# Kinetic Investigations of Quaternization Reactions of Poly[2-(dimethylamino)ethyl methacrylate] with Diverse Alkyl Halides

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**Kinetic investigations of the quaternization reactions of poly[2-(dimethylamino) ethyl methacrylate] (PDMAEMA) with alkyl halides (1-iodobutane, 1-iodoheptane, and 1-iododecane) are carried out at different temperatures. For this purpose, a PDMAEMA ($M_n$ = 17.8 kDa, $Đ$ = 1.35) synthesized via reversible addition fragmentation chain transfer polymerization is utilized. The progress of the quaternization reactions is followed by proton nuclear magnetic resonance. As expected, the rate of quaternization is higher with increasing temperature. The experimental data are used to determine the following kinetic parameters: order of the reaction, Arrhenius' pre-exponential factor, and activation energy. To the best of knowledge, this is the first contribution that provides detailed kinetic data of the quaternization reactions on PDMAEMA.**

## 1. Introduction

In the last two decades, cationic polymers have been widely studied for potential antimicrobial applications due to its effectivity against bacteria, such as gram-positive and gram-negative, and virus; furthermore, they possess low toxicity.[1,2] Reversible-deactivation radical polymerization (RDRP) methods have enabled accessing this kind of polymers with low dispersity ($Đ$) and good control of the molar mass.[3,4] Reversible addition-fragmentation chain transfer (RAFT) polymerization, a well-established RDRP technique, permits to synthesize a wide range of well-defined polymers from a variety of monomers.[5,6]

Poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) has a tertiary amine structure as pendant group, which in an acidic medium or as a quaternary ammonium salt acquires a cationic character.[7] Quaternized PDMAEMA is a versatile polymer that can be applied in antimicrobial systems,[8] such as films with porous surfaces of narrow size,[9] cationic coatings for silica nanoparticles,[10] recognition elements against bacteria,[11] tandem systems based on polymer-nanoparticles $Ca(OH)_2$-$Mg(OH)_2$ with fungicide properties,[12] or functionalized cellulose surfaces for preparation of fibers or nanocrystals.[13,14] Among different synthetic techniques, RAFT polymerization has been utilized for the synthesis of PDMAEMA, where reaction parameters such as the chemical nature of the chain transfer agent (CTA), concentration of reagents, and reaction medium have significant effects on the control of molar mass, $Đ$, and chemical structure of derived polymers.[15,16]

Despite the wide use of quaternized PDMAEMA, and cationic polymers in general, there are few contributions related to kinetic investigations and models of quaternization reactions of amino groups in PDMAEMA. Armes and co-workers have extensively reported diverse investigations related to quaternized PDMAEMA systems since mid-1990s.[17–19] To mention a couple of relevant examples, for instance, they systematically demonstrated that the cloud point of PDMAEMA aqueous solutions increases with the degree of quaternization (DQ) of the homopolymer.[18] In addition, they also reported on the effect of the molar mass on the cloud point of PDMAEMA aqueous solutions showing that this property is strongly influenced by the degree of polymerization; this study was systematically performed by investigating a PDMAEMA library covering a broad range of molar mass.[19] More recently, Yañez-Macias et al. carried out the synthesis of PDMAEMA via RAFT polymerization to obtain polymers of different molar mass, which, in a subsequent reaction, were quaternized with methyl iodine at different

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degrees.[20] The authors evaluated the effect of molar mass and DQ on a well-known thermoresponsive property of these materials (i.e., low critical solution temperature (LCST)) in aqueous solutions and in a broad temperature range. It was observed that an increase in the LCST is related, in general, to an augment in the DQ and/or a decrease in the polymer molar mass. Zhao et al. achieved the synthesis of copolymers based on poly(methyl methacrylate) and PDMAEMA followed by a subsequent quaternization of the PDMAEMA units with undecenyl bromide at low DQ (5 to 10 mol%).[21] The results showed that higher DQs favored an increase in the glass transition temperature of the copolymers and that these materials can find potential applications in antifogging and antimicrobial coatings. However, to the best of our knowledge, there are not contributions in the literature describing detailed kinetic studies of PDMAEMA quaternization reactions with different alkyl halides.

