Electronic Supplementary Material (ESI) for Polymer Chemistry.

ELECTRONIC SUPPLEMENTARY INFORMATION

Enhanced stability of conductive polyacetylene in ladder-like surface-grafted brushes

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Characterization of mixed SAMs on gold containing DS-DTCA photoiniferter and ODT

In order to evaluate the content of active photoiniferter groups in the mixed SAMs formed from the feed solutions containing DS-DTCA and inert ODT thiol in various ratios, FTIR spectra of the formed monolayers samples were recorded (figure S1). The ratios of the integral intensities (A) of the bands assigned to -NH- group (3251 cm^{-1}) and -CH_2- group (2854 cm^{-1}) (deconvoluted spectra in figure S2) were compared for the mixed SAMs. The band at 3251 cm^{-1} can be assigned to DS-DTCA molecules while the band at about 2854 cm^{-1} should be assigned mainly to C-H stretching vibrations of ODT molecules. Thus, the higher the ratio, A(3251 cm^{-1})/A(2854 cm^{-1}), the higher the concentration of photoiniferter groups on the surface.

FTIR measurements of the formed mixed SAMs revealed a monotonic relation between the SAM composition (reflected by the mentioned above ratio) and the content of DS-DTCA in the feed solution (figure S3 A). Some deviation was observed only for the SAM prepared using the solution containing 67 mol-% of DS-DTCA that indicated slightly preferential adsorption of ODT in that case. Such a behavior can be explained by generally higher adsorption rate of thiols comparing to disulfides on gold.[1] However, application of respective disulfide instead of ODT reverses the preferences in adsorption of the components is similar mixed SAMs.[2] Contact angle measurements revealed the same trend. We used the Israelachvili-Gee equation[3] (eq. S1) in order to evaluate the obtained contact angle data.

$$(1+\cos\theta)^2 = x_1 \cdot (1+\cos\theta_1)^2 + x_2 \cdot (1+\cos\theta_2)^2 \qquad \text{(eq. S1)}$$

where:

θ – contact angle for a mixed SAM,

θ_1, θ_2 – contact angles for single component SAMs,

x_1, x_2 – molar fractions of given components in SAM.

Figure S3 B presents the experimental data for given feed solutions (black squares) and the respective theoretical values of $(1+\cos\theta)^2$ as calculated from eq. S1 (red squares) based on the composition of the feed solutions and measured θ_1 (97±5° for the SAM composed of ODT) and θ_2 (51±3° for the SAM composed of DS-DTCA) values. The experimental data generally match with the values determined from the eq. S1 indicating that the compositions of the SAMs are similar to the ones of feed solutions. Only one experimental point (x_1=0.67) deviates slightly from the theoretical prediction indicating that for this feed solution there are some preferences for incorporation of ODT into the mixed SAM with respect to the feed composition.

