

Supporting information

Substitution Position Effect on Photoluminescence Emission and Chain Conformation of Poly(diphenylacetylene) Derivatives

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Experimental Methods

1) Materials:

The *p*- and *m*-PTMSDPA polymers were synthesized according to the previous reports (refs. 10, 11 in paper). The polymers used in this study have high weight-average molecular weights (M_w) of 4.18×10^6 and 5.23×10^6 g/mol, respectively, and polydispersity indices ($PDI = M_w/M_n$) of 2.5 and 3.2, respectively.

2) Preparation of polymer solutions and films:

The polymers were dissolved in toluene to prepare highly dilute solutions with concentrations of less than $< 1.0 \times 10^{-5}$ M. The polymers were dissolved in toluene to prepare films with thickness of about 30 nm by using spin-coating method.

3) Measurements:

The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of *p*- and *m*-PTMSDPA were evaluated using gel permeation chromatography (GPC, Shimadzu A10 instruments, Polymer Laboratories, PLgel Mixed-B (300 mm in length) as a column, and HPLC-grade tetrahydrofuran as eluent at 40 °C), based on a calibration with polystyrene standards. UV-vis absorption spectra were measured on a JASCO V-650 spectrophotometer, and photoluminescence spectra were recorded on a JASCO ETC-273 spectrofluorometer. Photoluminescence quantum yields of *p*- and *m*-PTMSDPA in toluene solution were

determined relative to quinine sulfate solution in 1N H₂SO₄. The solid state quantum yields were obtained relative to 9,10-diphenylanthracene in poly(methyl methacrylate) (PMMA) matrix ($\Phi_{re} = 0.83, 10^{-3}$ M). XRD measurements were performed at room temperature using a X-ray diffractometer (PANalytical X'Pert PRO-MPD) in Korea Basic Science Institute (Daegu). The samples were mounted directly into the diffractometer. The experiment was carried out using CuK α (1.54Å) radiation operating at 40kV and 25mA. The time-resolved emission spectra were measured on a streak camera using a femtosecond laser pulse from an optical parametric amplifier (Hamamatsu Photonics C4780). The center wavelength of 420 nm was used as the excitation light source. The width of the laser pulse was approximately 3 nm and the repetition rate was 5 nsec. These measurements were conducted at room temperature in air. Low energy conformations of both *p*- and *m*-PTMSDPA polymers were searched for 10-mer model compounds by molecular mechanics using MMFF force fields with Monte Carlo minimization procedures, and their equilibrium geometries were obtained using AM1 semi-empirical calculation as implemented in the Spartan program (Spartan'08 (Version 1.0.0), Wavefunction, Inc., www.wavefun.com). The intrinsic viscosity-molecular weight relationship was obtained using an in-line configured viscometer (Viscotek T60A) and an SEC instrument (in THF at 40 °C). The viscosity index volume, α was obtained by $[\eta] = KM^\alpha$ from the Mark-Houwink-Sakurada plot on the basis of the universal calibration curve, where $[\eta]$ is the intrinsic viscosity and M is the absolute molecular weight. The α values of *p*-PTMSDPA and *m*-PTMSDPA were determined in a range of $2.5 \times 10^5 \sim 2.5 \times 10^6$ g/mol and $1.0 \times 10^5 \sim 1.0 \times 10^6$ g/mol, respectively. High-speed (rapid scan) AFM (NVB500, Olympus, Tokyo) was used for single-molecules imaging in the tapping mode with a soft small cantilever (BL-AC7EGS, Olympus) having a spring constant of 0.2 N/m and a resonance frequency of 1 MHz in a liquid. Polymers were dissolved in tetrahydrofuran to prepare ca. 1.0×10^{-6} mol/L concentration solutions. A mica film was used as the substrate. The polymer solutions were cast onto the mica substrate surfaces. Single-molecules imaging was carried out in decamethyltetrasiloxane at room temperature. The setpoint of the amplitude was set to 0.9 for a soft tapping.

Figure S1 UV-visible absorption and PL emission (excitation wavelength 430 nm) spectra of *p*- and *m*-PTMSDPA in a) solution ($c = 1.0 \times 10^{-5}$ mol/L in toluene) and b) film (prepared by spincoating method; thickness 10 nm) (solid: absorption; open: PL emission; circle: *p*-PTMSDPA; square: *m*-PTMSDPA).