Hence, this research work focused on obtaining sufficient experimental kinetic data of different quaternization reactions of PDMAEMA to determine important kinetic parameters. For this purpose, a PDMAEMA of 17.8 kDa was prepared via RAFT polymerization and utilized as main reagent to investigate quaternization reactions with three alkyl halides: 1-iodobutane, 1-iodoheptane, and 1-iododecane. The quaternization reactions were carried out at different temperatures to obtain the corresponding polymeric ammonium salts as well as the following kinetic parameters: Order of the reaction ($n$), Arrhenius pre-exponential factor ($A$), and activation energy ($E_a$). These estimated parameters can provide useful kinetic information for optimizing quaternization reactions for the preparation of well-defined cationic PDMAEMAs, which could find interesting applications mainly in biological systems such as antimicrobial agents[8,12] or DNA/RNA delivery systems.[22]

## 2. Experimental Section

### 2.1. Materials

1-Iodobutane (BuI) (Alfa Aesar), 1-iodoheptane (HeI) (Sigma-Aldrich), 1-iododecane (DeI) (TCI Chemicals), chain transfer agent (CTA) 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (Boron Molecular), radical initiator 4,4′-azobis(4-cyano valerianic acid) (ACVA) (Sigma-Aldrich), trioxane (Sigma-Aldrich), methanol (Sigma-Aldrich), and ethanol (Sigma-Aldrich) were used as received. The monomer 2-(dimethylamino)ethyl methacrylate (DMAEMA) (Sigma-Aldrich) was stirred in the presence of a commercially available inhibitor remover (Sigma-Aldrich) for hydroquinone derivatives or 4-*tert*-butylcatechol.

### 2.2. Characterization Techniques

Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded on a spectrometer Bruker Avance 300 MHz at room temperature. Samples were dissolved in deuterated chloroform ($CDCl_3$) or deuterated methanol ($CD_3OD$).

Size-exclusion chromatography (SEC) measurements were performed on a Shimadzu system equipped with a CBM-20A system controller, a LC-10AD pump, a RID-10A refractive index detector, and a PSS SDV-linear S column (5 µm particle size) using a chloroform/trimethylamine/isopropanol (94:4:2) mixture as eluent and at a flow rate of 1 mL min$^{-1}$ at 40 °C. The system was calibrated with a linear calibration curve built from poly(methyl methacrylate) standards of narrow dispersity (400–100 000 g mol$^{-1}$).

Elemental analyses (EA) for carbon, hydrogen, nitrogen, and sulfur were performed using a Leco CHNS-932 Elemental Chemical Analyzer, whereas elemental analysis of halogens (i.e., iodine) was measured in an Euro EA 3000 analyzer.

