

Demonstrating the δ_1 -Helicity and Nanomechanical Function of Self-Organizable Dendronized Polymethacrylates and Polyacrylates

Katerina A. Andreopoulou,[†] Mihai Peterca,^{†,‡} Daniela A. Wilson,[†] Benjamin E. Partridge,[†] Paul A. Heiney,[‡] and Virgil Percec^{†,*}

[†]Roy & Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, United States

[‡]Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6396, United States

*E-mail: percec@sas.upenn.edu; tel.: +1-215-573-5527; fax.: +1-215-573-7888

Table of Contents

1. Cu-Catalyzed Radical Polymerization of First Generation Dendritic Monomers	S2
Table ST1	S2
2. Modeling of “Drop-Downs” in Polymer Backbone in δ_0- and δ_4-Columns	S3
Figure S1	S3
3. Optical Microscopy of 12-CH₂O-PMA	S4
Figure S2	S4
Figure S3	S4
4. Self-Assembly of Chiral Dendronized Monomers and Polymers Investigated by CD and UV..	S5
Figure S4	S5
Figure S5	S6
Figure S6	S6

1. Cu⁰-Catalyzed Single-Electron Transfer Living Radical Polymerization (SET-LRP) of First Generation Dendritic Monomers

Table ST1. Experimental Parameters for Cu⁰-Catalyzed SET-LRP of First Generation Dendritic Monomers at 23 °C

Polymer	[M] ₀ /[I] ₀ /[Cu ⁰] ₀ /[L] ₀	Solvents (v, mL)	M _n (th) (g/mol)	M _n (GPC) (g/mol)	M _w /M _n	Time (h)	Conv. (%)
12-4EO-PMA (11)	5/(CH ₃) ₂ CBr(CO ₂ Et)/Cu ⁰ /bpy 20:1:1:3	DMSO (0.3) THF (0.5)	24835	16370	1.65	24	94%
12-4EO*-PMA (12)	6/(CH ₃) ₂ CBr(CO ₂ Et)/Cu ⁰ /bpy 20:1:1:3	DMSO (0.3) THF (1.0)	25195	30230	1.70	24	80%
12-CH ₂ O-PMA (13)	7/(CH ₃) ₂ CBr(CO ₂ Et)/Cu ⁰ /bpy 20:1:1:3	DMSO (0.25) THF (0.45)	21115	17568	1.78	24	93%
16-4EO-PMA (14)	8/PhC(O)CHCl ₂ /Cu ⁰ /PMEDA 20:1:1:1	DMSO (0.2) cyclohexane (1.0)	28309	90600	1.85	21	98%
12-4EO-PAc (15)	9/CH ₃ CHBr(CO ₂ Me)/Cu ⁰ /Me ₆ -TREN 20:1:1:1	DMSO (0.3) DME (0.5)	24607	11280	1.34	24	55%
12-4EO*-PAc (16)	10/CH ₃ CHBr(CO ₂ Me)/Cu ⁰ /Me ₆ -TREN 20:1:1:1	DMSO (0.3) THF (1.0)	24887	7020	1.20	24	37%

2. Modeling of “Drop-Downs” in Polymer Backbone in δ_0 - and δ_4 -Columns

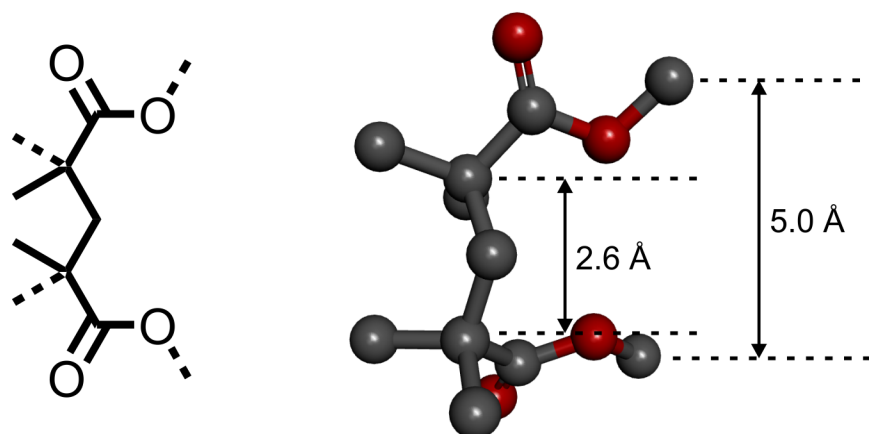


Figure S1. Model showing a conformation of the polymethacrylate backbone which separates adjacent dendrons by 5 Å. This conformation might be required to provide the “drop-downs” required in the δ_0 - and δ_4 column models (Figure 2).