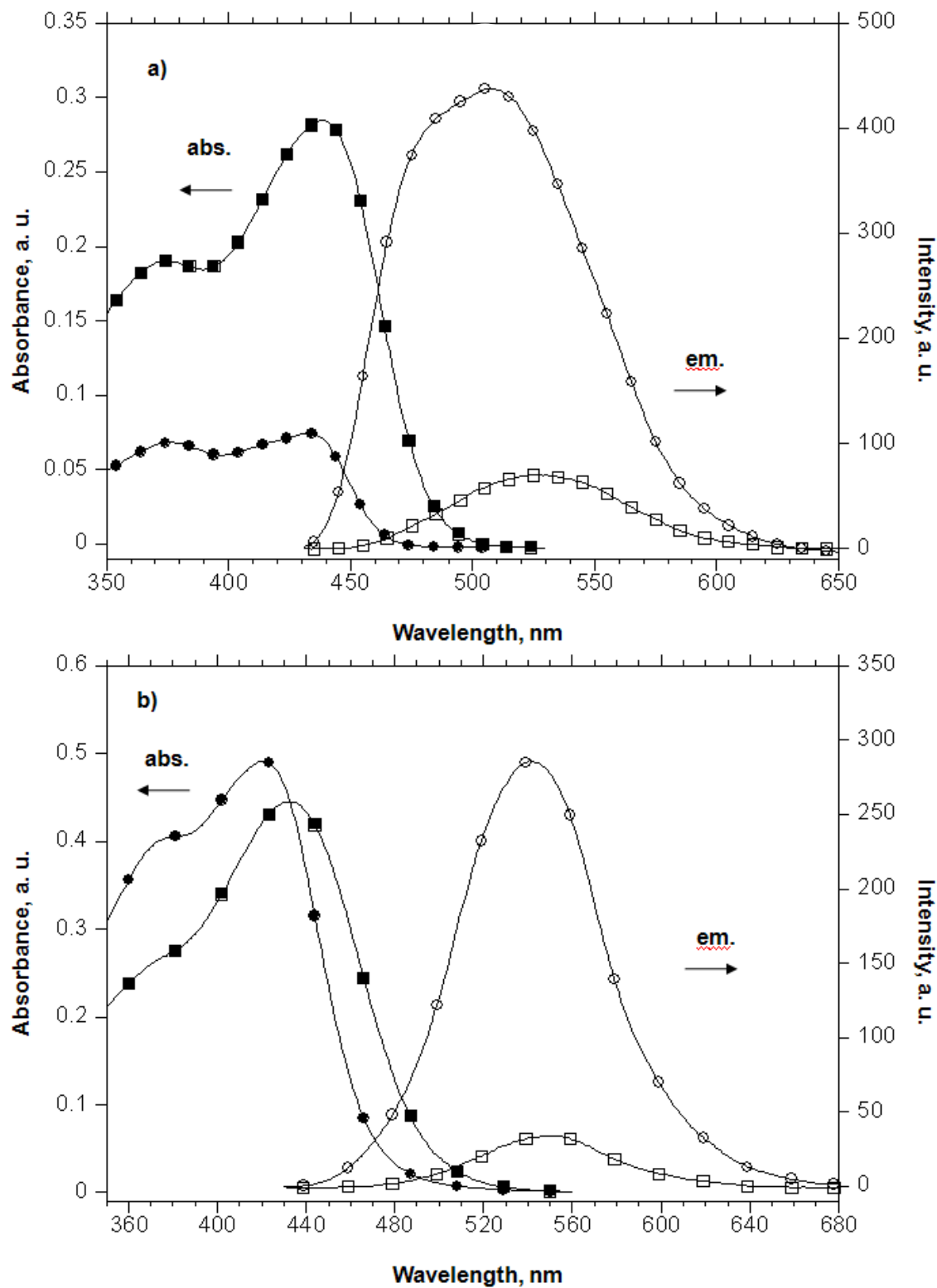


Table S1. Fluorescence Lifetimes of *p*-PTMSDPA and *m*-PTMSDPA in Films and Toluene Solutions^a

