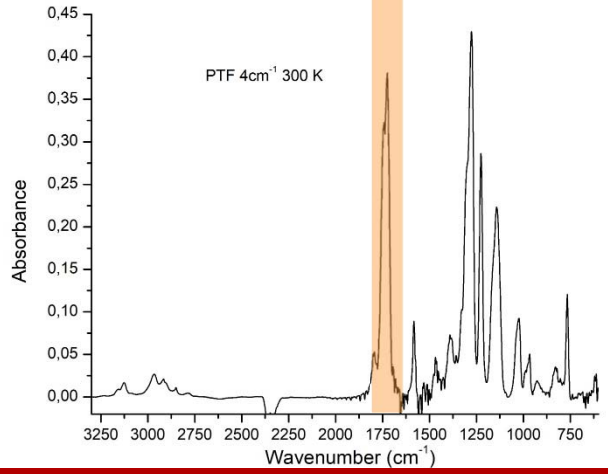
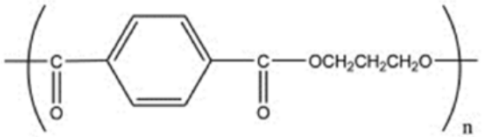
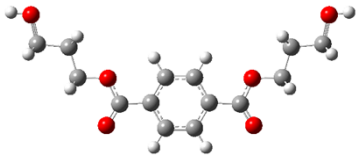
FTIR





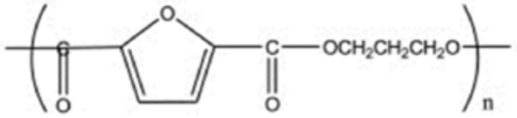
PTT

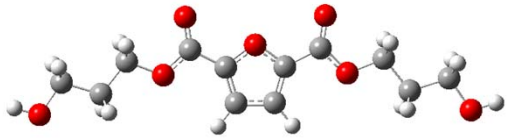




1717 cm^{-1} (-C=O stretching)

PTF





1722 cm^{-1} (-C=O stretching)

- Araujo, C. F.; Nolasco, M. M.; Ribeiro-Claro, P. J. A.; Rudic, S.; Silvestre, A. J. D.; Vaz, P. D.; Sousa, A. F. Macromolecules 2018, 51 (9), 3515-3526
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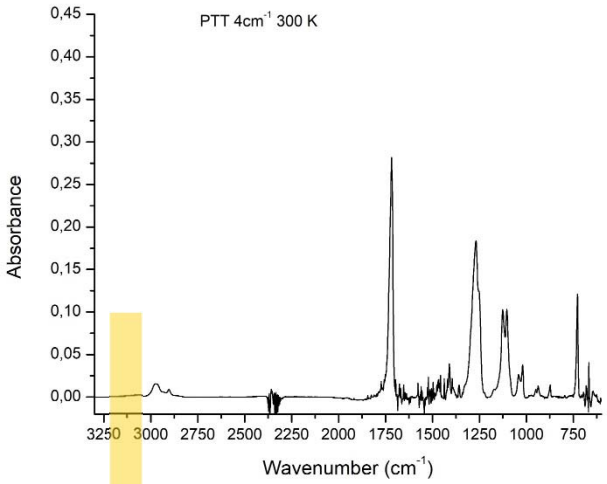
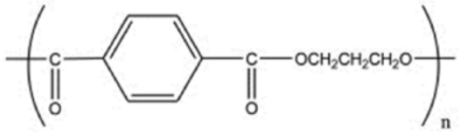
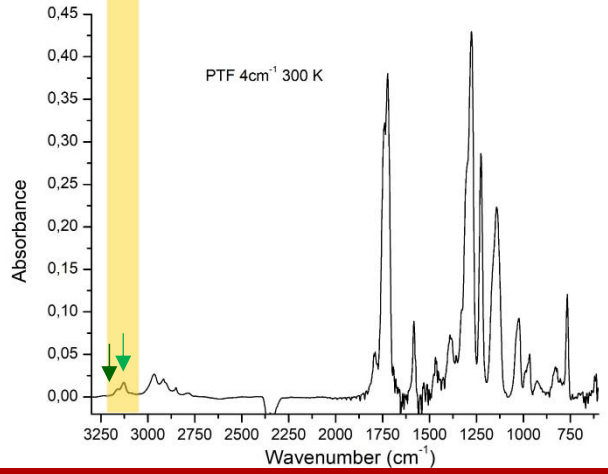
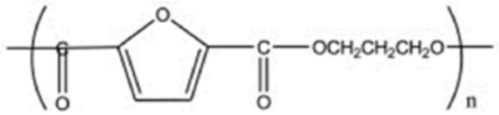


