Supporting Information

Chain Conformation, Molecular Dynamics and Thermal Properties of Poly(*n*-methylene 2,5-furanoates) as a Function of Methylene Units Sequence Length.

George Papamokos,[1*] Theodoros Dimitriadis,[1] Dimitrios N. Bikiaris,[2] George Z. Papageorgiou,[3] George Floudas[1,*]

[1] Department of Physics, University of Ioannina, 451 10 Ioannina, Greece

[2] Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24, Thessaloniki, Macedonia, Greece

[3] Chemistry Department, University of Ioannina, P.O. Box 1186, 45110 Ioannina, Greece

Corresponding Authors: George Floudas; E-mail: gfloudas@uoi.gr

George Papamokos; E-mail: gpapamokos@seas.harvard.edu

Content

(a) DFT calculations of the Gaussian scam grid, energetics and heat capacities for the monomers, dipole moments for the PEF nonamer and calculated IR spectra for the PEF trimer.

(b) Experimental DSC results obtained on heating/cooling with 10 K/min.

(c) Indicative fits to the α- and β-processes as a function of alkyl chain length.

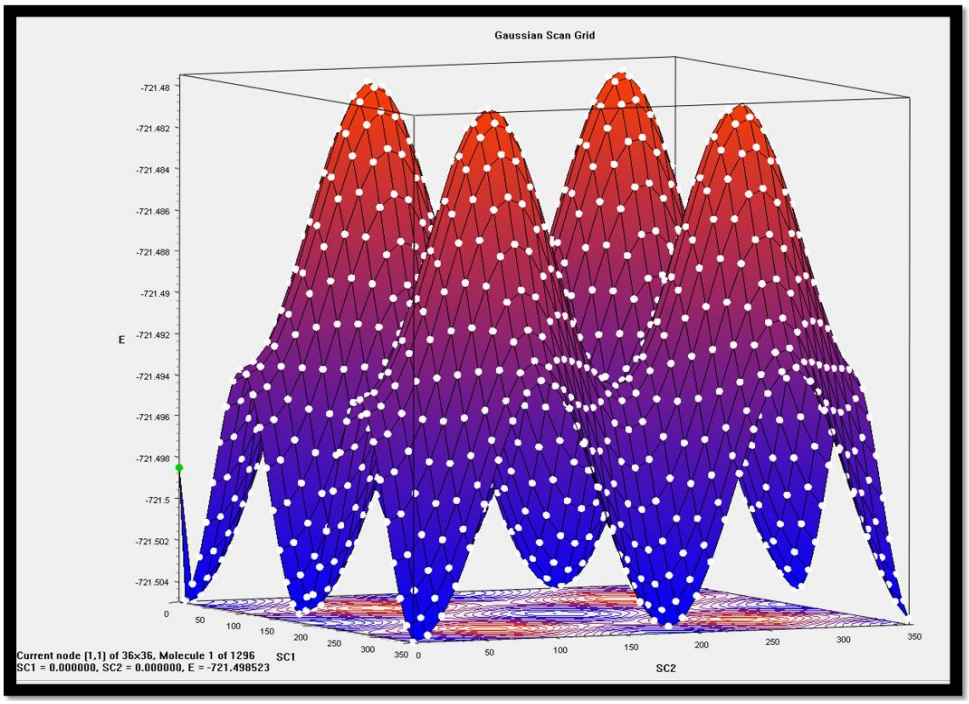


Figure S1. The gaussian scan grid at the DFT-ωB97XD level of theory and the 6-31+(d,p) basis set generated by the two scan coordinates **SC1** and **SC2** – dihedral angles $\mathbf{d_1}$ and $\mathbf{d_2}$ ($\mathbf{O_{ring}}$-$\mathbf{C_{ring}}$-**C=O**). Increment step for each coordinate: 10 degrees. Number of scan points: 1296.

Table S1. Energetics of monomers and heat capacities of FDCA and MF, EF, PF, BF, PEF, HF, OF monomers optimized at the DFT- wb97XD level of theory and the aug-ccPVTZ basis set.

Molecule	Eel (kcal/mol)	C_{v1}^{*} (cal/mol K) at *T*=298.15 K
FDCA anti	-381030.4	33.1
FDCA syn	-381029.6	33.2
FDCA cros	-381030.1	33.1
MF C1	-452899.8	41.6
MF C2	-452899.5	41.6
MF C3	-452899.0	41.6
MF C4	-452899.6	41.6
EF C1	-477566.6	46.7
EF C2	-477566.1	46.8
EF C3	-477565.5	46.8
EF C4	-477566.5	46.8
PF C1	-502238.6	51.4
PF C2	-502238.3	51.5
PF C3	-502237.9	51.5
PF C4	-502238.3	51.5
BF C1	-526910.6	56.3
BF C2	-526910.1	56.3
BF C3	-526909.6	56.3
BF C4	-526910.4	56.3
PeF C1	-551581.9	61.1
PeF C2	-551581.5	61.1
PeF C3	-551581.0	61.1
PeF C4	-551581.6	61.1
HF C1	-576253.2	65.9
HF C2	-576252.8	65.9
HF C3	-576252.3	66.0
HF C4	-576253.0	65.9
HeptF C1	-600924.4	68.7
HeptF C2	-600924.1	70.7
HeptF C3	-600923.6	70.8
HeptF C4	-600924.2	68.8
OF C1	-625595.7	73.6
OF C2	-625595.3	73.6
OF C3	-625594.8	73.6
OF C4	-625595.5	73.6

Table S2. Energetics and dipole moments of the **PEF** nonamer for the five initial conformations optimized at the PM7 semi-empirical level of theory.