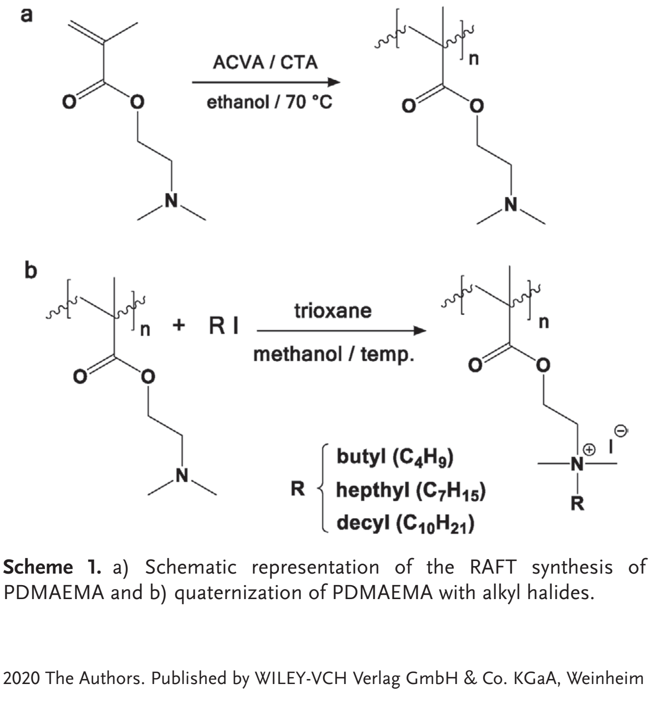
### 2.3. Synthesis

#### 2.3.1. RAFT Synthesis of PDMAEMA

236 g (1.503 mol) of DMAEMA, 3.63 g (0.009 mol) of CTA, 0.42 g (0.0015 mol) of initiator, and 395 g of ethanol were added into a 1 L jacketed glass reactor equipped with a magnetic stirrer (**Scheme 1**a). The reaction mixture was degassed with argon sparging under a vigorous stirring (500 rpm) for 15 min. Thereafter, the reaction system was kept under an argon atmosphere throughout the course of the reaction. The polymerization was carried out at 70 °C for 16 h. The final molar mass and monomer conversion were obtained by SEC and $^1$H NMR investigations, respectively. The purification of the obtained PDMAEMA was performed by evaporating a certain amount of ethanol solvent and followed by the precipitation of the concentrated polymer solution in hot water under a vigorous stirring. Finally, the product was dried under vacuum at 40 °C for 2 d and obtained as a light-yellow powder.

#### 2.3.2. Quaternization Reactions of PDMAEMA

A solution containing 10 wt% of PDMAEMA and 1 wt% of trioxane (internal standard) in methanol was placed in a round-bottom flask equipped with magnetic stirring



**Scheme 1.** a) Schematic representation of the RAFT synthesis of PDMAEMA and b) quaternization of PDMAEMA with alkyl halides.

**Table 1.** Reaction conditions of the investigated quaternization reactions; in all cases, equimolar amounts of alkyl halide with respect to the amino pendent groups in the PDMAEMA were utilized.

| ID | Alkyl halide[a)] [µL] | Temperature [°C] |
|---|---|---|
| BuI-30Q | BuI - 728 | 30 |
| BuI-40Q | BuI - 728 | 40 |
| BuI-50Q | BuI - 728 | 50 |
| BuI-60Q | BuI - 728 | 60 |
| HeI-30Q | HeI - 1050 | 30 |
| HeI-40Q | HeI - 1050 | 40 |
| HeI-50Q | HeI - 1050 | 50 |
| HeI-60Q | HeI - 1050 | 60 |
| DeI-30Q | DeI - 1366 | 30 |
| DeI-40Q | DeI - 1366 | 40 |
| DeI-50Q | DeI - 1366 | 50 |
| DeI-60Q | DeI - 1366 | 60 |

[a)] All systems required 6.4 mmol of alkyl halide.

(Scheme 1b). Subsequently, the respective alkyl halide was added under vigorous stirring at the predetermined temperature (30, 40, 50, and 60 °C) under ambient atmosphere. The purification process was based on the evaporation of methanol, then the product was washed two times with ethylic ether and dried under vacuum. Aliquots from the reaction mixtures were withdrawn at different times to measure consumption of the corresponding alkyl halides via $^1$H-NMR spectroscopy (following the signal related to the $\alpha$ CH$_2$-I protons). **Table 1** summarizes the conditions of the different quaternization reactions investigated in this work taking as a base 1 g of polymer, which is equivalent to 6.4 mmol of DMAEMA units to be quaternized (molar mass of DMAEMA is 157.21 g mol$^{-1}$; the contribution of the RAFT to the molar mass of the utilized PDMAEMA was neglected). Thus, the amount utilized of each alkyl halide was 6.4 mmol (1:1 molar ratio for the quaternization reaction), which corresponds to 1.17 g for BuI (184.02 g mol$^{-1}$), 1.44 g for HeI (226.1 g mol$^{-1}$) and 1.71 g for DeI (268.18 g mol$^{-1}$).

## 3. Results and Discussion

### 3.1. Synthesis and Characterization of PDMAEMA

A PDMAEMA with a monomodal molar mass distribution, a relatively low dispersity ($Đ$ = 1.35), and average number molar mass of $M_n$ = 17.8 kDa was obtained via RAFT polymerization (see Figure S1, Supporting Information). **Figure 1**a displays the $^1$H NMR spectrum of the DMAEMA monomer, where the signals *a* and *a′* correspond to the vinyl protons in the region of 6.10 and 5.56 ppm, respectively. Figure 1b displays the $^1$H NMR spectrum PDMAEMA, where the vinyl protons of the DMAEMA monomer are absent demonstrating the effectiveness of the utilized purification method. The presence of broad signals without multiplicity in the PDMAEMA spectrum (Figure 1b) is an additional indication of the formation of macromolecules of relative high molar mass.

