

Supporting Information

Temperature Controlled Dispersion of Carbon Nanotubes in Water with Pyrene-Functionalized Poly(N-cyclopropylacrylamide)

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1. Experimental

1.1 Materials and Methods

All chemicals and solvents were commercially available and used as received unless otherwise stated. Tetrahydrofuran (THF) was distilled over sodium. Spectra/Por 3 (MWCO 3500) were used as dialysis membranes. Poly(pentafluorophenylacrylate) PPFPA with a molecular weight of 25000 g/mol ($M_w/M_n = 1.32$) was synthesized according to a previously reported procedure.¹ p-PNCPA with 5 mol% pyrene side groups was synthesized according to the Scheme 1 (shown in Section 2). Raw single-walled carbon nanotubes (SWNTs) [batch number R0487] were purchased from Carbon Nanotechnologies (Houston, TX), containing 27 wt% impurity (mostly Fe-based catalyst). These nanotubes were used without further purification. SWNT suspensions were prepared by mixing dry SWNTs in 0.1 wt% aqueous solutions of p-PNCPA, followed by sonication for 10 minutes at 50 W using a VirTis Virsonic 100 ultrasonic cell disrupter (SP industries, Warminster, PA). Composites of p-PNCPA/SWNT were made by drying 5 ml of suspension on a quartz slide at a given temperature.

1.2 Characterization

All ¹H-NMR spectra were recorded on a Bruker 300 MHz FT-NMR spectrometer in deuterated solvents. Chemical shifts (δ) were given in ppm relative to TMS. Gel permeation

chromatography (GPC) was performed in THF to determine molecular weights and molecular weight distributions (M_w/M_n) of polymer samples with respect to polystyrene standards. Calibration was done using polystyrene standards. UV/Vis spectra were recorded on a Jasco V-630 photo spectrometer. Fluorescence measurements were performed on a Perkin Elmer LS 50B luminescence spectrometer. IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer using an ATR unit. FD-masses were measured on a MAT 95 Finnigan mass spectrometer.

Cryo-TEM images were taken with an FEI Tecnai G2 F20 operated at 200 kV equipped with cryogenic accessories. The samples were frozen in liquid ethane using an FEI Vitrobot apparatus. Images were recorded with a Gatan Tridiem GIF-CCD camera attached to the microscope. Viscosity of the suspensions as function of shear rate was measured using an AR-G2 rheometer (TA Instruments, Newcastle, DE) equipped with 40 mm parallel plate geometry. A gap of 1000 μm was maintained as per the recommended procedure for the instrument. This rheometer is equipped with a Peltier control system that provides accurate control ($\pm 0.1^\circ\text{C}$) of temperature between 10 and 90°C . Turbidity (actually decadic absorbance at 400 nm) measurements were made with a USB2000 UV/Vis spectrometer (Ocean Optics, Dunedin, FL) using a quartz cuvette. Scanning electron microscopy was performed with a FEI Quanta 600 FE-SEM on composites coated with a 5 nm layer of Pt/Pd. Sheet resistance of the composites was measured using a custom-built 4-point probe apparatus. The details of the instrument and measurement technique has been published elsewhere.² The data presented in Table 1 are the average values of 10 measurements per sample. Volume conductivity was calculated by taking the inverse of the product of the sheet resistance and composite thickness. Hydrodynamic radius of p-PNCPA was measured using a Zeta Phase Angle Light Scattering (PALS) instrument

(Brookhaven Instruments Corporation, Holtsville, NY) equipped with a 90 Plus particle sizing accessory and a temperature control system that provides accurate temperature control from 6 to 100°C, with an accuracy of $\pm 0.1^\circ\text{C}$. All measurements were made in a glass cuvette at a detection angle of 90° .