	PM7		
Conf.	**Energy (kJ/mol)**	**Dipole moment (debye)**	**Energy dif. with respect to C1 conformer (kJ/mol)**
C1	-6836.59	1.8	
C2	-6860.66	6.1	-24.07
C3	-6468.93	1.8	367.66
C4	-6468.13	2.6	368.46
C5	-6432.80	7.1	403.79

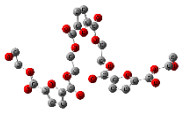
Table S3a. IR spectra of PEF trimer sensitive to gauche -trans isomerism of EG (Gaussview 6 output)

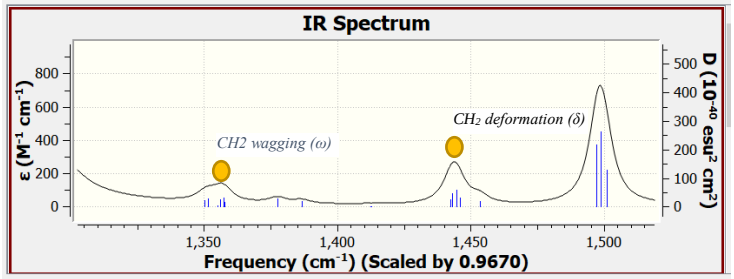
PEF-Trimer / B3LYP/6-311++G(d,p) – (Araujo, C. F. et al. Macromolecules 2018 reproduced in this work)

