

SYNTHESIS OF BRUSH COPOLYMERS CARRYING PHOSPHORYLCHOLINE MOIETIES

Marijus Jurkūnas*, Vaidas Klimkevičius, Ričardas Makuška

Faculty of Chemistry and Geoscience, Vilnius University, Lithuania

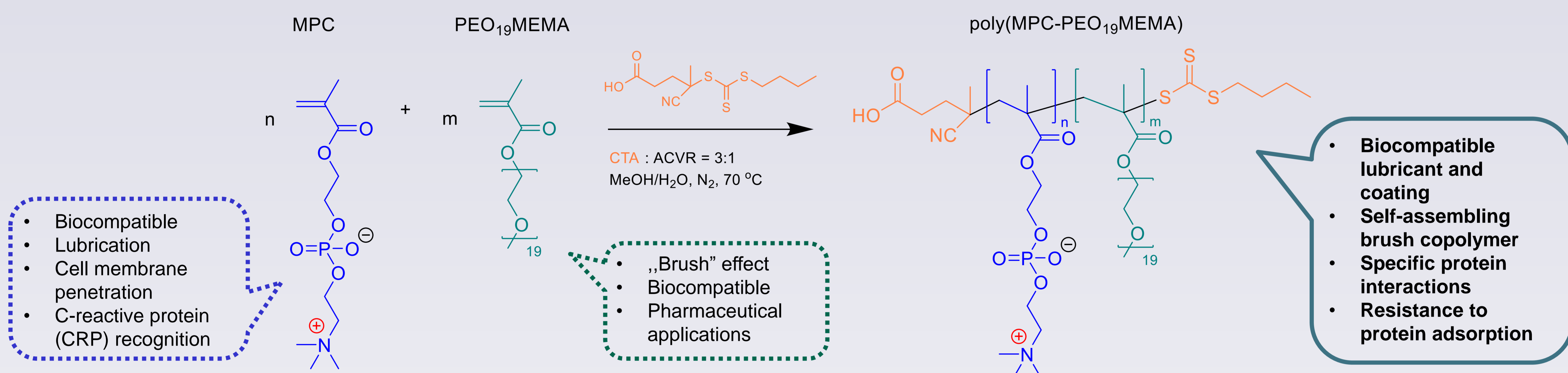
*marijus.jurkunas@chf.stud.vu.lt



Introduction

Hydrophilic polymers with phosphorylcholine head groups, such as poly(2-methacryloyloxyethyl phosphorylcholine) (pMPC), are antifouling materials that are suitable for direct penetration across cell plasma, imitation of bio-membrane structure, specific binding with C-reactive protein (CRP), fluid lubrication [1], etc. Polymers with MPC units offer possibilities to be used as biosensors [2], drug delivery agents [3], and bioinert materials [4]. Such kind of copolymers has huge potential to treat various diseases such as xerostomia, dysgeusia, etc. which requires continuous use of artificial saliva substitutes. It is known that MPC could be polymerized using RAFT technique [5]. In the present work, a zwitterionic monomer MPC and an amphiphilic macromonomer poly(ethylene oxide) methyl ether methacrylate (PEO₁₉MEMA) were selected to design a new zwitterionic brush copolymers that have promising potential for biomedical applications such as artificial tears and saliva.