Polymer	in film				in toluene			
	$\tau_1 (f_1)$	$\tau_2 (f_2)$	$\tau_3 (f_3)$	χ^2	$\tau_1 (f_1)$	$\tau_2 (f_2)$	$\tau_3 (f_3)$	χ^2
<i>p</i> -PTMSDPA	0.167 (0.70)	0.538 (0.26)	1.586 (0.04)	2.270	–	0.611 (0.92)	1.286 (0.08)	2.994
<i>m</i> -PTMSDPA	0.094 (0.89)	0.336 (0.10)	1.304 (<0.01)	2.948	–	0.114 (0.99)	0.481 (<0.01)	8.004

^a monitor wavelength is 550 nm, τ_1 , τ_2 and τ_3 are lifetimes (nsec), f_1 , f_2 and f_3 are fractional intensities, χ^2 is the reduced chi-square, the films were prepared by spincoating method (thickness 10 nm), the solution concentration (*c*) was fixed at 1.0×10^{-6} mol/L.

Detailed description on photophysical properties

In the Tsuchihara's reports^{1,2}, the spectrum analysis was not described in detail. At first, we re-investigated the photophysical properties of both *p*- and *m*-PTMSDPA. **Figure S1** shows the UV-visible absorption and PL emission spectra of *p*- and *m*-PTMSDPA in a) solution and b) film. Both polymers show two characteristic absorption maxima in solution: $\lambda_{\max, \text{abs}}$ 375 nm (ϵ_{\max} 2595 M⁻¹cm⁻¹) and 430 nm (2908 M⁻¹cm⁻¹) for *p*-PTMSDPA; $\lambda_{\max, \text{abs}}$ 375 nm (ϵ_{\max} 4016 M⁻¹cm⁻¹) and 440 nm (5823 M⁻¹cm⁻¹) for *m*-PTMSDPA. The absorption band of *m*-PTMSDPA appears at a longer wavelength as compared to that of *p*-PTMSDPA. The molar absorptivity of *m*-PTMSDPA is approximately 2 times larger than that of *p*-PTMSDPA. The yellow color of *m*-PTMSDPA in a solution was actually much darker than that of *p*-PTMSDPA in a solution at the same concentration. Their emission maxima wavelengths ($\lambda_{\max, \text{em}}$) are 504 and 528 nm, respectively. The *p*-PTMSDPA shows about 10 times more intense emission relative to the *m*-PTMSDPA in the same concentration. The same tendency is also shown with their films as displayed in Figure S1b.

Study on the time-resolved emission decay helps us to further comprehensively understand the dynamic fluorescence property of the polymers. **Table S1** summarizes the fluorescence lifetimes of *p*- and *m*-PTMSDPA in films and solutions. The photoemission decays of both polymers in films obeyed triexponential decay, while biexponential was required to adequately fit the observed decay dynamics in a solution. Their emissions in films are characterized by a shorter dominant fluorescence lifetime (τ_1) rather than longer ones (τ_2 , τ_3), whereas the emissions in solutions comes exclusively from the longer-lived excited species. The shorter-lived emission excited species of the film was presumably due to a rapid energy transfer into the energy trapping sites. It should be also noted that the dominant fluorescence lifetimes (0.167 ns in film; 0.611 ns in toluene) of *p*-PTMSDPA are much longer than those (0.094 ns in film; 0.114 ns in toluene) of *m*-PTMSDPA. This result well agrees with the facts that the steady state fluorescence properties of *p*- and *m*-PTMSDPA are very different, that is, the $\lambda_{\max, \text{em}}$ of *p*-PTMSDPA is shorter, and the emission intensity is much greater than are those of *m*-PTMSDPA.

Reference

1. K. Tsuchihara, T. Masuda, T. Higashimura, *J. Am. Chem. Soc.* 1991, **113**, 8548.
2. K. Tsuchihara, T. Masuda, T. Higashimura, *Macromolecules* 1992, **25**, 5816.

Figure S2. PL emission spectrum of unsubstituted poly(diphenylacetylene) in film (excitation wavelength 430 nm, thickness $\approx 20 \mu\text{m}$).

