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Copolymerization of a Cationic Double-Charged Monomer and Electrochemical Properties of the Copolymers

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ABSTRACT: The free radical copolymerization of 1,3-bis(*N*,*N*,*N*-trimethylammonium)-2-propylmethacrylate dichloride (di-M) with acryloyloxyethyltrimethylammonium chloride (Q), diallyldimethylammonium chloride (DADMAC), and acrylamide (A) yielded novel polyelectrolytes and allowed for assessing the influence of the charge density and charge location on the monomer reactivity. Copolymerizing di-M and Q, two monomers with comparable chemical structure but differing by factor two in the number of charges, the reactivity of Q was higher than the reactivity of di-M. However, the difference diminished with increasing ionic strength. Despite 4-fold less cationic charge per monomer unit length, the reactivity of DADMAC was much lower than the reactivity of di-M. This clearly demonstrates the dominating influence of the location of the growing radical. The difference of the reactivity ratios for di-M/A was less than for di-M/Q. At low di-M fraction in the di-M/A monomer feed, di-M was even preferred. Decreasing intrinsic viscosity with increasing di-M fraction in the di-M/A monomer feed confirmed the electrostatic influence on the copolymer chain propagation. The counterion activity correlates well with the linear average charge density. However, deviation from theoretical values suggests the impact of the charge distribution.

Introduction

Water-soluble synthetic polyelectrolytes have found a multitude of practical applications. The majority is based on electrostatic interaction in solution, at interfaces, or with a variety of different surfaces. Typical application fields are water purification, paper production, optoelectronics, personal care, and biotechnology, only to list some. The increasing importance of polyelectrolytes stimulates academic research to continue.[1] The research includes the synthesis of novel polyelectrolyte structures, the study of their solution and interaction behavior, and the discovery of novel applications. As a matter of fact, the majority of new water-soluble polyelectrolyte structures have been obtained by polymer modification or copolymerization but comparably less have been synthesized polymerizing new monomers. With the availability of novel charged monomers it becomes interesting, from the scientific point of view, to study first their polymerization behavior and their physical-chemical properties. Such research creates the basis for the technical synthesis and potential future applications. In some cases, basic studies on novel monomers can contribute to obtain general answers to open scientific questions.

Recently, 1,3-bis(*N*,*N*,*N*-trimethylammonium)-2-propylmethacrylate dichloride (di-M), for which the chemical structure is shown in Figure 1, became available.[2] It is a cationic monomer with two charged quaternary ammonium groups per methacrylic monomer unit. Its homopolymerization yields cationic polyelectrolytes with a charge density similar to DNA. Preliminary studies of the homopolymerization revealed considerable deviations from ideal polymerization kinetics but confirmed theoretically expected counterion condensation.[3] It is obvious and interesting also to study the copolymerization of this double-charged cationic monomer. For the selection of comonomers several aspects are of particular interest such as the novelty of the resulting copolymers, the contribution to unanswered questions concerning the reactivity of charged monomers as a function of their chemical structure, and potential applications of the copolymers.

It is known that the polymerization of ionic monomers in aqueous solution is strongly affected by electrostatic interactions. Very complex dependency of the kinetics on the ionic strength/monomer concentration has been reported or suggested for diallyldimethylammonium chloride (DADMAC),[4] di-M,[3] as well as ionized methacrylic acid.[5] It has further been suggested that the distance between the charge and the reactive double bond and the charge density at the growing chain end strongly influence the polymerization kinetics.[4,6] The copolymerization of the double-charged cationic monomer di-M with other cationic comonomers offers the opportunity to evaluate the electrostatic influence as a function of the monomer structure. For example, the copolymerization of di-M with acryloyloxyethyltrimethylammonium chloride (Q) or DADMAC can provided data to which extent the position of the cationic charge, its distance from the polymer backbone, and the number of charges, the charge density, are the dominating parameters. Moreover, in the case of DADMAC, the presence of one charge per 0.5 nm caused significant differences of the reactivity ratios (*r* values) when copolymerized with neutral monomers such as A. The reactivity of A was found to be much higher.[4,7−9] Contrarily, almost similar reactivity ratios or even a higher ratio was found for the cationic monomer if the cationic component for the copolymerization with neutral monomers was a methacrylic ester possessing one charge per 0.25 nm,[6,8] but more separated from the polymer backbone. It is interesting to study the copolymerization of A with di-M for scientific comparison with Q and DADMAC. In addition, there is a multitude of information available related to the copolymerization of A not least due to the extensive practical use of A.

The copolymerization of cationic monomers with A is not only of academic interest but has also practical purpose. The molar mass of cationic homopolymers is frequently limited due to the pronounced electrostatic hindrance of the chain propagation. Therefore, cationic monomers are copolymerized with A to obtain higher molar masses.[8,10−12] For instance, the copolymerization of A with monocharged Q[13] and DADMAC[4,14,15] are industrial processes with product volumes of thousands of tons per year. However, increasing the molar mass of the

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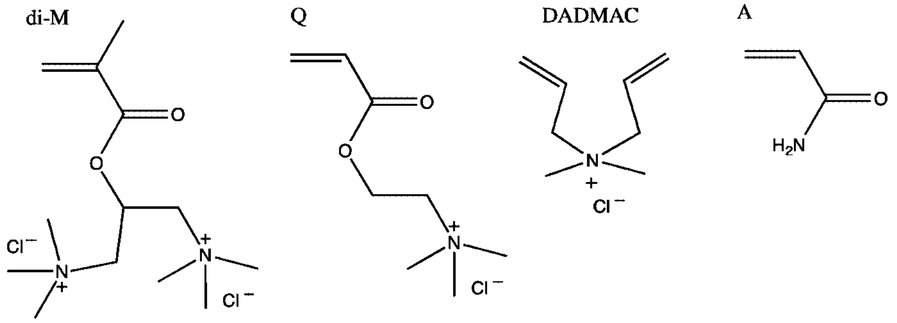

Figure 1. Chemical structures of the monomers 1,3-bis(N,N,N-trimethylammonium)-2-propylmethacrylate dichloride (di-M), acryloyloxyethyltrimethylammonium chloride (Q), diallyldimethylammonium chloride (DADMAC), and acrylamide (A).

polyelectrolyte through copolymerization with neutral A reduces the average charge density of the polyelectrolytes. A compromise has to be found between the charge density and the molar mass for final applications. Copolymerization of A with the double-charged di-M offers potential advantages. Higher overall charge density could be obtained using a lower molar fraction of the cationic comonomer.

The aim of this work is to report not yet existing reliable basic data on the copolymerization of di-M with other cationic and neutral comonomers and to compare the reactivity as a function of the chemical structure and the reaction conditions. In addition, the solution behavior was analyzed. Specifically, the free radical copolymerization in aqueous solution of the cationic double-charged monomer di-M with the cationic monocharged monomers Q and DADMAC as well as with the neutral monomer A will be reported. Analysis of the solution properties of di-M/A copolymers completes the study. The chemical structures of all monomers used here are presented in Figure 1.