Scheme of the synthesis of statistical and block copolymers of MPC and PEO₁₉MEMA



Synthesis and characterization of the copolymers

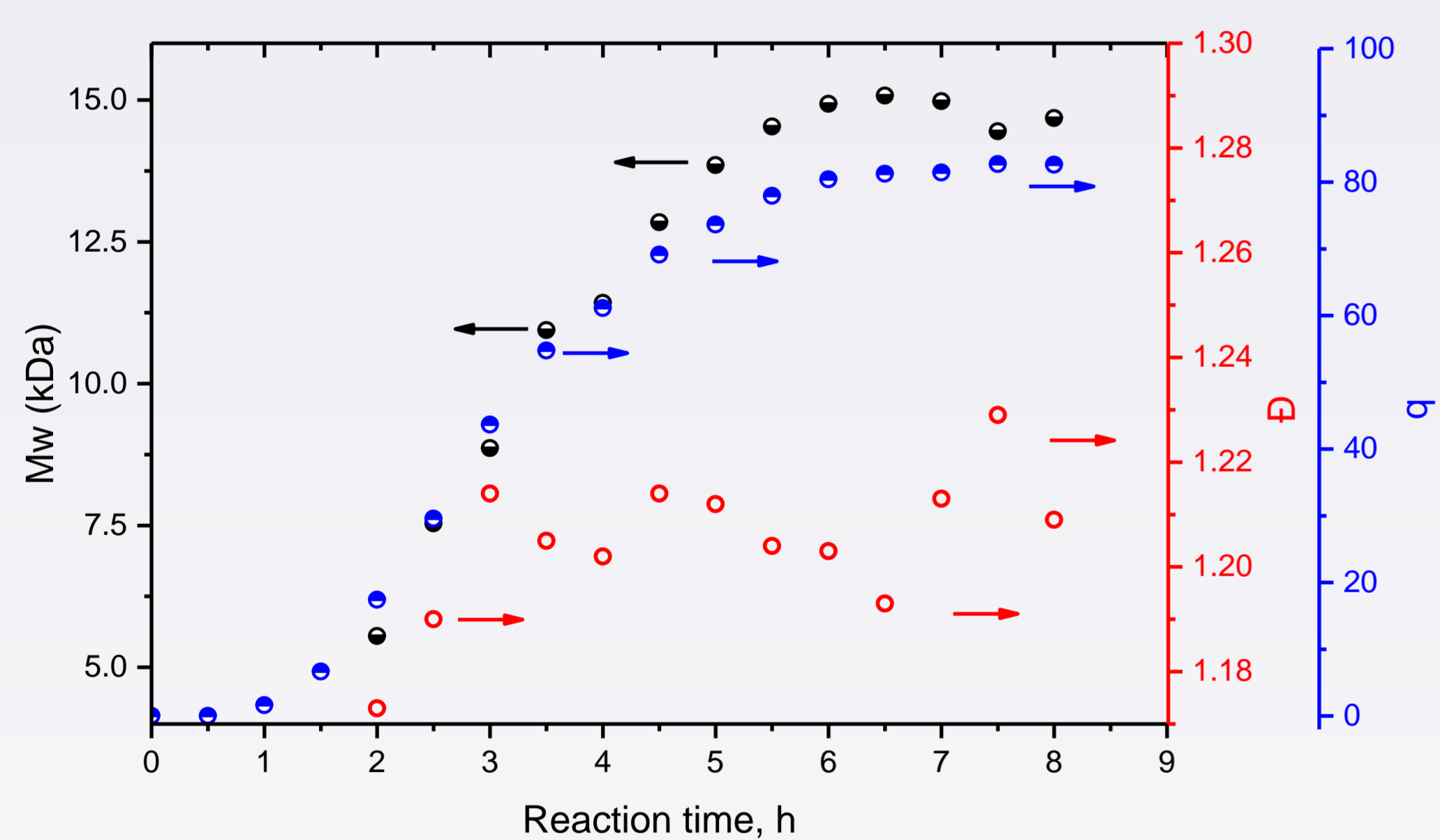


Fig 2. Kinetics of MPC polymerisation

Table 1. Main characteristics of statistical and block copolymers

Copolymer composition, MPC mol%	Degree of polymerization, DP (n+m)	Molecular weight, M _n	Dispersity index, Đ		
p(MPC- <i>stat</i> -PEO ₁₉ MEMA)	57	85	48800	1.38	
	81.1	134	56200	1.39	
p(MPC)- <i>block</i> -p(PEO ₁₉ MEMA)	34.4	22+42	64	46800	1.59
	57.8	37+27	64	36900	1.42
	78.1	57+16	73	31800	1.33