2. Synthesis

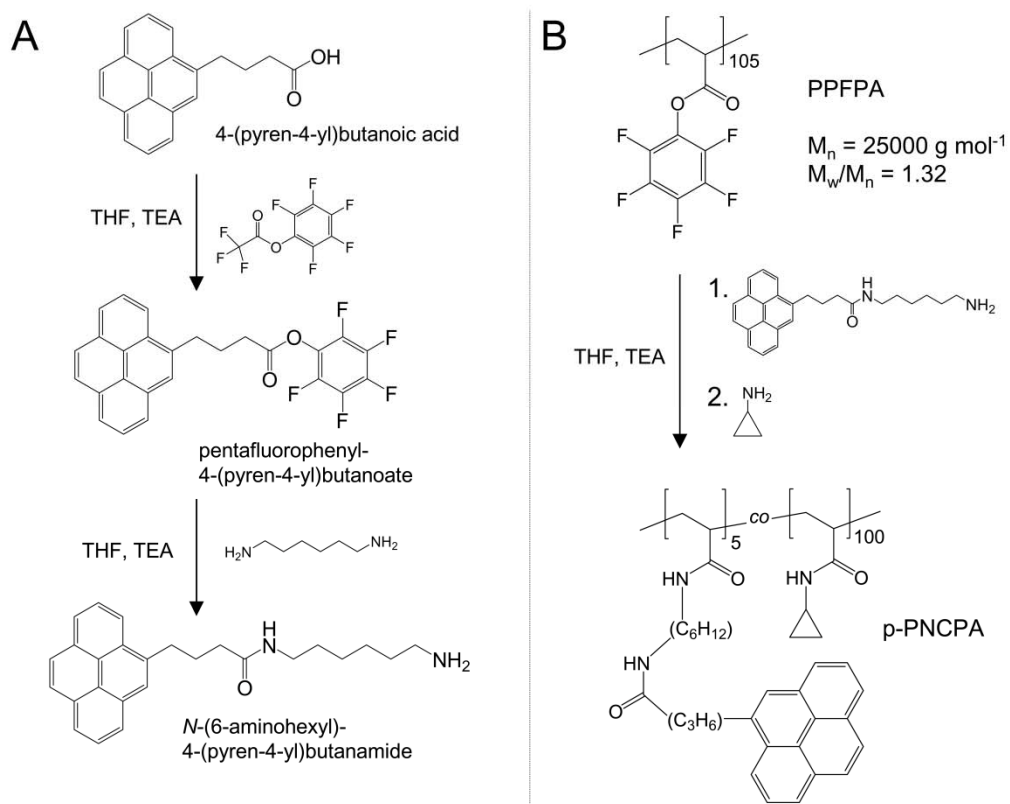
2.1 Synthesis of pentafluorophenyl-4-(pyren-4-yl)butanoate (see scheme 1, route A). 3.00 g (0.010 mol) 4-(pyren-4-yl)butanoic acid and 4.31 mL (0.031 mol) triethylamine (TEA) were dissolved in 25 mL dry THF and 8.74 g (0.031 mol) pentafluorophenyl trifluoroacetate was added drop wise. The solution was stirred for 12 h at room temperature, then diluted with 300 mL dichloromethane and transferred into a separation funnel. The organic phase was washed three times with 50 mL of water, dried with sodium sulfate and concentrated in vacuum. The product was isolated through precipitation into hexane. After filtration and drying in vacuum at 40°C , 3.23 g (0.0071 mol – 71 %) yellow colored pentafluorophenyl-4-(pyren-4-yl)butanoate was obtained. $^1\text{H-NMR}$ (CDCl_3): δ /ppm: 8.27 (d, 1H), 8.13 (m, 4H), 8.03 (s, 2H), 7.99 (t, 1H), 7.86 (d, 1H), 3.47 (t, 2H), 2.77 (t, 2H), 2.32 (quin, 2H); FT-IR (ATR-mode): 2944 cm^{-1} (C-H – valence), 1774 cm^{-1} (C=O reactive ester band), 1517 cm^{-1} (PFP - C=C aromatic band), 1100 cm^{-1} (C-O ester band); MS (FD) m/z (%): 454.3 (100.00), 455.3 (27.58), 456.3 (4.51)