Experimental Section

Materials. 1,3-Bis(*N*,*N*,*N*-trimethylammonium)-2-propylmethacrylate dichloride was supplied as powder by Taminco N.V. (Gent, Belgium).[2] Acrylamide, four times recrystallized, was purchased from Applichem GmbH (Darmstadt, Germany), acryloyloxyethyltrimethylammonium chloride, 80 wt% in water, was obtained from Sigma-Aldrich GmbH (Schnelldorf, Germany), and diallyldimethylammonium chloride (DADMAC), 65 wt% aqueous solution, was supplied by Aldrich Chemical Co., Inc. (Milwakee, WI). (Caution: A is toxic in contact with skin and inhalation and may cause genetic damage.) 2,2′-Azobis(2-methylpropionamidine) dihydrochloride (AMPHC) (Sigma-Aldrich, Steinheim, Germany) was used as initiator. The water for all solutions and mixtures was bidistilled. A mixture of acetone/methanol 75/25 vol %, HPLC grade, (Applichem-Axon Laboratory AG, Switzerland) was used to precipitate the copolymers in the withdrawn samples.

Copolymer Synthesis and Conversion Analysis. The 30 mL glass reactor used to perform all copolymerizations was equipped with stirrer, condenser, gas inlet, and a heating/cooling jacket. A thermostat adjusted the reaction temperature within ±1 K. Oxygen was removed from the initial comonomer feed solution prior to the reaction by purging with argon during 30 min at room temperature. The initiator was added right before reaching the polymerization temperature. During the polymerization, the reactor was continuously purged with argon. Samples of 0.3−0.4 g were withdrawn in defined time intervals of two to five minutes. The copolymerizations were continued up to about 25% conversion.

The residual monomer was analyzed using a HPLC system composed of an injector 7725i (Rheodyne, USA), a stainless steel filter, a precolumn (all Waters, USA), a pump L-6000, and a UV detector L-4000H operating at 193 nm (both Hitachi, Japan). The stationary phase was a Nova-Pak cartridge housed in a radial compression system, RMC 8 × 10 (Waters, USA) operating at 180 $kg \cdot cm^{-2}$. The mobile phase was a mixture of acetonitrile/bidistilled water, 50/50 wt%, containing 0.005 $mol \cdot L^{-1}$ dibutylamine phosphate, pH = 3 was adjusted with orthophosphoric acid.

Table 1. Summary of the General Experimental Conditions and Designation of the Copolymerization Experiments, $T = 323 \pm 1$ K

no.	series	[di-M]+[Q] ($mol \cdot L^{-1}$)	[di-M]+[A] ($mol \cdot L^{-1}$)	[di-M]+ [DADMAC] ($mol \cdot L^{-1}$)	[I] ($mol \cdot L^{-1}$)
1	di-M/Q02	0.2			4.7×10^{-3}
2	di-M/Q05	0.5			4.7×10^{-3}
3	di-M/A05		0.5		4.7×10^{-3}
4	di-M/DADMAC			1.45	1.2×10^{-2}

The samples withdrawn from the reactor were first mixed with 3 mL of acetone/methanol to precipitate and isolate the copolymer. The residual monomers remained in solution. Then 1 mL of the supernatant was centrifuged to complete the separation. Subsequently, 0.5 mL of the supernatant was diluted with water to ensure monomer peak detection within the calibrated detectable range. Finally, 0.02 mL of this diluted solution was injected into the HPLC. The HPLC system was calibrated as previously described,[16] however, adaptation to the monomers used here was necessary. Briefly, di-M, Q, DAMAC, and A solutions of known concentration were used for the calibration. The peak area of appropriate signals served as calibration parameter. The HPLC working conditions, such as flow rate (2−4 $mL \cdot min^{-1}$) and elution time, were adapted for the detection of each monomer. It has to be mentioned that the signal from the azo-initiator appears with the same elution time as the Q monomer. However, due to the comparably much lower concentration of the initiator the contribution is negligible. Further, the signal from A overlaps with the signal of acetone from the precipitant agent. Therefore, the acetone signal was analyzed separately and subtracted from the A signal employing an additional calibration procedure.

The monomer consumption rate R_p was calculated from the slope $-d[M]/dt$ at conversions lower than 10−15%, where the linear regression was characterized by $r^2 > 0.99$. Table 1 lists the general conditions for all polymerization experiments. Several monomer feed compositions have been copolymerized for each series.

Copolymer Composition and Reactivity Ratios. The copolymer compositions were calculated from residual monomer concentration data. The mathematical procedure was described elsewhere in detail.[17] Briefly, the residual monomer concentration in the withdrawn samples analyzed at different reaction times yields $-d[M_1]/dt$ and $-d[M_2]/dt$. Consequently, the instantaneous copolymer composition can be determined at any time of the copolymerization. Nevertheless, the procedure is based on the assumption that side reactions such as transfer to batch components have no significant influence on the kinetics and copolymer composition.

In addition to the experimental influences, the values of the copolymerization reactivity ratios could depend on the mathematical treatment of the raw data, the mathematical correlation of the instantaneous copolymer composition with the initial monomer feed composition.[18] Linear and nonlinear procedures are available and

Table 2. Relationships to Calculate the Counterion Activity Coefficient f_a

case	f_a	
	Manning[31]	Gueron/Weisbuch[32]
$\xi < 1$	$\exp(-\xi/2)$	
$\xi > 1$	$(1/\xi)\exp(-1/2)$	$0.7\xi^{-1}$

commonly used.[19−24] In this contribution, the calculations of the monomer reactivity ratios r_1 (di-M) and r_2 (other comonomers) were carried out according to the low conversion linear methods reported by Fineman−Ross,[20] and Kelen−Tüdös,[21] as well as the nonlinear least-squares (NLLS) fitting method proposed by Tidwell and Mortimer.[24]

Statistical Microstructure. The distribution of the monomer sequence along the copolymer chain was calculated based on the terminal copolymerization model as described by Igarashi.[25] This method calculates statistically the molar fractions of the monomer dyad sequences M_1-M_1, M_1-M_2, and M_2-M_2 as a function of reactivity ratios and compositions.

In addition, the mean monomer sequence lengths μ_1 and μ_2 were calculated using Pyun's equations.[26,27] μ_1 is the average of M_1 monomer units that follow each other consecutively in a sequence uninterrupted but bounded on each end of the sequence by M_2 units. The appropriate holds for μ_2.