PTT

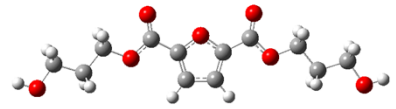




PTF



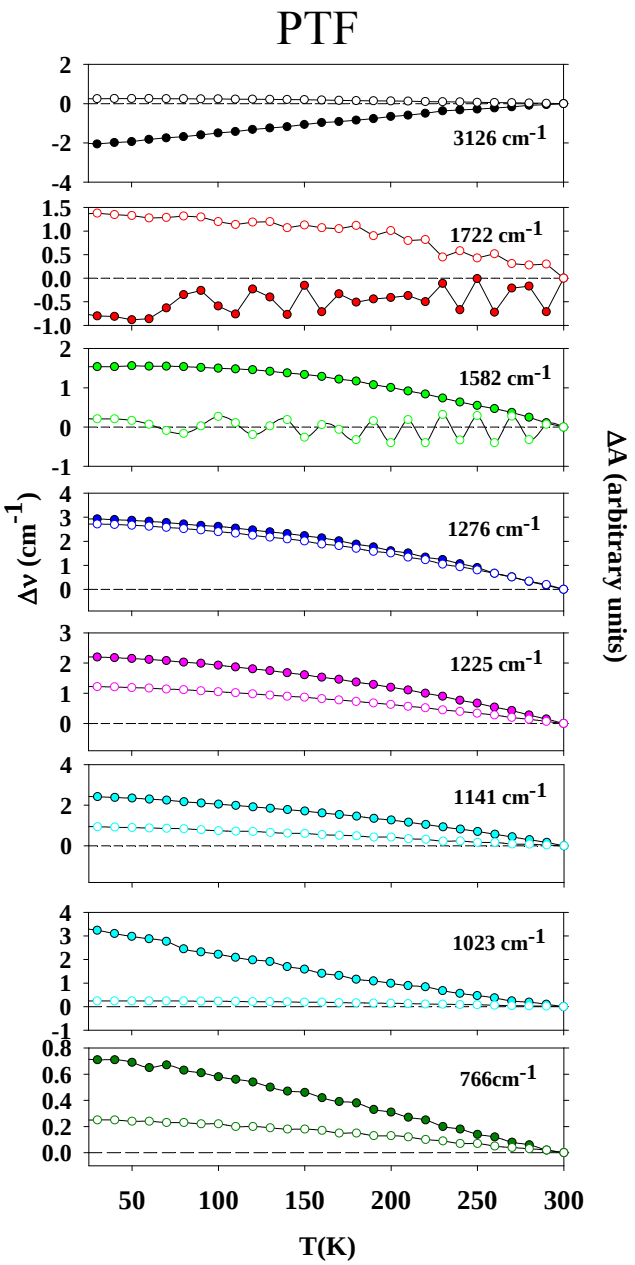
$\nu_{sym}(C\text{-}H)_{ring}$: 3155 cm^{-1}