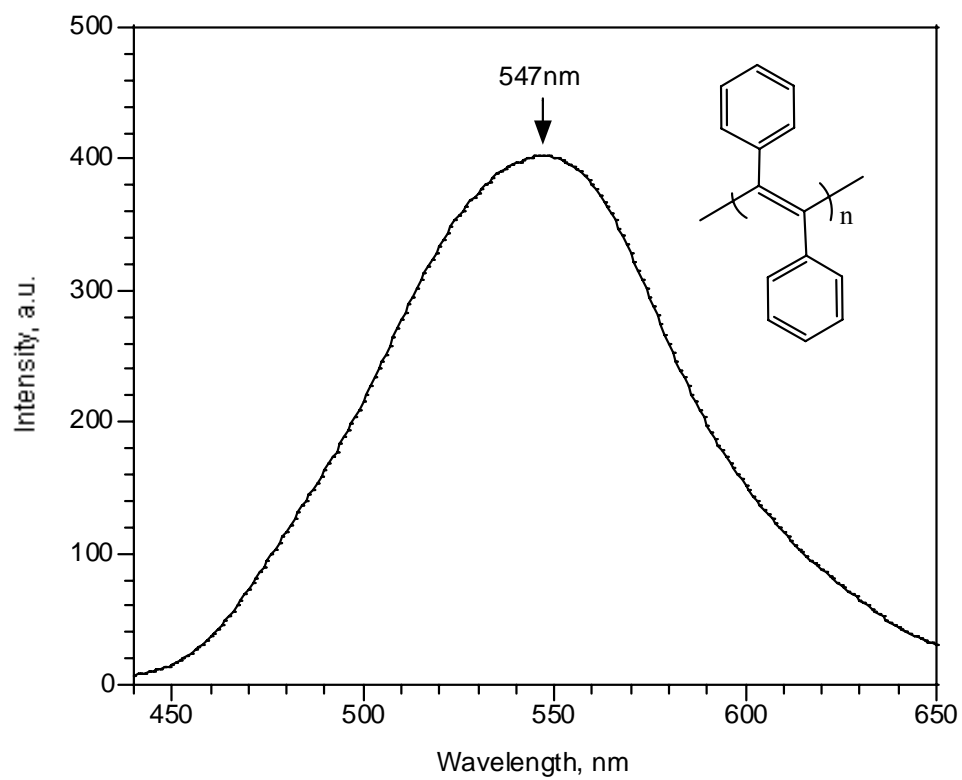


Figure S3. X-ray diffraction (XRD) patterns of *p*-PTMSDPA and *m*-PTMSPDA in cast film (thickness $\approx 30 \mu\text{m}$).

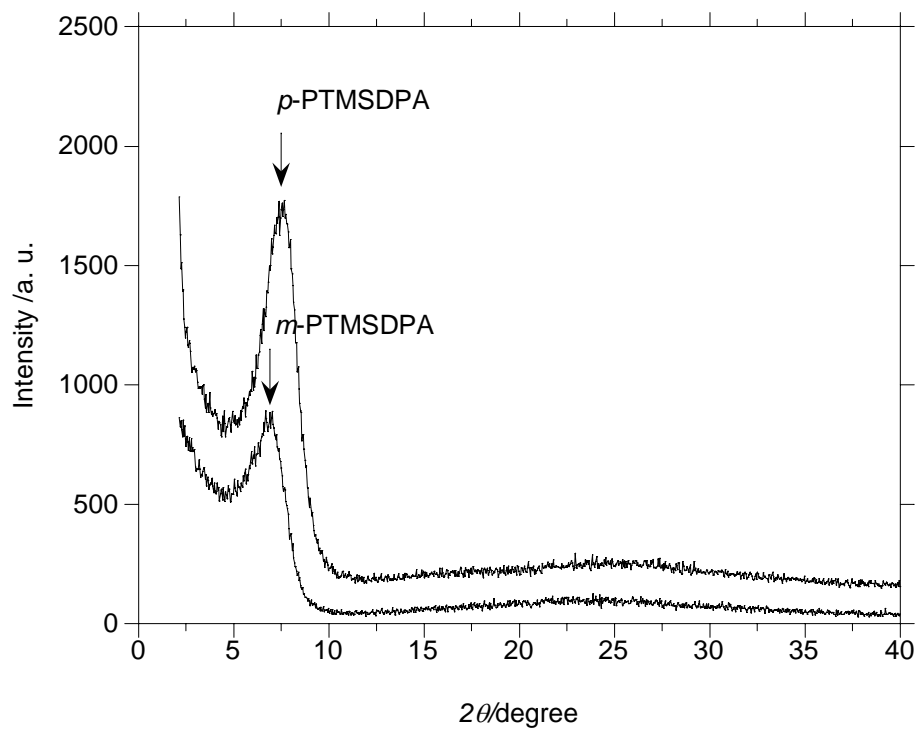


Figure S4. Schematic representation for the zigzag structure and the dihedral angle in the energy-minimized structure of 10-mer model compound of *p*-PTMSDPA polymers as obtained with AM1 geometry. Side views is shown as space-filling model, in which carbon atoms appear in gray, silicons in red, and hydrogens in white. For viewing clarity, hydrogen atoms are omitted for the top views in tube model.