3. Optical Microscopy of 12-CH₂O-PMA

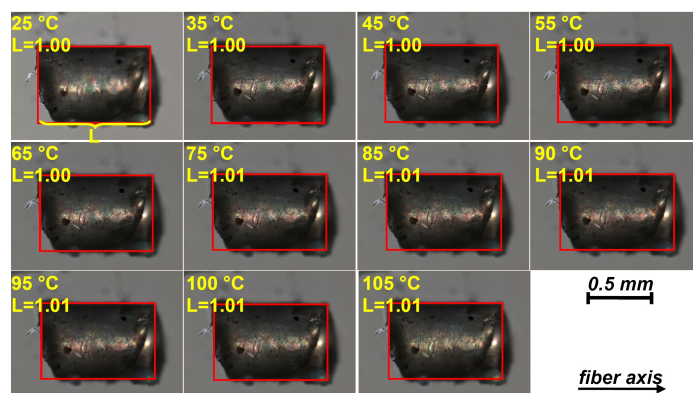


Figure S2. Macroscopic thermal expansion of an oriented fiber of 12-CH₂O-PMA. Temperature and length relative to length at 25 °C, *L*, are indicated.

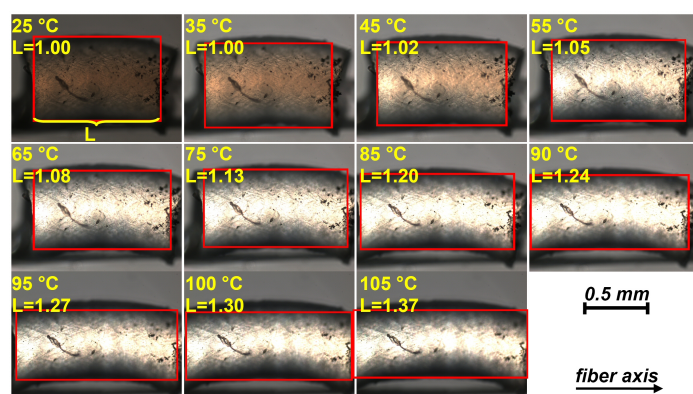


Figure S3. Macroscopic thermal expansion of an oriented fiber of 16-4EO-PMA. Temperature and length relative to length at 25 °C, *L*, are indicated.

