

## Article

# Cationic Polyelectrolytes Containing Perfluorinated Groups: Synthesis and Self-Assembly Properties in Aqueous Solutions

Periklis Didaskalou, Martha Kafetzi and Stergios Pispas \* 

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Avenue, 11635 Athens, Greece; periklis06@gmail.com (P.D.); mkafetzi91@gmail.com (M.K.)  
\* Correspondence: pispas@eie.gr; Tel.: +30-210-727-3824

**Abstract:** In this work, the synthesis and solution self-assembly of partially fluorinated cationic polyelectrolytes based on post-polymerization-modified poly(2-(dimethylamino) ethyl methacrylate), incorporating hydrophobic fluorinated groups along the polymer chain, is reported. The post-polymerization modification aims to establish amphiphilic characteristics and strong polyelectrolyte properties to the polymer. Therefore, the self-organization characteristics in aqueous media are expected to be affected. The poly(2-(dimethylamino) ethyl methacrylate) (PDMAEMA) homopolymer precursor is synthesized using RAFT polymerization. A quaternization reaction on the amine side groups using heptadecafluoro-10-iododecane results in the poly((2-dimethylamino) ethyl methacrylate-co-quaternized heptadecafluoro-10-iododecane (2-dimethylamino) ethyl methacrylate) (PQFD) amphiphilic statistical copolymers. We intentionally study statistical copolymers in our research of DMAEMA-based polyelectrolytes as there are not many studies about such materials. We have also chosen the incorporation of highly hydrophobic perfluorinated groups to study the changes in the solution properties of the initial hydrophilic homopolymer. The successful synthesis is supported by size-exclusion chromatography (SEC), <sup>1</sup>H-NMR, and FTIR experiments. The self-assembly of the copolymers in aqueous solutions along with the dependence of the properties of the resulting aggregates on the pH, temperature, and ionic strength of the solution are studied using light scattering methods (DLS, ELS) and fluorescence spectroscopy (FS). The structural characteristics of the aggregates depend on composition, solution preparation protocol and solution pH, and temperature.

**Keywords:** amphiphilic statistical copolymers; RAFT polymerization; aggregates; polyelectrolytes; fluorinated polymers



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## 1. Introduction

Limited research reports concerning the synthesis and properties of statistical copolymers were published until the last decade, because such polymers presented poorly defined molecular properties and wide molecular weight distributions. However, recent progress in controlled radical polymerization strategies enabled the design and synthesis of well-defined statistical copolymers, with control over their molecular characteristics. As a result, in recent years, several research groups have been focusing their efforts on the synthesis and self-assembly of amphiphilic statistical copolymers. The synthesis of amphiphilic statistical copolymers is fast and easy, which makes their industrial production very attractive. In addition, their self-assembly in aqueous solutions produces distinctive nanostructures that are worth studying in more detail [1]. Nanostructures resulting from the self- or co-organization of statistical copolymers have certain advantages over micelles derived from block copolymers. For example, structures originated from statistical copolymers can benefit more from a weak interaction, thus producing more dynamically reversible structures as opposed to normally kinetically frozen structures from block copolymers. This type of copolymer can be prepared in two ways: either by a partial, hydrophobic modification of a water-soluble homopolymer [2–5] or by the polymerization of at least two distinct

hydrophilic and hydrophobic monomers. The hydrophilic/hydrophobic fraction of the statistical copolymer affects the most its self-assembly behavior. In the case the hydrophobic content is comparatively low, intramolecular self-folding dominates and the subsequent formation of single-chain aggregates, whose cores are composed of hydrophobic domains, is favored. When the hydrophobic content increases, intermolecular self-assembly occurs and multichain aggregates are formed [6,7]. In this study, we focus on the synthesis of statistical copolymers with a low hydrophobic content of perfluorinated side groups.

Polyelectrolytes (PELs) are a very important category of polymers that seems to allure research interest ever more [8,9]. One of their most significant properties is their solubility in water and their similarities with biopolymers. Furthermore, they present the ability to charge neutral particles, allowing them to disperse in aqueous solution. In addition to the hydrophilic nature of the polyelectrolytes, a supplemental and imperative phenomenon to be taken into account comes from the favorable entropic contribution of the counter ions to the free energy of mixing the polymer with the solvent [10]. The polyelectrolyte water solubility combined with their tendency to interact with oppositely charged polyelectrolytes and biomacromolecules to form complexes has led to a high number of applications such as “smart” materials used as drug-carriers in the human body. PELs are also used in the manufacture of implants with increased biocompatibility and in the production of membranes used for dissolution and filtration purposes.

Polymers that are responsive to external stimuli are defined as polymers that undergo relatively high and direct physical or chemical changes when changes in their environmental conditions occur [11,12]. These polymers recognize the stimulus as a signal, determine its magnitude, and change their chain configuration as an immediate response to it. There are many different stimuli that regulate the polymer response and can be classified as either chemical (e.g., pH, ionic strength) or physical (e.g., temperature) stimuli [13–16]. Such responses of polymeric systems are very useful in biological applications, such as drug delivery [12,17], biotechnology [18], and chromatography/separation [17]. Some polymeric systems are able to correspond to two or more stimuli, for example, they are temperature-responsive but also respond to pH changes [19,20]. On the other hand, there are studies that report the simultaneous imposition of two stimuli for a response from the polymer, which is called double-responsive [19].

Reversible addition fragmentation chain transfer polymerization (RAFT) exhibits many advantages concerning the synthesis of smart polymers, including statistical and block copolymers [21]. First, it provides the synthesis of well-defined polymers of predetermined molecular characteristics [21,22]. The molecular weight and the composition of the resulting polymer can be manipulated by fitting the polymerization conditions. RAFT can be used for a variety of monomers and can provide many different macromolecular architectures. In addition, experimental conditions for RAFT polymerization are mild and manageable, with the absence of catalysts, and the polymerization process can be conducted in aqueous media [21,23].

In this study, we report on the synthesis of cationic polyelectrolytes that contain perfluorinated hydrophobic groups using the RAFT polymerization and post-polymerization functionalization techniques. The synthesized polyelectrolytes were obtained from the partial chemical modification of a poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) homopolymer precursor. In the first stage, a PDMAEMA homopolymer was synthesized using RAFT polymerization. Then, the amino groups of the polymer were partially modified with heptadecafluoro-10-iododecane by means of a quaternization reaction. The introduction of different contents of fluorinated groups led to the preparation of amphiphilic copolymers of different compositions. The amphiphilic characteristics of the copolymers is attributed to the fact that the DMAEMA segments are hydrophilic while the fluorinated DMAEMA (QFDMAEMA) segments are hydrophobic. The monomer 2-(dimethylamino)ethyl methacrylate (DMAEMA) was selected for this study because it is a weak cationic electrolyte and its polymers are responsive to changes in pH, temperature, and ionic strength [24–26]. The interesting part about this approach for preparing

DMAEMA-based polyelectrolytes lies in the introduction of the perfluorinated groups in the polymer chain. Fluorinated polymers in general tend to have a low dielectric constant and refractive indexes and they are highly hydrophobic and resistant to aging and oxidation. Pairing these abilities with the properties of DMAEMA-based electrolytes gives these polymers very unique properties. Additionally, the use of statistical copolymers based on DMAEMA instead of block copolymers is also a new approach as there are not many studies on this research direction. Following the successful synthesis of the copolymers, interest turned to their study in water at the structural and supramolecular level. The primary purpose was to study their self-assembly in aggregates when inserted in aqueous solutions and the dependence of their properties on the change in the solution physicochemical parameters. One goal of this study was to obtain a clear picture of whether the response of these polyelectrolytes to external stimuli is affected by increasing the content of hydrophobic groups in the polymer.

