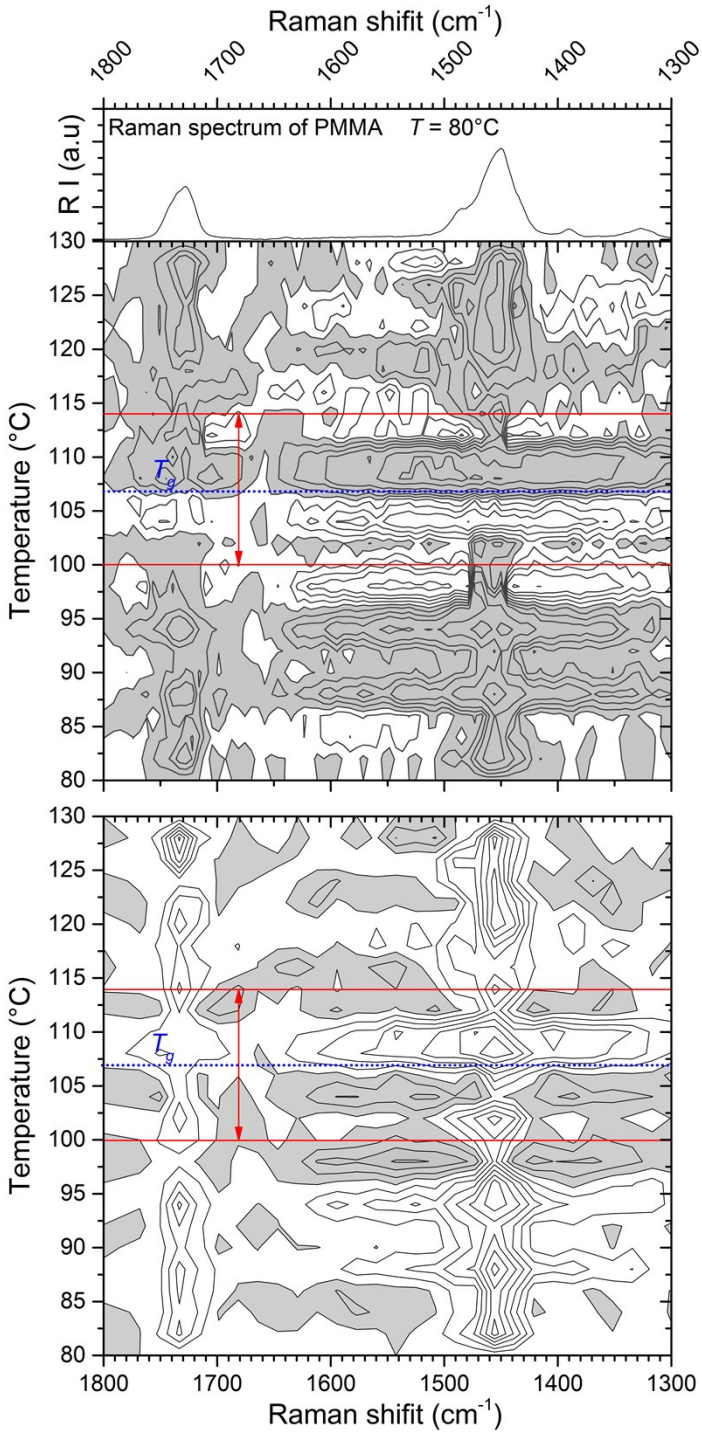