C1

gauche

EG

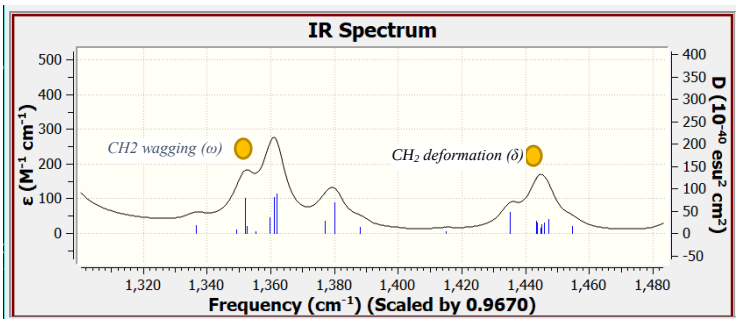




C2

gauche

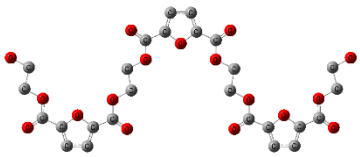
EG

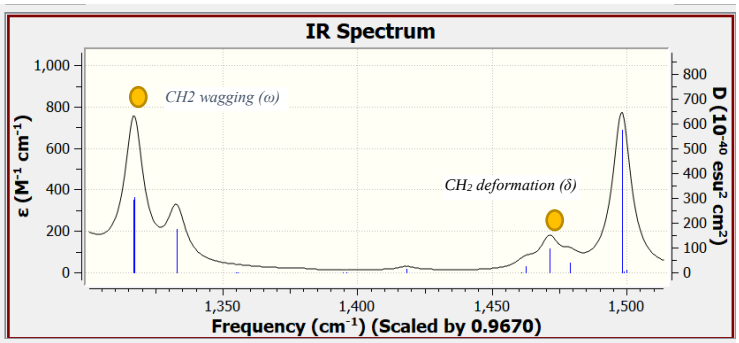


C3

trans

EG

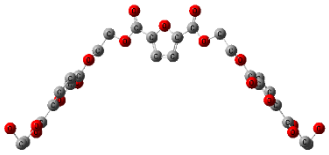


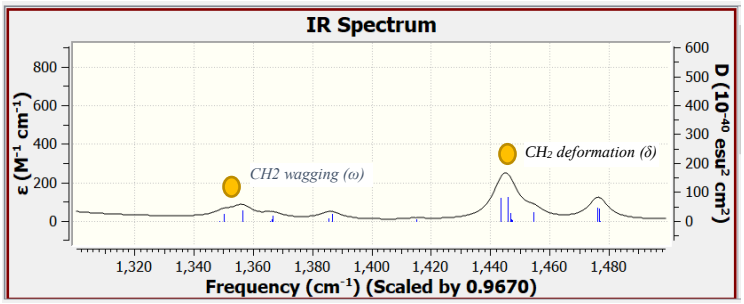


C4

gauche

EG

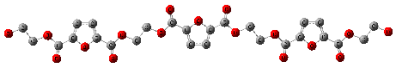


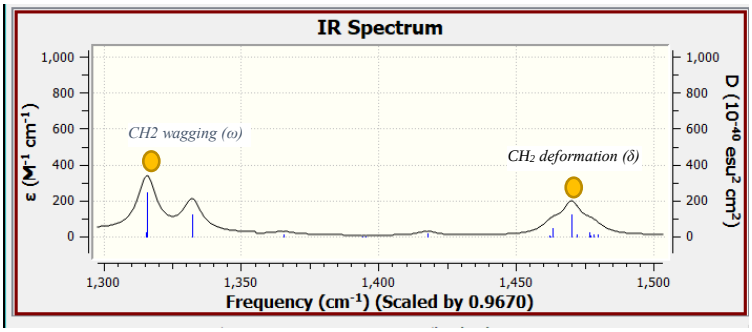


C5

trans

EG



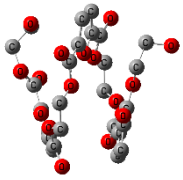


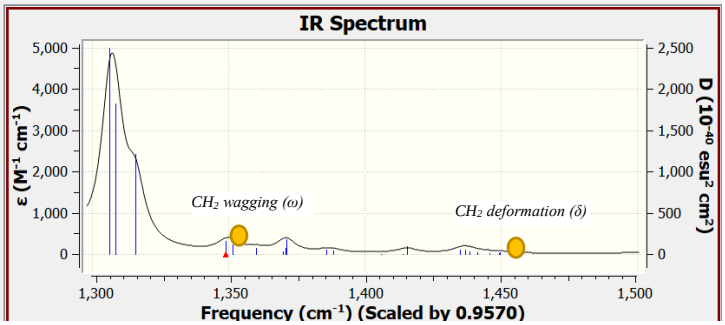
PEF-Trimer / RwB97XD/6-311++G(d,p) present work

C1

gauche

EG

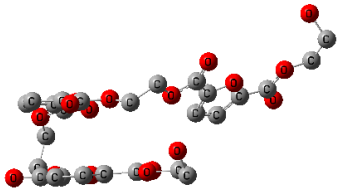


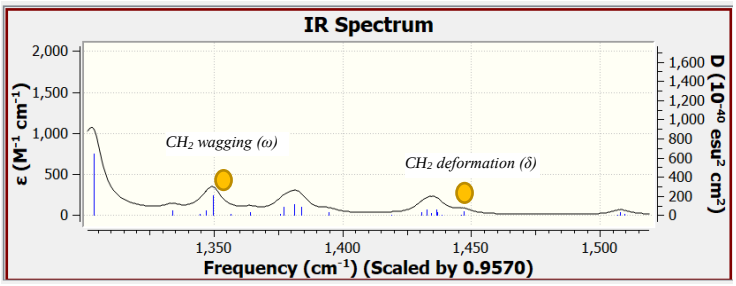


C2

gauche

EG

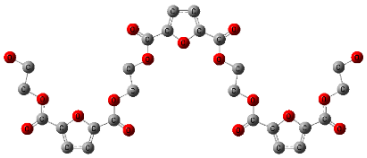


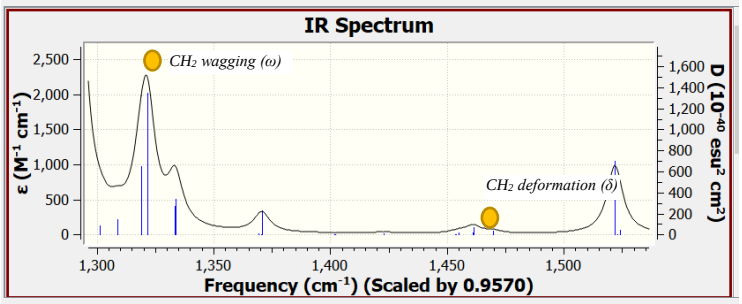


C3

trans

EG

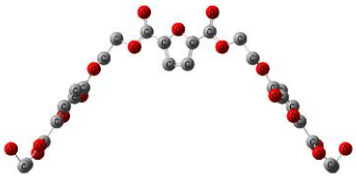


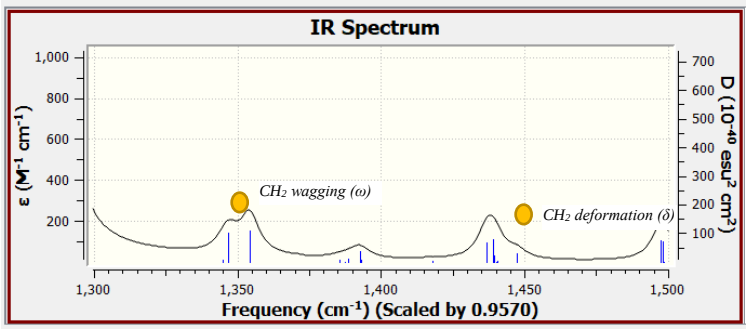


C4

gauche

EG

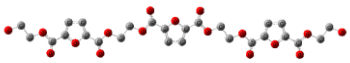




C5

trans

EG



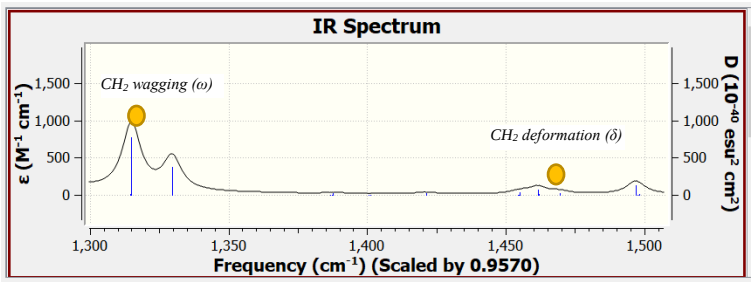
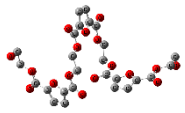