2.2 Synthesis of N-(6-aminohexyl)-4-(pyren-4-yl)butanamide (see scheme 1, route A). 7.77 g (0.067 mol) hexamethylenediamine and 0.93 mL (0.0067 mol) TEA were dissolved in 80 mL dry THF and 3.04 g (0.0067 mol) pentafluorophenyl-4-(pyren-4-yl)butanoate dissolved in 30 mL dry THF was added drop wise. The solution was stirred for 12 h at room temperature, then diluted

with 400 mL dichloromethane and extracted four times with 80 mL of water, respectively. The organic phase was separated and dried with sodium sulfate. After removal of the solvent in vacuum, 2.07 g (0.0054 mol – 80 %) yellow colored *N*-(6-aminohexyl)-4-(pyren-4-yl)butanamide was obtained. ¹H-NMR (DMSO): δ /ppm: 8.35 (d, 1H), 8.22 (m, 4H), 8.10 (s, 2H), 8.02 (t, 1H), 7.90 (d, 1H), 7.83 (t, 1H), 3.29 (t, 2H), 3.06 (q, 2H), 2.46 (t, 2H), 2.24 (t, 2H), 2.00 (quin, 2 H), 1.35 (t, 2H), 1.23 (m, 6H); FT-IR (ATR-mode): 3300 cm⁻¹ (N-H – amide valence), 2928 cm⁻¹ (C-H – valence), 1643 cm⁻¹ (C=O amide band I), 1550 cm⁻¹ (C=O amide band II); MS (FD) m/z (%): 386.3 (89.14), 387.4 (58.24), 774.0 (100.00), 775.0 (62.55), 776.0 (3.09)

2.3 Synthesis of p-PNCPA (see Scheme 1, Route B). 2 g PPFPA and 2 mL (0.0143 mol) TEA were dissolved in 20 mL dry THF and 162 mg ($4.201 \cdot 10^{-4}$ mol) *N*-(6-aminohexyl)-4-(pyren-4-yl)butanamide was subsequently added. This solution was stirred 3 h under nitrogen atmosphere at room temperature. Afterwards, 2 mL (0.029 mol) cyclopropylamine was added. After an additional 12 hours of stirring, the solvent was removed by evaporation in vacuum. The residue was suspended in 10 mL of water and dialyzed against diluted ammonia for ~ 12 h. The clear dialyzed solution was evaporated and the residue was twice dissolved in 5 mL of methanol and precipitated into diethyl ether. After centrifugation and drying in vacuum at 40°C, 0.61 g of colorless p-PNCPA was obtained. ¹H-NMR (MeOD): δ /ppm: 8.13 (m), 3.21 (s), 2.71 (s), 2.38 (s), 2.06 (br s), 1.59 (br s), 0.67 (d); FT-IR (ATR-mode): 3280 cm⁻¹ (N-H – amide valence), 2940 cm⁻¹ (C-H – valence), 1643 cm⁻¹ (C=O amide band I), 1540 cm⁻¹ (C=O amide band II). *N*-(6-aminohexyl)-4-(pyren-4-yl)butanamide was synthesised in two steps. First, 4-(pyren-4-yl)butanoic acid was activated with pentafluorophenyl trifluoroacetate and then reacted with an

excess amount of hexamethylenediamine resulting in *N*-(6-aminohexyl)-4-(pyren-4-yl)butanamide (Route A). p-PNCPA was synthesized through a polymer analogous to PPFPA with *N*-(6-aminohexyl)-4-(pyren-4-yl)butanamide and cyclopropylamine (Route B).



Scheme 1. Overview of reactions described in detail in the above text.