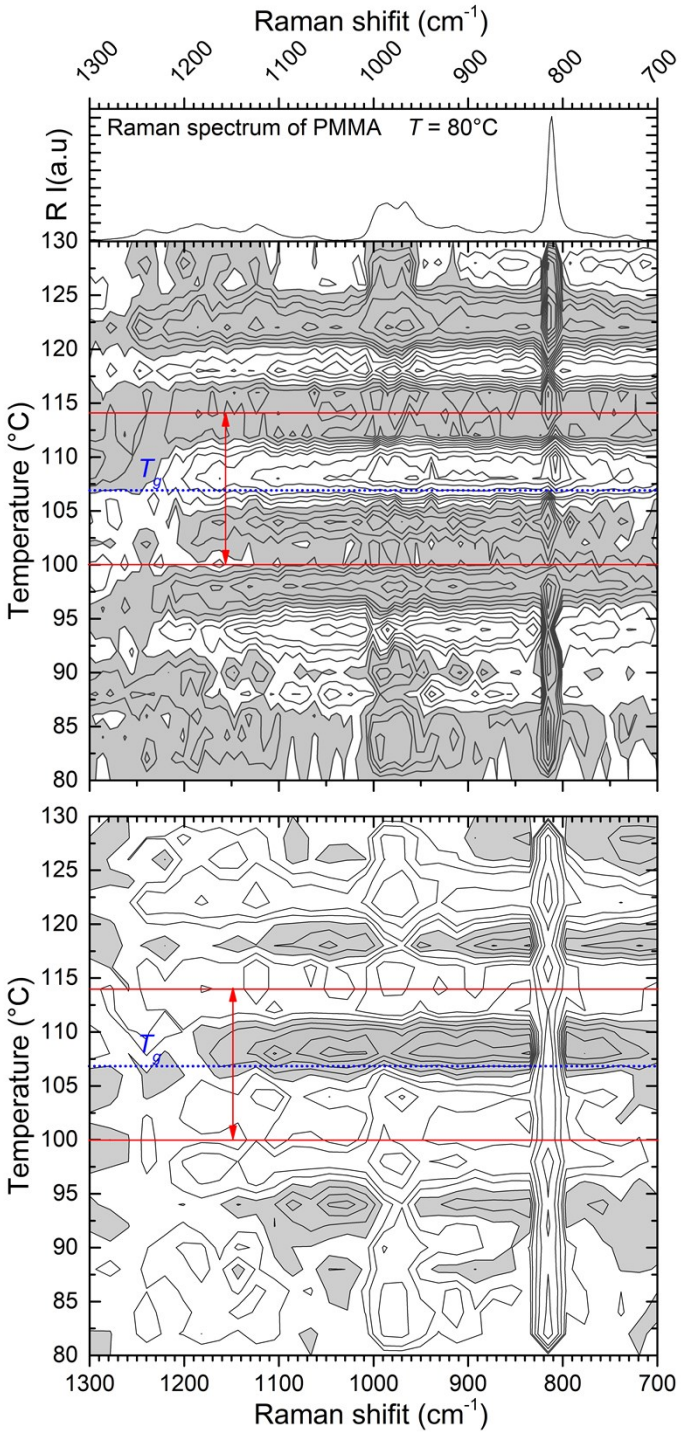
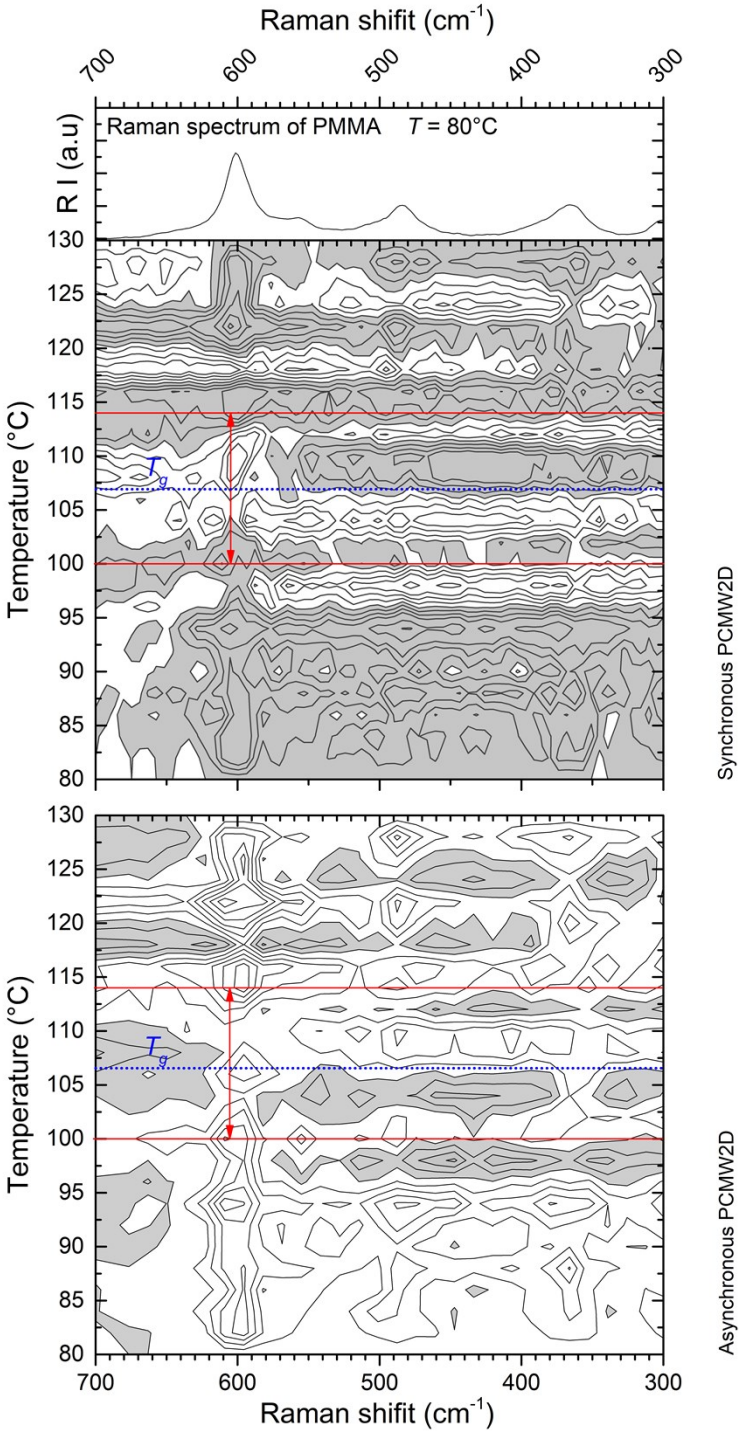
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