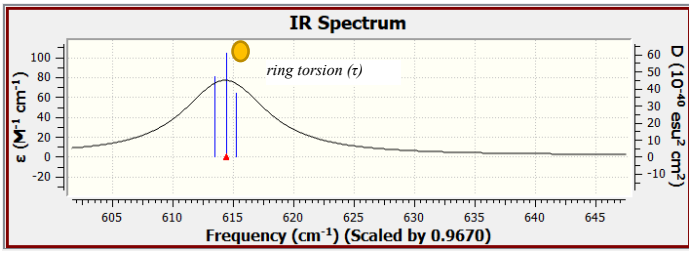
Table S3b. IR spectra of PEF trimer sensitive to *syn-anti* isomerism of FDCA (Gaussview 6 output)

PEF-Trimer / B3LYP/6-311++G(d,p) – (Araujo, C. F. et al. Macromolecules 2018 reproduced in this work)

C1

anti
FDCA

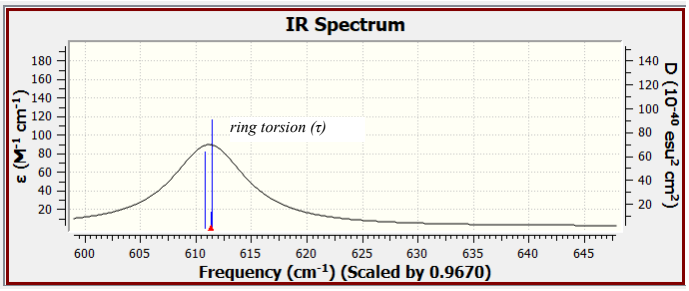




C2

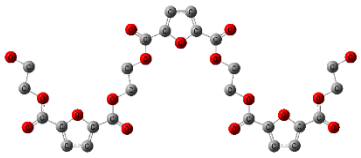
anti-
syn

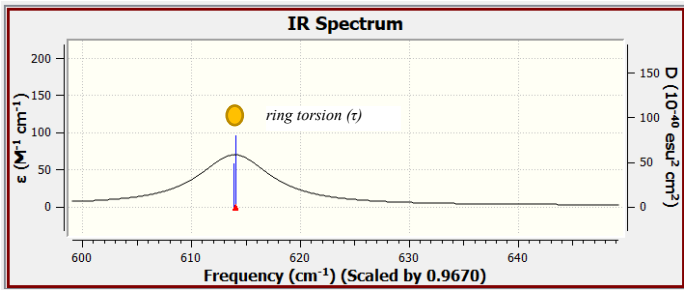
FDCA



C3

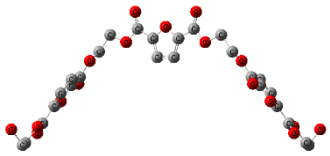
anti
FDCA

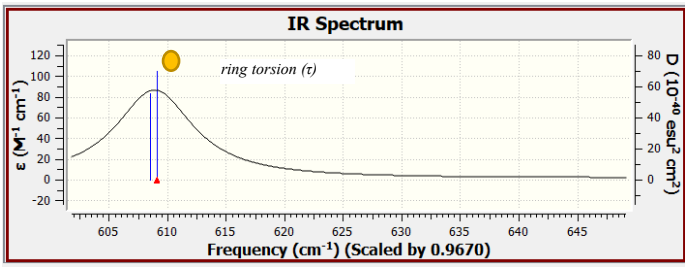




C4

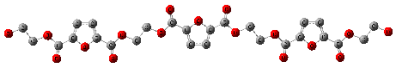
syn
FDCA

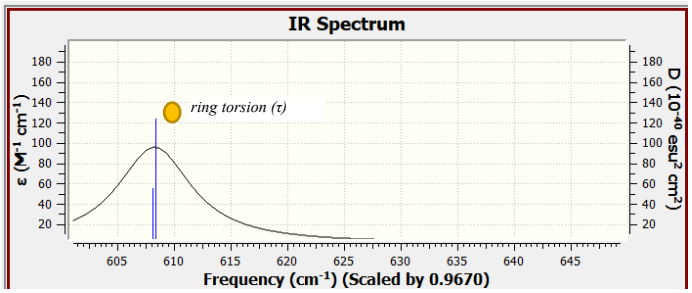




C5

syn
FDCA

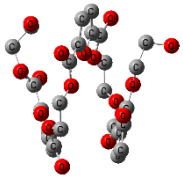