Di-M/A Copolymer Analysis and Solution Behavior. The di-M/A copolymer composition of samples intended for the study of the solution behavior was analyzed by argentometric titration using a 736 GP Titrino (Metrohm, Switzerland). The chloride content in aqueous polymer solutions of known copolymer concentration, obtained by gravimetry of parallel samples, directly yields the composition of the binary copolymer.[28]

The intrinsic viscosity, [η], of samples dissolved in 0.5 M NaCl was determined at 20 ± 0.1 °C using a Viscologic TI1 capillary viscometer, capillary 0.58 mm (Sematech, Nice France). [η] was obtained from plots according to Huggins.[29]

Counterion activity measurements were performed by direct potentiometry at 20 ± 0.1 °C under inert gas atmosphere using a model 692 pH/ion meter.[28,30] A titration lid equipped with a chloride selective electrode, a double junction reference electrode (Ag/AgCl/KNO_3), holes for inert gas in- and outlet, and a pipet sealed the titration vessel. The equipment and accessories were purchased from Metrohm (Switzerland). Calibration curves were measured before and after each data set with NaCl standard solutions (Merck, Switzerland). Experiments were repeated at least in duplicate.

Table 2 summarizes relationships derived by Manning[31] and Gueron and Weisbuch[32] to calculate counterion activity coefficients, f_a, for the two limiting cases $\xi < 1$ and $\xi > 1$. ξ is the linear charge density parameter (Manning parameter), defined as $\xi = l_B/b$, where b is the average charge distance between two charges on an infinitely long stiff linear polyelectrolyte chain, calculated as $b=L/N$ with L the contour length and N the total number of charges. l_B is the Bjerrum length, which has a value of 0.712 nm in water at 20 °C.

Results and Discussion

Copolymerization Diagrams. Copolymerization diagrams presenting the dependence of the instantaneous copolymer composition on the initial monomer feed composition have been constructed based on the data of the monomer conversion analysis. Figure 2 shows copolymerization diagrams, the molar fraction of di-M in the produced copolymer (di-$M^P = f_1$) as a function of the molar fraction of di-M in the monomer feed (F_1) for the series di-M/Q02, di-M/Q05, di-M/A05, and di-M/DADMAC, for which the reaction conditions are summarized in Table 1. The subscript 1 denotes monomer 1, which is di-M throughout this paper.

Similarly shaped dependencies are visible in Figure 2 for the copolymerization series di-M/Q02, di-M/Q05, and di-M/A05.

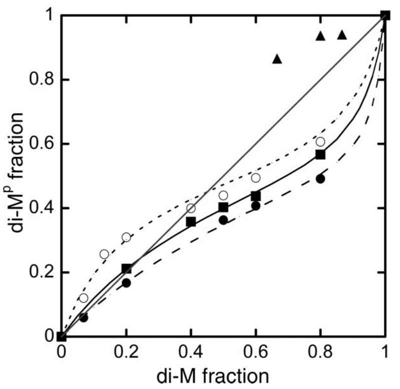

Figure 2. Molar fraction of di-M in the copolymer (f_1) as a function of the molar fraction of di-M in the feed (F_1). Experimental results: for di-M/Q, (■) [di-M] + [Q] = 0.5 mol·L^{-1}, (●) [di-M] + [Q] = 0.2 mol·L^{-1}; for di-M/A, (○) [di-M] + [A] = 0.5 mol·L^{-1}; and for di-M/DADMAC, (▲) [di-M] + [DADMAC] = 1.45 mol·L^{-1}. The curves represent fits with reactivity ratios calculated according to Tidwell−Mortimer (Table 3). Grey line: $f_1 = F_1$.

Differently, the di-M/A curve clearly crosses the ideal copolymerization line $f_1 = F_1$. This is characteristic for copolymerizations termed azeotropic. Over a relatively wide range of low di-M molar feed fraction, di-M is preferably consumed. This range of preference of di-M is diminished to about <0.2 for the di-M/Q05 series. Almost coincidence with the ideal line is observed up to 0.2. Finally, the plot for the di-M/Q02 series remains below the ideal curve for almost the entire range of di-M feed fraction and for the conditions studied here. Ideality seems to exist only at very low di-M fraction.

Whereas the copolymerization of di-M with Q and di-M with A yielded copolymers at total monomer concentrations as low as 0.5 and 0.2 mol·L^{-1}, the series di-M/DADMAC required a minimum concentration of 1.45 mol·L^{-1} for obtaining copolymers. And even at this total monomer feed concentration, copolymerization was only observed if the di-M molar feed fraction was above 0.6. If the di-M molar feed fraction was lower, the reaction only yielded di-M homopolymers. It is noteworthy that, despite the 4-fold lower charge density per monomer unit length of DADMAC, its reactivity is inferior of the reactivity of di-M. Decreasing the fraction of di-M in the monomer feed di-M/DADMAC is accompanied by decrease of the ionic strength and, consequently, by less electrostatic screening and stronger electrostatic repulsion. For example, comparing 0.8 and 0.2 di-M molar fraction, the average number of charges per monomer is reduced by 25%, from 1.6 to 1.2. Further increase of the total monomer concentration was not possible without provoking unfavorable nonintended side effects such as incomplete dissolution of di-M or autoacceleration at low conversion.[3] While an aqueous solution concentration of up to 4 mol·L^{-1} is not a problem for DADMAC,[5] the solubility of di-M is limited to about 1.9 mol·L^{-1}. Preliminary homopolymerization studies revealed that autoacceleration could already occur at di-M concentrations slightly higher than 1 mol·L^{-1}.[3] Therefore, the majority of copolymerizations in this first study have been performed at relatively low total concentrations, 0.5 and 0.2 mol·L^{-1}.

Reactivity Ratios. The experimental results presented in Figure 2 have been treated according to Fineman−Ross,[20] Kelen−Tüdös,[21] and Tidwell−Mortimer[24] to calculate the reactivity ratios $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. As will be presented below, the chain length of the copolymers was sufficient to apply these methods. The reactivity ratios are defined as the ratio of the propagation constants of the homopolymerization (k_{11} and k_{22}) and copolymerization (k_{12} or k_{21}) of the two components of the monomer feed, M_1 and M_2. For di-M/DADMAC, the

