Specificity of counterion binding to a conjugated polyelectrolyte: a combined MD and NOESY investigation

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This Supporting Information contains the computed build-up curves of the NOE used to construct the simplified NOESY spectra from the simulation trajectories as well as basic information about the meaning of radial distribution functions.

Figure S1: PTAA monomeric unit (left) neutralized with a tetrabutylammonium counterion (right). Notation of chemically distinct hydrogen atoms is added to the structure for further reference.
Diagonal peaks

The signal intensities at mixing time $t_m = 0$ correspond to number of chemically distinct hydrogen atoms in the repeating unit of the simulated system. The signal intensities decrease with increasing mixing time due to the longitudinal relaxation.

Figure S2: Dependence of diagonal peaks signal intensities ($I$) on the mixing time ($t_m$), calculated for simulated 0.2 mol L$^{-1}$ solutions of TBACl. ■ – hydrogen atoms nearest to the central TBA$^+$ nitrogen atom (H$_1$), ○ – hydrogen atoms bound to the second most inner TBA$^+$ carbon atom (H$_2$), ▲ – hydrogen atoms, bound to the third carbon atom from the central TBA$^+$ nitrogen atom (H$_3$), ▼ – hydrogen atoms bound to the outer TBA$^+$ carbon atom (H$_4$).

The farther from the central N atom the proton is, the slower is its relaxation. This dependence is also expected from equation (2) in the main paper. In general, faster molecular dynamics of a proton leads to lower $J(n\omega_0)$ and longer relaxation time.

Figure S3: Dependence of diagonal peaks signal intensities ($I$) on the mixing time ($t_m$), calculated for the simulated 0.2 mol L$^{-1}$ solution of PTATBA. The markers for protons from TBA$^+$ ions are the same as in Figure S2. The markers for protons from PTAA: ■ – aliphatic hydrogen atoms (H$_{al}$), ▲ – aromatic hydrogen atoms (H$_{ar}$),
Intramolecular cross-peaks

Figure S4: Dependence of intensity and of the sign of intramolecular cross-peaks intensities in simulated TBACl system on the mixing time $t_m$. – $H_1/H_2$, – $H_1/H_3$, – $H_1/H_4$; – $H_2/H_3$, – $H_2/H_4$; – $H_3/H_4$.

Signal intensities at mixing time $t_m = 0$ are zero since no magnetization exchange has taken place yet. At the beginning of mixing (low values of the mixing time) the signals start to increase (in the absolute sense) with the increase of the mixing time ($t_m$). This initial increase of signals is followed by a subsequent decrease to zero. In Figure S4, all the signals are negative. This feature is a consequence of the fact that the system dynamics is fast when compared to the Larmor frequency of the instrument.

Figure S5: Dependence of intramolecular cross-peaks intensities of simulated PTATBA system on the mixing time ($t_m$). – $H_{al}/H_{ar}$; – $H_1/H_2$, – $H_1/H_3$, – $H_1/H_4$; – $H_2/H_3$, – $H_2/H_4$; – $H_3/H_4$.

In Figure S5, all the signals, except the signal corresponding to the interaction between $H_3$ and $H_4$ type hydrogen atoms, are positive as a result of a slow dynamics of PTATBA system.
**Intermolecular cross-peaks**

**TBA⁺ counterion hydrogen atoms - aliphatic PTAA hydrogen atom**

![Graph showing cross-peaks intensities]

Figure S6: Dependence of cross-peaks intensities corresponding to dipole-dipole interactions between aliphatic hydrogen atoms of oligoion (H_{al}) and TBA⁺ hydrogen atoms (H₁–H₄) on the mixing time (t_m). ■ – H_{al}/H₁, ■ – H_{al}/H₂, ▲ – H_{al}/H₃ and ▼ – H_{al}/H₄.

The build-up curves are similar to the ones for counterion/counterion interaction in the case of PTAA presence (Figure S5) corresponding to a slow dynamics of these interactions. The signals display similar maximum intensity regardless of the kind of the proton (see the main article for discussion). While the initial changes of signal intensities are quite similar for all the protons, they start to differ at longer mixing times.

**TBA⁺ counterion hydrogen atoms - aromatic PTAA hydrogen atom**

The build-up curves are similar to the previous ones (Figures S5 and S6) corresponding to a slow dynamics of interactions between aromatic (H_{ar}) hydrogen atom and hydrogen atoms from TBA⁺ counterion. The signals display similar dynamics at the beginning but start to differ for longer mixing times.
Figure S7: Dependence of cross-peaks intensities corresponding to dipole-dipole interactions between aromatic hydrogen atoms of oligoion (H_ar) and TBA⁺ hydrogen atoms on the mixing time (t_m). Legend: ■ – H_ar/H₁, ○ – H_ar/H₂, ▲ – H_ar/H₃ and ▼ – H_ar/H₄.
Radial distribution function

The radial distribution function $g_{ij}(r)$, or more generally the pair distribution function, is a function that measures the probability density of finding a particle $j$ at a radial distance $r$ of another particle $i$. It can also be seen as a reduced local density of particles $j$ at a radial distance $r$ of another particle $i$.\(^1\)

$$g_{ij}(r) = \frac{\rho_{ij}(r)}{\rho_0}$$  \(1\)

The number of particles $j$ contained in a spherical shell of thickness $dr$ at a radial distance $r$ of a particle $i$ is then $4\pi\rho_0 g_{ij}(r)r^2dr$.\(^2\)

In the present study, the pair distribution functions were calculated between different types of atoms using the following procedure: distances between two atoms of different type (e.g. between oxygen atoms and Li\(^+\) counterion) were calculated for all the atom pairs and the calculated distances were then sorted into histogram with bin width ($\Delta r$) of 10 pm. $g(r)$ was finally computed following the expression for the $k$-th bin:

$$g(r^{(k)}) = \frac{N_{AB}^{(k)}V}{4\pi(r^{(k)})^2\Delta r N_A N_B}$$  \(2\)

where $N_{AB}^{(k)}$ is the number of distances that corresponds to the $k$-th bin, $V$ is the volume of the system, $N_A$ and $N_B$ is number of atoms A and B in the system, respectively (e.g. number of oxygen atoms and Li\(^+\) counterions), $r^{(k)}$ is the distance of the $k$-th bin for which $g(r)$ is calculated.

Beyond depicting how the density of counterions varies with the distance of those counterions from the oxygen or sulfur atoms of PTAA, the $g(r)$ functions can be also used to compute spatial averages of meaningful quantities. One of such quantities is for example the $\langle 1/r^6 \rangle$ average which is related to the average dipolar coupling the different spins, which might be computed as:

$$\langle \frac{1}{r^6} \rangle = \int_0^{\infty} \frac{1}{r^6} g(r)4\pi r^2 dr = 4\pi \int_0^{\infty} \frac{g(r)}{r^3} dr$$  \(3\)
References

(1) Hill, T. L. *An Introduction to Statistical Thermodynamics*; Dover Publications, Inc, New York, USA, 1986; pp 301–303.

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