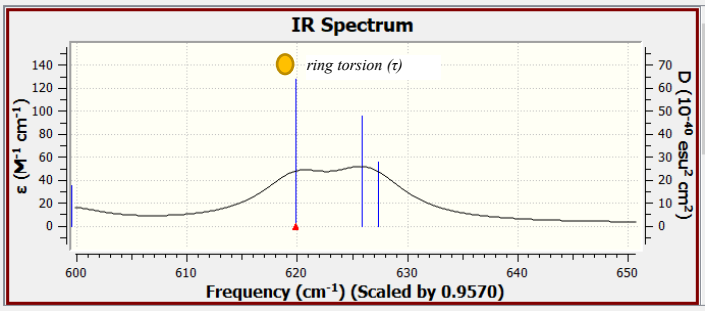


PEF-Trimer / RwB97XD/6-311++G(d,p) present work

C1

anti
FDCA

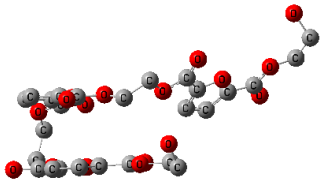


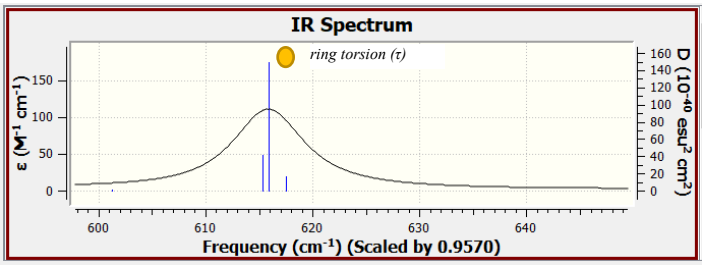


C2

anti-
syn

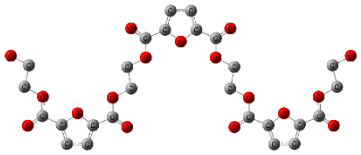
FDCA

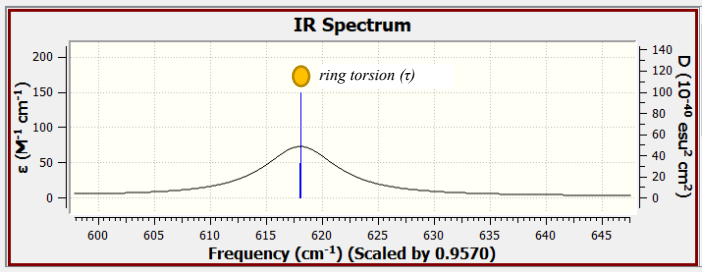




C3

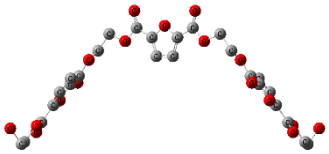
anti
FDCA

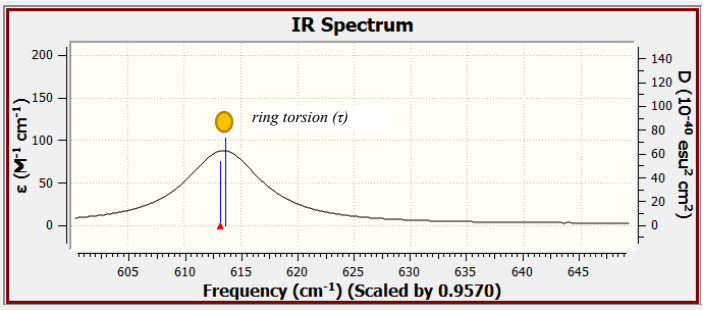




C4

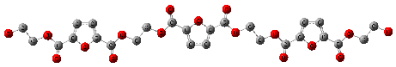
syn
FDCA





C5

syn
FDCA



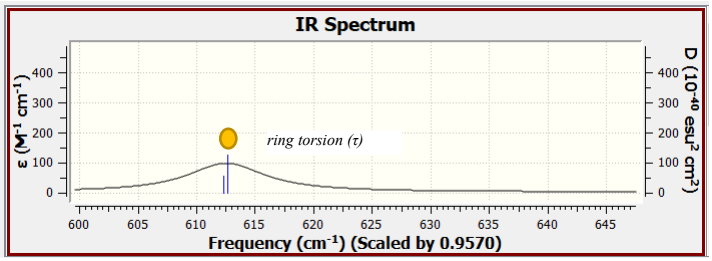
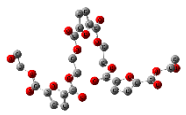


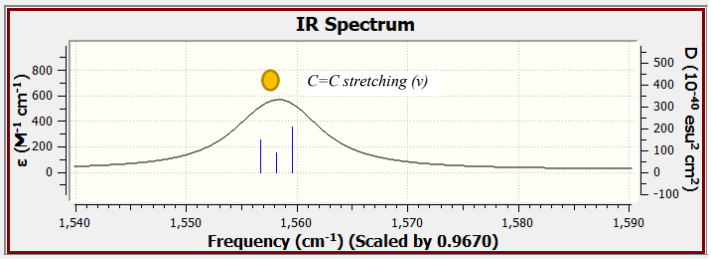
Table S3b. IR spectra of PEF trimer sensitive to *syn-anti* isomerism of FDCA (Gaussview 6 output)