## 2. Materials and Methods

### 2.1. Materials

The monomer, 2-dimethylamino ethyl methacrylate (DMAEMA), was purchased from Alfa Aesar and was purified by passing through a column packed with inhibitor remover before polymerization. The column used was the 311332 inhibitor remover column from Sigma Aldrich. Azobisisobutyronitrile (AIBN) was used as the initiator and 4-cyano-4-[(dodecyl sulfanylthio carbonyl)-sulfanyl] pentanoic acid (CDP) as the CTA. Both of them were purchased from Sigma Aldrich. The quaternization agent utilized was heptadecafluoro-10-iododecane (qf17) and was also purchased from Sigma Aldrich. As solvents for this study, tetrahydrofuran (THF), n-hexane, 1,4 dioxane, and deuterated chloroform ( $\text{CDCl}_3$ ), purchased from Sigma Aldrich, were also used.

### 2.2. Synthesis of the PDMAEMA Homopolymer Precursor

The monomer was first purified from the inhibitor it contained (hydroquinone monomethyl ether) by passing through a column filled with the appropriate resin (Sigma Aldrich 311332, St. Louis, MO, USA). Then, 3 g of the inhibitor-free DMAEMA monomer (3.2 mL), 0.1211 g of CTA (4-cyano-4-[(dodecyl sulfanylthio carbonyl)-sulfanyl] pentanoic acid), 0.00493 g of AIBN, which is the initiator, and 11.8 mL of dioxane solvent were placed in a spherical flask. The final volume of the solution was 15 mL. The stoichiometric molecular weight (10,000 g/mol) of the polymer was what determined the required amount of CTA. The CTA/initiator molar ratio used to form the homopolymer was CTA/AIBN = 10 and the volume of solvent used was such that the concentration of monomer in the solvent was 20%. Mixing of reagents was followed by degassing of the solution using high-purity nitrogen gas, for twenty minutes. After degassing, the spherical flask was placed in an oil bath at a temperature of 70 °C. The duration of the polymerization was 18 h. After this period, the solution was cooled for about 15 minutes at a temperature of −8 °C in order to terminate polymerization, and the free radicals were deactivated by opening the flask to air after returning to room temperature. Finally, the polymer was recovered by precipitation in a ten-fold excess of nonsolvent (hexane). After precipitation, the supernatant liquid was removed and the polymer, now free of unreacted monomer, was collected and placed in a vacuum oven for a week for drying.

### 2.3. Synthesis of the P(DMAEMA-co-QFDMAEMA) (PQFD) 90:10 and 80:20 Statistical Copolymers

The PDMAEMA homopolymer underwent a partial conversion of its tertiary amine groups into quaternary ones using heptadecafluoro-10-iododecane. The addition of hydrophobic fluorinated groups turned the polymer system into an amphiphilic one.

Two copolymers of different compositions were prepared, one with a 10% modification of the tertiary amino group (per mol) and one with a 20% modification of the tertiary amino group (per mol). The preparation method was the same in both cases and the only thing that was changed was the amount of heptadecafluoro-10-iododecane used.

The quaternization reaction was performed in a spherical flask containing a dilute solution (2% *w/v*) of the PDMAEMA polymer in tetrahydrofuran (THF), and with moderate stirring, the required amount of heptadecafluoro-10-iododecane was added. The reaction lasted 72 h under continuous stirring at room temperature. Afterward, the copolymers were precipitated in a ten-fold excess of hexane and were stored in the refrigerator for one day. The supernatant was removed the next day and the copolymers were placed in a vacuum oven for drying.

#### 2.4. Self-Assembly of the P(DMAEMA-co-QDMAEMA) (PQFD) Statistical Copolymers

The amphiphilic copolymers synthesized were studied according to their molecular structure and based on their ability to self-assemble in aqueous solutions forming aggregates. Two different protocols were used for the production of self-assembled polymeric nanoparticles. The first protocol included the direct dissolution of the copolymers in distilled water. The second one concerned the initial dissolution of the copolymers in THF, the addition of the mixture in distilled water, and then the evaporation of the organic solvent, by heating the mixture [27]. Specifically, the first protocol included the addition of the appropriate volume of distilled water of pH 7, in a specific quantity of copolymer. The resulting mixture was left overnight at room temperature and studied the following day, in order to fully dissolve the copolymer and the solution to be in thermodynamic equilibrium. By implementing this protocol, samples of concentrations of  $1 \times 10^{-3}$  g/mL were prepared. The second protocol involved the dissolution of a specific quantity of copolymer in 1 mL of THF and, subsequently, the injection of the resulting solution in the appropriate volume of distilled water of pH 7, under vigorous stirring. After two minutes of stirring, the latter mixture was heated until the THF was evaporated and the final aqueous solution of  $1 \times 10^{-3}$  g/mL concentration was obtained. The final solutions were kept at room temperature overnight and studied the following day. The pH studies were implemented by carrying out the same preparation process, regardless of the protocol that was followed in order to prepare the aqueous solutions. After the thermodynamic equilibrium of the solutions was achieved, a certain volume of each aqueous solution was taken in order to regulate the pH. Appropriate volumes of 0.1 M HCl were added in order to tune the pH of the aqueous solutions at pH 3, while appropriate volumes of 0.1 M NaOH were used to tune the solutions at pH 10. The final solutions where the pH was regulated at 3 and 10, respectively, were left for 3 h before conducting the measurements, in order to achieve equilibrium.

#### 2.5. Characterization Methods

##### 2.5.1. Size-Exclusion Chromatography

The molecular weight and molecular weight distribution of the synthesized homopolymer were determined using size-exclusion chromatography (SEC), using a Waters instrument, consisting of a Waters 1515 isocratic pump, a set of three  $\mu$ -Styragel mixed-composition separation columns (pore range  $10^2$ – $10^6$  Å), and a Waters 2414 refractive index detector (balanced at 40 °C). The setup was controlled by Breeze software. The mobile phase was tetrahydrofuran, which contained 5% *v/v* triethylamine at a flow rate of 1 mL/min at 30 °C. The instrument was calibrated with standard polystyrene samples with narrow molecular weight distributions and average molecular weights in the range of 2500 to 123,000 g/mol.

##### 2.5.2. <sup>1</sup>H-NMR Spectroscopy

<sup>1</sup>H-NMR spectra were obtained on a Bruker AC 600 FT-NMR spectrometer. Chemical shifts were presented in ppm with the tetramethylsilane (TMS) signal as the reference. The preparation of the samples for the <sup>1</sup>H-NMR measurements included the dissolution of 10 mg of the copolymer in 0.7 mL of deuterated chloroform and the transfer of the solution into an NMR tube. The spectral analysis was performed using MestReNova software from MestRelabs.

### 2.5.3. ATR-FTIR Spectroscopy

The mid-infrared measurements ( $550\text{--}4000\text{ cm}^{-1}$ ) were performed using a FTIR spectrometer (Equinox 55 by Bruker Optics, Billerica, MA, USA), equipped with a single-reflectance ATR germanium crystal (Dura-Samp1IR II by SensIR Technologies).

### 2.5.4. Fluorescence Spectroscopy

The spectra were recorded with a NanoLog fluorescence spectrometer (by Horiba Jobin Yvon), using a laser diode as the excitation source (NanoLED, 440 nm, pulse width 100 ps) and a UV TBX-PMT series detector (250–850 nm) by Horiba Jobin Yvon. The method used is described below.