3. ^1H -NMR Spectra of p-PNCPA

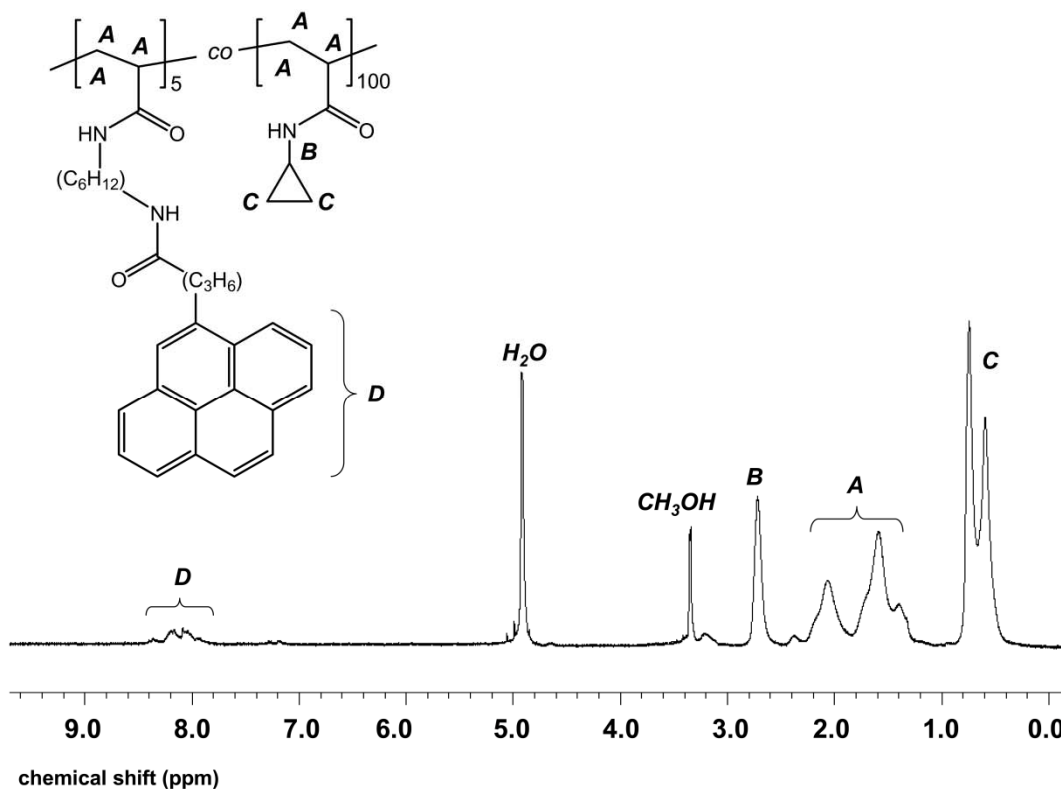


Figure S1. ^1H -NMR spectra of p-PNCPA measured in deuterated methanol.

^1H -NMR spectroscopy confirmed successful synthesis of the copolymer p-PNCPA. The characteristic signals of the aromatic pyrene side groups at 8.13 ppm, as well as the cyclopropylamide repeating units at 2.71 ppm and 0.67 ppm, were assigned. The amount of incorporated pyrene side groups was determined by calculating the ratio of the integrals of the aromatic pyrene protons and the single signal of the cyclopropyl proton at 2.71 ppm. However, the obtained value of 5 mol% pyrene fits to the calculated value demonstrating the efficiency of the polymer reaction.

4. UV/Vis Absorption and Fluorescence Emission Spectra of p-PNCPA

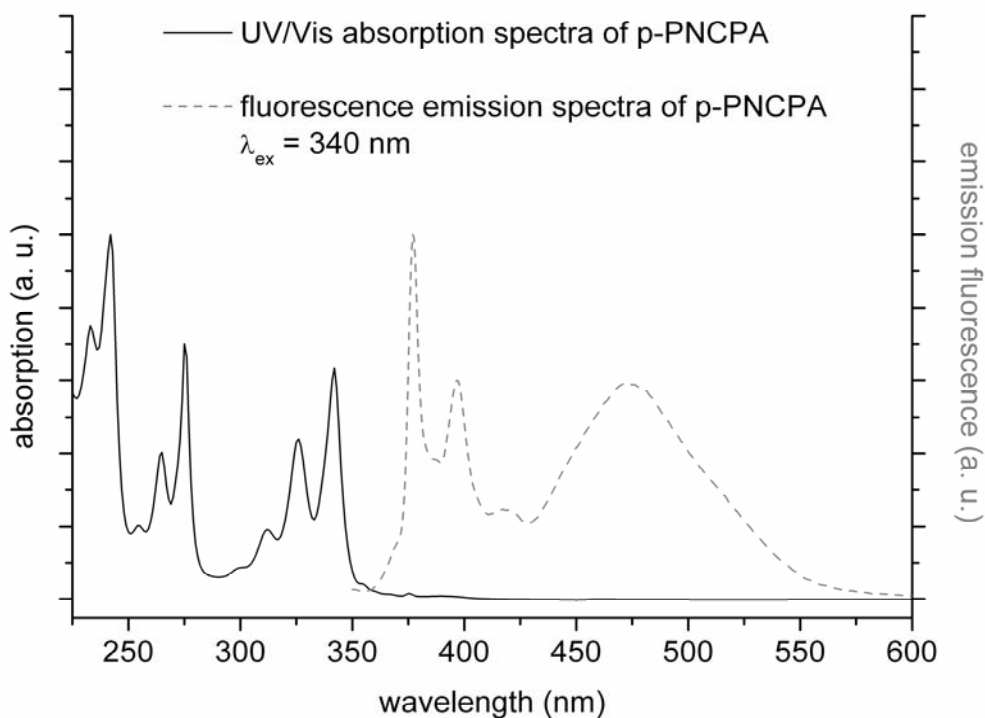


Figure S2. UV/Vis absorption and fluorescence emission spectra of p-PNCPA measured in methanol.