PEF-Trimer / B3LYP/6-311++G(d,p) – (Araujo, C. F. et al. Macromolecules 2018 reproduced in this work)

C1

anti
FDCA

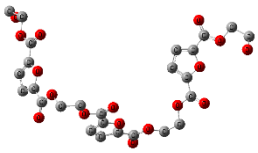


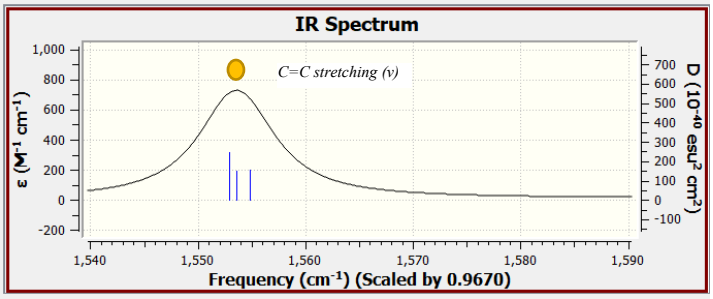


C2

anti-
syn

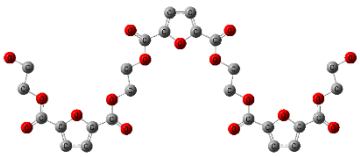
FDCA

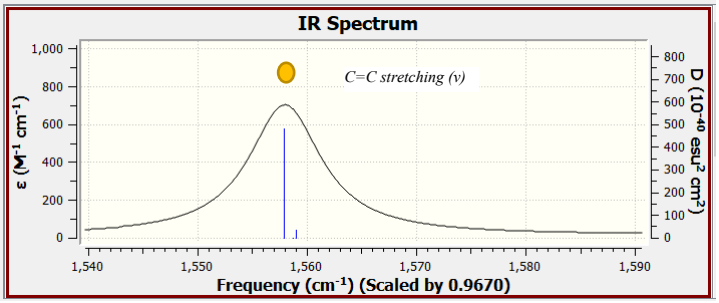




C3

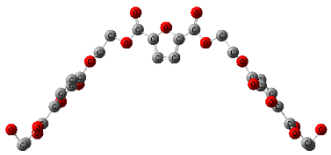
anti
FDCA

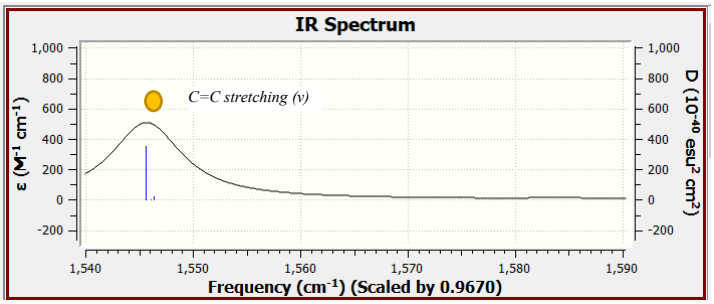




C4

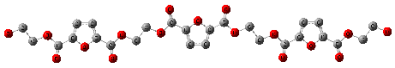
syn
FDCA

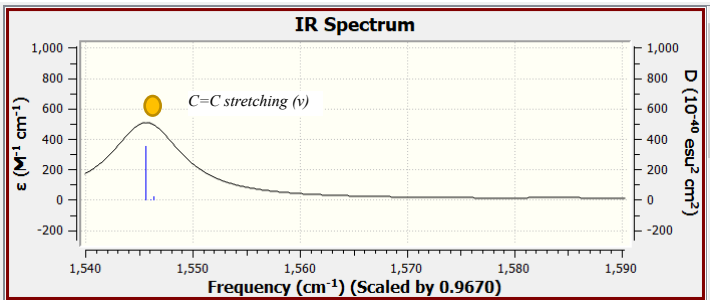




C5

syn
FDCA

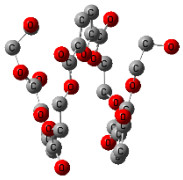


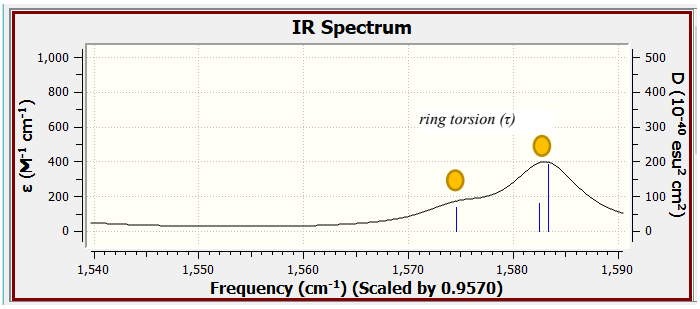


PEF-Trimer / RwB97XD/6-311++G(d,p) present work

C1

anti
FDCA

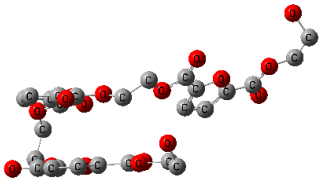


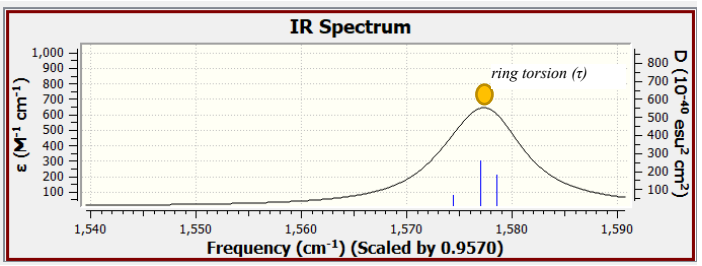


C2

anti-
syn