Polymer solutions were prepared at a concentration range of  $10^{-3}\text{--}10^{-8}\text{ g/mL}$  and these solutions were traced with pyrene solution (in acetone) in a ratio of 1  $\mu\text{L/mL}$  of polymer solution. The solutions were kept at rest away from sunlight for 24 h to allow pyrene to be encapsulated in the hydrophobic domains of the copolymer aggregates, and they were then measured. The  $I_1/I_3$  ratio was evaluated in relation to the concentration of the polymer in the aqueous solution.

### 2.5.5. Dynamic Light Scattering

Dynamic light scattering measurements were performed using the ALV/CGS-3 Compact Goniometer System (ALV GmbH, Langen, Germany), equipped with a JDS Uniphase 22 mW He-Ne laser operating at 632.8 nm, connected to a 288-channel digital coupler ALV-5000/EPP multi-tau and an ALV/LSE-5003 electronic light scattering unit to control the gradual movement of the goniometer carrying the detector and controlling the end position switch. The intensity of the scattered radiation and the correlation functions were recorded five times and analyzed by the method of cumulants and the CONTIN algorithm, which provides the distribution for the apparent hydrodynamic radius using the inverse Laplace transformation of the auto-correlation function and by using the Stokes–Einstein equation. For this study, solutions of a concentration of  $1.0 \times 10^{-3}\text{ g/mL}$  at pH 7 were prepared and were let to rest for one day.

In the case of the pH study, the solution pH was altered from 7 to 3 and 10, in order to study the properties at neutral, acidic, and basic pH, respectively. In order to change the pH from neutral to basic, an appropriate volume of 0.1 M aqueous NaOH solution was added dropwise to adjust the pH from 7 to 10. In order to change the pH from neutral to acidic, an appropriate volume of 1 M aqueous HCl solution had to be added to change the pH from 7 to 3. In both cases, the solutions were allowed to rest for one day to reach equilibrium and then DLS measurements were performed at  $90^\circ$  angle.

In the case of the temperature study, measurements were made at a  $90^\circ$  angle and in the temperature range from  $25^\circ\text{C}$  to  $55^\circ\text{C}$ , with a step of  $5^\circ\text{C}$ . The solution was kept at rest in each temperature for 15 min, before the measurement, in order to achieve equilibrium.

Finally, in the case of the ionic strength study, increasing volumes of a 1 M NaCl aqueous solution were added to achieve different salt concentrations in the copolymer solution. The measurements were made at an angle of  $90^\circ$  and at final salt concentrations:

$C_{\text{NaCl}}$	0.001	0.011	0.021	0.03	0.048	0.092	0.201	0.334	0.429	0.5 M
	M	M	M	M	M	M	M	M	M	

The respective measurements were performed after 15 min had passed from each NaCl solution addition.

### 2.5.6. Electrophoretic Light Scattering— $\zeta$ -Potential

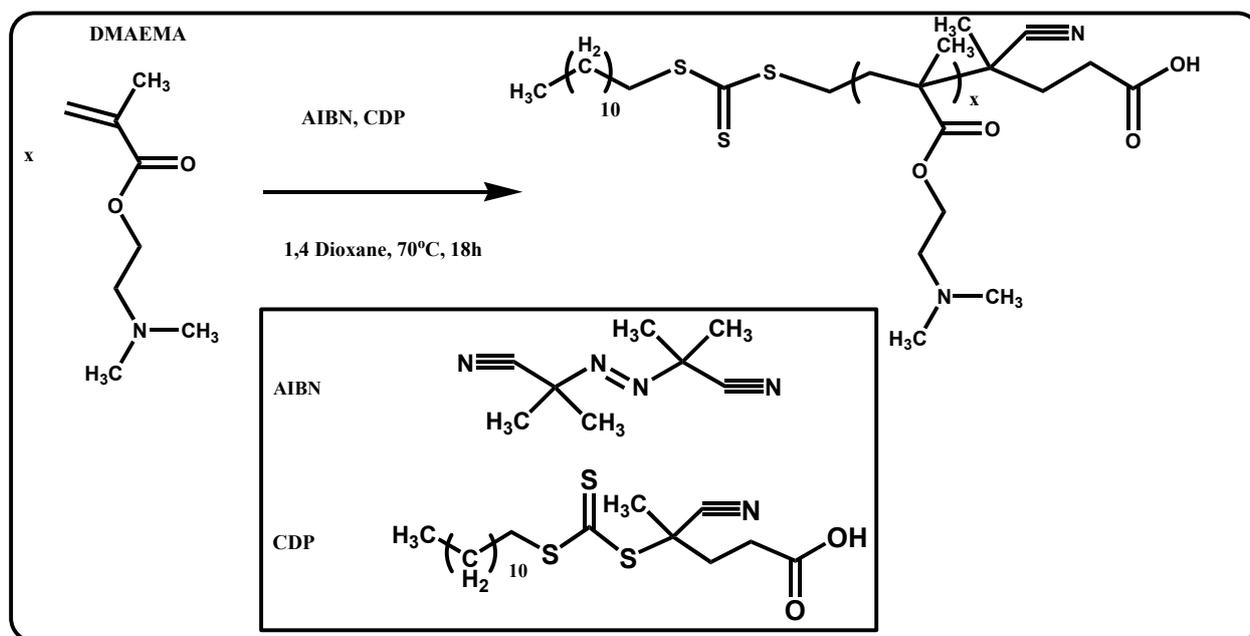
The  $\zeta$ -potential was measured on a Malvern system (Nano Zeta Sizer) equipped with a He-Ne 4 mW laser with wavelength  $\lambda = 633\text{ nm}$ . A photodiode was used as a detector and the scattered radiation was measured at an angle of  $173^\circ$ . Electrokinetic measurements to determine the mobility and  $\zeta_p$  values of colloids were performed using the LDV (Laser Doppler Velocimetry) technique and the Smoluchowski approach. The reported  $\zeta_p$  values

were the average of 100 measurements. The copolymer solutions were prepared in the same way that was described in the DLS studies.

### 3. Results and Discussion

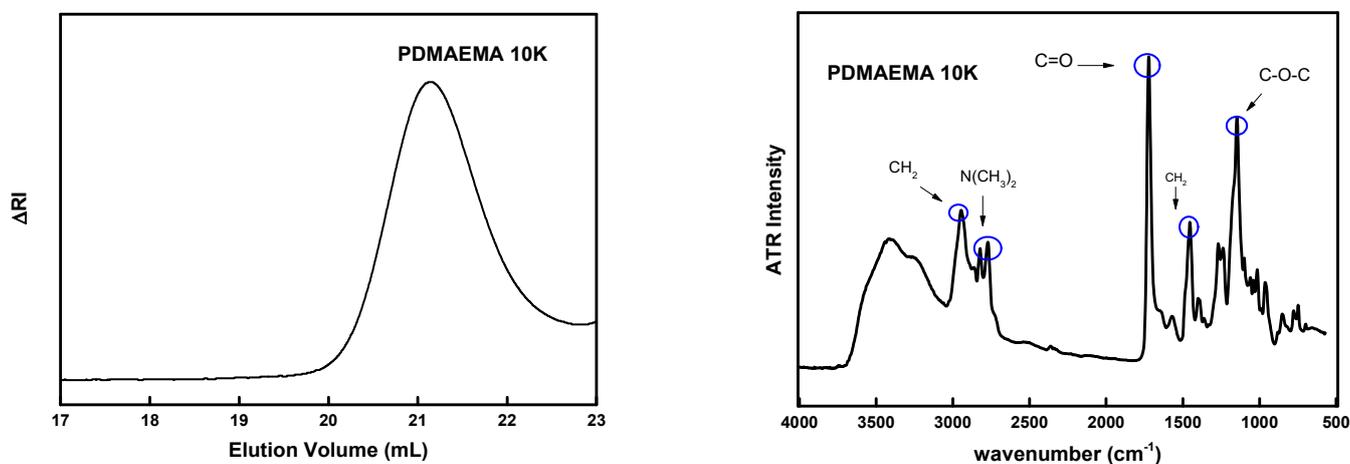
#### 3.1. Synthesis of the PDMAEMA Homopolymer Precursor

The polymerization reaction utilized for the synthesis of the PDMAEMA homopolymer precursor is shown in Scheme 1.



