

SYNTHESIS AND PROPERTIES OF CATIONIC CATECHOL BRUSH COPOLYMERS

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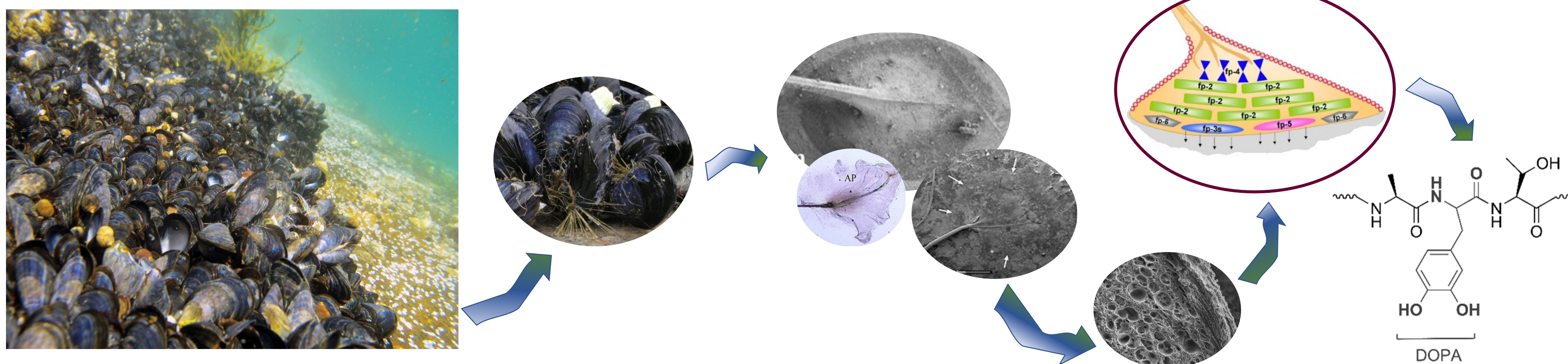
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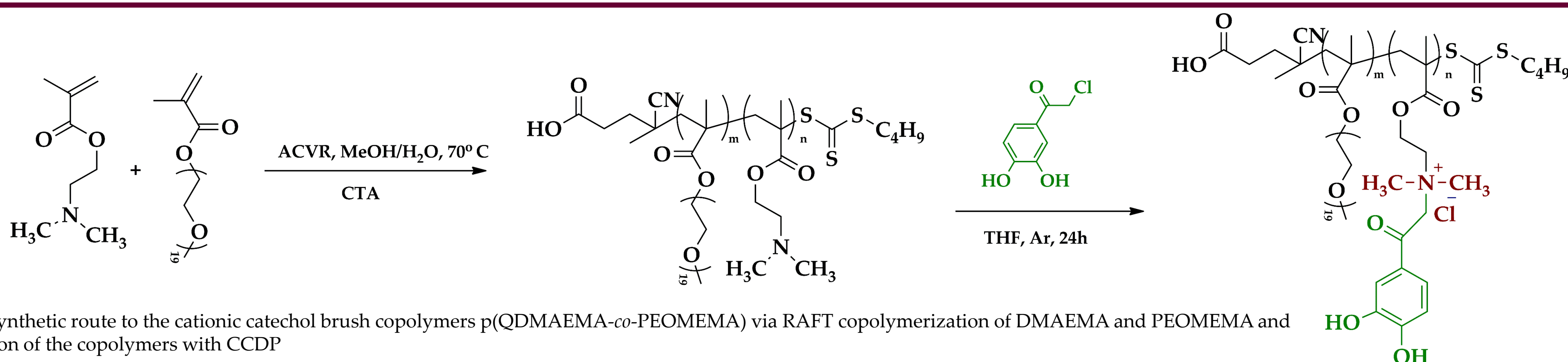


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Synthesis and application of bio-inspired polymeric materials have always been one of the main fields of materials science. In recent years, more and more attention has been given to mussel protein mimetic polymers containing catechol groups, known as the mussel-mimetic bioadhesives. These mussel-mimetic, polydopamine-containing polymers have been proven to be highly suitable for various applications in biomedicine such as biosensors, drug delivery, cancer cell imaging, medicine glue, hydrogel, and coatings [1]. Such extensive use of these biopolymers is due to their good antibacterial properties, complexation, and excellent adhesion to various surfaces and compounds under various environmental conditions [2]. In addition, they excel non-toxicity and biocompatibility [3].