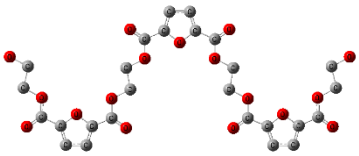
FDCA

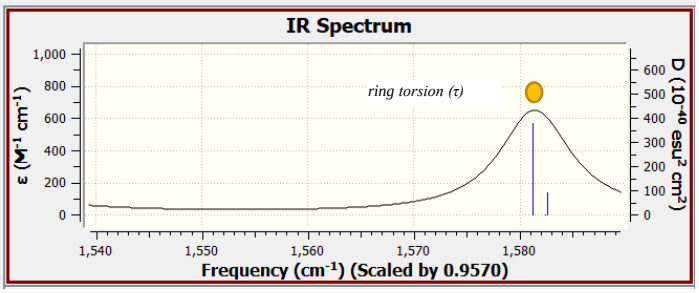




C3

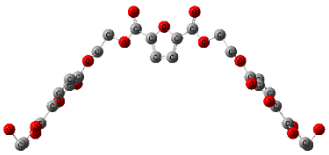
anti
FDCA

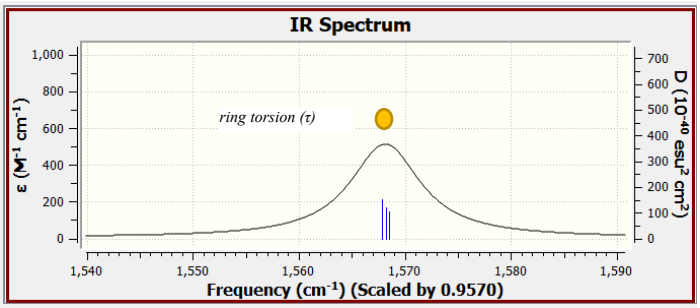




C4

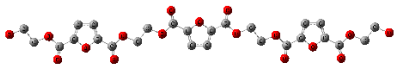
syn
FDCA





C5

syn
FDCA



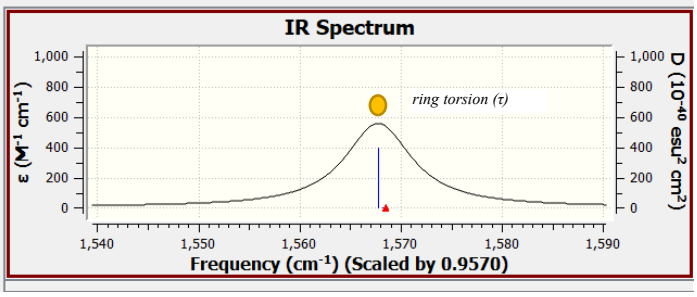


Table S4. Glass temperatures obtained from DSC during heating apparent melting temperatures and heats of fusion obtained with 10 K/min following cooling with the same rate.

Sample	*n*	T_g (K)	Δc_p (J/gK)	ΔH (J/g)	T_m (K)
PEF	2	351.5	0.28	54.0	485.7
PPF	3	316.1	0.32	15.4	446.3
PBF	4	323.2	-	48.2	441.9
PPeF	5	284.9	0.38	-	-
PHF	6	277.8	-	45.5	415.9
PHeptF	7	269.5	0.45	-	-
POF	8	275.2	-	51.6	412.8
PNF	9	264.4	0.46	-	-
PDeF	10	265.5	-	61.6	380.2
PDoF	12	266.6	-	52.3	380.8