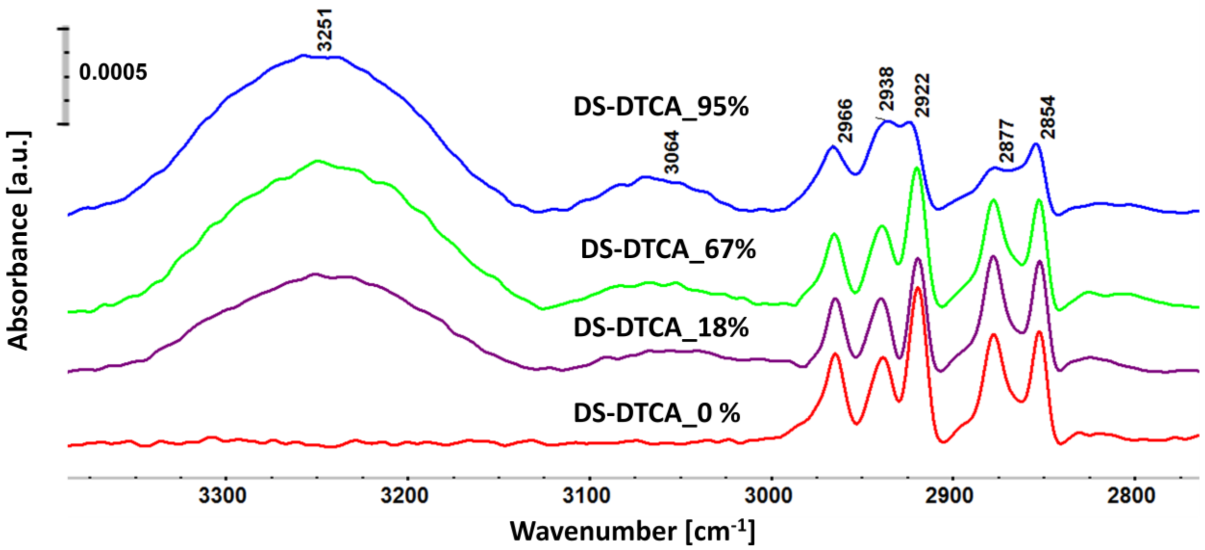

Figure S1. FTIR spectra of the mixed SAMs containing various amounts of deposited DS-DTCA and ODT molecules used for grafting poly(TPM) brushes.

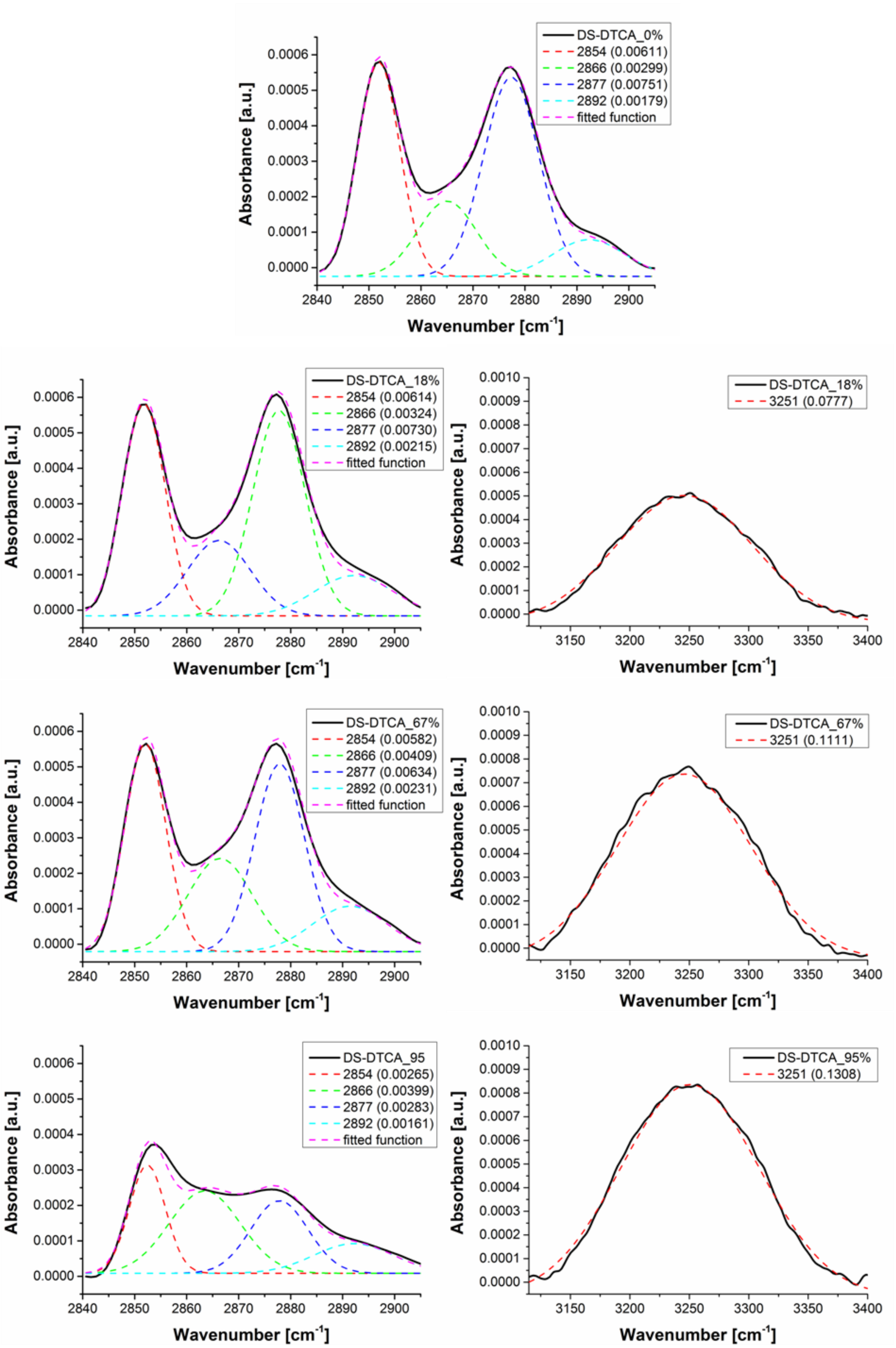

Figure S2. Zoomed in and deconvoluted selected FTIR bands of the mixed SAMs containing various amounts of DS-DTCA (mol-% given in the legends) and ODT. Calculated integral intensities of the bands are presented in brackets next to wavenumbers of the bands maxima.