Several different methods are used to obtain polymers with catechol moieties; however, the modification of preformed polymers by compounds carrying catechol groups remains supreme mainly due to the wide choice of starting polymer base and a wider possible choice of compounds suitable for the modification. Among synthetic polycations, poly(*N,N*-dimethylaminoethyl methacrylate) (pDMAEMA) is of great importance. Because of the reactivity of its amino groups, this polymer has much potential for facile modification reactions. Modification of pDMAEMA and its copolymers with catechol bearing substitutes, gives cationic catechol-containing polymers. Moreover, it possesses responsiveness to pH, temperature, and ionic strength, which gives unique properties to DMAEMA (co)polymers and their modified derivatives [4].



Scheme 1. Synthetic route to the cationic catechol brush copolymers p(QDMAEMA-co-PEOMEMA) via RAFT copolymerization of DMAEMA and PEOMEMA and quaternization of the copolymers with CCDP

In this study, we demonstrated possibilities to synthesize well-defined gradient cationic catechol brush copolymers p(QDMAEMA-co-PEO₁₉MEMA) with DP close to 100 and Đ less than 1.18 and characterized their properties by ¹H NMR, FT-IR, UV-vis spectroscopy, and water contact angle measurements. For attachment of catechol (DOPA) moieties, DMAEMA units of the copolymers were quaternized with 2-chloro-3,4-dihydroxyacetophenone (CCDP). We also report the optimized quaternization procedure of DMAEMA units in the copolymers, enabling us to reach the degree of quaternization up to 100 %. Kinetics of RAFT copolymerization were studied by size exclusion chromatography (SEC) and ¹H NMR, which allowed calculating copolymerization rate and the evolution of copolymer composition during copolymerization.