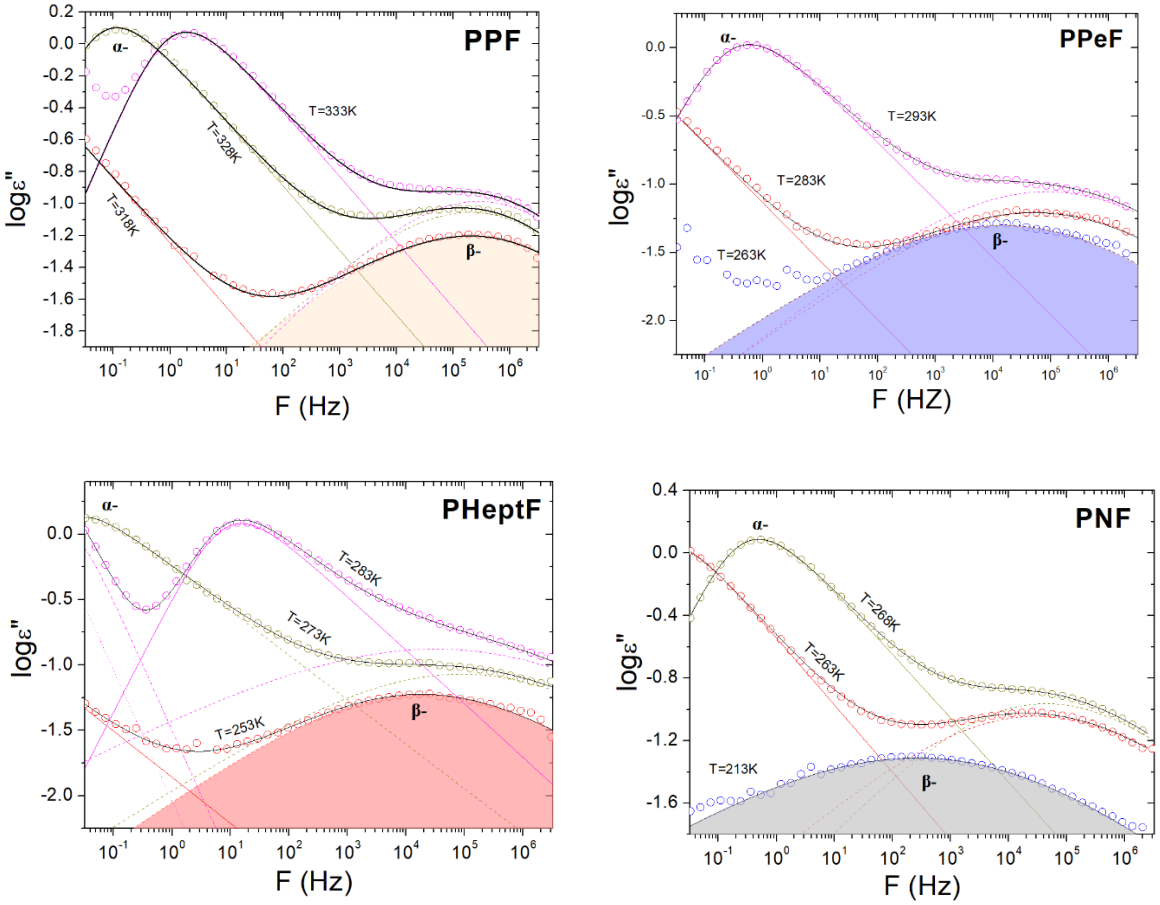


Figure S2. Representative dielectric loss curves at selected temperatures obtained on heating for **PPF** (*n*=3), **PPeF** (*n*=5), **PHeptF** (*n*=7) and **PNF** (*n*=9) together with fits to a summation of two HN functions corresponding to a faster β-process (shown in color) and the slower segmental process (α_{am}).

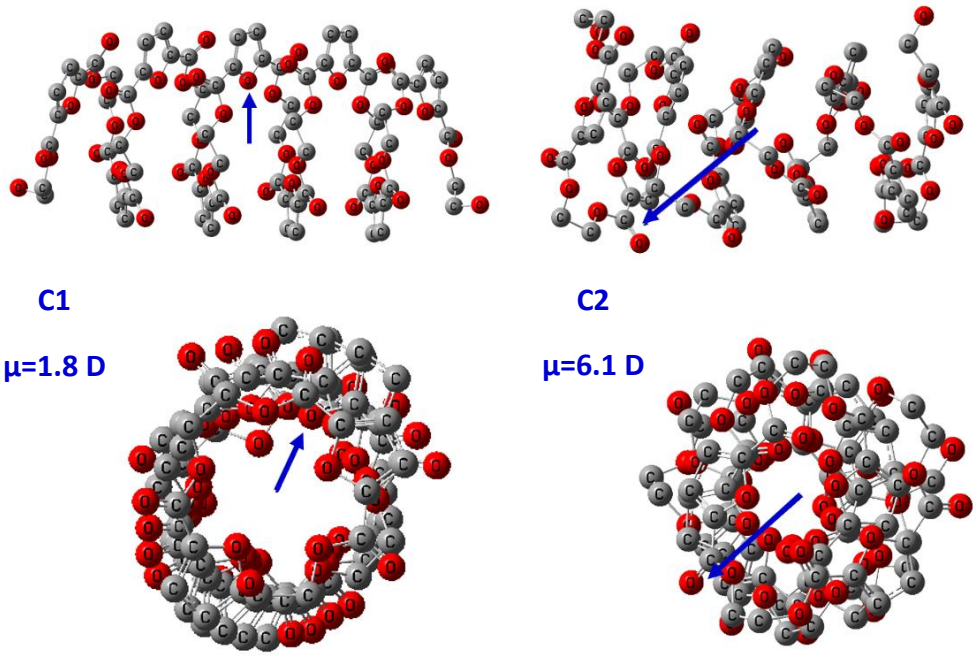


Figure S3. Pictorial representation of the C1 (left) and C2 (right) conformations of the nonamer after minimization at the semi-empirical level (PM7). (Up) View along the helical axis. (Down) View with the helical axis perpendicular to the plane. The dipole moment vector is indicated in blue.