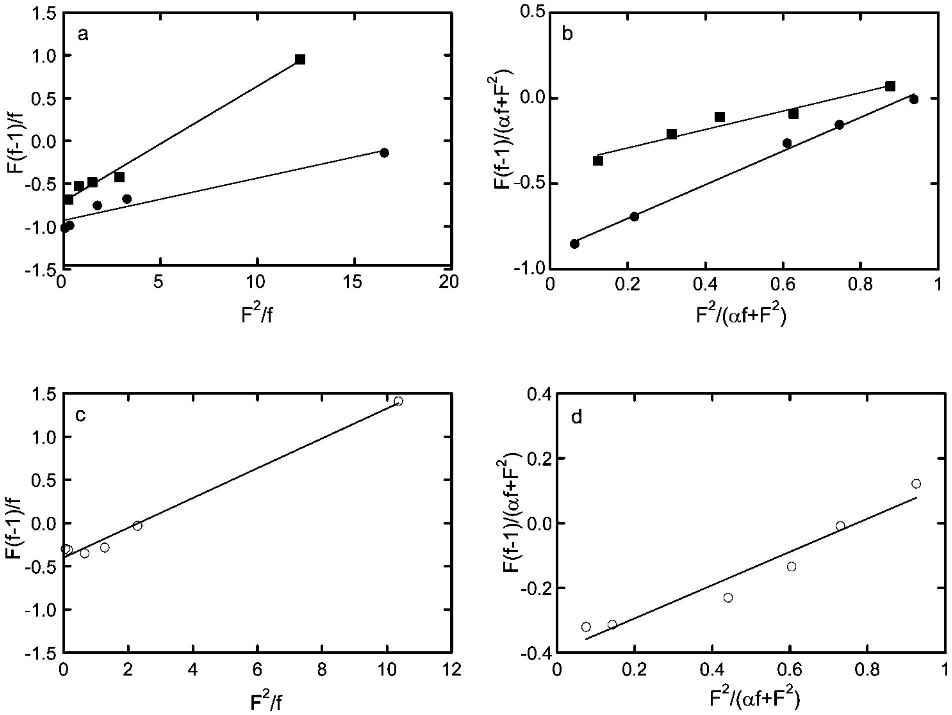

Figure 3. Determination of reactivity ratios for di-M/Q and di-M/A: (a) Fineman−Ross [di-M] + [Q] = (■) 0.5 mol·L^{-1}, r^2 = 0.99; (●) 0.2 mol·L^{-1}, r^2 = 0.95; (b) Kelen−Tüdös [di-M] + [Q] = (■) 0.5 mol·L^{-1}, r^2 = 0.94; (●) 0.2 mol·L^{-1}, r^2 = 0.99; (c) Fineman−Ross [di-M] + [A] = (○) 0.5 mol·L^{-1}, r^2 = 0.94; (d) Kelen−Tüdös [di-M] + [A] = (○) 0.5 mol·L^{-1}, r^2 = 0.99. (Note the different scale for the *y*-axes in parts b and d.)

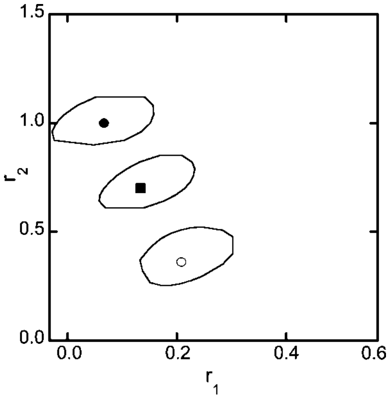

Figure 4. Joint confidence regions at 95% probability for the reactivity ratios of [di-M] + [Q] = (■) 0.5 mol·L^{-1} and (●) 0.2 mol·L^{-1} and [di-M] + [A] = (○) 0.5 mol·L^{-1}.

number of experimental points was not sufficient for such calculation for the reasons explained in the previous paragraph. Figure 3 shows the Fineman−Ross and Kelen−Tüdös plots. Figure 4 presents the joint confidence intervals at 95% probability calculated as proposed by Tidwell and Mortimer. Here $F = [M_1]/[M_2]$ and $f = d[M_1]/d[M_2]$ denote the monomer concentration ratio in the comonomer feed and the instantaneous copolymer composition with M_1 always being di-M. The parameter α is defined as $\alpha = \sqrt{(F^2/f)_{max}(F^2/f)_{min}}$.[21]

It was not the intention of this research to determine very precise reactivity ratios for the monomer pairs included here, but to identify principal differences of the monomer reactivity and their correlation with the chemical structure of the monomers, in particular the charge density and the location of the radical position in relation to the charges. Nevertheless, the data is considered as sufficiently reliable for such conclusions. Table 3 lists the reactivity ratios for all three data treatments. Good agreement is obvious. For Fineman−Ross, the errors refer to the slop and intercept. For Kelen−Tüdös, a procedure was used recommended by these authors.[33] The accuracy of the Tidwell−Mortimer r-values was obtained from the extension of the confidence intervals in Figure 4.

Overall, the majority of both reactivity ratios, r_1 and r_2, has values of <1, with the exception of $r_2 \approx 1$ for di-M/Q at 0.2 mol·L^{-1} total monomer concentration. Copolymerizations for which both r_1 and r_2 are <1 can be classified as statistical azeotropic copolymerizations. Azeotropic behavior could already be concluded free of doubt for di-M/A from Figure 2, but is now also confirmed for di-M/Q at 0.5 mol·L^{-1} total monomer concentration, although the crossing with the ideal line occurs at relatively low di-M molar feed fraction. Moreover, for all copolymerizations the tendency to form alternating copolymers is expected because of $r_1 \times r_2 < 1$ in all cases.

The copolymerizations of di-M/Q and di-M/A show, as expected, higher reactivity for the less charged Q and the neutral A. However, the incorporation of di-M increases with the ionic

Table 3. Reactivity Ratios of di-M (M_1, r_1), Q and A (M_2, r_2) at Different Total Monomer Concentrations

	Fineman−Ross			Kelen−Tödös			Tidwell−Mortimer		
$[M_1]+[M_2]$ (mol·L^{-1})	r_1	r_2	$r_1 \times r_2$	r_1	r_2	$r_1 \times r_2$	r_1	r_2	$r_1 \times r_2$
Copolymerization di-M/Q									
0.5	0.13 ± 0.01	0.70 ± 0.04	0.09	0.13 ± 0.08	0.9 ± 0.13	0.12	0.14 ± 0.1	0.72 ± 0.1	0.10
0.2	0.05 ± 0.01	0.93 ± 0.05	0.05	0.09 ± 0.1	1.10 ± 0.1	0.10	0.07 ± 0.1	1.00 ± 0.1	0.07
Copolymerization di-M/A									
0.5	0.17 ± 0.01	0.43 ± 0.05	0.07	0.21 ± 0.04	0.55 ± 0.03	0.12	0.22 ± 0.08	0.36 ± 0.15	0.08

Table 4. Structural Data for the Copolymers di-M/Q and di-M/A. M_1, Where F_1, and μ_1 Refer to di-M, M_2 and μ_2 Refers to Q or A

		molar dyad fraction in the copolymer				
		blocks		alternation		
$[M_1] + [M_2]$ (mol·L^{-1})	F_1	M_1-M_1	M_2-M_2	M_1-M_2	μ_1	μ_2
		Copolymerization di-M/Q				
0.5	0.80	0.20	0.07	0.73	1.18	1.55
	0.60	0.07	0.19	0.73	1.11	1.92
	0.50	0.05	0.24	0.70	1.01	2.07
	0.40	0.03	0.32	0.65	1.07	2.30
	0.20	0.01	0.60	0.41	1.04	3.70
0.2	0.80	0.10	0.11	0.79	1.06	2.03
	0.60	0.04	0.22	0.73	1.05	2.45
	0.50	0.02	0.30	0.67	1.04	2.75
	0.20	<0.01	0.66	0.33	1.01	5.90
	0.06	<0.01	0.88	0.12	1.00	16.50
		Copolymerization di-M/A				
0.5	0.80	0.25	0.04	0.71	1.34	1.23
	0.60	0.10	0.11	0.78	1.21	1.36
	0.50	0.06	0.18	0.75	1.17	1.46
	0.40	0.04	0.25	0.71	1.14	1.55
	0.20	0.02	0.40	0.58	1.10	1.80
	0.13	0.01	0.50	0.50	1.07	2.04

strength comparing the two di-M/Q series. Interestingly, and somewhat surprising, the copolymerization series di-M/A showed azeotropic behavior, preferring the incorporation of the double-charged cationic monomer di-M at low molar fraction of di-M in the comonomer feed. These findings will be discussed in detail below.