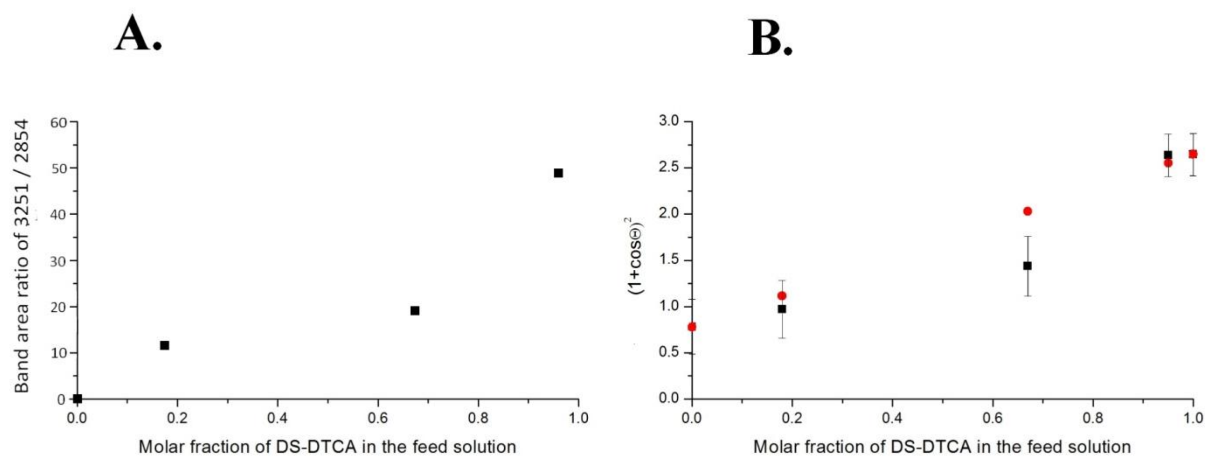

Figure S3. A) Relation of the ratios of the integral intensities of the bands 3251 cm^{-1}/ 2854 cm^{-1} in the respective SAMs versus DS-DTCA content in the feed solution; B) relation given by eq. S1 as calculated for various molar fraction of DS-DTCA in the feed solutions. Experimental results based on the measured contact angles of the mixed SAMs are presented as black squares and the theoretical values calculated using eq. S1 and contact angle values of single component SAMs are presented as red squares.

Estimation of the conductivity of the doped poly(TPM) brushes

Electrical conductivity (σ) of the brushes were calculated using a basic formula (eq. 1), where S – tip-surface contact area, l – average length of surface grafted poly(TPM) chains, and R – electrical resistance of the polymer brushes calculated as an average reciprocal slope of the curves in the linear parts of the TUNA ramp I-U plots in the voltage range between -0.1 V and +0.1 V.

$$\sigma = \frac{l}{RS} \qquad (1)$$

Tip-surface contact area (S) for Pt/Ir coated conductive tip used in TUNA measurements (with nominal tip radius of 25 nm) was estimated to be on the level of 10^{-17} m^2. The average length of the poly(TPM) chains (l) was taken as a dry brushes thickness (10^{-8} m, see Fig 3A). The electrical resistance of the obtained polymer brushes (R) was estimated based on the histograms shown in Fig. 5. For example, the value of 10^9 Ω was determined for poly(TPM)_95 (Fig. 5 C) based on the average value dI/dU = 10^3 pA/V.

[1] C. D. Bain, H. A. Biebuyck, G. M. Whitesides, *Langmuir,* 1989, **5**, 723–727.
[2] E. M. Benetti, E. Reimhult, J. de Bruin, S. Zapotoczny, M. Textor, G. J. Vancso, *Macromolecules*, 2009, **42**, 1640.
[3] J. N. Israelachvili, M. L. Gee, *Langmuir*, 1989, **5**, 587.