**Scheme 1.** Synthetic route for the PDMAEMA homopolymer precursor.

The SEC and ATR-FTIR analysis (Figure 1) proves the successful polymerization at high monomer conversion as there are no peaks in the SEC chromatogram that can be attributed to the monomer, and especially because there is no peak corresponding to the vibration of the C=C double bond in the ATR-FTIR spectrum. The molecular weight and molecular weight distribution of the PDMAEMA homopolymer as determined by SEC are shown in Table 1, and the polymer characteristic groups were identified with ATR-FTIR spectrometry. The results are shown below.



**Figure 1.** SEC chromatogram (left) and ATR-FTIR spectrum (right) of the PDMAEMA homopolymer precursor.

**Table 1.** Molecular characteristics of the PDMAEMA precursor and the quaternized PQFD amphiphilic copolymers.

Sample	$M_w$ (g/mol) <sup>1</sup>	$M_w/M_n$ <sup>1</sup>	%DMAEMA <sup>2</sup>	%QDMAEMA <sup>2</sup>
PDMAEMA 10 K	6450	1.14	100%	-
PQFD 10%	8200 <sup>3</sup>	-	93%	7%
PQFD 20%	8750 <sup>3</sup>	-	90%	10%

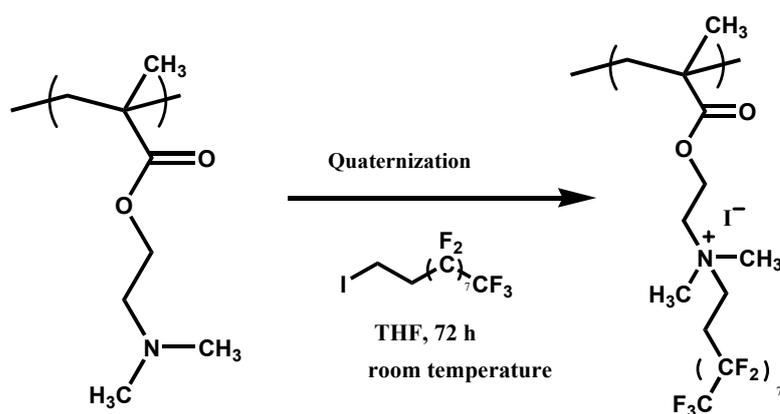
<sup>1</sup> Determined by SEC, <sup>2</sup> Determined by <sup>1</sup>H-NMR, <sup>3</sup> Determined by combination of SEC and <sup>1</sup>H-NMR data.

In the ATR-FTIR spectrum of the PDMAEMA homopolymer (Figure 1), the absorption bands at  $2948\text{ cm}^{-1}$  correspond to C-H bond vibrations of the  $-\text{CH}_2$  groups (asymmetric extension) [28], and those at wavenumbers of  $2821\text{ cm}^{-1}$  and  $2771\text{ cm}^{-1}$  correspond to bond vibrations of the tertiary amine groups  $-\text{N}(\text{CH}_3)_2$  [29,30]. The peak at  $1719\text{ cm}^{-1}$  corresponded to bond vibrations of the ester carbonyl. At  $1454\text{ cm}^{-1}$ , an asymmetric bend corresponding to the C-H bonds of  $-\text{CH}_2$  is observed [28]. At  $1146\text{ cm}^{-1}$ , the bond vibration of the  $\text{O}=\text{C}-\text{O}-\text{C}$  group of the ester group can be observed [31]. However, according to the literature, at these wavenumbers, the vibration of the C-N bond is also expected [32]. We believe that there is an overlap of the peaks and, thus, we cannot distinguish which band corresponds to each of the two chemical groups. Based on the literature, the vibration of  $\text{O}=\text{C}-\text{O}-\text{C}$  is considered to be stronger.

### 3.2. Synthesis of the PQFD 90:10 and 80:20 Statistical Copolymers

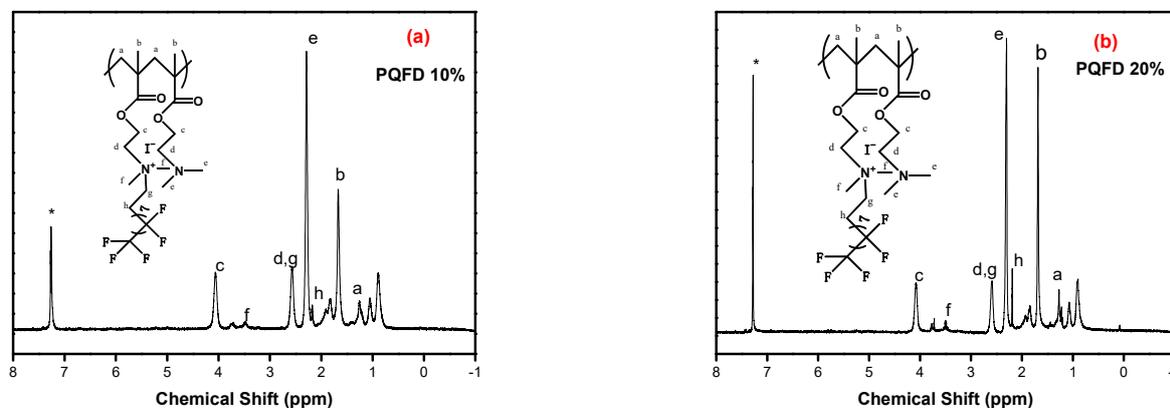
The introduction of the perfluorinated chains in the PDMAEMA homopolymer was pursued in order to prepare highly amphiphilic copolymers and investigate at which degree the presence of highly hydrophobic perfluorinated groups on the hydrophilic polymer chain affects the polymer solution properties. It is expected that by introducing hydrophobic groups in the polymer chain, it will now form aggregates when found in aqueous media, even under conditions that no aggregation is observed for the PDMAEMA homopolymer, due to the fact that the fluorinated groups want to avoid contact with water. It is also expected that by increasing the content of the perfluorinated groups on the PDMAEMA chain, aggregation properties and their dependence on external stimuli may be affected.

The quaternization reaction utilized for the incorporation of the perfluorinated qf17 groups in the PDMAEMA homopolymer chain is shown in Scheme 2.