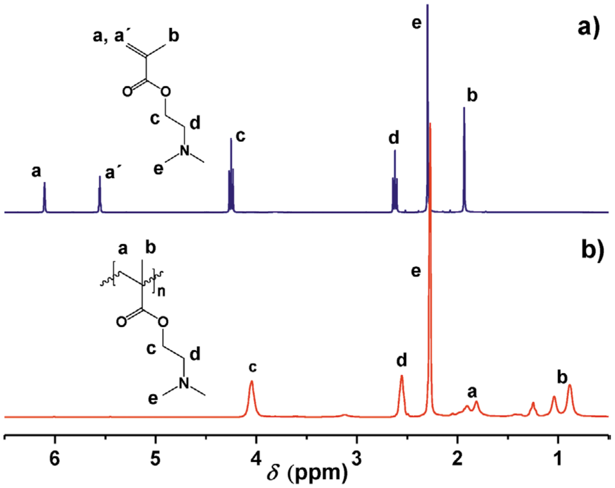


**Figure 1.** a,b) $^1$H NMR (300 mHz, CDCl$_3$) spectra of DMAEMA monomer and PDMAEMA.

### 3.2. Quaternization of PDMAEMA and Characterization

Quaternization reactions of PDMAEMA with the different alkyl halides were carried out at different temperatures (30, 40, 50, and 60 °C) under ambient atmosphere. Under the investigated experimental conditions, oxidation of the utilized alkyl halide can be neglected as these reactions might only proceed at higher temperatures (>100 °C) and/or in the presence of strong acids (e.g., dimethyl sulfoxide) or heavy metals.[23] Furthermore, potential evaporation of the utilized alkyl halides can also be disregarded due to their relatively high boiling point (>100 °C for butyl iodine). Thus, the alkyl halide conversion was followed via $^1$H NMR analysis at different times taking as reference the passing of $x_1$ (≈2.95 ppm) and using the trioxane signal as an internal standard (≈4.9 ppm) (see **Figure 2**). The decrease in time of the integral values corresponding to $\alpha$ CH$_2$-I protons was an

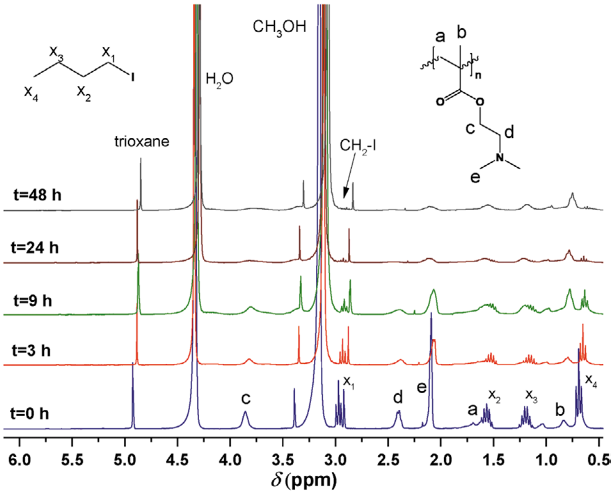


**Figure 2.** $^1$H NMR (300 mHz, CDCl$_3$) spectra of the quaternization reaction of PDMAEMA with BuI at 60 °C and different times showing the disappearance of the signal corresponding to $\alpha$ CH$_2$-I proton in the region of 2.95 ppm.