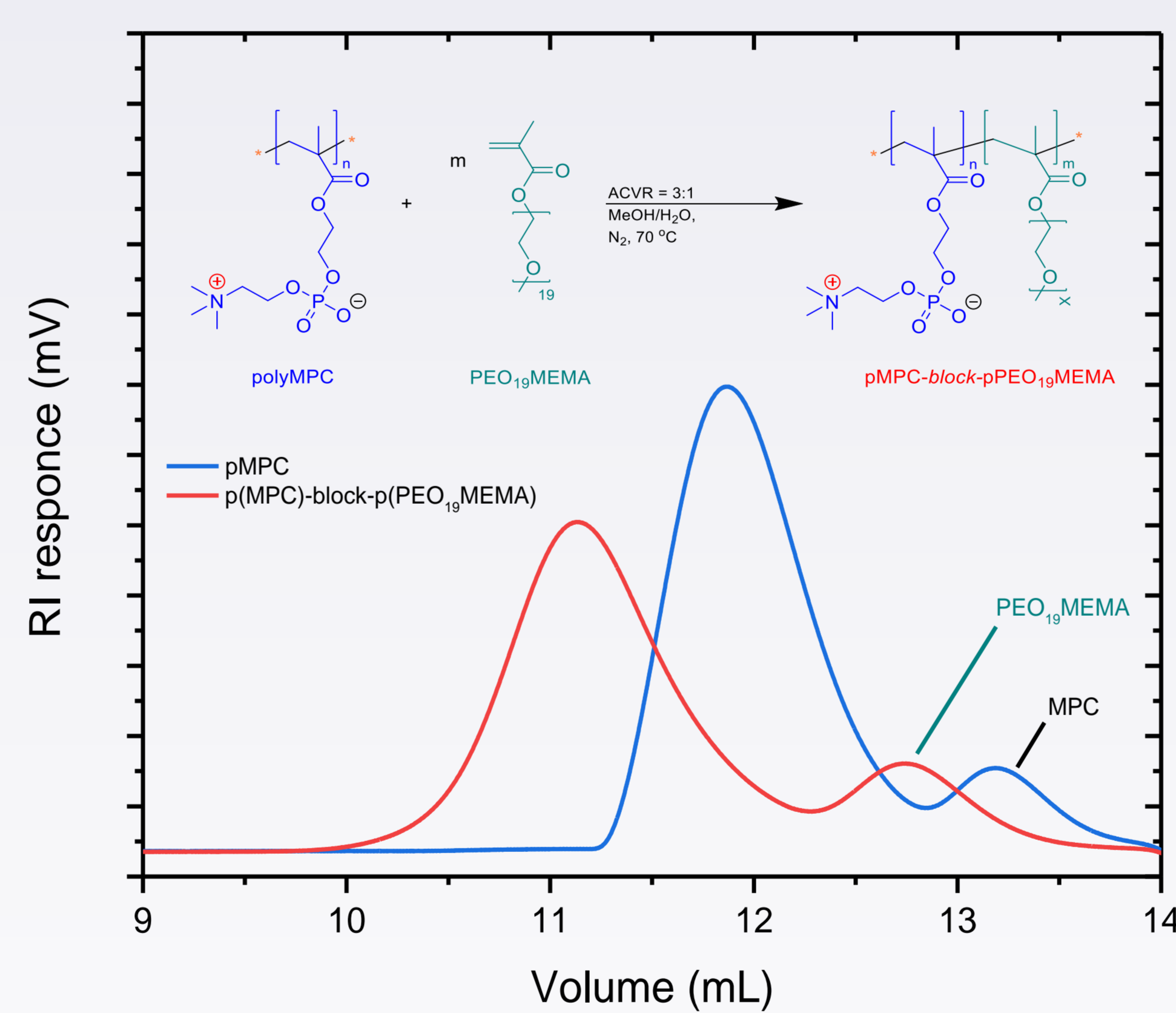


Fig 3. SEC eluograms of the reaction mixture taken after the first (blue) and second (red) steps of the block copolymerisation of MPC and PEO₁₉MEMA