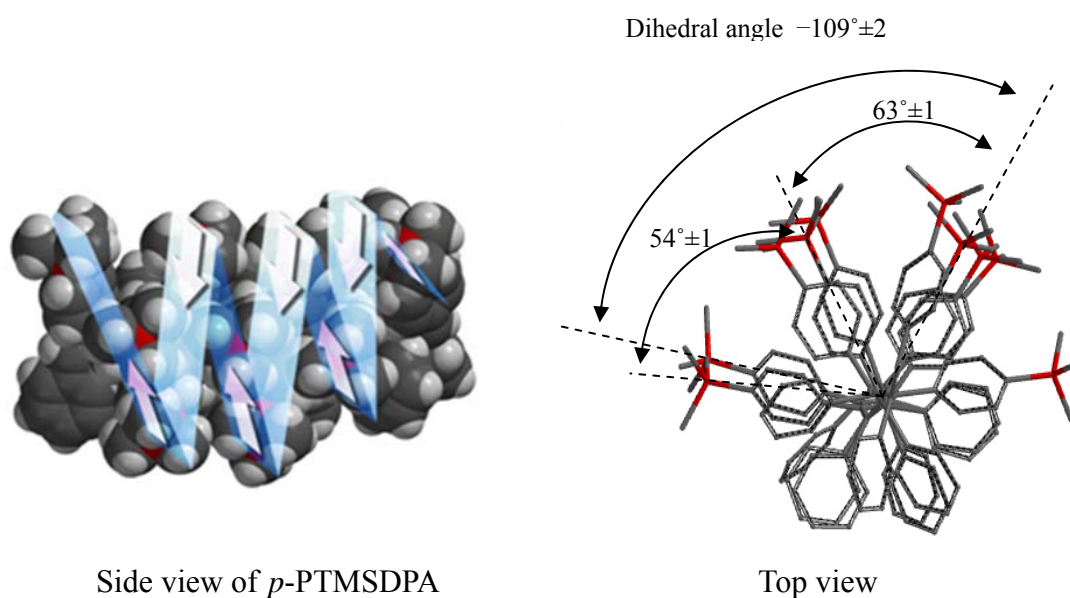


Figure S5. Schematic representation for the helix-like structure and the dihedral angle in energy-minimized structure of 10-mer model compound of *m*-PTMSDPA polymers as obtained with AM1 geometry. Side view are shown as space-filling model, in which carbon atoms appear in grey, silicons in red, and hydrogens in white. For viewing clarity, hydrogen atoms are omitted for the top views in tube model. *p*-PTMSDPA