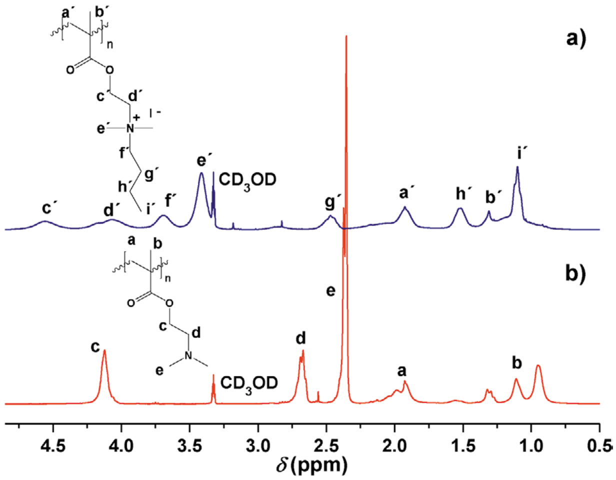


**Figure 3.** a) $^1$H NMR (300 mHz, CDCl$_3$) spectrum of BuI-Q60 compared to b) nonquaternized PDMAEMA precursor.

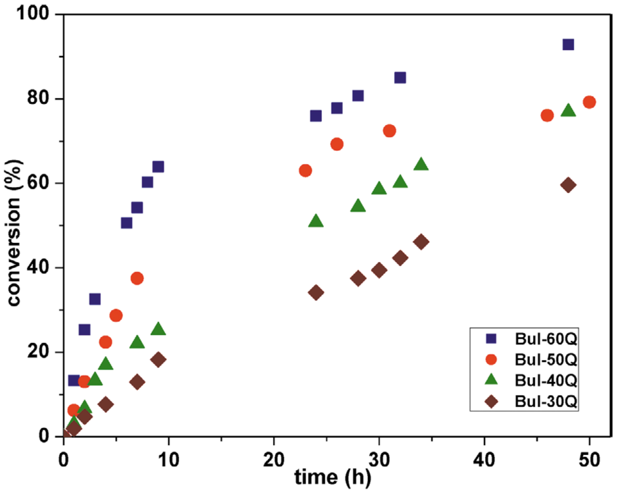


**Figure 4.** Quaternization of PDMAEMA with BuI at different temperatures.

evidence of the progress of the quaternization reaction; besides the decrease in intensity of the characteristic signals related to the alkyl halides (e.g., for BuI $x_2$ (1.7 ppm), $x_3$ (1.4 ppm) and $x_4$ (0.7 ppm)) was another fact to elucidate the consumption of these compounds. In Figure 2, the NMR spectra revealed broad signals for methanol and water; the presence of these solvents might have provoked the observed shift of the PDMAEMA signals as compared to the NMR spectrum of Figure 1b.

**Figure 3** compares the $^1$H NMR spectrum of the purified quaternized PDMAEMA BuI-Q60 (Figure 3a) to its nonquaternized polymer precursor (Figure 3b) in CD$_3$OD, where differences can be observed in terms of the chemical shifts of some signals. For instance, the signal at 4.56 ppm (Figure 3a) corresponding to the protons $c'$ ($\alpha$ O−C=O) undergoes a shift to lower field with respect to nonquaternized polymer precursor due to a higher polarity as a result of the quaternization of the pendant amino group. Protons corresponding to signals $d'$ (4.07 ppm) and $e'$ (3.41 ppm) with vicinal coupling to the nitrogen atom exhibited a displacement in their chemical shifts to the region of higher frequencies with respect to nonquaternized polymer precursor. These changes can also be ascribed to a larger ionic strength as consequence of the quaternization of the side amino group.[24] Note that in the quaternized PDMAEMA spectrum, new signals $f'$ (3.69 ppm), $g'$ (2.46 ppm), $h'$ (1.52 ppm), and $i'$ (1.10 ppm) arise as a result of the quaternization process.

The kinetic data obtained in this work at different temperatures are summarized in the conversion versus time plots displayed in **Figures 4–6** for the alkyl halides BuI, HeI, and DeI, respectively. These experimental data were utilized for estimating the kinetic parameters of a well-established kinetic model, which will be discussed in detail next.

Figure 4 displays experimental conversion (as determined by $^1$H NMR) as a function of time for each investigated quaternization reaction with BuI at different temperatures. As expected, an increase in reaction temperature yielded a higher conversion for a given reaction time; this fact is related to an increase in the frequency of collisions between the molecules. For instance, at 48 h of reaction time, the BuI-60Q system (60 °C) showed a yield of ≈93%, whereas in the BuI-30Q system (30 °C) the yield was ≈59%. This behavior is also representative for the other investigated reaction systems with HeI (Figure 5) and DeI (Figure 6).

The alkyl length of the utilized halides has also a significant impact on reaction rate. In general, for a given reaction time and temperature, halides with longer alkyl chains are less reactive than halides with shorter alkyl chains; this trend can be observed in **Figure 7**, where reached limiting conversions are shown for all investigated reactions.

The purified materials of the quaternization reactions at 60 °C were additionally investigated by EA in an attempt to corroborate the yields obtained by $^1$H NMR; based on the percentage of halogen (iodide) present in each polymer, it is possible to estimate the conversion or yield of these reactions. Hence, quaternization results obtained by EA for compounds BuI-60Q (88%), HeI-60Q (92%), and DeI-60Q (88%) are similar to those obtained by $^1$H NMR spectroscopy (see Figure 7).