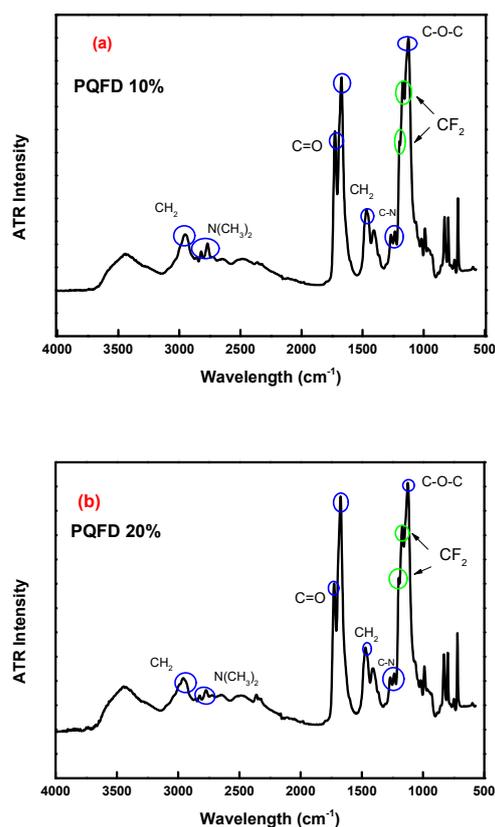
**Scheme 2.** Quaternization reaction of the PDMAEMA precursor by insertion of the qf17 fluorinated groups.

The successful quaternization reaction was verified both qualitatively and quantitatively by implementing ATR-FTIR and the <sup>1</sup>H-NMR experiments, respectively. The composition of each copolymer was determined by utilizing the corresponding <sup>1</sup>H-NMR spectrum and specifically by comparing the integrals of the peaks that correspond to a specific characteristic proton group. Determination of the copolymer composition and

homopolymer precursor molecular weight led to the calculation of the molecular weights of the statistical copolymers obtained after quaternization. The  $^1\text{H-NMR}$  and ATR-FTIR spectra of both copolymers are shown in Figures 2 and 3, respectively, and their molecular characteristics are presented in Table 1.



**Figure 2.**  $^1\text{H-NMR}$  spectra of the (a) quaternized PQFD 10% and (b) quaternized PQFD 20% amphiphilic copolymers. The peak at 7.2 ppm (\*) is assigned to the solvent protons.



**Figure 3.** ATR-FTIR spectra of the (a) quaternized PQFD 10% copolymer and (b) quaternized PQFD 20% copolymer.

The characteristic chemical shifts were determined based on literature data [33]. The peak a at 1.28 ppm in Figure 2a,b corresponds to the protons of the skeletal  $\text{CH}_2$  groups, while peak b is assigned to the methyl group protons. Peaks c and d found at 4.07 ppm and 2.62 ppm, respectively, correspond to protons of ethyl groups. Characteristic peak e appearing at 2.32 ppm is assigned to protons of the tertiary amine group. Protons of the qf17 group that is attached to certain amino groups are found at 2.62 and 2.18 ppm, respectively. It is obvious that the peaks of the d and g proton overlap. Finally, the

methacrylate group f protons of the quaternary amine group are affected by the reagent qf17. The abovementioned protons are related to the peak that appears at 3.5 ppm.

The e and f proton peaks that appear at 2.32 ppm and 3.5 ppm were used to determine the composition of the two copolymers, respectively. As a result, the quaternization/modification degree of the first statistical copolymer obtained was calculated to be 10%, while that of the second one was equal to 20%. Through determination of the composition of the copolymers and by taking into account the molecular weight of the precursor PDMAEMA homopolymer and the molecular weight of the qf17 reagent, the values of the molecular weights of the two copolymers were calculated.

The assignment of the peaks in the ATR-FTIR spectra of the PQFD copolymers was performed using the PDMAEMA spectrum as the basis. The symmetrical vibration peaks of the C–F bonds of the CF<sub>2</sub> groups (Figure 3) appeared at approximately 1170 cm<sup>-1</sup> and 1195 cm<sup>-1</sup> according to the literature [34]. The peak at 1675 cm<sup>-1</sup> is attributed to the bond stretching vibration of the C=O bond of the ester carbonyl [35]. The results support the chemical composition of the obtained copolymer after quaternization and are in agreement with NMR analysis.

### 3.3. Self-Assembly of PQFD Amphiphilic Copolymers in Aqueous Media

Studies on the ability of the resulting copolymers to self-assemble in aqueous media were conducted by implementing fluorescence spectroscopy and light scattering techniques. Fluorescence spectroscopy was used for determining the Critical Aggregate Concentration (CAC) [36–40] of each copolymer and also to investigate more thoroughly the increased hydrophobic character of the nanoaggregates induced by the fluorinated side chains that are expected to compose the hydrophobic domains of the formed nanostructures. Pyrene was used as the probe in order to carry out the fluorescent studies at different pH values and temperatures. DLS was used to determine the hydrodynamic radius ( $R_h$ ) and the size polydispersity index (PDI) of the formed aggregates. The PDI was extracted by using the cumulant method, while  $R_h$  was obtained by both the cumulant method and the CONTIN algorithm. Finally, ELS was used to determine the  $\zeta$ -potential value for copolymer aggregates at different pH values.

#### 3.3.1. Fluorescence Spectroscopy Results

Polymer solutions in a range of concentrations of 10<sup>-8</sup>–10<sup>-3</sup> g/mL were prepared and traced with pyrene for determining the CAC value for the copolymers PQFD 10% and PQFD 20%. Polymer solutions were prepared with both the H<sub>2</sub>O and the THF protocols. CAC values were determined for PQFD 20% in both protocols but, in the case of PQFD 10%, it was determined only for the solution prepared by the THF protocol due to the nature of the results that were given by the solutions prepared by the H<sub>2</sub>O protocol. The results are presented in Table 2 (where plots of I<sub>1</sub>/I<sub>3</sub> ratio vs. copolymer concentration are shown in Figure S1 and pyrene emission spectra at different conditions are shown in Figures S2–S5).

**Table 2.** AC values for PQFD amphiphilic copolymer solutions prepared by the H<sub>2</sub>O and THF protocols.

Sample	CAC Value
PQFD 10% (H <sub>2</sub> O protocol)	-
PQFD 20% (H <sub>2</sub> O protocol)	6.2 × 10 <sup>-5</sup> g/mL
PQFD 10% (THF protocol)	4.7 × 10 <sup>-5</sup> g/mL
PQFD 20% (THF protocol)	9.9 × 10 <sup>-6</sup> g/mL

Fluorescence spectroscopy was also used to determine the ability of hydrophobic-fluorinated domains of the resulting PQFD 10% and PQFD 20% nanostructures in aqueous media to encapsulate pyrene. Both protocols were also used for the preparation of copolymer solutions of  $c = 1 \times 10^{-3}$  g/mL concentration, at pH 3, 7, and 10, and measurements took place at 25 °C and 50 °C. The experiments were carried out in order to examine the dependence of the nanoaggregate properties on the pH, temperature, and protocol used

for the solution preparation. In these experiments, the ratio  $I_1/I_3$  at each temperature was determined for each sample, as it indicates the level of hydrophobicity of the environment around pyrene and, indirectly, how well-defined the hydrophobic domains of the aggregates are in each case. It is expected that the value of the  $I_1/I_3$  ratio decreases when either the pH or temperature is increased, which results from the increase in hydrophobicity under conditions of high temperatures and high pH values. However, as can be seen in Table 3, this was not always the case in our experiments, indicating domains of moderate hydrophobicity in most cases. This observation should be related to the internal morphology of the PQFD aggregates, which are expected to contain small hydrophobic domains due to the partial modification of PDMAEMA with fluorinated side chains and the steric hindrance being exerted on these side chains during their organization in separate domains.

**Table 3.**  $I_3$  values for the PQFD amphiphilic copolymers at different pH and temperature conditions ( $c = 1 \times 10^{-3}$  g/mL).