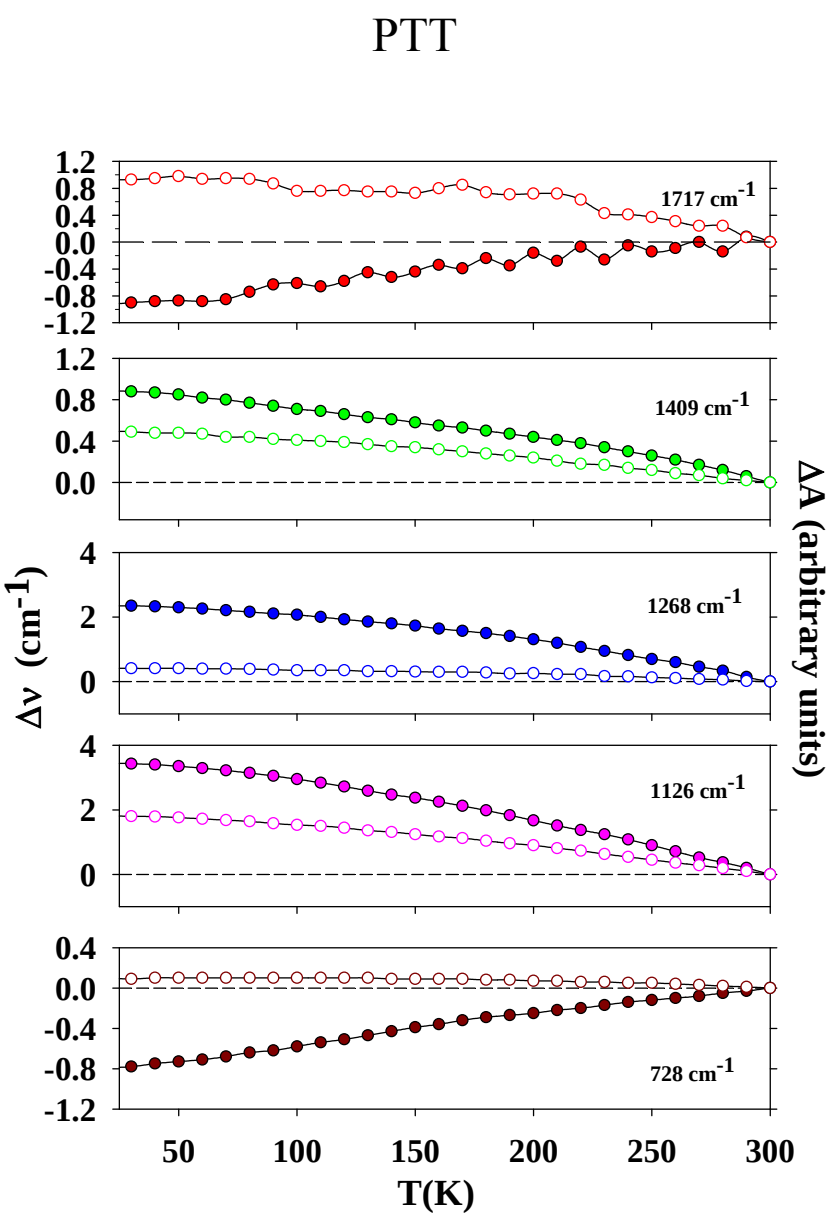


$\nu_{1\,asym}(C\text{-}H)_{ring}$: 3127 cm^{-}

- Araujo, C. F.; Nolasco, M. M.; Ribeiro-Claro, P. J. A.; Rudic, S.; Silvestre, A. J. D.; Vaz, P. D.; Sousa, A. F. Macromolecules 2018, 51 (9), 3515-3526
- Papamokos,G.; Dimitriadis,T; Bikiaris,D.N.; Papageorgiou,G.Z.; Floudas G.: Macromolecules 2019, 52, 6533−6546
- Irska, I.; Paszkiewicz, S.; Pawlikowska, D.; Dryzek, J.; Linares, A.; Nogales, A.; Ezquerra, T. A.; Piesowicz, E. Polymer 2021, 229,

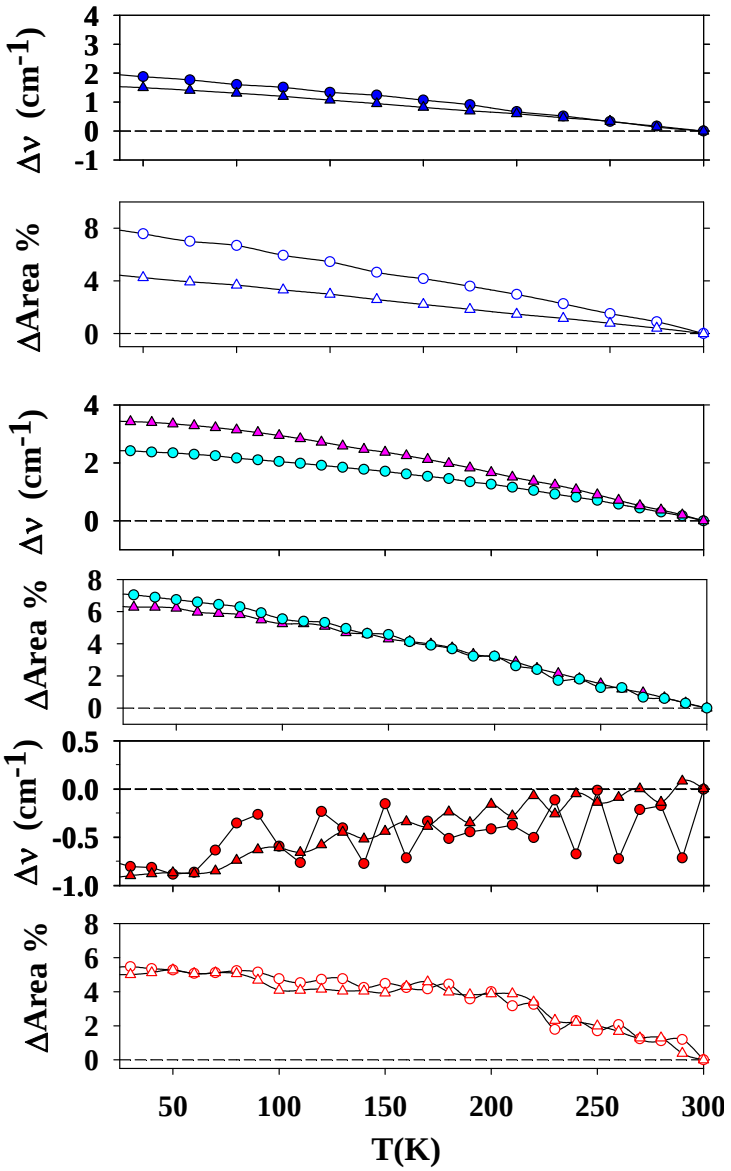
Poly(trimethylene 2,5-furanoate) (PTF) versus Poly(trimethylene terephthalate) (PTT)

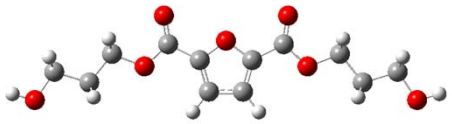




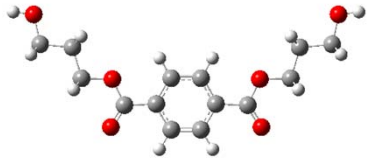
Poly(trimethylene 2,5-furanoate) (PTF) versus Poly(trimethylene terephthalate) (PTT)

PTT
PTF



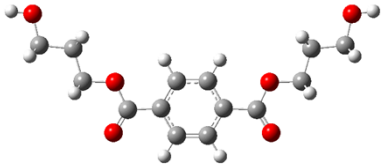


1276 cm^{-1} (**PTF C-O asymmetric stretching**)

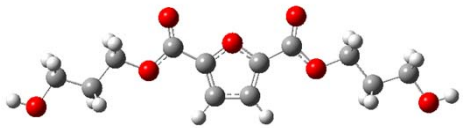


1268 cm^{-1} (**PTT C-O asymmetric stretching**, $CH)_{ring}$ rocking).

