



Cite this: *INEOS OPEN*,
2025, 8 (1–3), XX–XX
DOI: 10.32931/ineosopen

Received XX Month 20XX

Accepted 12 May 2025

<http://ineosopen.org>

ASSESSMENT OF POLARITY OF COMB-LIKE POLYELECTROLYTES USING A PYRENE PROBE

A. A. Solunina,* P. A. Fetin, and I. M. Zorin

*Institute of Chemistry, St. Petersburg State University,
Universitetskaya nab. 7–9, St. Petersburg, 199034 Russia*

Abstract

In recent years, particular attention has been drawn to the investigations on the application of comb-like polyelectrolytes as micellar catalysts. One of the most important parameters that determine the course of a catalytic reaction is the polarity of the medium in a micellar pseudophase. In this work, the polarity of a series of comb-like polyelectrolytes bearing different ionic groups was assessed using the pyrene polarity scale.

Key words: pyrene polarity scale, comb-like polyelectrolytes, micellar catalysis.

Introduction

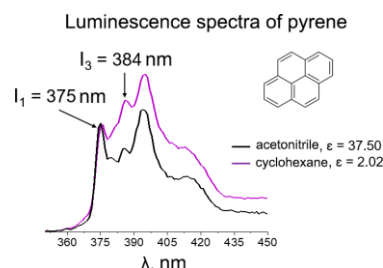
Comb-like polyelectrolytes comprise a multifunctional platform which can be used for solving a wide range of scientific and practical problems. High-molecular-weight compounds of this type are used as ion-exchange resins, reagents for micellar capillary electrophoresis and for ion-selective electrodes. The term comb-like polyelectrolyte refers to the polymerization product of a surfactant monomer containing a polymerizable group in the hydrophobic tail of the molecule.

In recent years, comb-like polyelectrolytes have been studied in micellar catalysis, in particular, in alkaline hydrolysis of esters and Suzuki coupling performed in an aqueous phase [1–4]. One of the characteristics affecting the reaction in the micellar pseudophase is the polarity of the surfactant. However, empirical definition of the polarity is very difficult. One of the approaches used to assess this characteristic can be probing micelles with luminescent labels [5]. It is known that some polycyclic aromatic hydrocarbons are sensitive to changes in the polarity of their microenvironment, which is reflected in a change in the ratio of peak intensities in their luminescence spectra [6, 7]. In particular, the pyrene polarity scale has been described in the literature, namely, the dependence of the ratio of characteristic luminescence peaks of pyrene on the dipole moment of the solvent molecules.

Herein, we report for the first time the polarity data of comb-like macromolecules that differ in the type of ionic groups.

Experimental section

A stock solution of pyrene in benzene with a concentration of 1 mg/mL was prepared. Aliquots of the stock solution (100 μ L) were placed in vials, then the containers were left at 25 $^{\circ}$ C for 24 h, until the complete evaporation of the solvent. Then



aliquots of the aqueous solutions of the studied polyelectrolytes (4 mL) with a concentration of 0.003 M of the monomer units were placed in the vials. The polymers were obtained according to the previously described methods [1–4]. The vials were closed and kept at 25 $^{\circ}$ C for 14 days, until the equilibrium was established in the systems.

For each solution, the luminescence spectrum was recorded on a FluoroMax-4 spectrofluorometer at room temperature in the wavelength range of 350–550 nm. The excitation wavelength was 335 nm. To assess the polarity, the ratio of intensities of the luminescence peaks at 375 ± 5 nm (I_1) and 384 ± 5 nm (I_3) was used.

Results and discussion

In this work, six comb-like polyelectrolytes bearing different ionic groups were investigated (Fig. 1). The resulting ratios of the luminescence peak intensities are presented in Table 1.

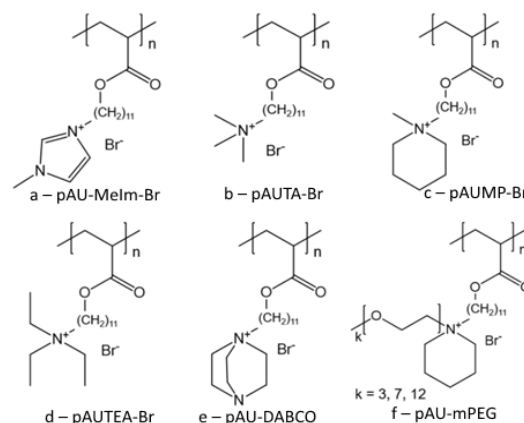


Figure 1. Structures of the polyelectrolytes explored: pAU-Melm-Br (a), pAUTA-Br (b), pAUMP-Br (c), pAUTEA-Br (d), pAU-DABCO (e), pAU-mPEG 160 ($k = 3$), pAU-mPEG 350 ($k = 7$), pAU-mPEG 550 ($k = 12$) (f).

Table 1. Ratios of intensities of the characteristic luminescence peaks of pyrene (I_1 : 375 ± 5 nm, I_3 : 384 ± 5 nm), solubilized by micelles of the comb-like polyelectrolytes with different terminal groups

Polymer	I_1/I_3
pAU-MeIm-Br	1.37
pAUTA-Br	1.44
pAUMP-Br	1.45
pAUTEA-Br	1.47
pAU-DABCO	1.49
pAUP-mPEG 160 (k=3)	1.62
pAUP-mPEG 350 (k=7)	1.62
pAUP-mPEG 550 (k=12)	1.62

An increase in the ratio of intensities of the characteristic luminescence peaks of pyrene corresponds to an increase in the dipole moment of the surrounding molecules (molecular fragments). In this case, the pAU-MeIm-Br molecules had the lowest value due to the redistribution of the positive charge over the imidazolium moiety. The resulting values of the I_1/I_3 ratio correspond to the polarity of ethyl acetate, the intermediate polarity values of 1.45–1.49 are close to that of *N*-methylacetamide (1.48), the presence of an ethylene glycol unit in the polar group led to a polarity value of 1.62, which correlates well with the value characteristic of poly(ethylene glycol) (1.64) [5].

pAUTA-Br, pAUMP-Br, pAUTEA-Br, and pAUP-mPEG with different lengths of the poly(ethylene glycol) moiety formed two groups with similar I_1/I_3 values. On the one hand, the absence of significant differences in the resulting parameters within each group may indicate the insensitivity of the method to small changes in the polarity of the functional group. On the other hand, a significant difference in the values obtained for pAUMP-Br and pAUP-mPEG series may indicate different localization of the pyrene molecules within the polyelectrolyte micelles.

Conclusions

In this work, the pyrene probe was used to assess the polarity of comb-like polyelectrolytes. It was shown that this approach can be used to differentiate the polarity of these macromolecules. The key effect on the polarity of the pyrene probe is exerted by the type of ionic groups in the polyelectrolyte.

Acknowledgements

This work was supported by the Russian Science Foundation (project no. 24-73-00193).

The authors are grateful to the Magnetic Resonance Research Centre and Chemical Analysis and Materials Research Centre of St. Petersburg State University.

Corresponding author

* E-mail: st076490@student.spbu.ru. Tel: +7(921)898-1092 (A. A. Solunina).

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