Statistical Microstructure. To obtain additional information about the copolymerization process, the molar fraction of the monomer dyad sequences M_1-M_1, M_2-M_2, and M_1-M_2 in the binary copolymer chain was analyzed. It represents the distribution of bonds between the same and different monomer units.[25] M_1-M_1 and M_2-M_2 refer to the so-called blockiness, while M_1-M_2 describes alternation. Further, mean monomer sequence lengths μ_1 and μ_2 of M_1 and M_2 have been calculated using an approach of Pyun.[27] Table 4 lists the results.

The authors are aware of the potential uncertainty of a statistical analysis, which is based on the terminal model neglecting effects of the penultimate and antepenultimate monomer units.[27,34,35] In the case of charged monomers such an effect cannot be excluded a priori. However, previous quantitative studies of such effects for the copolymerization of DADMAC with A revealed only slightly better agreement of experimental data with model calculations using the four reactivity rations obtained from the penultimate model.[36] These results justify the use of the terminal model here for di-M/Q and di-M/A. Nevertheless, experimental evidence is needed to confirm this conclusion.

Alternation tendency clearly dominates for the majority of copolymerization conditions, confirmed by values of >0.5 for the molar dyad fractions of M_1-M_2. Only for di-M/Q at the lowest di-M molar feed fractions (below 0.2), blockiness of Q or A becomes increasingly important. Comparing the di-M/Q copolymerizations performed at different total monomer concentrations, the blockiness of M_2-M_2 is more pronounced at lower total monomer concentration, which corresponds to lower ionic strength. The statistical calculations further confirm the alternating tendency previously concluded from the composition and reactivity studies.

Decreasing the ionic strength by lowering the total feed concentration reduces electrostatic screening leading to a lower reactivity especially of the double-charged monomer di-M. As a consequence, the probability of forming either the homodyad (M_1-M_1) or the heterodyad linkages (M_2-M_1) becomes low. Under such conditions, the homopolymerization of the less electrostatically hindered monomers Q and A is preferred rather than their copolymerization with di-M. Hence, M_2-M_2 becomes the major dyad fraction. As well, lower reactivity of di-M results in reduced mean sequence lengths of di-M (μ_I) in the copolymers. Nonlinear dependencies of both M_1-M_1 and μ_I on the molar feed fraction of di-M becomes visible for all copolymerizations from appropriate plots of the data in Table 4 (Supporting Information Figure S1), but is most pronounced for di-M/A.

Monomer Consumption Rates. The results presented and discussed so far allow for conclusions concerning the copolymer composition obtained as a function of the reaction conditions. Whereas the determination of the copolymer composition as a function of the monomer feed composition, which yields the reactivity ratios, and statistical evaluation of the copolymer microstructure are reported for many copolymerizations, studies concerning the copolymerization rates and the kinetic orders of the polymerizing components are relatively rare.

In this study, the monomer consumption was analyzed to obtain the instantaneous copolymer composition. This method yielded monomer consumption rates, R_p(X) for the initial phase, low conversion phase, of the copolymerization of di-M with the other comonomers. Figure 5 presents these kinetic results. (X) refers to the analyzed monomer.

Figure 5a shows the monomer consumption rates of di-M as a function of the di-M initial concentration in the feed. Figure 5c presents such data for the monomers A, Q and DADMAC. Figure 5b repeats the data of Figure 5a but now as a function of the monomer feed composition. While the first presentation (5a) reflects the real concentrations, the second one (Figure 5b) allows for a better correlation with the plots in the copolymerization diagrams in Figure 2.

Figure 5c shows for the two more reactive monomers, Q and A, as generally expected for polymerization processes, a monomer consumption rate increasing linearly with the concentration in a double logarithmic plot. From the regression, formal monomer reaction orders were obtained as $\alpha = 1.28$ for A analyzing series di-M/A05, and as $\alpha = 1.78$ and $\alpha = 2.01$ for Q analyzing series di-M/Q05 and di-M/Q02 0.2, respectively. The reaction order α of A is in the range as previously found for homopolymers of A at concentrations $[A] < 0.5$ mol·L^{-1}, reported as $\alpha = 1.25$ as lowest value[37,38] and $\alpha = 1.5$ as highest value.[39] No reaction order was obtainable from the few points for DADMAC. However, a much lower DADMAC consumption rate is clearly visible and a lower reaction order can be hypothesized likewise. Interestingly, in the concentration range 0.1−0.2 mol·L^{-1} where data are available to compare series d-M/Q05 and di-M/Q02, the consumption rate of the monomer Q is higher for the series di-M/Q02, at totally lower feed concentration. However, at conditions where the initial Q concentration is the same in the series di-M/Q05 and di-M/Q02, it has to be considered that the amount of di-M differs and certainly influences the reaction.

Completely different kinetic behavior is visible in Figure 5a and b. For di-M/A05 and di-M/Q02, the reaction order has positive values at low di-M concentration, passes a maximum, before it decreases. The slope for the di-M/Q05 copolymerization is always negative for the concentration range studied here. However, a positive slope cannot be excluded for lower di-M concentrations. R_p(di-M) has the same order of magnitude for the copolymerizations with Q and A performed at the same total monomer feed concentration 0.5 mol·L^{-1}. More similarity exists at higher di-M feed fraction/concentration. Despite the almost 3-fold total concentration of the di-M/DADMAC series, R_p(di-M) is in the same order of magnitude as for di-M/Q05 and di-M/A05. The strong concentration dependence of R_p(di-M) for this series, with di-M being the more reactive mono-