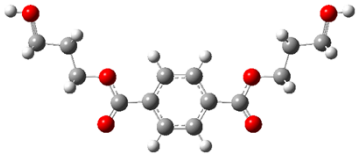
1143 cm^{-1} (**PTF $(C\text{-}H)_{ring}$ rocking**, $(C\text{-}O)_{ring}$ stretching, C-O stretching),



1126 cm^{-1} (**PTT $(CH)_{ring}$ rocking**, C-O asymmetric stretching).



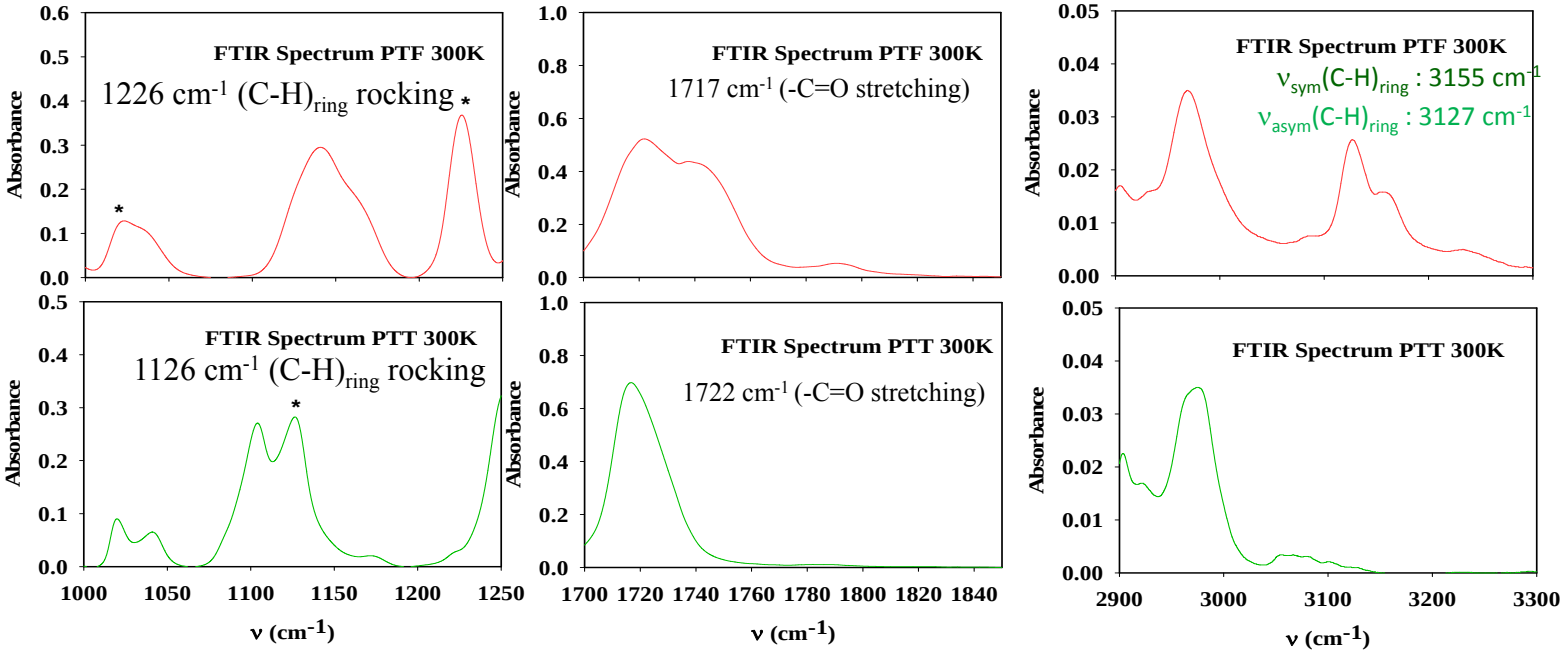
1722 cm^{-1} (-C=O stretching)

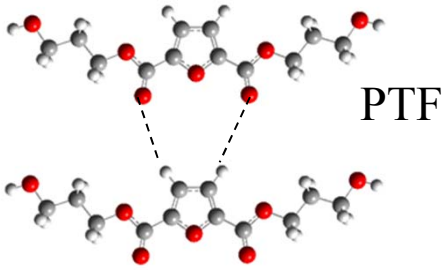


1717 cm^{-1} (-C=O stretching)