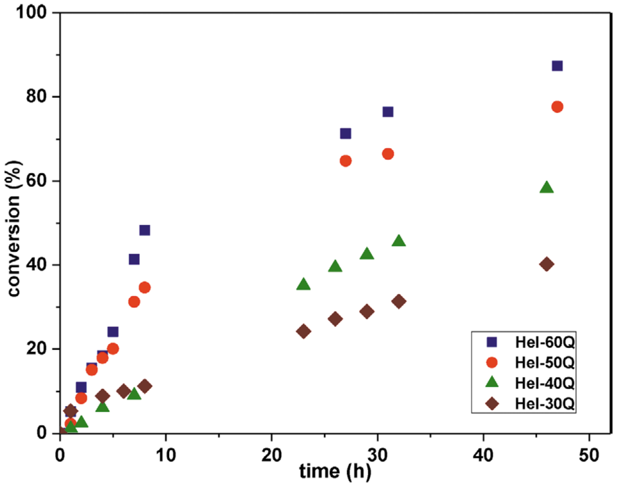


**Figure 5.** Quaternization of PDMAEMA with HeI at different temperatures.

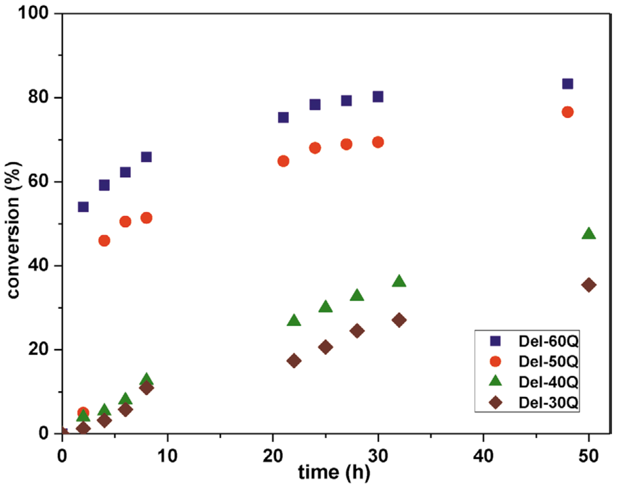


**Figure 6.** Quaternization of PDMAEMA with DeI at different temperatures.

### 3.3. Kinetic Model

As mentioned in the previous section, the $\alpha$ $CH_2$-I signal of alkyl halides in the $^1H$ NMR analysis was monitored to estimate the conversion of the quaternized reactions and its evolution in time. Thereafter, a linear fitting of the obtained experimental data to a linearized kinetic model with a reaction order $n = 2$ (see next) yielded the reaction profiles displayed in **Figures 8–10** as the inverse of concentration [L mol$^{-1}$] versus time [h].

The equation of a simple kinetic model with a reaction order $n = 2$ at constant volume is shown in Equation (1), where $dC_A/dt$ represents the rate of the reaction, $t$ is time, $k$ is the reaction rate constant, and $C_A$ is the concentration of a reagent A (i.e., halide concentration in this work)

$$\frac{dC_A}{dt} = -kC_A^2 \qquad (1)$$

The integration of (1) yields the linearized version of this equation as shown in Equation (2), wherein the value of the