Sample		$I_1/I_3$		
		25 °C	50 °C	
PQFD 10%	H <sub>2</sub> O protocol	pH 3	1.36	1.55
		pH 7	1.6	1.53
		pH 10	1.41	1.43
	THF protocol	pH 3	1.64	1.55
		pH 7	1.55	1.53
		pH 10	1.4	1.48
PQFD 20%	H <sub>2</sub> O protocol	pH 3	1.5	1.53
		pH 7	1.21	1.45
		pH 10	1.44	1.31
	THF protocol	pH 3	1.61	1.56
		pH 7	1.58	1.51
		pH 10	1.51	1.41

### 3.3.2. pH Effects on the Self-Assembly Behavior of PQFD Copolymers—Light Scattering Results

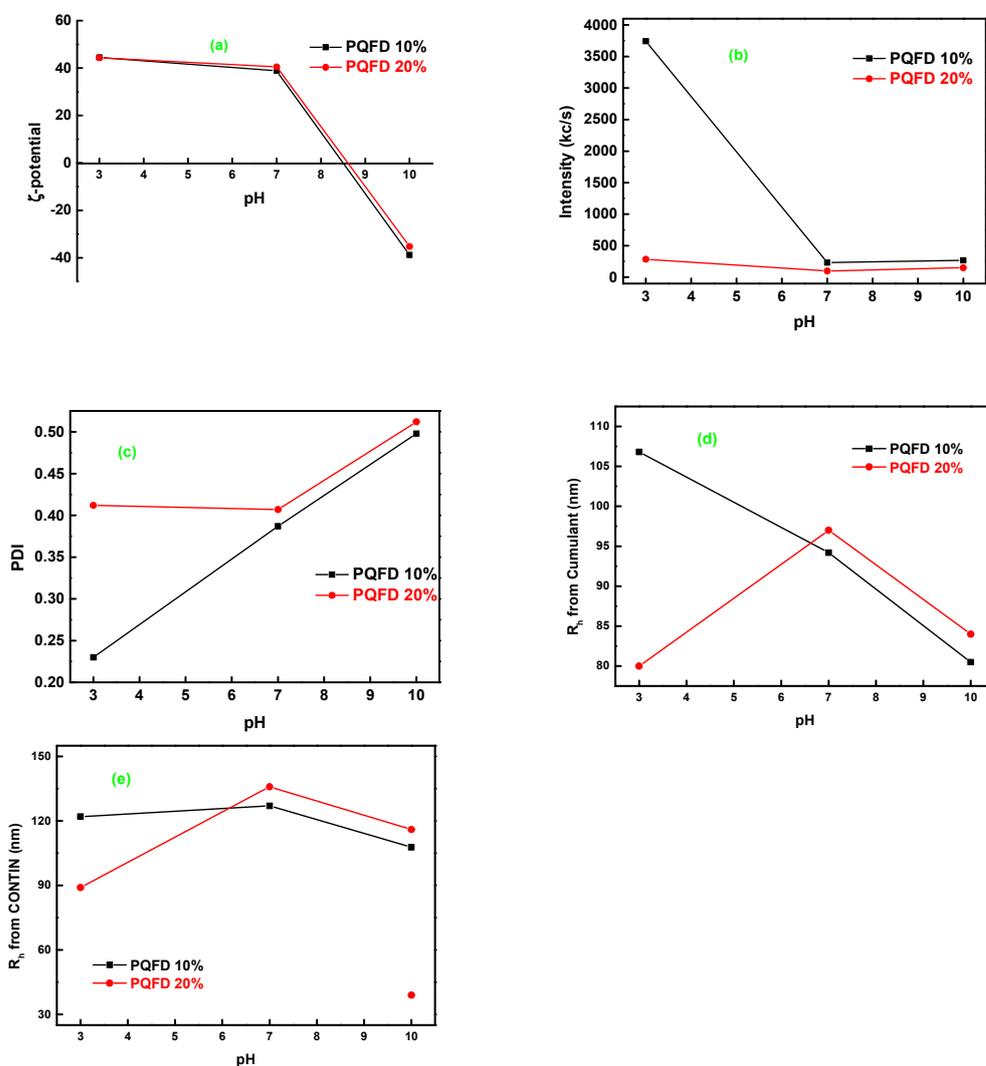
The effect of pH changes on the properties of the formed aggregates as a result of the self-assembly of amphiphilic statistical PQFD copolymers in aqueous solutions was examined by dynamic and electrophoretic light scattering, as well as by fluorescence spectroscopy.

According to the literature, the PDMAEMA homopolymer is a weak polybase and behaves as a responsive cationic polyelectrolyte due to the balance between protonation and deprotonation of the tertiary amine side groups, which depends on solution pH. At neutral pH, PDMAEMA is a hydrophilic homopolymer due to the partial protonation of the amino groups, and the species present in the solution are in the form of single chains. With the increase in pH at basic values (pH = 9 and above), complete deprotonation of the amino groups occurs, resulting in the reduction in electrostatic interactions and the formation of aggregates. The reduction in pH to acidic values results in the complete protonation of the amino groups of PDMAEMA, whereby the electrostatic interactions increase and therefore the hydrophilicity also increases. Therefore, at acidic pH, PDMAEMA is more soluble than at basic pH values and, therefore, particles of smaller mass and size are expected.

The fact that part of the amino groups is permanently positively charged, due to the partial incorporation of the qf17 reagent, is expected to affect the properties depending on the fluorination degree. It is also important to note that each quaternary amino group carries a perfluorinated chain. This means that in each solution of different pH, there will be hydrophobic segments on the polymer chains and, for this reason, aggregates are expected to be observed in the solution. The size of the aggregates will be affected by the pH according to the properties of nonquaternized DMAEMA segments, as mentioned above.

In Figure 4, plots of  $\zeta$ -potential, scattering intensity, size polydispersity index,  $R_h$ , obtained by the cumulant method, and  $R_{h,c}$ , obtained by CONTIN versus pH, are presented for the aqueous solutions of samples PQFD 10% and PQFD 20% prepared by the H<sub>2</sub>O

protocol. Figures S6 and S7 present the results from solutions prepared by the THF protocol. In Tables 4 and 5, the results obtained by light scattering techniques for all the samples are presented.



**Figure 4.** Dependence of (a)  $\zeta$ -potential, (b) scattering intensity, (c) PDI, (d)  $R_h$  (from cumulant method), and (e)  $R_h$  (from CONTIN) of the PQFD 10% and PQFD 20% copolymer solutions ( $H_2O$  protocol) on pH variations.