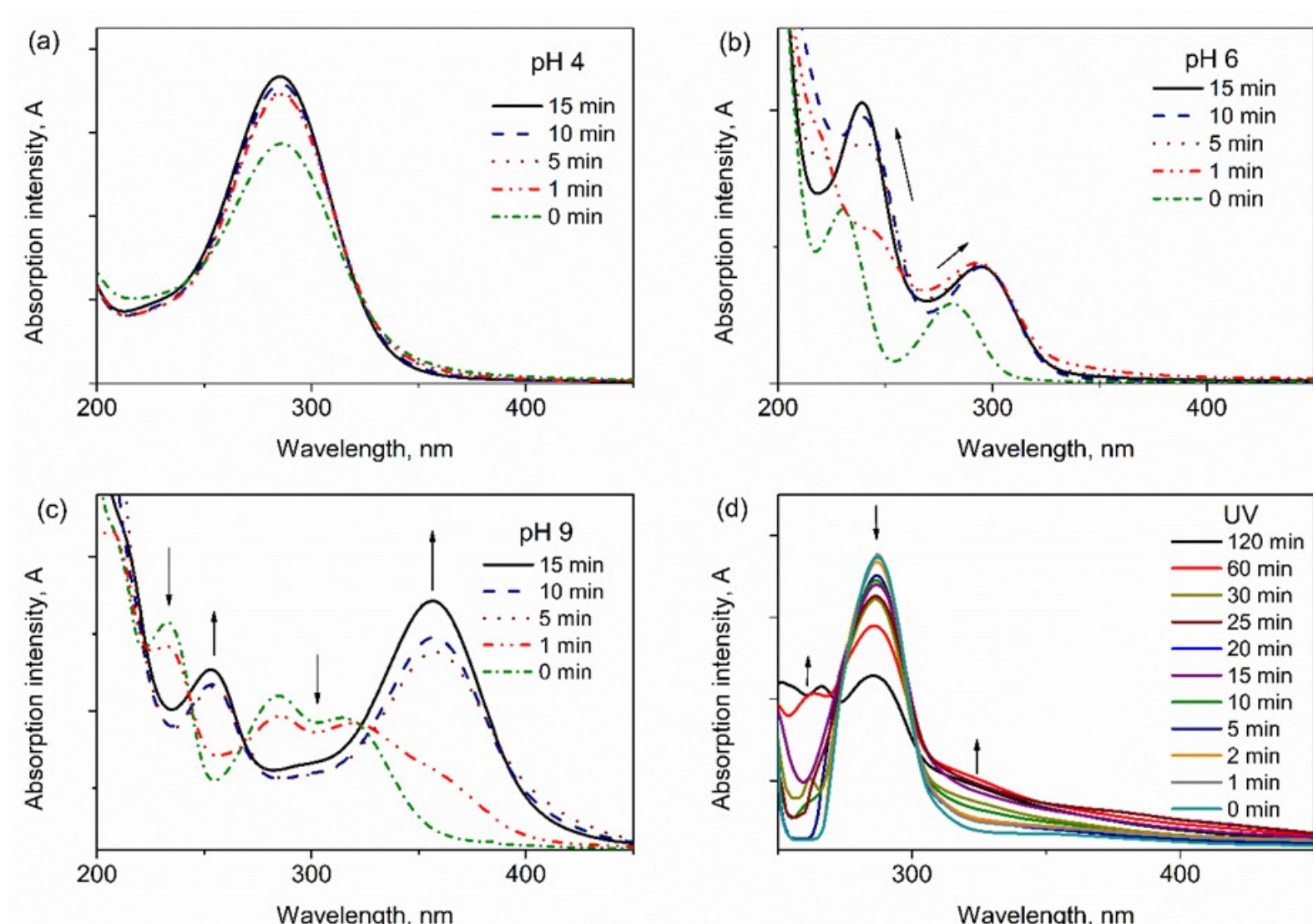


Figure 1. UV-vis spectra of aqueous solutions of the copolymer p(QDMAEMA-co-PEOMEMA) (52:48, mol %) before experiment and stored for 1, 5, 10 and 15 min. at pH 4 (a), pH 6 (b), and pH 9 (c), and UV-vis spectra of aqueous solutions (pH 4) of the copolymer p(QDMAEMA-co-PEOMEMA) (d) (52:48, mol %) after UV irradiation for 0, 1, 2, 5, 10, 15, 20, 25, 30, 60 and 120 min