UV/Vis absorption (black solid curve, conc. 0.172 mg/mL in methanol) and fluorescence emission spectroscopy (grey dashed curve, conc. 0.00172 mg/mL in methanol, $\lambda_{\text{ex}} = 340 \text{ nm}$) were performed to investigate the synthesized p-PNCPA. Both spectra clearly show the characteristic peaks of the pyrene side groups of the copolymer, indicating a successful reaction.

5. Transition Temperature of p-PNCPA Using Dynamic Light Scattering (DLS)

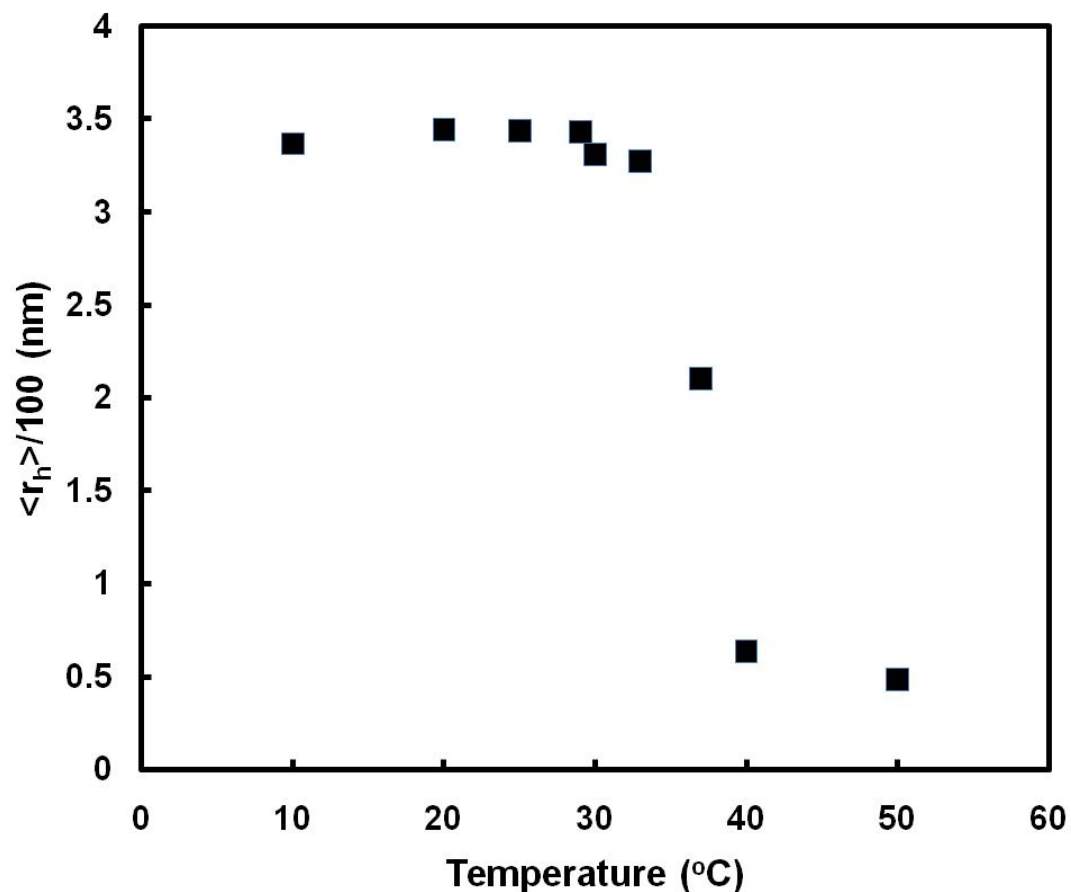


Figure S3. Hydrodynamic radius of p-PNCPA as a function of temperature in water. The concentration of p-PNCPA in the solution was 0.1 wt% and the scattering angle was set at 90°C.