**Table 4.** Effect of pH on the properties of copolymer PQFD 10% aqueous solutions.

Preparation Protocol	pH	Intensity (kC/s)	$R_h$ from Cumulants (nm)	PDI	$R_h$ from CONTIN (nm)	%wt	$\zeta$ -Potential
$H_2O$	3	3743	107	0.230	122	99	+44 mV
	7	232	94	0.387	127	98	+39 mV
	10	268	81	0.498	108	98	-38 mV
THF	3	389	303	0.433	58	50	+48 mV
					449	50	
	7	1052	548	0.47	36	10	+32 mV
					99	29	
					744	61	
	10	642	150	0.498	47	38	-35 mV
					285	62	

**Table 5.** Effect of pH on the properties of copolymer PQFD 20% aqueous solutions.

Preparation Protocol	pH	Intensity (KC/s)	R <sub>h</sub> from Cumulants (nm)	PDI	R <sub>h</sub> from CONTIN (nm)	%wt	ζ-Potential
H <sub>2</sub> O	3	285	80	0.412	89	98	+44 mV
	7	99	97	0.407	136	98	+40 mV
	10	150	84	0.512	39 116	31 69	−35 mV
THF	3	787	2060	0.389	50 958	20 80	+0.6 mV
	7	937	18,980	0.338	102 973	11 89	+27 mV
	10	655	3550	0.436	34 555	10 90	−27 mV

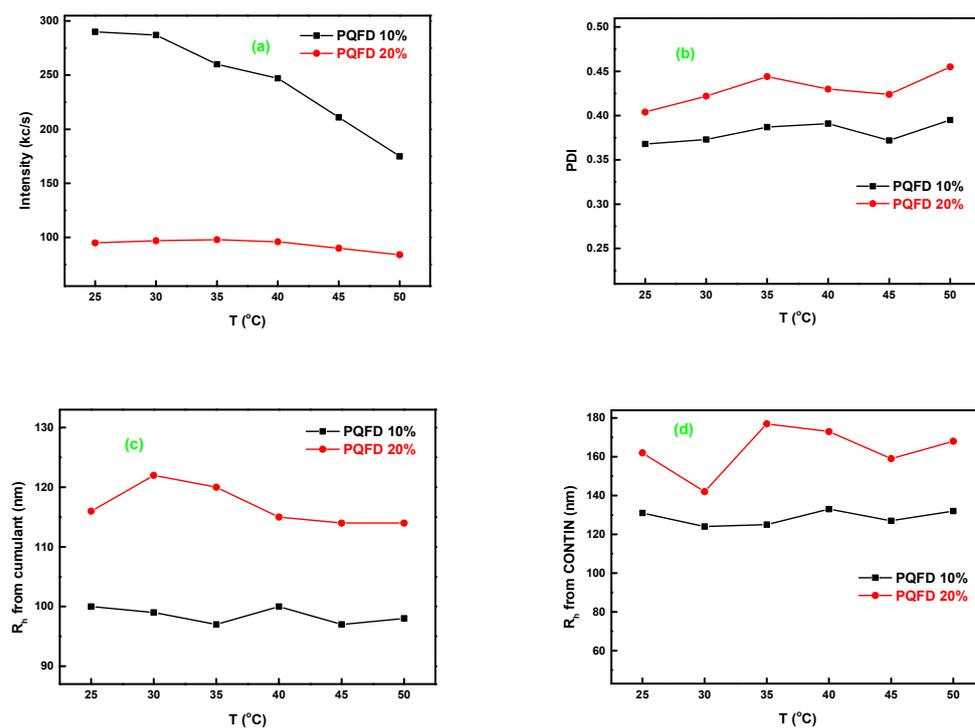
From the ELS results, one can see that as the pH value increases, the ζ-potential value decreases. This occurs because as the pH increases, the protonation of the amino groups decreases. In some cases though, we can observe that the ζ-potential value does not always follow that rule. For example, in some cases, the ζ-potential value at pH 3 is lower than that at pH 7 despite the fact that at pH 3, complete protonation of the amino groups takes place, while at pH 7, the protonation is partial. This can be attributed to the fact that this method measures the electric charge on the surface of the aggregates and it is possible that some protonated amino groups may be hidden inside the aggregate structure while more iodine anions are attached on the surface. This is directly related to the actual nanoscale morphology of the aggregates formed by the statistical copolymers, which may not be of the core-corona structure expected for amphiphilic diblock copolymers. The internal morphology should depend on the folding characteristics of the amphiphilic polyelectrolyte chains that are dictated by the tendency of the hydrophobic perfluorinated side groups to associate and the electrostatic repulsions from existing charges. There is the possibility that the hydrophobic domains in the PQFD aggregates have a patchy, multidomain structure reminiscent of compound micelles of block copolymers.

From the DLS results, after CONTIN analysis, it is evident that in many of the copolymer solutions (and mostly in those from the THF protocol), there are multiple populations of different-size aggregates. The cumulant method shows that in most cases, the samples at pH 7 have the largest aggregates, while the samples at pH 3 have the smallest. In general, it is observed that in the copolymer solutions prepared by the THF protocol, larger aggregates are formed than in the solutions prepared by the H<sub>2</sub>O protocol. The scattering intensity determined in each copolymer solution (which is also proportional to the mass of the aggregates) follows the size of the aggregates (i.e., the larger the aggregates present in the solution are, the higher the value). The polydispersity in aggregate populations may also be related to the statistical nature of the amphiphilic copolymer chains.

### 3.3.3. Temperature Effects on the Self-Assembly Behavior of the PQFD Copolymers—Light Scattering Results

It is known that PDMAEMA is also a thermoresponsive polymer. In order to investigate the effect of temperature changes on the properties of copolymer solutions, dynamic light scattering and fluorescence spectroscopy measurements were performed.

In Figure 5, plots of scattering intensity, size polydispersity index, R<sub>h</sub>, obtained by the cumulants method, and R<sub>h</sub>, obtained by CONTIN, in dependence of temperature, as obtained by light scattering techniques, for the aqueous solutions of amphiphilic copolymers PQFD 10% and PQFD 20%, prepared by the H<sub>2</sub>O protocol, are shown. In Figures S8 and S9, the results obtained for the THF protocol are presented.



**Figure 5.** Dependence of (a) scattering intensity, (b) PDI, (c)  $R_h$  (from cumulants method), and (d)  $R_h$  (from CONTIN) of the PQFD 10% and PQFD 20% copolymer solutions ( $H_2O$  protocol) on temperature changes.

As can be seen in Figure 5 for the aggregates of the PQFD 10% copolymer in water, the solution temperature seems to not affect their size. Nonetheless, the intensity in this sample seems to be decreasing when the solution temperature is increasing. On the other hand, for the aggregates of the PQFD 20% copolymer in water, it can be seen that the intensity is constant while the size of the particles varies at lower temperatures and seems to be stabilizing at a certain value at higher temperatures.

The results in Figures S8 and S9 show that when both copolymer solutions are prepared by the THF protocol, multiple populations of aggregates are observed. Aggregates of different sizes are present at lower temperatures, but with the increase in temperature, finally only one population is observed. Additionally, for both copolymer solutions from the THF protocol, there is a tendency for aggregate size reduction when the solution temperature increases, which is accompanied by lower values of the scattered light intensity. This means that aggregates of lower mass are formed at higher temperature.

