Supporting Material to:

Spectroscopic Evidence for Stereocomplex Formation by Enantiomeric Polyamides Derived from Tartaric Acid

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Experimental details

PnDMT studied in this work were synthesized by polycondensation in solution of the corresponding α,ω-diamines and pentachlorophenyl di-*O*-metyl D- and L-tartrates according to previous report[8]. The crude polyamides resulting from synthesis were purified by reprecipitation from chloroform with ether addition and subsequently fractionated, if needed, in order to obtain comparable molecular weights and polydispersities for all the samples. Calorimetric measurements were performed with a Perkin-Elmer Pyris DSC instrument calibrated with indium. Sample weights of about 2-5 mg were used in a temperature range from -20 up to 300 ºC at heating and cooling rates of 10 ºC min^{-1} under a nitrogen atmosphere. Contact angles between water and solid surfaces were measured by means of an OCA 15+ contact angle measuring system supported by a SCA20 software (Dataphysics, Germany). Angle values were registered at room temperature after 30 seconds of dropping the water onto the polymer surface and at least 10 measurements were made.

Table 1. Contact Angles

Polyamide	Left	Right
P6DMT(D)	59	60
P6DMT(L)	59	61
P6DMT(D+L)	52	53

The ^{1}H NMR analysis of peak broadening of polyamides solutions was performed on a Bruker AMX-300 equipment at 300.13 MHz from samples dissolved in deuterated chloroform at 298.1 K. Spectra were acquired with a pulse width p1 of 2.8 μs (30 °), a relaxation delay of 2 s, 32 k data points and 128 scans. 50 mg of P6DMT(L) or P6DM(D+L) mixture were dissolved in 1 ml of $CDCl_3$ and NMR spectra from these samples were recorded at different intervals of time.

^{1}H NMR diffusion measurements were performed on a 400 MHz Bruker Avance Spectrometer using a bipolar pulse longitudinal eddy current delay (BPLED)[1] pulse sequence. The pulse sequence included a 5 ms delay to allow residual eddy currents to decay. Diffusion time (Δ) was set to 350 or 400 ms. The pulsed gradients were incremented from 2 to 95% of the maximum strength in sixteen spaced steps with a duration ($\delta/2$) of 3 to 4 ms. Data were acquired in $CDCl_3$ with sample rotation and the temperature was controlled at 298 K to minimizing convection effects.[2]

In PSGE experiments, the signal intensity of a given resonance experiment decays following the Stejskal-Tanner equation (1) as:

$I = I_o \exp(-\gamma^2 g^2 \delta^2 (\Delta - \delta/3) D)$　　　　(1)

where I and Io are the signal intensities in the presence and absence of the pulsed-field gradients respectively, γ is the gyromagnetic ratio (rad s G^{-1}), g is the strength of the diffusion gradients (G m^{-1}), D is the diffusion coefficient of the observed spins (m^2 s^{-1}), δ is the length of the diffusion gradients (s) and Δ is the time separation between the leading edges of the two diffusion pulsed gradients (s)

Figures 1, 2 and 3 show a semi-logarithmic of the NMR signal attenuations as versus $\gamma^2 g^2 \delta^2 (\Delta - \delta/3)$ (Stejskal-Tanner plot). For data processing the DOSY software package included in XWINNMR 3.5 was used and the data were also processed by a non linear least-squares fitting method with Origin 6.0 software.
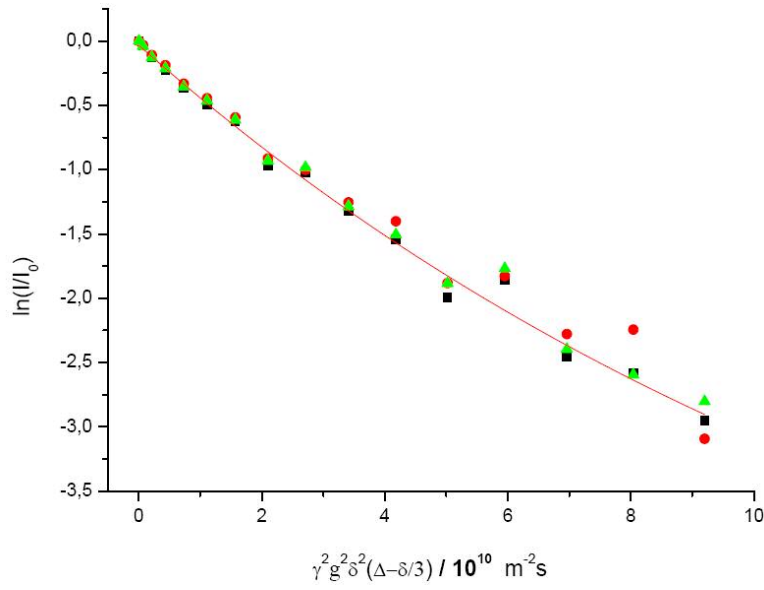
Figure 1. Stejskal-Tanner plot of signal attenuation for P6DMT(L) polyamide. Diffusion coefficient: $D=3.67 \times 10^{-11} \pm 0.08$ m^2 s^{-1}.
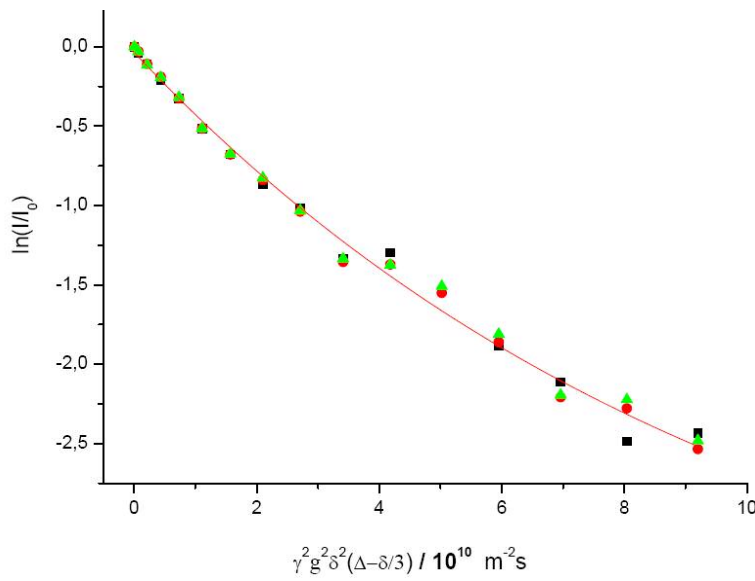