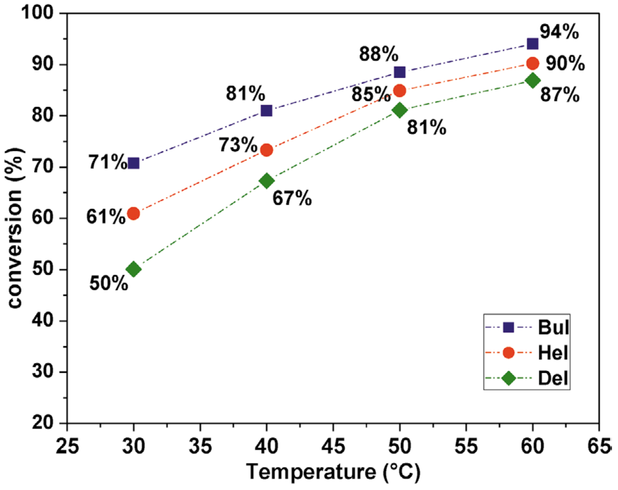


**Figure 7.** Observed limited conversions in quaternization reactions with alkyl halides.

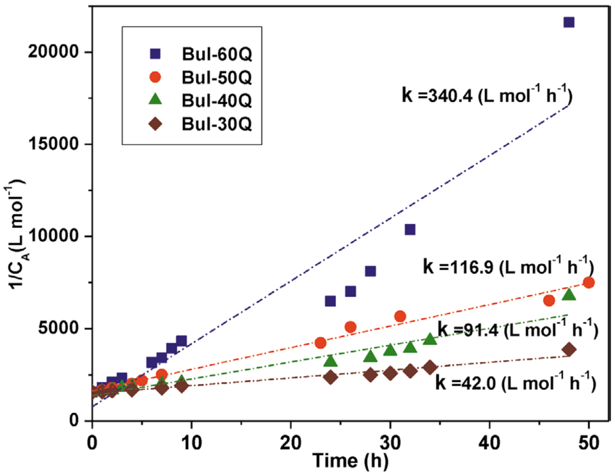


**Figure 8.** Kinetic plots of the quaternization of PDMAEMA with BuI at different temperatures.

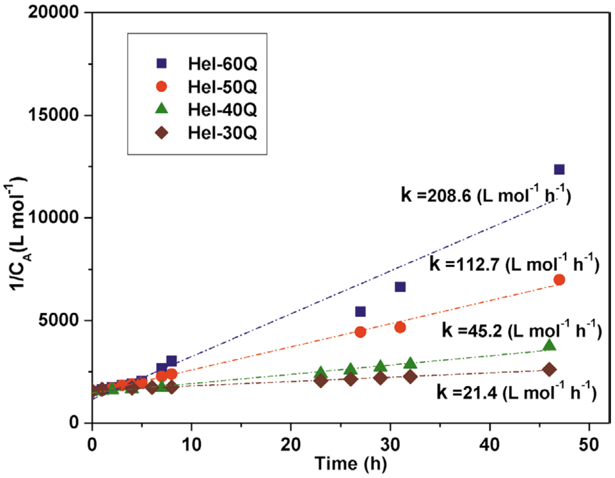


**Figure 9.** Kinetic plots of the quaternization of PDMAEMA with HeI at different temperatures.

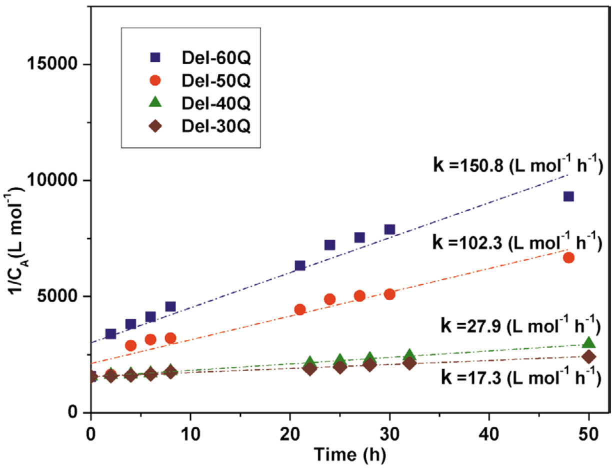


**Figure 10.** Kinetic plots of the quaternization of PDMAEMA with DeI at different temperatures.

slope of each curve is equivalent to the value of $k$ (reaction rate constant) at a constant temperature

$$\frac{1}{C_A} = kt + \frac{1}{C_{A0}} \tag{2}$$

Based on the experimental conditions of this work, $C_{Ao}$ has a value of $6.4 \times 10^{-4}$ mol $L^{-1}$ and $C_A$ is a function of conversion as shown in Equation (3), where % conv was estimated by $^1$H NMR analysis

$$C_A = C_{A0}\left(1 - \frac{\%\text{conv}}{100}\right) \tag{3}$$

Fittings of the obtained experimental data to the above-mentioned kinetic model are displayed in Figures 8–10 for the BuI, HeI and DeI quaternization systems, respectively. As expected, it can be observed that in all cases the highest values of the slopes in the plots of $1/C_A$ versus time (in the linearized version of the utilized kinetic model) are obtained at 60 °C (i.e., highest investigated reaction temperature). Additionally, the values of the slopes obtained in the experiments performed at lower reaction temperature are also lower, which confirms that the reaction rate constant is directly proportional to the reaction temperature. It is also worth mentioning that, in the investigated reactions, the length of the alkyl chain of the corresponding halide has an influence on the rate of these quaternization reactions (i.e., in general, higher reaction rates are observed for halides with a smaller alky chain).