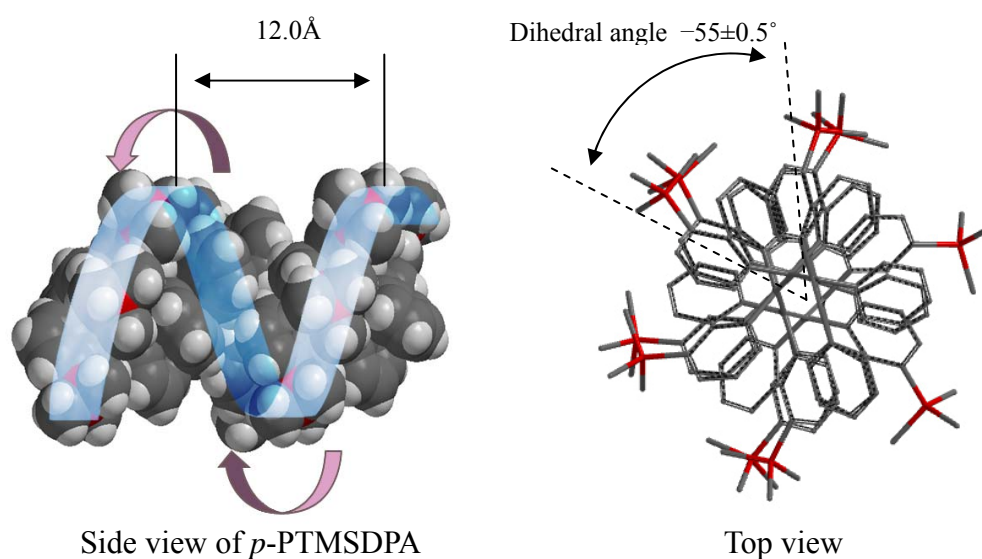
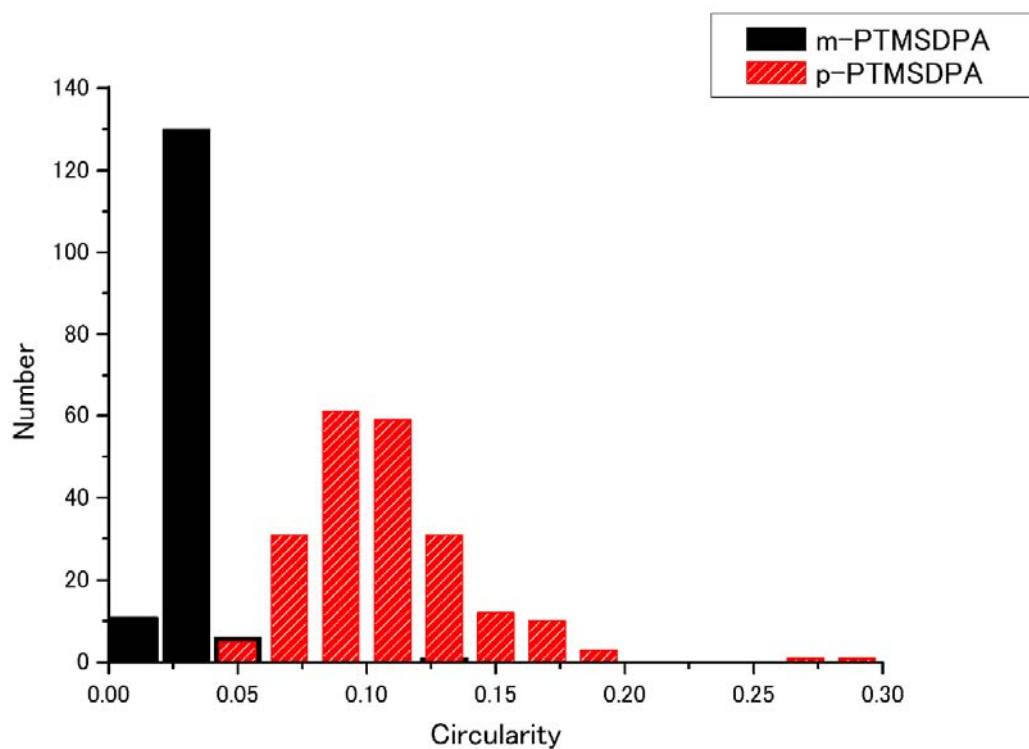


Figure S6. Histogram of the circularity distribution of *m*- and *p*-PTMSDPA that was measured based on the high-speed AFM images in Movies S1 and S2. The circularity of the meta-polymer is much smaller than that of the para-polymer. If the circularity is 0, the polymer would be an ideal rod molecule. If the circularity is 1.0, the polymer would be an ideal sphere molecule. This indicates that *m*-PTMSDPA is closer to rigid rod-like molecules while *p*-PTMSDPA is closer to globule molecules.



Movie S1. High-Speed AFM movie of a single-molecule of *m*-PTMSDPA on mica in decamethyl tetrasiloxane at room temperature. The scanning size is 236 x 177 nm². The scanning rate is 10.0 frames per second.
<http://webbuild.knu.ac.kr/~gkwak/m-PTMSDPA.avi>

Movie S2. High-Speed AFM movie of a single-molecule of *p*-PTMSDPA on mica in decamethyl tetrasiloxane at room temperature. The scanning size is 262 x 197 nm². The scanning rate is 19.9 frames per second.
<http://webbuild.knu.ac.kr/~gkwak/p-PTMSDPA.avi>