Poly(trimethylene 2,5-furanoate) (PTF) versus Poly(trimethylene terephthalate) (PTT)

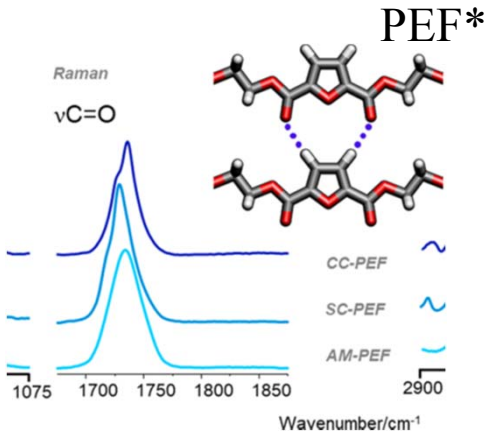
Hydrogen bonds





PTF

PEF*

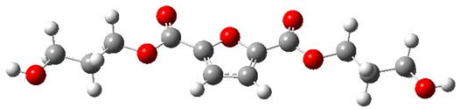


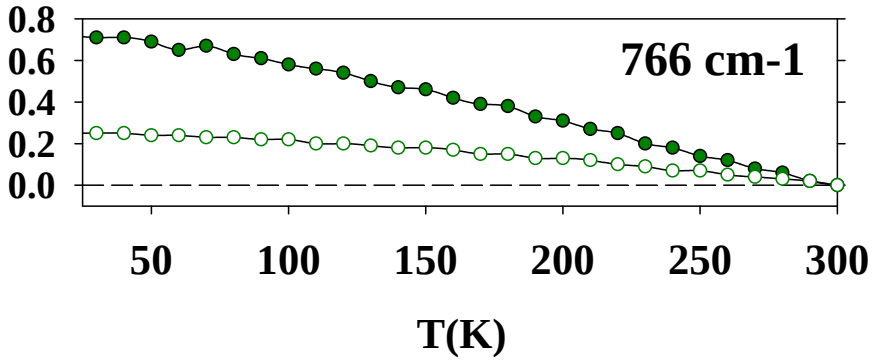
*Araujo, C. F.; Nolasco, M. M.; Ribeiro-Claro, P. J. A.; Rudic, S.; Silvestre, A. J. D.; Vaz, P. D.; Sousa, A. F. Macromolecules 2018, 51 (9), 3515-3526

Poly(trimethylene 2,5-furanoate) (PTF) versus Poly(trimethylene terephthalate) (PTT)

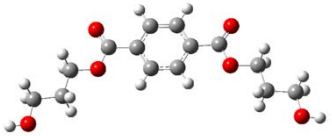
Hydrogen bonds

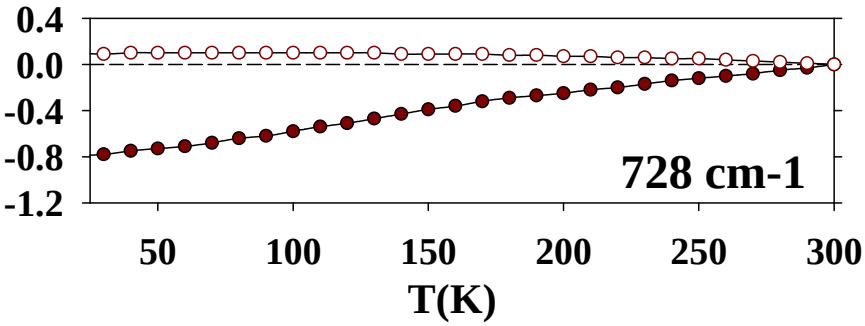
$\omega(C\text{-}H)_{ring} + \pi(C\text{-}O\text{-}C)$: 766 cm^{-1}