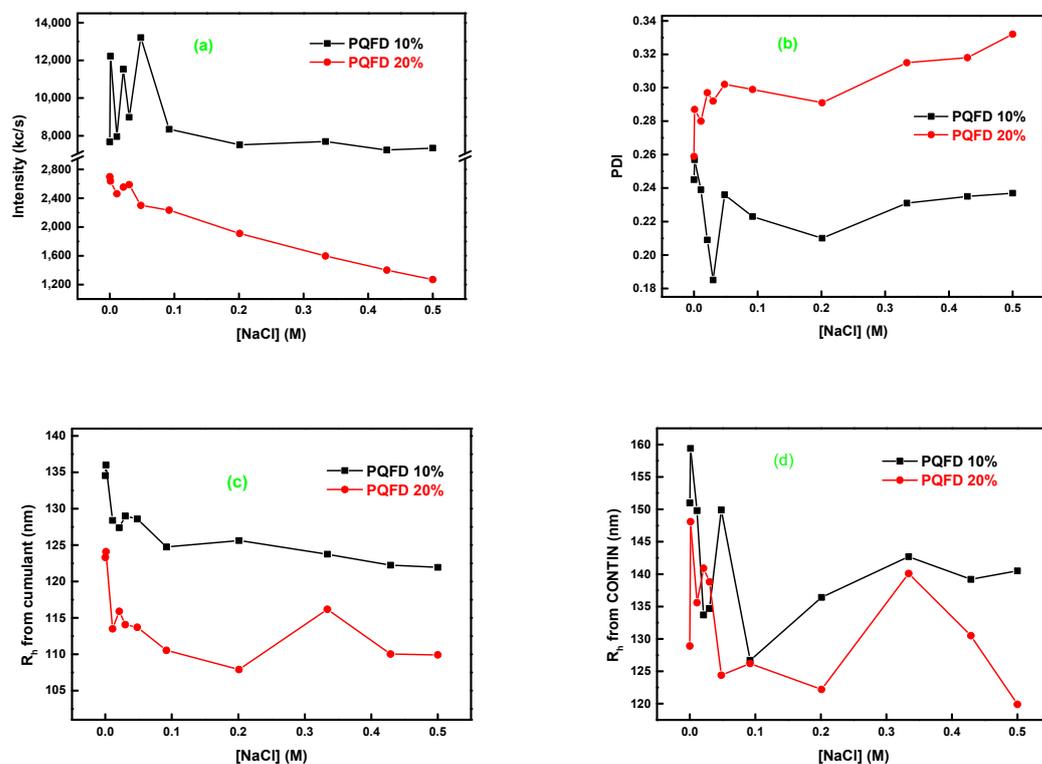
### 3.3.4. Ionic Strength Effects on the Self-Assembly Behavior of PQFD Copolymers—Light Scattering Results

The effect of ionic strength was also studied on PQFD copolymer solutions using dynamic light scattering, as the copolymers are hydrophobically modified polyelectrolytes and the salt concentration may affect their state of aggregation. In the analysis of the results, the small change in the concentration of the solution after each addition of NaCl solution has been taken into account.

As mentioned before, the PDMAEMA homopolymer is a weak polyelectrolyte and the properties of its aggregates (for example, the intensity of the scattered radiation and the hydrodynamic radius) change with the increase in the ionic strength of the solution. However, the present amphiphilic polyelectrolyte copolymers also bear fluorinated QFDMAEMA segments. Specifically, these QFDMAEMA segments carry quaternary amine groups that are permanently positively charged, conferring strong electrolyte properties to the copolymers. QFDMAEMA segments are present in small amounts in the copolymer

chains, compared to DMAEMA segments, but they present the ability of affecting the solution properties of the polymeric system.

In Figure 6, plots of the scattering intensity, PDI,  $R_h$ , from the cumulants method, and  $R_h$ , from CONTIN, as a function of salt concentration for the aqueous solutions of PQFD 10% and PQFD 20% prepared by the H<sub>2</sub>O protocol are shown. Respective plots for the THF protocol are given in Figures S10 and S11.



**Figure 6.** Dependence of (a) scattering intensity, (b) PDI, (c)  $R_h$  from cumulants, and (d)  $R_h$  from CONTIN for the PQFD 10% and PQFD 20% copolymer solutions (H<sub>2</sub>O protocol) as a function of ionic strength.

The fluctuations in the intensity of the scattered intensity observed at low salt concentrations are probably due to the change in the size of the aggregates as the ionic strength increases. Correspondingly, stabilization of the intensity of the scattered intensity around a certain value is attributed to the stabilization of the size of the aggregates (for example, when solvent penetrates into the aggregates and aggregate swelling occurs, while, afterward, the aggregate size stabilizes).

#### 4. Conclusions

A PDMAEMA homopolymer precursor synthesized by RAFT polymerization was chemically modified by quaternization with heptadecafluoro-10-iododecane at different degrees. Amphiphilic polyelectrolyte copolymers of the poly[(2-(dimethylamino) ethyl methacrylate)-*co*-(quaternized 2-dimethylaminoethyl methacrylate)] type (PQFD) were successfully obtained as evidenced by NMR and FTIR characterization. The modification with perfluorinated side groups resulted in a rich and interesting self-assembly behavior of the copolymers in aqueous solutions, which depends on the solution preparation protocol and copolymer composition. Critical aggregation concentrations could be determined in most cases using fluorescence spectroscopy with pyrene as the probe. Dynamic and electrophoretic light scattering experiments show that direct dissolution in water generally resulted in a lower number of aggregate species in solution compared to the organic solvent preparation protocol, which in turn gave solutions containing small- and large-size

copolymer aggregates. The aggregates formed were found to be influenced by changes in temperature and, to a lesser extent, in solution pH and ionic strength alterations.

The influence of external factors such as pH, temperature, and ionic strength on the self-assembly of the systems also presented differences depending on the respective preparation protocol. The overall observed solution behavior of the present macromolecular systems can be attributed in part to the high hydrophobicity of the perfluorinated side groups, the statistical nature of the hydrophobically modified polyelectrolytes, and to kinetic phenomena during self-assembly, due to the large incompatibility of perfluorinated segments with water and the hydrogenous parts of the macromolecular chains (which can also be related to the folding characteristics of the hydrophobic polyelectrolyte chains).

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/macromol2020013/s1>, Figure S1. Plots of the ratio of I1/I3 of pyrene spectra peaks as a function of concentration for the determination of CAC value: (a) PQFD 10% prepared in H<sub>2</sub>O protocol, (b) PQFD 20% prepared in H<sub>2</sub>O, (c) PQFD 10% prepared in THF protocol, and (d) PQFD 20% in THF protocol. Figure S2. Fluorescence spectra of pyrene for solutions of PQFD 10% at pH 3, 7, and 10, prepared by the H<sub>2</sub>O protocol at (a) 25 and (b) 50 °C. Figure S3. Fluorescence spectra of pyrene for solutions of PQFD 10% at pH 3, 7, and 10, prepared by the THF protocol at (a) 25 and (b) 50 °C. Figure S4. Fluorescence spectra of pyrene for solutions of PQFD 20% at pH 3, 7, and 10, prepared by the H<sub>2</sub>O protocol at (a) 25 and (b) 50 °C. Figure S5. Fluorescence spectra of pyrene for solutions of PQFD 20% at pH 3, 7, and 10, prepared by the THF protocol at (a) 25 and (b) 50 °C. Figure S6. Plots of (a) scattering intensity, (b) PDI, (c) Rh from cumulant method, (d) Rh from CONTIN algorithm, and (e)  $\zeta$ -potential of the PQFD 10% copolymer solutions (prepared by the THF protocol) as a function of pH. Figure S7. Plots of (a) scattering intensity, (b) PDI, (c) Rh from cumulant method, (d) Rh from CONTIN algorithm, and (e)  $\zeta$ -potential of the PQFD 20% copolymer solutions (prepared by the THF protocol) as a function of pH. Figure S8. Plots of (a) scattering intensity, (b) PDI, (c) Rh from cumulant method, and (d) Rh from CONTIN of the PQFD 10% copolymer solutions (prepared by the THF protocol) as a function of temperature. Figure S9. Plots of (a) scattering intensity, (b) PDI, (c) Rh from cumulant method, and (d) Rh from CONTIN of the PQFD 20% copolymer solutions (prepared by the THF protocol) as a function of temperature. Figure S10. Plots of (a) intensity, (b) PDI, (c) Rh from the cumulant method, and (d) Rh from CONTIN of the PQFD 10% copolymer solutions (prepared by the THF protocol) as a function of ionic strength. Figure S11. Plots of (a) intensity, (b) PDI, (c) Rh from the cumulant method, and (d)  $R_h$  from CONTIN of the PQFD 20% copolymer solutions (prepared by the THF protocol) as a function of ionic strength.

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