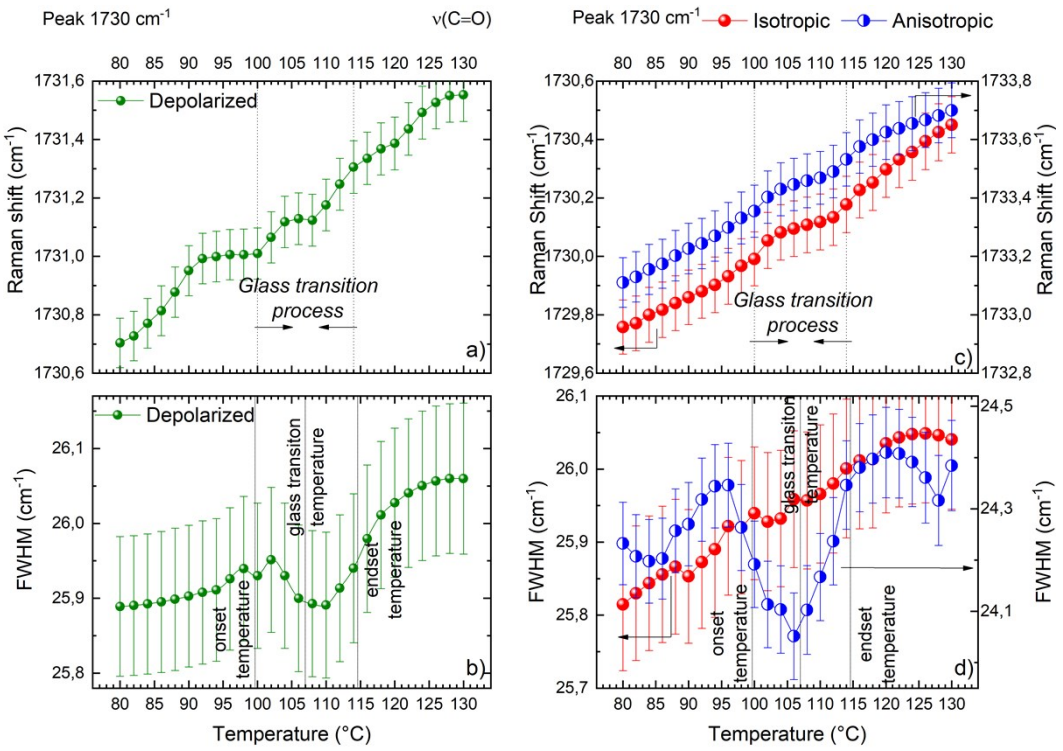

# Supplementary Figure.


Raman shifit (cm-1)
1800
1700
1600
1500
1400
1300
Raman spectrum of PMMA T = 80°C
R I (a.u)
Temperature (°C)
130
125
120
115
110
105
100
95
90
85
80
Tg
Tg
Raman shifit (cm-1)

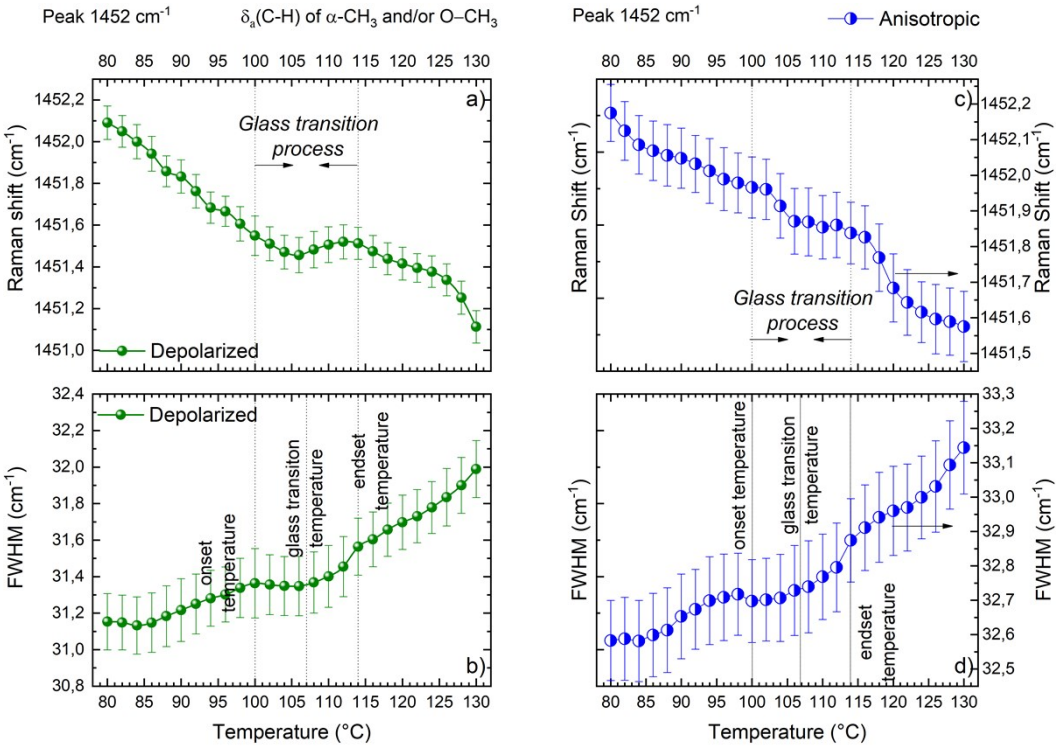

Raman shifit (cm-1)
1300
1200
1100
1000
900
800
700
Raman spectrum of PMMA T = 80°C
R I(a.u)
Temperature (°C)
130
125
120
115
110
105
100
95
90
85
80
Tg
Tg
Temperature (°C)
Raman shifit (cm-1)