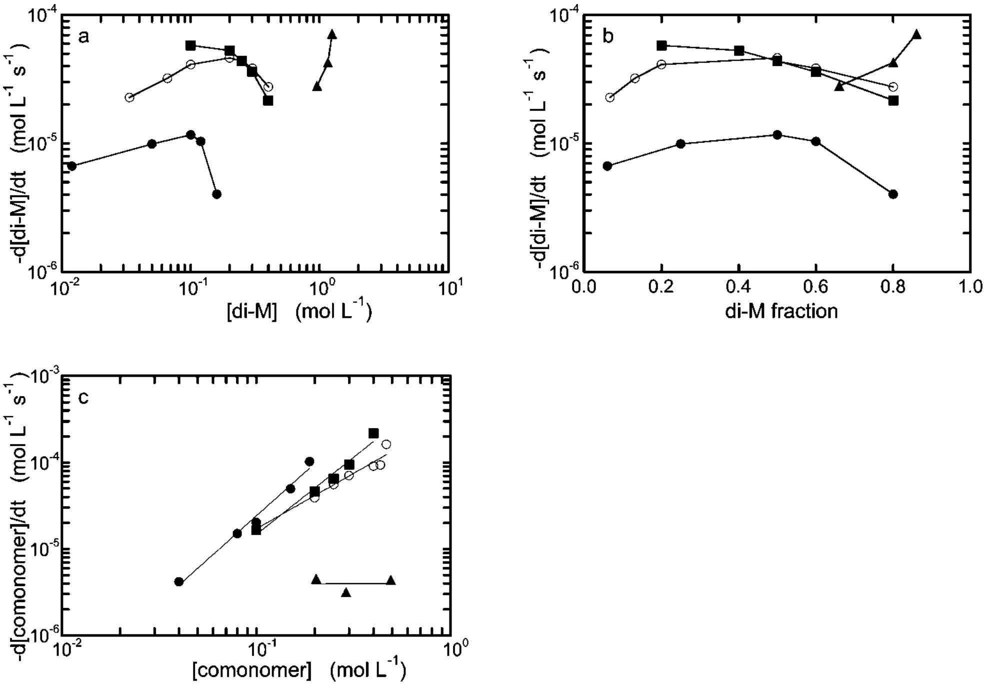

Figure 5. Monomer consumption rates R_p(X). R_p(di-M) as a function of (a) the initial di-M monomer feed concentration and (b) the di-M molar feed fraction for series (■) di-M/Q05, (●) di-M/Q02, (O) di-M/A05, and (▲) di-M/DADMAC. (c) R_p(Q) for series (■) di-M/Q05 and (●) di-M/Q02, R_p(A) for series (○) di-M/A05, and R_p(DADMAC) for series (▲) di-M/DADAMAC as a function of the Q, A, or DADMAC initial feed concentration.

mer here, corresponds to the high monomer reaction order $\alpha = 4.4$ experimentally determined for the di-M homopolymerization.[3]

It is suggested that the more reactive comonomers for all series kinetically behave as expected, however, the less reactive component behaves unusually. The kinetics of the latter correlates qualitatively with the increasing preference of Q and A at higher di-M feed fraction.

Prior to discussing the copolymerization of di-M with other cationic monomers and with acrylamide more in detail it is important reminding that nonideal conditions are present in these systems with a known potential to affect the polymerization kinetics. These are the permanent ionic character of the monomers di-M, Q and DADMAC, the methacrylic respectively acrylic structure of di-M and Q, and using water as solvent. It is currently understood, that acrylate monomers can introduce difficulties to the kinetic scheme by the presence of midchain radicals largely influencing propagation and termination mechanism.[40] For nonionized methacrylic acid in aqueous solution, solvent effects of kinetic origin have been reported.[41] In case of ionization of the latter, complex influence of the monomer concentration on the kinetics was suggested.[5] Here we copolymerize permanently charged monomers in water yielding strong and highly charged polyelectrolytes. It cannot be predicted a priori which effects have to be considered to which extent in addition to the strong electrostatic influences.

Copolymerization of di-M with Other Cationic Monomers. The copolymerization of di-M with the other two cationic monomers Q and DADMAC have been performed to identify the impact of the structural and electrochemical characteristics of the monomers on their reactivity, to distinguish between the influence of the charge density and the general chemical structure.

As it is obvious from Figure 1, the distance between the charged groups and the reactive double bond, the later position of the radical, is similar for Q possessing one positively charged quaternary ammonium group and di-M with two positively charged groups. However, this distance is much shorter for the DADMAC structure where only one methylene group separates the quaternary ammonium group from the double bond. On the other hand, the average linear charge distance *b* along a polyDADMAC chain is about 0.5 nm, which is the double of 0.25 nm estimated for polyQ and the 4-fold of 0.125 for a homopolymer of di-M.

The copolymerization results for the series di-M/DADMAC, revealing a higher reactivity for di-M, confirm, despite the two charges of di-M, that the spacing groups between the two charges and the radical position provide sufficient screening to reduce the electrostatic repulsion more as it is the case for the much less charged DADMAC. The results support previous conclusions that the distance between the growing radical position and the monomer charge is the dominating fact for the reactivity of charged monomers.[4,6,36]

In the case of the structurally similar monomers di-M and Q, the number of charges clearly determines the reactivity. The sensitivity of the reactivity ratios to the total monomer concentration supports the electrostatic interpretation. Higher total monomer feed concentration/higher ionic strength diminishes the difference between r_1 and r_2. In addition, as visible from Figure 5, the impact of the ionic strength on the monomer consumption rate is much more pronounced for di-M than for Q. This qualitative conclusion is based on results from, at present, two total monomer concentrations. Extension of the concentration range is needed for quantification.

Copolymerization of di-M with Acrylamide. Figure 6 presents the relative enrichment of di-M in copolymers of the series di-M/A05 as a function of increasing initial molar feed fraction of A. This plot clearly demonstrates the preference of the double-charged di-M if the neutral A becomes available in the surplus. Several influences have to be considered for the discussion of these results including both electrostatic and hydrophobic interactions.

Several studies of the free radical polymerization of water-soluble monomers in aqueous solutions discuss the importance of hydrophobic interactions.[42−45] Water-soluble polymers con-

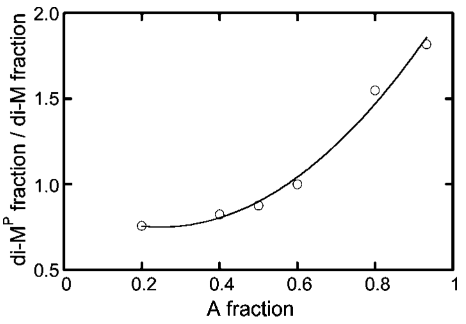

Figure 6. Relative amount of di-M in the di-M/A copolymer at different molar fractions of A in the monomer feed. [di-M] + [A] = 0.5 mol·L^{-1}, $T = 323$ K.