4. Self-Assembly of Chiral Dendronized Monomers and Polymers Investigated by CD and UV

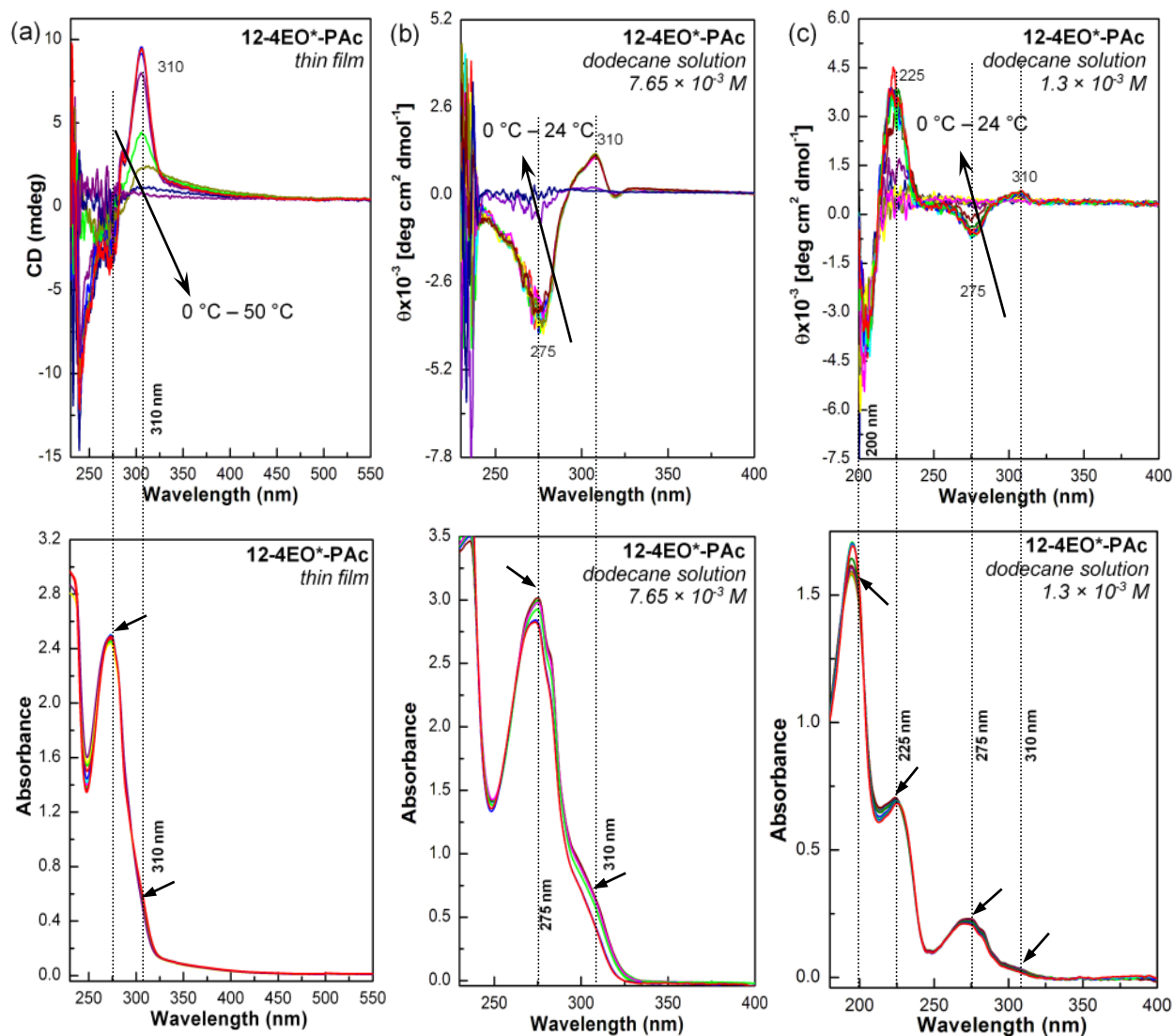


Figure S4. Temperature dependence of the (top) CD and (bottom) UV spectra of 12-4EO*-PAC in (a) spin-coated film cast from hexane (1.1 %, w/v), (b) dodecane solution (7.65×10^{-3} M), and (c) dodecane solution (1.3×10^{-3} M). Arrows indicate trends upon increasing temperature.

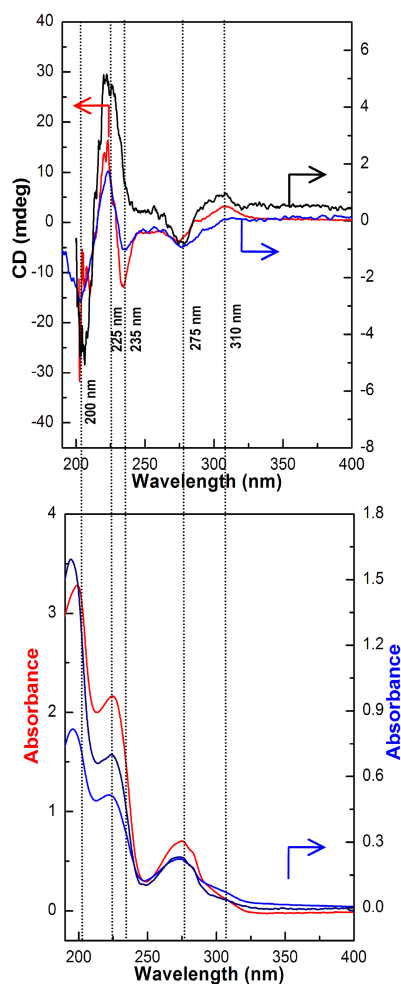


Figure S5. Comparison of the (top) CD and (bottom) UV spectra at 0 °C of 12-4EO*-PMA cast by spin-coating from hexane (3.2 %, w/v; **red line**), 12-4EO*-PAC in spin-coated film cast from hexane (1.1 %, w/v; **blue line**), and 12-4EO*-PAC in dodecane solution (1.3×10^{-3} M; **black line**).

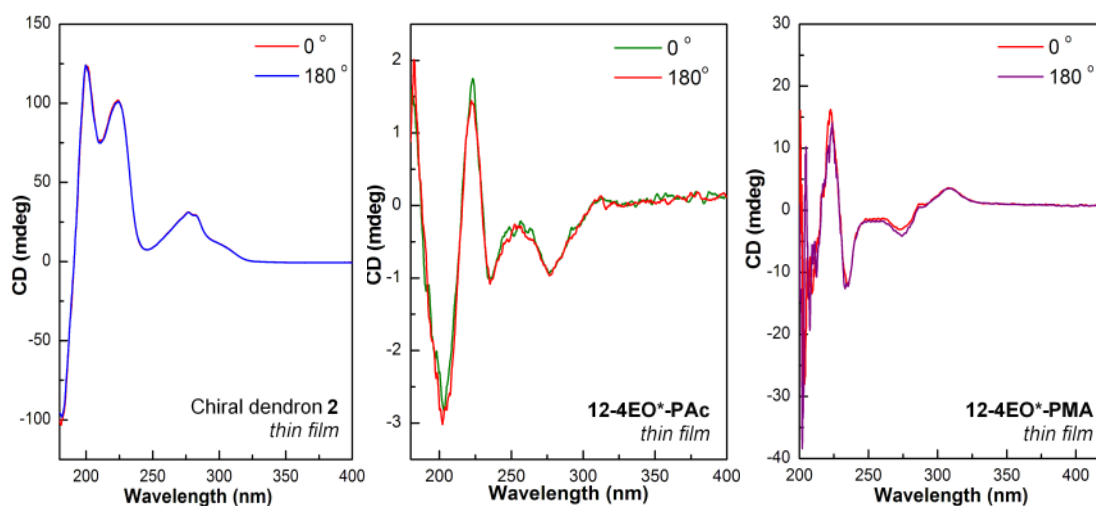


Figure S6. CD spectra recorded at relative rotations of 0° and 180° to verify the absence of linear dichroism of (left to right) chiral dendron 2, 12-4EO*-PAC, and 12-4EO*-PMA.