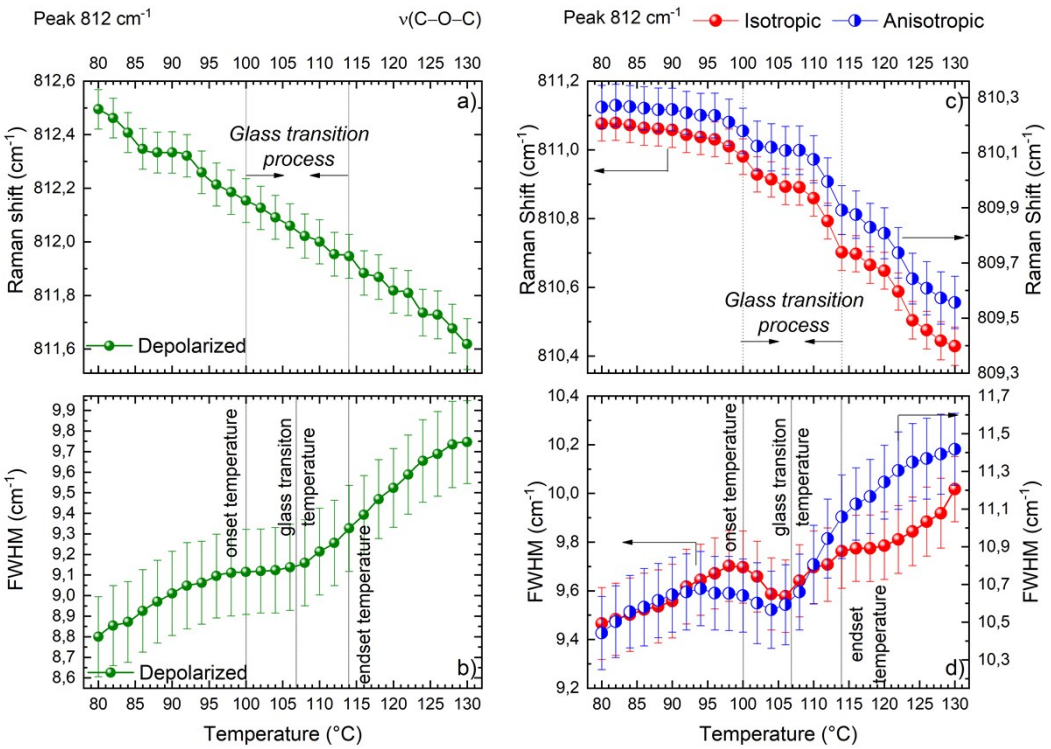

**Supplementary figure 1**. On the top the depolarized Raman spectrum of atactic PMMA, recorded at 80°C, is shown for the spectral regions a) from 1800 to 1300 $cm^{-1}$, b) from 1300 to 700 $cm^{-1}$ and c) from 700 to 300 $cm^{-1}$; below, for the same spectral regions, the synchronous and asynchronous Perturbation-Correlation Moving-Window two-dimensional correlations (PCMW2D) are shown for temperature perturbation from 80°C to 130°C, using the windows size of $2m + 1 = 3$ for all of them. The white color means positive PCMW2D correlation intensity, while the grey color represents negative correlation intensity. The horizontal lines pinpoint the glass transition temperature and its onset and endset temperatures, as reported in the Figures 4-10.



