Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information for

Molecular Dynamics Simulations of Oligoester Brushes: The Origin of Unusual Conformations

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Estimation of the maximum relaxation time of sizes of grafted chains

In order to estimate the length of the time interval of the production run, which will be used to analyse the structural characteristics of the grafted layer, we calculated the autocorrelation function $C_{H^2_{end-to-end}}(t)$ of the squared distance between the ends of the OLA chains $H^2_{end-to-end}$. Calculations were carried out over a 500 ns of the production run. The time dependence of $C_{H^2_{end-to-end}}(t)$ for the OLA chains at σ = 1.76 nm^{-2} (the highest considered grafting density) is presented on a semilogarithmic scale in Fig. S1. It is clear that more than one relaxation processes are involved. Fitting of $C_{H^2_{end-to-end}}(t)$ by the sum of two exponents shows that, firstly, initial decay includes whole spectrum of relatively fast process and, secondly, the characteristic time of the slowest process is ~ 80 ns. With this data it was decided to use the last 500 ns of the production run with total duration of 900 ns for the analysis of structural properties, which is approximately 6 times greater than the calculated relaxation time.

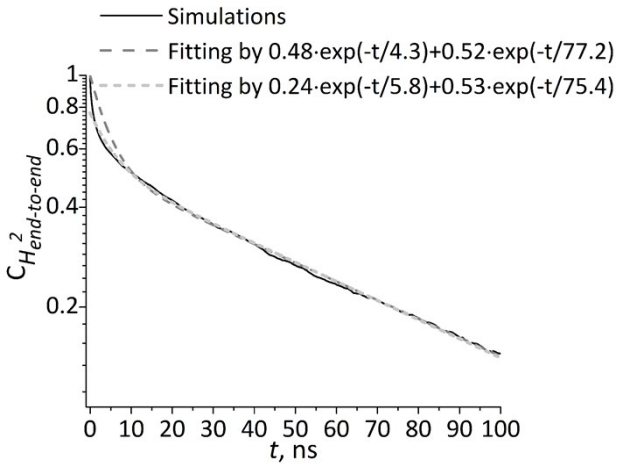

Fig. S1 Autocorrelation function $C_{H^2_{end-to-end}}(t)$ for the case σ = 1.76 nm^{-2}. The solid line shows the dependence calculated on the basis of the molecular dynamic trajectory, dashed and dotted – approximations by the sum of two exponents.

Shape of the density profiles and interpenetration between grafted and melt chains

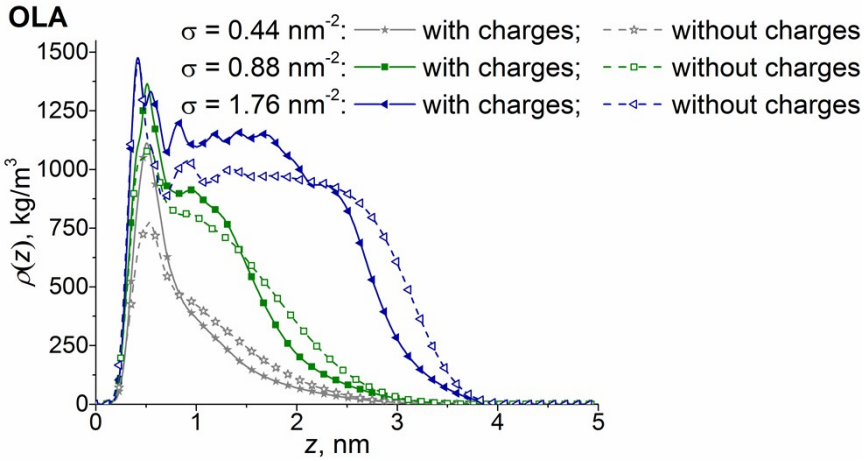

Fig. S2 Density profile for OLA chains in the systems with and without partial charges at various grafting density σ.

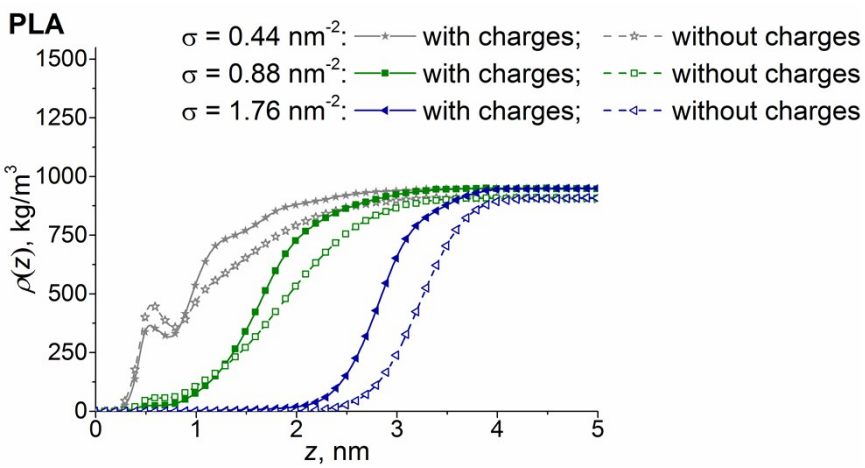

Fig. S3 Density profile for PLA chains in the systems with and without partial charges at various grafting density σ.

Density profiles in Fig. S2 and Fig. S3 allow one to calculate overlap parameter P_{ov} in order to evaluate the degree of interpenetration between grafted and melt chains using the following expression:[1]

$$P_{ov} = \frac{\int_0^\infty \rho_{OLA}(z)\rho_{PLA}(z)dz}{\int_0^\infty \rho_{OLA}(z)dz \int_0^\infty \rho_{PLA}(z)dz},$$

where $\rho_{OLA}(z)$ and $\rho_{PLA}(z)$ are the density profiles for OLA and PLA chains, correspondingly.

Calculated overlap parameter P_{ov} for the system studied is presented in Fig. S4. It is seen that the partial charges have almost no influence on the degree of interpenetration within the margin of error depending on the grafting density.

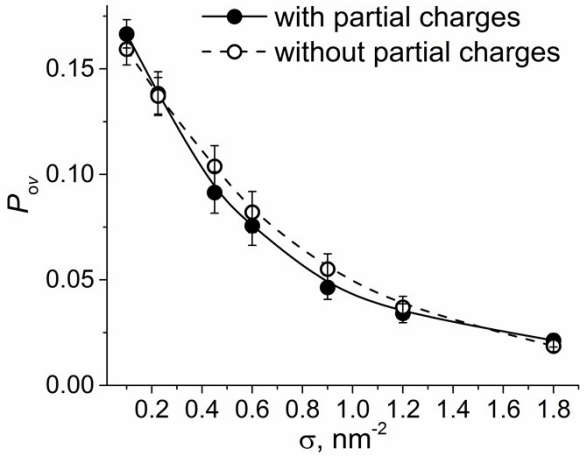

Fig. S4 Overlap parameter P_{ov} as a function of grafting density σ for the systems with and without partial charges.

References

1. Z. Benková and M. N. D. S. Cordeiro, *Langmuir*, 2015, **31**, 10254–10264.