Table 1. Characteristics of the copolymers p(DMAEMA-co-PEOMEMA) used for attachment of catechol moieties. [M]₀: [CTA]₀: [ACVA]₀ = 300:3:1, t = 24 h.

Sample	[DMAEMA] ₀ : [PEOMEMA] ₀	q, mol. %	Copolymer comp., DMAEMA, mol. %	M _n , g·mol ⁻¹	DP	Đ
1	25:75	90	23	71200	92	1.22
2	50:50	93	52	52700	94	1.14
3	75:25	96	71	33200	96	1.10

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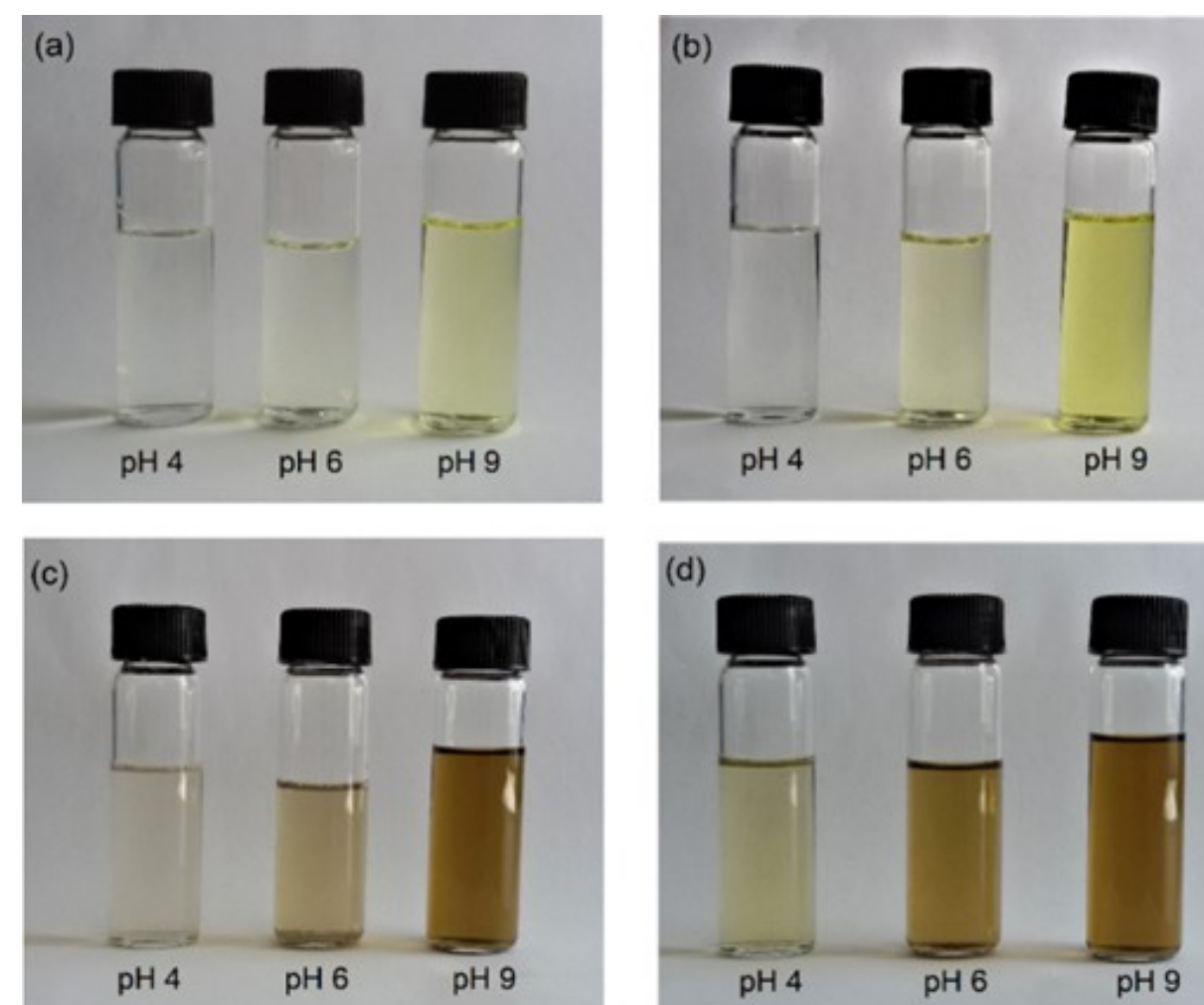