Figure 2. Stejskal-Tanner plot of signal attenuation for P6DMT(D) polyamide. Diffusion coefficient: $D=3.57 \times 10^{-11} \pm 0.08$ m^2 s^{-1}.
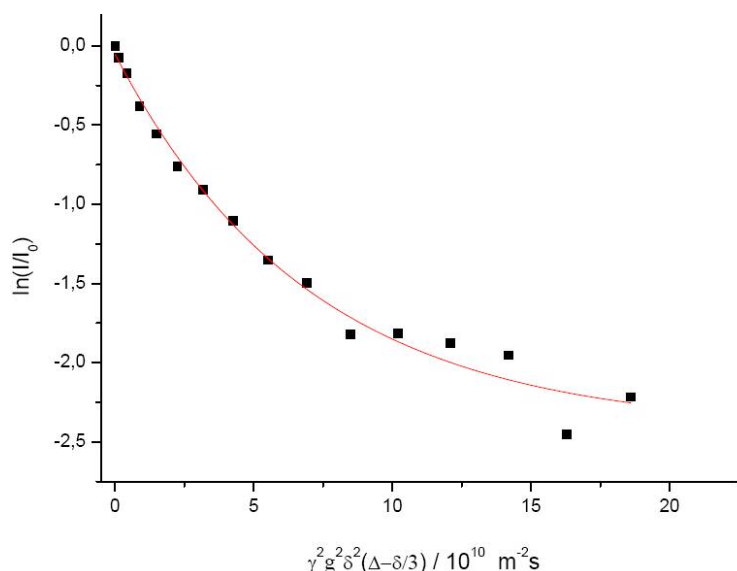
Figure 3. Stejskal-Tanner plot of signal attenuation for P6DM(D+L) mixture. Diffusion coefficient: $D = 2.22 \times 10^{-11} \pm 0.09 \ m^2 \ s^{-1}$.

Transmission infrared spectra of polytartaramide films were recorded on a Nicolet AVATAR 370 Fourier transform infrared spectrophotometer (FTIR). The P6DMT(L) FTIR sample was prepared by solvent casting from a chloroform solution (1% wt/v) on a KBr pellet. The P6DMT(D+L) sample was prepared by sandwiching between a KBr pellet and a teflon plate a small amount of the gel-like stereocomplex formed after a week in the bottom of a 1% wt/v chloroform solution. In both samples residual solvent was removed in a vacuum oven at 60º C for 48 hours before spectral recording.