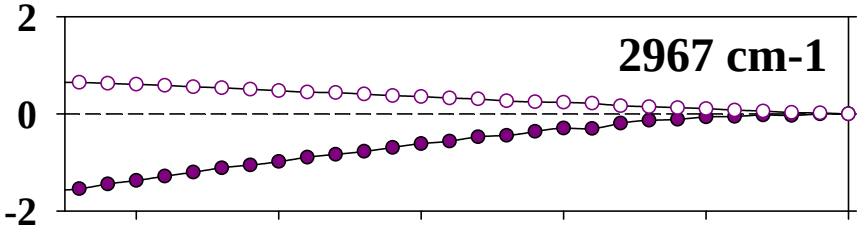


$\omega(C\text{-}H)_{ring}$: 728 cm^{-1}

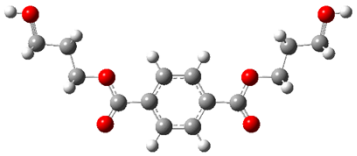


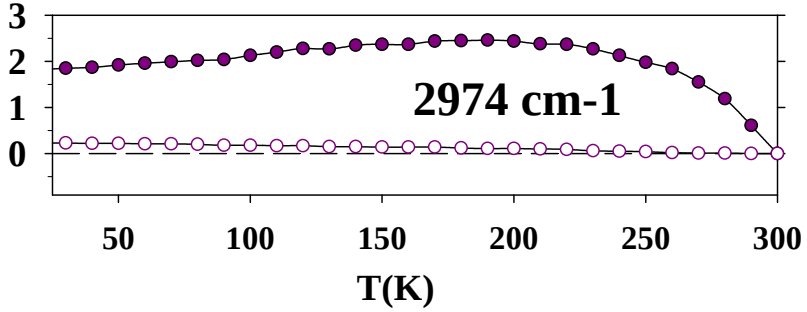


$\nu_{asym}CH_2$: 2967 cm^{-1}

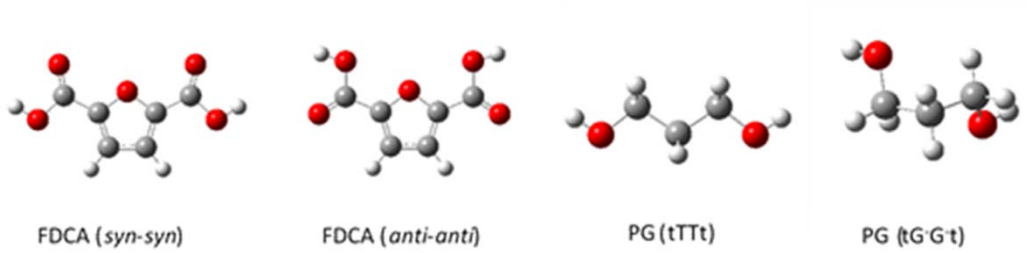


$\nu_{asym}CH_2$: 2974cm^{-1}



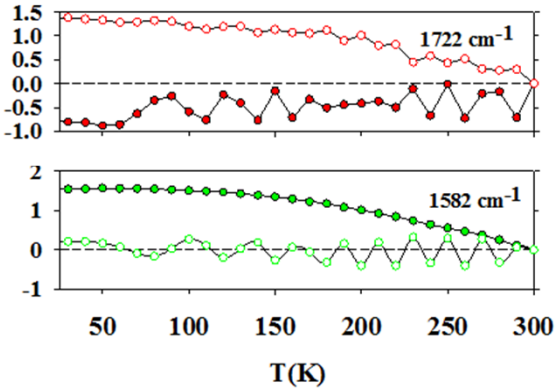


Poly(trimethylene 2,5-furanoate) (PTF) : Quantum mechanical molecular dynamics simulation



- Energy calculations by the DFT method predicts the FDCA syn-syn configuration to be <1 kcal/mol less stable than anti-anti configuration.
- At 160 K, RT is around 0,32 kcal/mol suggesting that the internal conversion of anti-anti-gauche to syn-syn-trans conformations in PTF could occur even at low temperatures.
- We focus on the following modes: i) -C=O stretching (around 1722 cm^{-1})
  ii) C=C stretching (1582 cm-1)

  because these bands exhibit opposite tendencies in their temperature dependences



Blue shift

Red shift

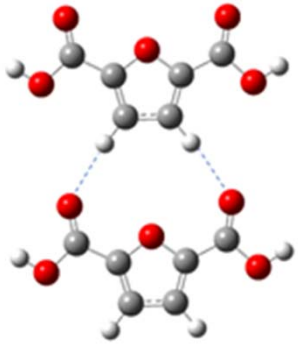
- Araujo, C. F.; Nolasco, M. M.; Ribeiro-Claro, P. J. A.; Rudic, S.; Silvestre, A. J. D.; Vaz, P. D.; Sousa, A. F. Macromolecules **2018**, 51 (9), 3515-3526
- Papamokos, G.; Dimitriadis, T.; Bikiaris, D. N.; Papageorgiou, G. Z.; Floudas, G. *Macromolecules* **2019,** 52 (17)

Poly(trimethylene 2,5-furanoate) (PTF) : Quantum mechanical molecular dynamics simulation

	C=O stretching sym	C=O stretching asym	C=C stretching
FDCA (*anti-anti*)	1774	1765	1591
FDCA (*syn-syn*)	1801	1783	1578
$FDCA_2$ (HB)	1798	1775	1579
	1791	**1772**	1574

- We can hypothesize that as temperature increases, the observed blue-shift of the C=O stretching band and concurrent red-shift of the C=C stretching band would be expected if an increment of the syn-syn conformations takes place.

HB (hydrogen bonding)



$FDCA_2$ (HB)

$$\Delta E_{dimer} = E_{dimer} - 2xE_{monomer} \text{ (kcal/mol)}$$

	$FDCA_2$ (HB)
ΔE_{dimer}	-4,29
d(C=O···H)	2,328

- Density-functional theory (DFT) method B3LYP (Becke's three parameter hybrid exchange functional plus the nonlocal correlation functional of Lee, Yang, and Parr. M06-2X functional (D3 version of Grimme's dispersion for dimers of FDCA. Gaussian 16 software.