In dynamic light scattering, the diffusive motion of particles in solution gives rise to fluctuations in the intensity of the scattered light on the μs timescale. The fluctuating signal is processed by forming an autocorrelation function, $g(\tau)$, where τ is the time delay. This experimentally obtained autocorrelation function is used to calculate the translational diffusion coefficient (D).

The hydrodynamic radius (R_H) of the polymer is then calculated using the Stokes- Einstein equation:

$$R_H = \frac{k_B T}{6\pi\eta(\tau)D} \quad (1)$$

where k_B is the Boltzmann's constant, T is temperature (in K), $\eta(\tau)$ is the viscosity of liquid medium and D is the translational diffusion coefficient. This procedure was carried out automatically in the program supplied with the instrument. The data shown in Fig. S3 is the average of 5 measurements. It can be seen that the R_H value of p-PNCPA is almost constant at temperatures below 30°C. At temperatures between 30 and 40°C, a sharp decrease in the radius of the polymer particles can be observed. This decrease is due to the coil-globule transition of the polymer.

4. Scanning Electron Microscopy

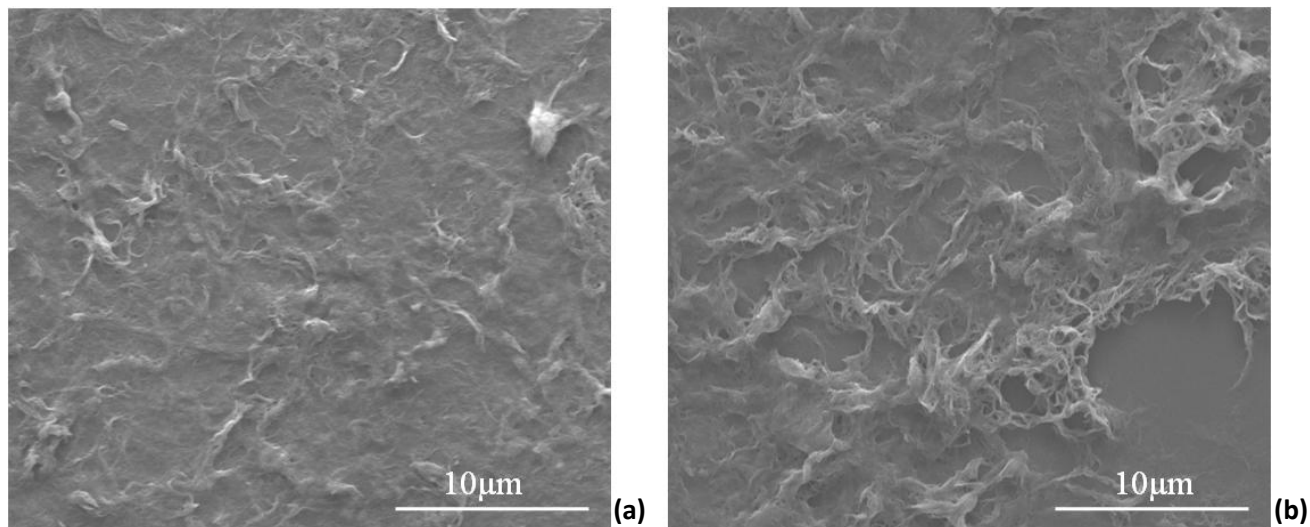


Figure S4. SEM images of p-PNCPA/SWNT composites dried at 20°C (a) and 50°C (b). SWNT concentration was 10 wt% in these composites.

It can be seen in Fig. S4 that SWNTs exist in a highly aggregated state in composites dried at 50°C, as compared to those dried at 20°C. It should be noted that SWNT concentration in these composites was 10 wt% and such high concentration results in aggregation of SWNTs, which is likely the reason for the observed aggregated microstructure in composites dried at 20°C.

References

- (1) Jochum, F. D.; Theato, P. *Polymer* **2009**, *in press*, doi:10.1016/j.polymer.2009.05.041.
- (2) Jan, C. J.; Walton, M. D.; McConnell, E. P.; Jang, W. S.; Kim, Y. S.; Grunlan, J. C. *Carbon* **2006**, *44*, 1974-1981.