The following spectra support the formation of the stereocomplex in the chloroform solution. The green coloured spectrum corresponds to amorphous P6DMT(L) (shown only for reference). The blue spectrum corresponds to an "as precipitated sample" (before any crystallization treatment, just dried at 60º C and vacuum for two days) and the red coloured spectrum shows the spectrum of P6DMT(D+L) after thermal treatment at 160º C for one hour. As can be seen, the red and blue spectra are nearly identical, suggesting complete crystallization for the "as precipitated" sample.
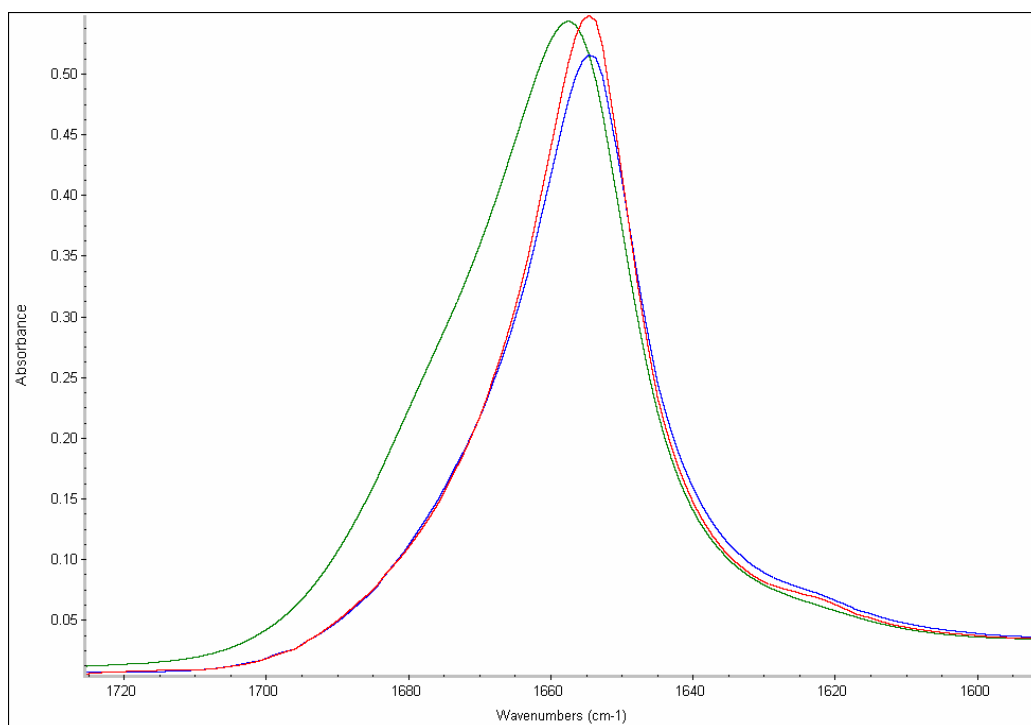
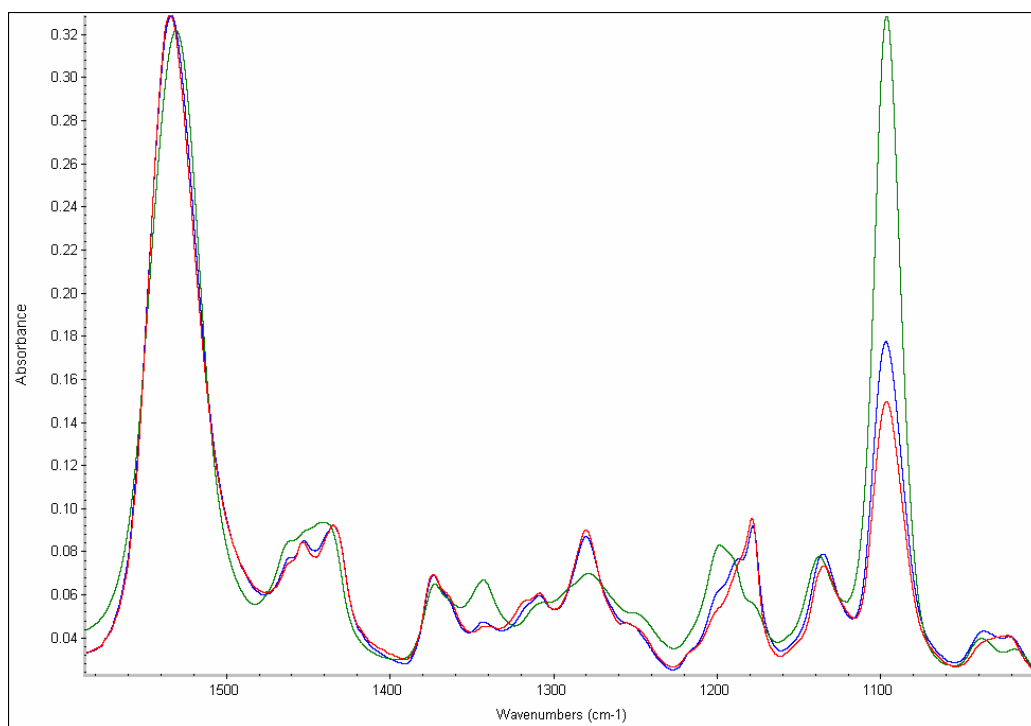Figure 4. FTIR spectra in the C=O stretching region (see text).

Figure 5. FTIR spectra in the 1000-1600 cm^{-1} region (see text).

References

1. Wu, D.; Chen, A.; Johnson, C.S. *J. Magn. Reson. A* **1995**, 115, 260.
2. Esturau, N.; Sánchez-Ferrando, F.; Gavin, J.A.; Roumestand, C.; Delsuc, M.A. *J. Magn. Reson.* **2000**, 142, 323.