Conclusions

- The temperature dependence of the FTIR bands of PTF and PTT exhibit a similar behavior (red shift) with exception of those related to hydrogen bonding(blue shift)
- Quantum mechanical simulation (Functional Density Theory (DFT)) for PTF reveals that syn-syn conformations and hydrogen bonding are likely to occur in the vitreous state.
- The existence of hydrogen bonding in PTF may affect the "shape" of the β-relaxation in comparison to that of PTT.
- More Quantum mechanical simulation is needed in order to compare PTT and PTF (Work in progress¡¡)

Acknowledgements

The authors gratefully acknowledge the financial support of the Spanish Ministry of Science and Innovation (MICINN) through PID2019-107514GB-I00 / AEI / 10.13039/501100011033.

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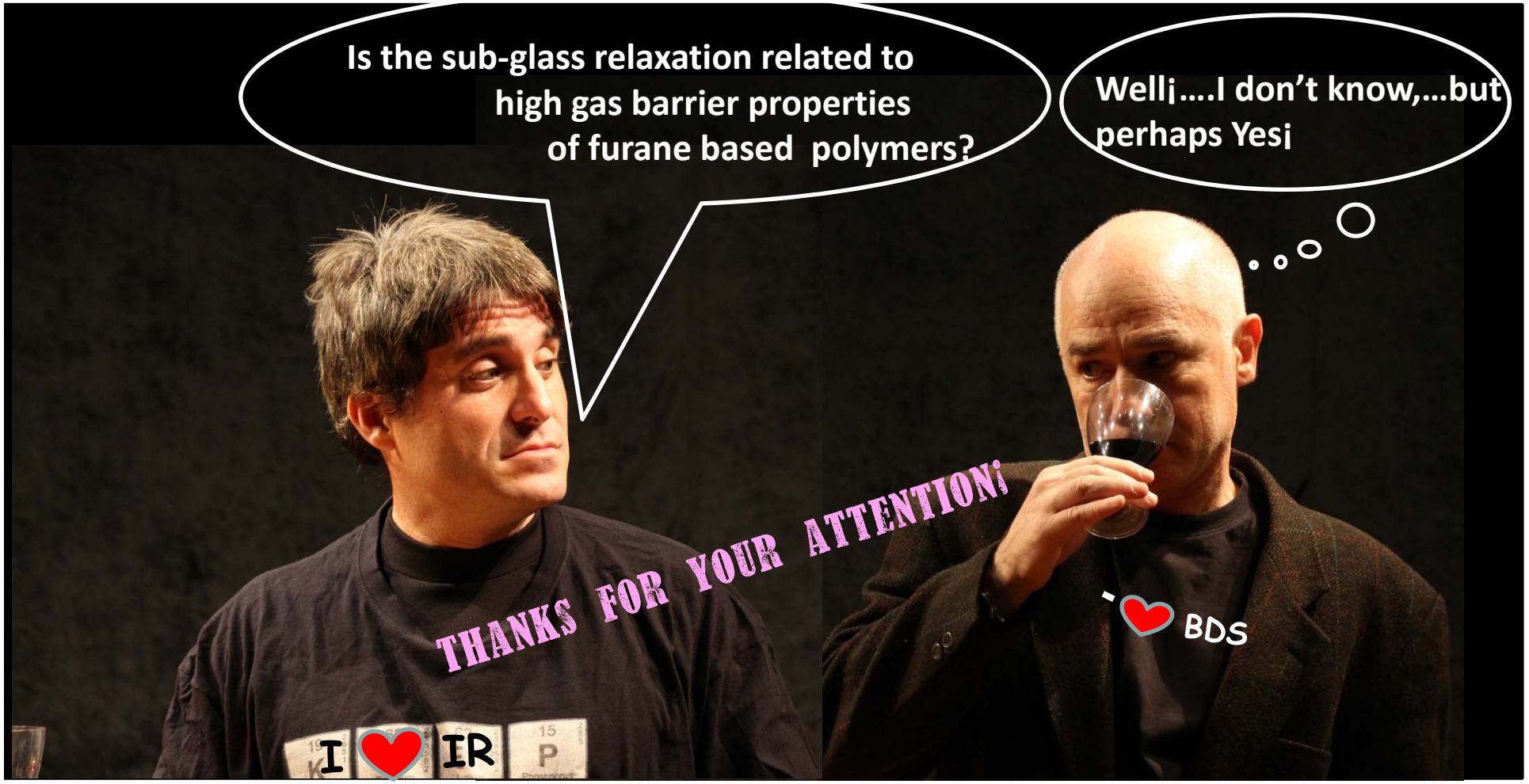
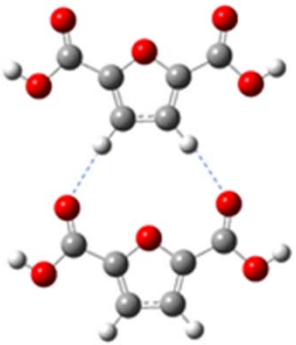


