Chain Structure and β Conformation of Poly (9,9-dioctylfluorene) (PFO) with Different Molecular Weight Delivering from Solution to Film in Drop-casting Process

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Supporting information

1. The calculation method of the proportion of β-conformation in PFO film\(^1\).

The proportion of β conformation in PFO film can be calculated according to Lambert-Beer’s law (Eq. S1), where \(c_\alpha\) and \(c_\beta\) are the concentrations of α conformation and β conformation, respectively, \(A\) (obtained from experiments) is the absorbency and \(\varepsilon\) is the absorption coefficient. In UV-vis absorption spectra of PFO films, it is difficult to obtain the \(\varepsilon\) for α conformation and β conformation. Thus, we used the method of molecular simulation to the absorption spectra to calculate the proportion of \(\varepsilon_\beta/\varepsilon_\alpha^2\).

\[
\alpha\% + \beta\% = 1 \quad (S1)
\]

\[
\beta\% = \frac{c_\beta}{c_\beta + c_\alpha} = \frac{A_\beta \times \varepsilon_\alpha}{A_\beta \times \varepsilon_\alpha + A_\alpha \times \varepsilon_\beta} \quad (S2)
\]

By defining six monomer units as the conjugation length\(^3\), we optimized the symmetry geometries of PFO chains for the approximate calculation of \(\varepsilon\) using Density Functional Theory (DFT)\(^4\). To calculate the oscillator strengths (f), Time-Dependent Density Functional Theory (TD-DFT) was used\(^5\), as this method has been found to give reliable results\(^6\). DFT and TD-DFT are both with a B3LYP hybrid functional basis set level of 6-31G\(^*\). All calculations were performed using the Gaussian 03 package\(^7\). The oscillator strengths (f) of the two conformations are 4.46 for
α conformation at 386 nm and 4.83 for β conformation at 437 nm. Thus, the proportion of ε_β/ε_α can be obtained from Eq. S3 and Eq. S4, where k is a constant and ν is the vibration frequency of two conformations. We can approximately calculate the proportion of β conformation in each UV-vis absorption spectra of PFO films using Eq. S2 and Eq. S4. Then the proportion of α conformation can be easily got by Eq. S1.

\[ f = k \int \varepsilon dv, \quad f \propto \varepsilon \]  \hspace{1cm} \text{(S3)}

\[ \frac{\varepsilon_\beta}{\varepsilon_\alpha} = \frac{f_\beta}{f_\alpha} = \frac{4.83}{4.46} = 1.08 \]  \hspace{1cm} \text{(S4)}

2. Calculation method of the aggregates of fractal dimension (d_f) in solution by static light scattering (SLS)

In solution, the scattering intensity of polymer aggregates has the following power relationship with the test angle:

\[ I(q) = \left(\frac{K}{R_s}\right) C M_{app} (q R_{app})^{-d_f} \]

Where \( I(q) \) is the scattering light intensity, \( K \) is a constant factor, \( R_s \) is the solvent Rayleigh ratio, \( C \) is the polymer concentration, \( q \) is the scattering vector and \( M_{app} \) and \( R_{app} \) are the apparent mass and apparent radius, respectively. The fractal dimension \( d_f \) of the aggregation can be obtained from \( I(q) \) and \( q^{-d_f} \).

3. Influence of Concentration on the β Conformation Formation of PFO in pure THF solvent.
4. Relationship between the volatilization time and the $\beta$ conformation contents which were calculated from Figure 9a and Figure 9c.

Table S1. the $\beta$ conformation contents which were calculated from the normalized UV-vis absorption spectra of the films with the change of volatilization time when the initial concentration was 10 mg/mL and 20 mg/mL.

<table>
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<th>Volatilization time</th>
<th>0s</th>
<th>30s</th>
<th>60s</th>
<th>90s</th>
<th>120s</th>
<th>150s</th>
<th>180s</th>
<th>210s</th>
<th>240s</th>
<th>270s</th>
<th>300s</th>
<th>330s</th>
<th>360s</th>
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<tr>
<td>10mg/mL</td>
<td>0</td>
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<td>29.0</td>
<td>32.8</td>
<td>34.5%</td>
<td>35.4%</td>
<td>35.9%</td>
<td>36.2%</td>
<td>36.3%</td>
<td>36.4%</td>
<td>36.5%</td>
<td>36.5%</td>
</tr>
<tr>
<td>20mg/mL</td>
<td>0</td>
<td>8.6%</td>
<td>26.3%</td>
<td>34.8</td>
<td>36.7</td>
<td>37.0%</td>
<td>37.2%</td>
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<td>37.3%</td>
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REFERENCES


(3) Ng, M. F.; Sun, S. L.; Zhang, R. Q. *J. Appl. Phys.* 2005, 97, 103513.