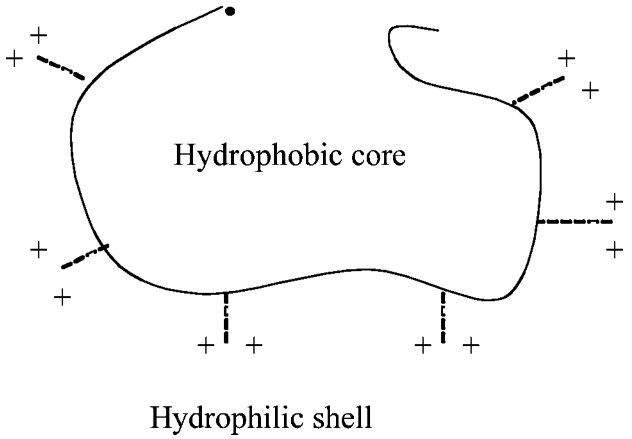

Figure 7. Schematic representation of the micelle-like copolymer conformation.

taining a long hydrocarbon chain and short hydrophilic branches of the type COX (where X = OH, NH_2, SO_3^-, etc.) have been considered as compounds exhibiting surface activity. While, for example, the carbonyl groups of A are practically bonded with water molecules, only some of the carbonyl groups take part in the formation of H-bonds in the polymers. Such difference in the solvation of monomer and polymer by water emphasizes the importance of hydrophobic interactions in aqueous solutions of polymers and copolymers derived from A or other acrylic water-soluble monomers.[43,44] The aqueous solution of such polymers have been reported to form micelle-type associates consisting of a hydrophobic core and a hydrophilic outer shell, as schematized in Figure 7 for the copolymer type studied here.

The chain propagation takes place in these associates. As a consequence, the copolymer composition depends on the capability of the comonomer to enter the core,[43−45] and the composition of the monomer mixture within the associates could even differ from that one of the monomer feed. However, it is still uncertain whether this is on the time scale of kinetic steps to affect the kinetics.

The copolymerization data for di-M/A indicate preferential incorporation of di-M at low di-M feed fraction. This could suggest a higher capability of di-M to enter such potential associates if A is available in excess. As the amount of A in the monomer feed increases, both the polymerization rate and the molar mass increase,[46,47] enhancing the importance of the micelle-associates. However as demonstrated in Figure 2, the di-M fraction in the di-M/A copolymer continuously increases with the di-M feed fraction even if di-M is not the preferred monomer. Hence, the charge density in the copolymer increases making now the incorporation of the charged monomer more difficult. Generally, hydrophobic interactions vary for acrylic and methacrylic monomers.

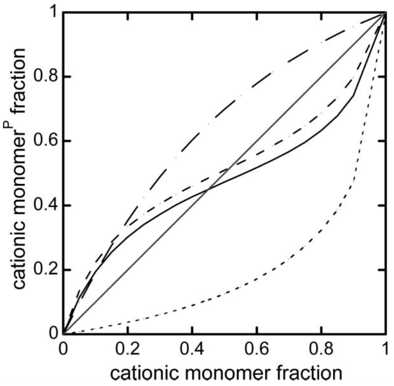

Figure 8. Molar fraction of the cationic monomer in the copolymer (f_1) as a function of the molar fraction of the cationic monomer in the feed (F_1) calculated from reactivity ratios of the copolymerization of A with: (—) di-M, (— —) DMAEM, (--) DMAEA=Q, (•••) DADMAC. Grey line: $f_1 = F_1$.

Table 5. Reactivity Ratios of the Copolymerization of A (r_2) with Cationic Monomers (r_1) and Average Linear Charge Distance *b* of the Corresponding Cationic Homopolymer

monomer	r_1	r_2	$r_1 \times r_2$	*b* (nm)	ref.
DMAEM	2.46	0.49	1.2	0.25	4
DMAEA[a]	0.34	0.29	0.098	0.25	4
di-M	0.22	0.36	0.08	0.125	
DADMAC	0.06	6.4	0.38	0.5	5

[a] Same as Q.

Comparison of the Copolymerization of Acrylamide with di-M and Other Cationic Monomers. Differences are observed when comparing the reactivity ratios obtained here for the di-M/A copolymerization with those reported for the copolymerization of A (M_2) with other cationic monomers (M_1) such as DADMAC or cationic derivatives of methacrylic acid, acrylic acid, methacrylamide and acrylamide. Higher reactivity and preferred incorporation of the neutral A into the copolymers with charged monomers is expected from the electrochemical point of few. However, this is observed only for DADMAC/A over the entire range of feed composition. Values in the range of about $1 < r_1 < 2.5$ and $0.25 < r_2 < 0.6$ have been reported for cationic methacrylic derivatives. Differently, the range was $0.34 < r_1 < 0.48$ and $0.29 < r_2 < 0.95$ for the analog acrylic derivatives.[6,8] These ratios indicate preference of the cationic methacrylic derivatives and azeotropic copolymerizations for the acrylic analogs with preference of the cationic monomer at its low feed fractions.

Figure 8 and Table 5 provide selected representative comparisons for the copolymerization of A with di-M, DADMAC, quaternized dimethylaminoethylacrylate (DMAEA = Q, synonym frequently used for acryloyloxyethyltrimethylammonium chloride), and quaternized dimethylaminoethylmethacrylate (DMAEM).

The reactivity of the cationic monomers is in the order of DMAEM ≫ DMAEA > di-M ≫ DADMAC. Hence, the reactivity of di-M does not correspond with the general observation that the reactivity of methacrylic cationic derivatives is higher than the reactivity of the acrylic derivatives and even A. The more hydrophobic methacrylic monomer is suggested having a higher capability to enter the core of potential polymer associates. The hydrophobic interactions are strong enough to overcome electrostatic repulsions. The less hydrophobic acrylic monomer has this higher capability only if its molar feed fraction is low. At higher feed fraction when copolymer chains of higher charge density are produced, the electrostatic repulsion dominates preferring the neutral A. In the case of the double-charged methacrylic di-M the electrostatic effects are stronger than in

Table 6. Synthesis Conditions (Total Monomer Feed Concentration [di-M] + [A]), Chemical Composition (Molar Fractions of di-M and A in the Copolymer), and Intrinsic Viscosity ($[\eta]_H$) of di-M/A Copolymers and Polydi-M in 0.5 M NaCl at $T = 20$ °C

polymer	[di-M]+[A] (mol ·L^{-1})	di-M^P	A^P	$[\eta]_H$ (mL·g^{-1})
di-M/A-1	0.5	0.30	0.70	141
di-M/A-2	0.5	0.42	0.58	109
di-M/A-3	1.0	0.47	0.53	135
di-M/A-4	1.0	0.55	0.45	138
polydi-M	1.91	1.0	0	233

Table 7. Experimental and Calculated Counerion Activity Coefficients (f_a) for Copolymers and Homopolymers of Different Average Linear Charge Distance b

polymer	b (nm)	$f_{a,\mathrm{experimantal}}$[a]	$f_{a,\mathrm{Manning}}$	$f_{a,\mathrm{Gueron/Weisbuch}}$
di-M/A-1	0.44	0.61−0.49	0.37	0.43
di-M/A-2	0.30	0.40−0.30	0.26	0.29
di-M/A-3	0.27	0.37−0.29	0.23	0.26
polyQ	0.25	0.33−0.27	0.21	0.25
di-M/A-4	0.22	0.25−0.21	0.19	0.22
polydi-M	0.12	0.18−0.12	0.10	0.12

[a] First value for the lowest experimental concentration and second value for the highest concentration.

the monocharged analog causing azeotropic behavior as for the acrylics. The reactivity of DADMAC was even less than for di-M in the di-M/DADMAC series. This is in agreement with the data in Table 5.