Poly(trimethylene 2,5-furanoate) (PTF) : Quantum mechanical molecular dynamics simulation

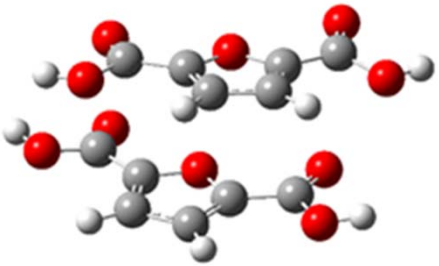
	C=O stretching sym	C=O stretching asym	C=C stretching
FDCA (*anti-anti*)	1774	1765	1591
FDCA (*syn-syn*)	1801	1783	1578
$FDCA_2$ (HB)	1798	1775	1579
	1791	**1772**	1574
$FDCA_2$ (π-π)	**1813**, 1805	**1783**	**1576**, 1574
		1744	

- We can hypothesize that as temperature increases, the observed blue-shift of the C=O stretching band and concurrent red-shift of the C=C stretching band would be expected if an increment of the syn-syn conformations takes place.

HB (hydrogen bonding)



$FDCA_2$ (HB)

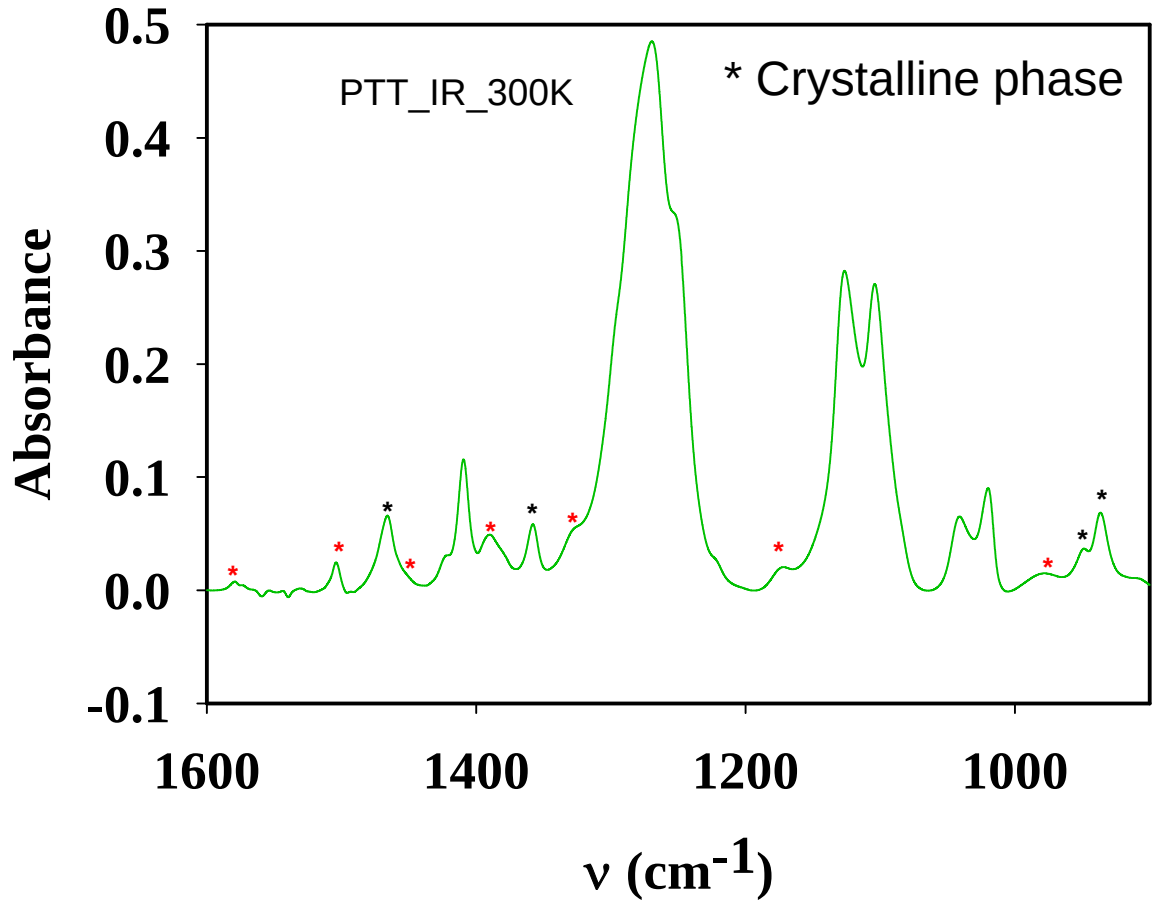


$FDCA_2$ (π-π)

	$FDCA_2$ (HB)	$FDCA_2$ (π-π)
ΔE_{dimer}	-4,29	-6,38
d(C=O···H)	2,328	
d(π···π)		3,330
Crystal[a]	2,47	3,39

Poly(trimethylene terephthalate) (PTT)

FTIR



- K.J. Kim, J.H. Bae, Y.H. Kim. Polymer 42 (2001) 1023-1033