The activation energy ($E_a$) is normally defined as the minimum energy that a system requires for undergoing a chemical transformation. Therefore, the reaction rate constant has a relationship with $E_a$, which obeys the Arrhenius equation as a function of temperature ($T$) (Equation (4))

$$k = A^* e^{-\left(\frac{E_a}{RT}\right)} \tag{4}$$

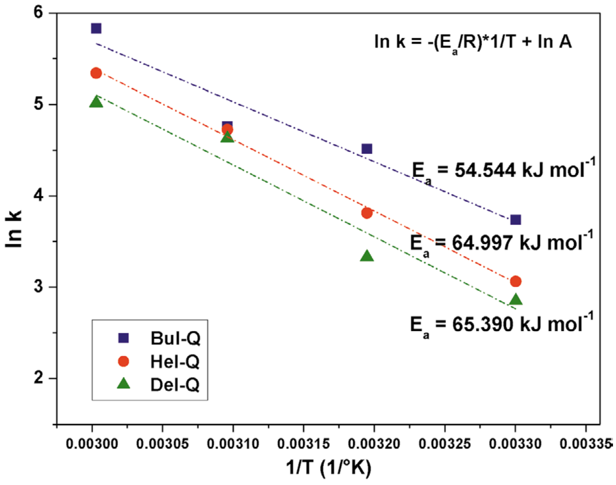


**Figure 11.** Plot of ln($k$) versus 1/$T$ for BuI, HeI, and DeI systems for the estimation of $E_a$.

**Table 2.** Energies of activation obtained from the kinetic profiles for quaternization in PDMAEMA with BuI, HeI, and DeI.

| System | $E_a$ [kJ mol$^{-1}$] | $A$ [L mol$^{-1}$ s$^{-1}$] |
|---|---|---|
| BuI-Q | 54.544 | $2.887 \times 10^7$ |
| HeI-Q | 64.997 | $9.399 \times 10^8$ |
| DeI-Q | 65.390 | $8.245 \times 10^8$ |

where $A$ represents the so-called frequency factor and is a measure of the frequency of collisions between molecules, and $R$ is the universal gas constant. The experimentally determined values of $k$ can be utilized to estimate $E_a$ from the slope of a fitting of the linearized version of the Arrhenius' equation. Plots ln$k$ versus $1/T$ and their respective linear fitting are displayed in **Figure 11** for the investigated quaternization reactions. The obtained $E_a$ and $A$ values for each quaternization system are summarized in **Table 2**. The data shown in Table 2 indicate, in general, that halides of longer alkyl chains require more energy to be able to quaternize pendant amine groups of PDMAEMA, which may be ascribed to diffusional effects of the corresponding alkyl halide and polymer chains.[25]

## 4. Conclusions

A PDMAEMA ($Đ$ = 1.35 and $M_n$ = 17.8 kDa) was synthesized by RAFT polymerization. Thereafter, quaternization reactions of this polymer with BuI, HeI, and DeI were investigated at different temperatures in order to estimate the kinetic parameters such as reaction rate constants $k$, $E_a$, and $A$. Fittings of the obtained experimental conversion versus the time to a linearized version of second-order reaction kinetic model allowed the estimation of $k$ at different temperatures and for the three different alkyl halides. Next, from the obtained $k$ values at different temperature, it was possible to estimate the $E_a$ of three investigated reactions. The obtained results revealed that lower $E_a$'s are required to perform these quaternization reaction for halides with shorter alkyl chain lengths (i.e., $E_a$ = 54.544 kJ mol$^{-1}$ for BuI, 64.997 kJ mol$^{-1}$ for HeI, and 65.390 kJ mol$^{-1}$ for DeI). The herein described experimental method and the obtained kinetic parameters can be used as a reference for optimizing the conditions of quaternization reactions of polymers with amino pedant groups to access cationic polymeric materials, which, either pristine or in combination with other (nano-)compounds (e.g., nanoparticles), can be useful as novel antimicrobial or fungicidal systems[8,12] or in other biological applications (e.g., DNA/RNA delivery systems).[22] Future contributions in this direction will include the kinetic analysis and comparison of similar quaternization reactions utilizing other series of alkyl halides (e.g., alkyl bromides).

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

antimicrobial polymers, cationic polymers, kinetic parameters, quaternized PDMAEMA, RAFT polymerization

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