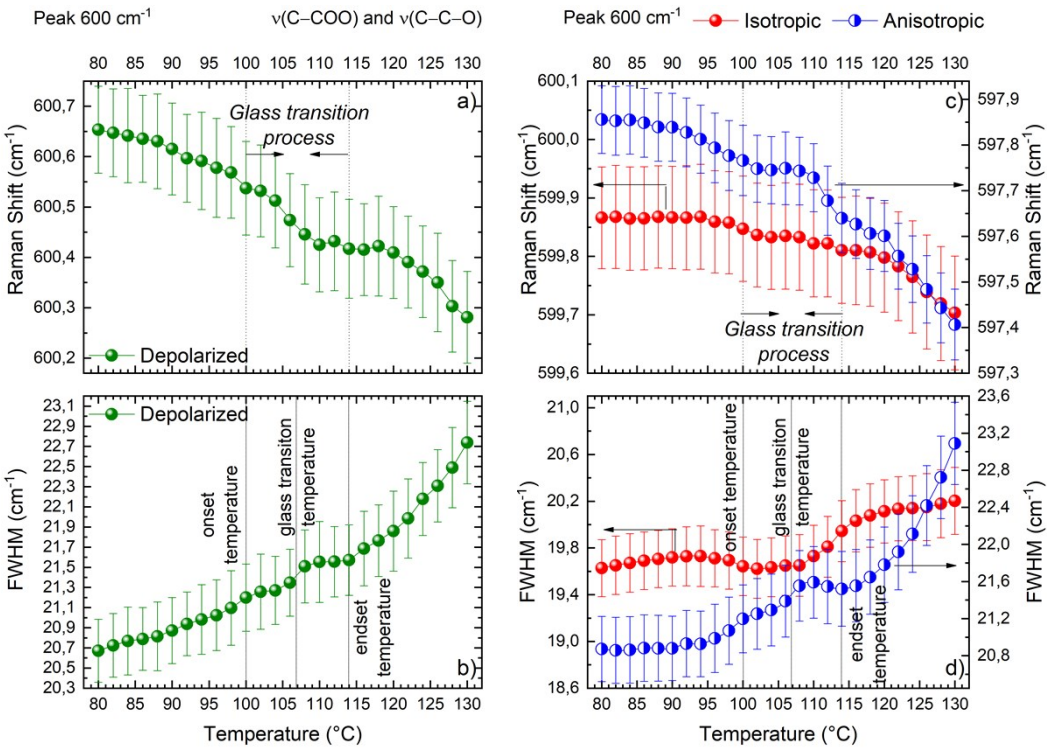

**Supplementary Figure 4**. Raman shift and full width at half maximum (FWHM) of the Raman peak at around 1730 $cm^{-1}$ associated with ν(C=O) of atactic PMMA, **a)** and **b)** recorded in the depolarized Raman spectrum (green dots), and **c)** and **d)** recorded in the isotropic (red dots) and anisotropic (blue dots) Raman spectrum, as a function of the sample temperature from 80°C to 130°C, highlighting the temperature range from 100°C to 114°C where the glass transition process takes place, and the pinpointed glass transition temperature at 107°C.




**Supplementary Figure 5**. Raman shift and full width at half maximum (FWHM) of the Raman peak at around 1452 $cm^{-1}$ associated with $\delta_a$(C–H) of α-$CH_3$ and/or O–$CH_3$ of atactic PMMA, **a)** and **b)** recorded in the depolarized Raman spectrum (green dots), and **c)** and **d)** recorded in the anisotropic Raman spectrum (blue dots), as a function of the sample temperature from 80°C to 130°C, highlighting the temperature range from 100°C to 114°C where the glass transition process takes place, and the pinpointed glass transition temperature at 107°C.




**Supplementary Figure 6**. **a)** Raman shift and full width at half maximum (FWHM) for the Raman peak at around 812 $cm^{-1}$ associated with ν(C–O–C) of atactic PMMA, **a)** and **b)** recorded in the depolarized Raman spectrum (green dots), and **c)** and **d)** recorded in the isotropic (red dots) and anisotropic (blue dots) Raman spectrum, as a function of the sample temperature from 80°C to 130°C, highlighting the temperature range from 100°C to 114°C where the glass transition process takes place, and the pinpointed glass transition temperature at 107°C.




**Supplementary Figure 7**. **a)** Raman shift and full width at half maximum (FWHM) for the Raman peak at around 600 $cm^{-1}$ associated with ν(C–COO), and with ν(C–C–O) of atactic PMMA, **a)** and **b)** recorded in the depolarized Raman spectrum (green dots), and **c)** and **d)** recorded in the isotropic (red dots) and anisotropic (blue dots) Raman spectrum, as a function of the sample temperature from 80°C to 130°C, highlighting the temperature range from 100°C to 114°C where the glass transition process takes place, and the pinpointed glass transition temperature at 107°C.