Figure 2. Colour of acidic, close to neutral and alkaline aqueous solutions of the copolymer p(QDMAEMA-co-PEO₁₉MEMA) (52:48, mol %) before (a) and stored at room temperature for 1 day (b), 1 week (c) and 3 weeks (c).

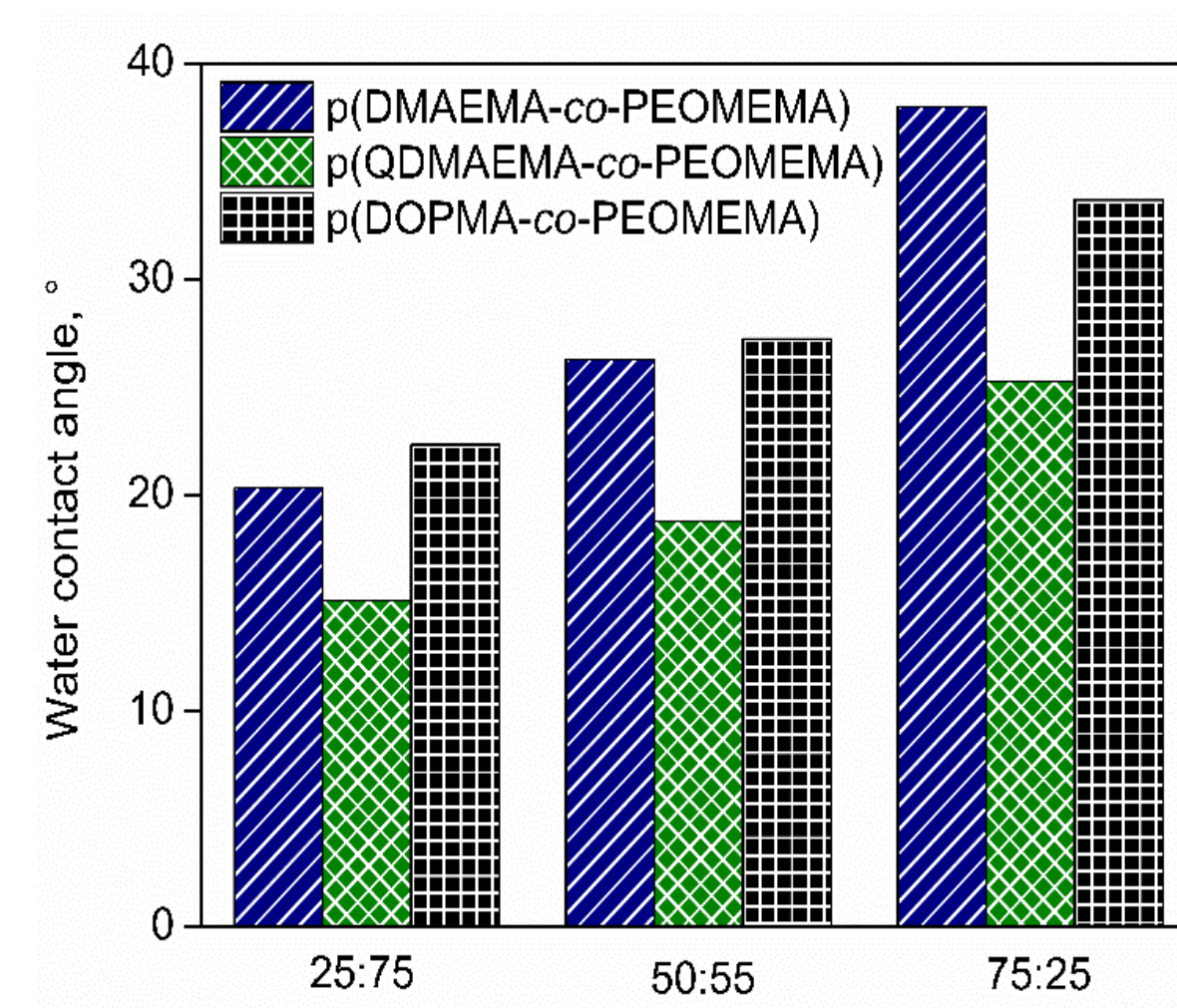


Figure 3. Water contact angle of the copolymers p(DMAEMA-co-PEOMEMA) (a-c) and p(QDMAEMA-co-PEOMEMA) (d-f), both with composition 23:77, 52:48, and 71:29 mol. %,.

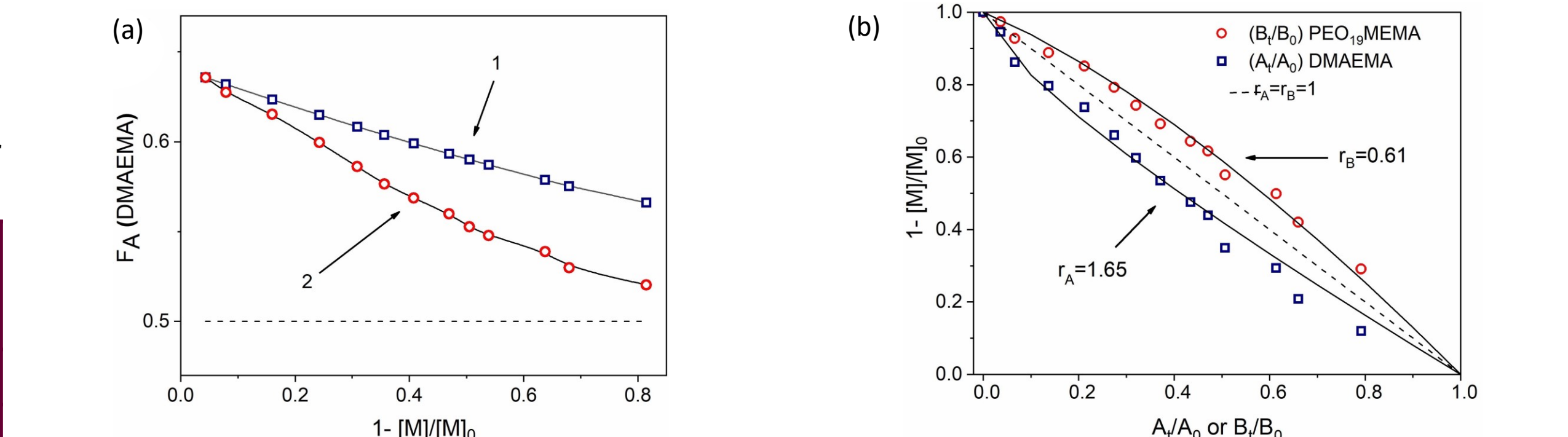


Fig. 4. RAFT copolymerization of DMAEMA and PEOMEMA (52:48 mol: (a) evolution of DMAEMA content in gradient copolymers as a function of the sum monomer conversion (apparent normalized chain length) during RAFT copolymerization (2); changes in cumulative copolymer composition (1); (b) sum monomer conversion plotted against relative residual concentration of DMAEMA (A_i) or PEOMEMA (B_i) during copolymerization. Reactivity ratios of the monomers r_A = 1.65 (DMAEMA) and r_B = 0.61 (PEOMEMA). Diagonal represents ideal copolymerization with r_A = r_B = 1

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