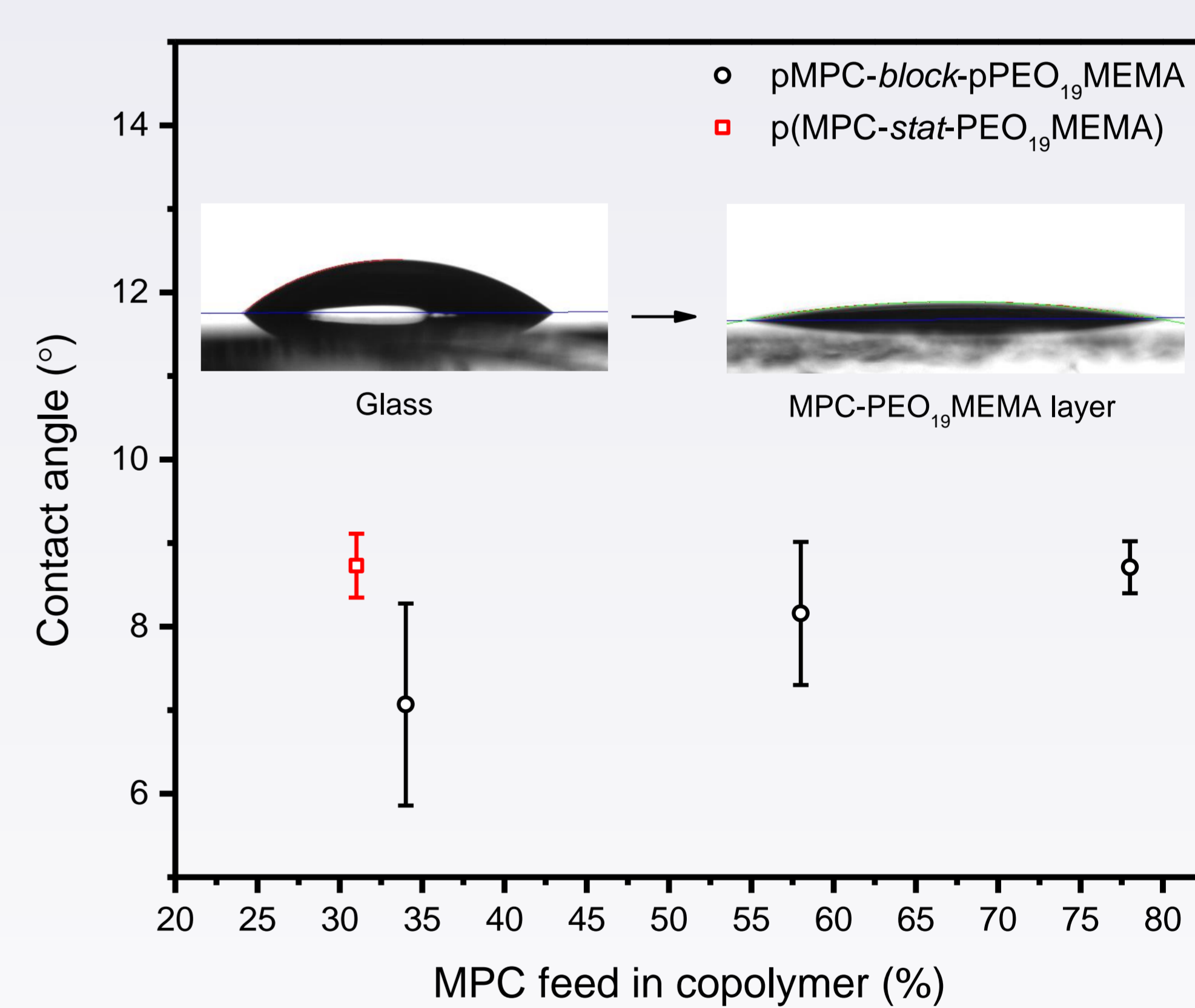


Fig 4. Wettability of statistical and block copolymers of MPC and PEO₁₉MEMA

Conclusions

A series of statistical brush copolymers with degree of polymerization (DP) up to 130 and dispersity index Đ 1.3–1.4 containing different amount of MPC units were synthesized. In the series of the block copolymers, the block of pMPC was rather monodisperse (Đ about 1.2) but the chain extension by the units of PEO₁₉MEMA was less successful giving diblock brush copolymers with higher dispersity (Đ 1.3–1.6). Hydrophilicity of the synthesized copolymers was evaluated by the water contact angle method which showed high hydrophilicity of synthesized copolymers. Study of biolubrication properties of the synthesized zwitterionic statistical and diblock brush copolymers of MPC and PEO₁₉MEMA is in progress.

References

[1] T. Goda, K. Ishihara, Y. Miyahara, Critical update on 2-methacryloyloxyethyl phosphorylcholine (MPC) polymer science, *J. Appl. Polym. Sci.* 132 (2015) 41766. <https://doi.org/10.1002/APP.41766>.

[2] P. Barathi, B. Thirumalraj, S.M. Chen, S. Angaiyah, A simple and flexible enzymatic glucose biosensor using chitosan entrapped mesoporous carbon nanocomposite, *Microchem. J.* 147 (2019) 848–856. <https://doi.org/10.1016/J.MICROC.2019.03.083>.

[3] G. Xie, C. Ma, X. Zhang, H. Liu, X. Guo, L. Yang, Y. Li, K. Wang, Y. Wei, Biocompatible zwitterionic phosphorylcholine polymers with aggregation-induced emission feature, *Colloids Surfaces B Biointerfaces*. 157 (2017) 166–173. <https://doi.org/10.1016/j.colsurfb.2017.05.070>.

[4] Z. Zhang, Y. Zhou, Z. Zhou, Y. Piao, N. Kalva, X. Liu, J. Tang, Y. Shen, Synthesis of enzyme-responsive phosphoramidate dendrimers for cancer drug delivery, *Polym. Chem.* 9 (2018) 438–449. <https://doi.org/10.1039/C7PY01492A>.

[5] N. Bhuchar, Z. Deng, K. Ishihara, R. Narain, Detailed study of the reversible addition–fragmentation chain transfer polymerization and copolymerization of 2-methacryloyloxyethyl phosphorylcholine, *Polym. Chem.* 2 (2011) 632–639. <https://doi.org/10.1039/C0PY00300J>.