Solution Behavior of di-M/A Copolymers. Table 6 contains information concerning the di-M/A copolymers and the di-M polymer, for which the electrochemical solution behavior was studied.

The intrinsic viscosity of the di-M/A copolymers, as a measure for the molar mass, depends on the synthesis conditions and, if these are kept constant, in particular on the chemical composition of the resulting copolymer. The copolymers used here were obtained from copolymerizations at relatively low total concentrations up to about 25−30% conversion. Residual monomer and initiator have been removed by dialysis against water controlled by conductivity measurements. One has to consider that the viscosity of the polymerizing batches becomes already relatively high at this conversion. Moreover, due to the different reactivity of the two monomers a drift of the monomer feed composition is probable. To limit the polydispersity of the chemical copolymer composition, the majority of the copolymers for the electrochemical studies were produced at monomer feed compositions for which $f_1 \approx F_1$ can be expected. Nevertheless, a certain level of molar mass and composition polydispersity remains due to the 20−30% variation of the total monomer concentrations with progressing polymerization. For polydi-M, a number average molar mass $M_n = 3.25 \times 10^5$ g·mol^{-1} was measured by membrane osmometry.[48] The intrinsic viscosities of the copolymers let assume lower moderate molar masses. It is advantageous that the copolymerization diagram of di-M/A crosses the ideal polymerization line at about 0.45 molar di-M fraction. Mathematically results for copolymers with di-M^P = 0.5 the same average linear charge density as for polyQ. The experimental comparison of the counterion activity coefficients is therefore interesting.

Table 7 summarizes the theoretical and experimental values of the counterion activity coefficient f_a for the copolymers of Table 6 and homopolymers of di-M and Q. The concentration dependence of f_a is visualized in Figure 9. The plots in Figure 9 show a decrease of f_a with increasing concentration. The decrease is more pronounced for copolymers with lower di-M^P fraction. In addition, the comparison of the experimental and theoretical values in Table 7 reveals slightly higher experimental values.

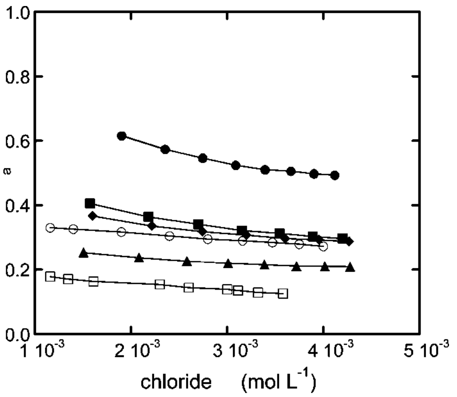

Figure 9. Counterion activity coefficient f_a of (●) di-M/A-1, (■) di-M/A-2, (♦) di-M/A-3, (▲) di-M/A-4, (○) polyQ, and (□) polydi-M, $T = 20$ °C.

Comprehensive counterion activity studies with model polyelectrolytes of the poly(vinylbenzyltrialkylammonium) type with $b = 0.25$ nm previously revealed an influence of the concentration and the chain length on the polyion-counterion interaction. Only for degrees of polymerization higher than 400 no concentration dependence was present at comparable concentration range. For shorter chains, the concentration dependence became increasingly pronounced.[30] According to the detailed discussion presented there, the concentration dependent behavior of f_a observed here for di-M/A copolymers and the homopolymers can be attributed to the moderate chain length and chain length polydispersity.

A difference between values calculated from theoretical models and experimental data was also found previously for the model polymers. The difference between theory and experiment increased with decreasing chain length.[30] So far, the copolymers behave as expected for polydisperse samples of moderate molar masses; their experimental f_a values are slightly higher than calculated from theories and increase with dilution.

However, additional facts should not be neglected for di-M/A copolymers of lower average charge density. For example, the molar ratio of the double-charged di-M to A is 3:7 in the copolymer di-M/A-1. That means, each double-charged monomer unit is separated by 2−3 neutral A units. As a consequence, despite the mathematical average of $b = 0.44$ nm, the distance between the double-charged di-M units amounts in reality to 0.75 to 1.0 nm, a distance for which counterion condensation should not be present. On the one hand, this heterogeneous charge distribution should reduce the counterion condensation resulting in deviations from the theory. On the other hand, the flexibility of the spacer group between the charges and the polymer backbone as well as of the chain segment of the A units between the di-M units will diminish the reduction and limit the deviation from the theory as observed for di-M/A-1. The deviation from the theory is for this sample only a little more pronounced.

Overall, the results presented in Table 7 and Figure 9 confirm very good correlation and graduation of the average linear charge density and the polyion-counterion interaction quantified by f_a for all polymers.

Conclusions

The copolymerization of the cationic double-charged monomer di-M with the cationic monocharged monomers Q and DADMAC and the neutral monomer A allowed for evaluating the impact of the charge density and the overall chemical structure on the kinetics and mechanism of the reactions. The distance between the quaternary ammonium groups and the radical position, the charge density, and the ionic strength in the polymerizing batch were identified as major influences determining the copolymer composition and kinetics. However, in particular obvious when copolymerizing di-M with A, hydrophobic interactions have also to be considered and can probably not be neglected. They compete with electrostatic influences. The latter was confirmed by comparison of the copolymerization of A with di-M and monocharged acrylic and methacrylic esters of similar chemical structure. Due to the two charges, di-M behaves more like the acrylic ester and not like the more hydrophobic methacrylic structure. Interestingly, homopolymerization of di-M was clearly preferred for the monomer pair di-M/DADMAC, despite the 4-fold higher charge density produced with di-M in the polymer chain.

The analysis of the monomer consumption rates showed concentration dependencies as expected for the preferred comonomer but unusual kinetic orders for the less reactive monomer. However, comprehensive interpretation and reliable conclusions will need more experimental data for comparable and extended concentration ranges and ionic strength.

The chain lengths of the majority of copolymers produced at conditions suitable for kinetic mechanistic studies were limited. To avoid strong end group effects, the copolymers for electrochemical studies had to be produced under modified conditions yielding sufficient chain lengths. Decreasing charge density of di-M/A copolymers seems to cause increasing deviation from theoretically expected polyion-counterion interaction. Heterogeneous charge distribution, locally high charge density at the position of the di-M monomer unit and neutrality at the A segment, could be the reason. However, final conclusions require studies with uniform model copolymers.

Overall, the copolymerization study of di-M provides the first kinetic mechanistic results for this monomer, which can be used as a basis for copolymerization process design and development.

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Supporting Information Available: Figure S1, illustrating the data of Table 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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