Nano-Structuration by Self-Assembly in *N*-Alkyl Thiazolium and Triazolium Side-Chain Polymethacrylates

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ABSTRACT

Amphiphilic polymers are tunable systems to construct supramolecular hierarchically self-assembled structures. Six families of heterocyclic polymethacrylates (PMTAs) bearing 1,3-thiazole and 1,2,3-triazole pendant groups with alkyl and succinate spacers were chemically modified by quaternization reaction of the azole heterocycles with five alkylating agents (methyl, butyl, octyl, dodecyl and hexadecyl iodide) leading to a library of 30 different amphiphilic polyelectrolytes (PMTAs-RI). These polymers have been characterized in bulk by small and wide angle x-ray scattering (SAXS, WAXS) and differential scanning calorimetry (DSC). Quaternization induces a dramatic effect (increase) on the glass-transition temperature T_g , being strongest for methyl iodide members. Increasing the length of the quaternizing agent, plasticization is first observed, followed by a further increase of T_g . This effect, together with evidences of a second T_g and crystallization for the members with the longest quaternizing agents, could be attributed to the presence of well-developed alkyl nano-domains evidenced by the structural investigation. WAXS and SAXS results have been consistently interpreted by assuming nano-structuration driven by the amphiphilicity balance of polyelectrolytes. The different morphologies revealed by SAXS have been characterized, assigning a plausible chemical nature to the phases involved in each case. The non-polar fraction has been considered as the control parameter defining the main features of the achieved morphology. By increasing this parameter, structures ranging from hexagonally packed non-polar cylinders in a polar matrix to the inverse situation have been found, passing through lamellar phases. Under some conditions, within the polar lamellae a third phase formed by cylinders of heterocycles has even been determined. We have checked the validity of the scenario proposed by comparing

the sizes deduced from the SAXS analysis with the expected characteristic lengths of the associated moieties, inferring thereby how alkyl side groups arrange within the nano-domains. On the basis of the complete picture achieved, the type of nano-structures formed by this class of polymers can be predicted, if the chemical composition including the quaternization degree is known.

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1. INTRODUCTION

Nowdays it is well-established the block copolymers can self-assemble in different morphologies, i.e. , in solid state, in solution and also at the interface, depending on the incompatibility between phases, the interaction parameter, the molecular weight and the composition of copolymers, among others specific in solution, such as solvent, temperature, pH, ionic strength, etc. There have been also many reports on the nanostructuration of polyethylene precisely copolymerized with acrylic acid (AA),¹,² phosphonic acid (PA),³ and 1-methylimidazolium bromide (ImBr) with molar fraction lower than 10%, to be considered as ionomers.⁴ These ion-containing polymers offer current potential as ion conductors for energy storage or conversion, membranes for water purification or desalination, electroactive materials for actuators or sensors, and shape memory materials.^{5, 6}

On the other hand, ammonium polyionenes, which are polymers containing quaternary nitrogen atoms in the polymer main chain, have also been studied in terms of structure-morphology-properties relationships. Semicrystalline imidazolium polyesters with long spacers (imidazolium-C₁₁-sebacate-C₆, imidazolium-C₁₁-sebacate-C₁₁, bis(imidazolium)ethane-C₆-sebacate-C₆, and bis(imidazolium)ethane-C₁₁-sebacate-C₁₁), exhibit well-defined lamellar thicknesses between the imidazolium groups, indicating that imidazolium groups are at the surface of the alkylene group crystal lattice.⁷ Moreover, bis(imidazolium) polyesters have higher glass transition temperature and/or melting transition than their mono-imidazolium analogs.

It is also important to consider the amine size on the thermal, mechanical and rheological properties of these polyionenes, i.e. size of the amine in amine neutralized sulfonated polystyrenes the reduces the strength of the ion dipole interaction by preventing close approach of the amine sulfonate groups.⁸ Bulky aliphatic amine-based cations tend to either decrease or lead to less significant increases of T_g, melt viscosity, and modulus, while these properties increase compared to those of the unsulfonated polymer when a metal⁹ or ammonium cation is used.⁸ The cation size is also crucial to the developed morphologies due to the different association energies of cations with anions and ether oxygens in the case of polyesters.¹⁰

In spite of all these research to the best of our knowledge none has been focused on the structural analysis of amphiphilic homopolymeric materials in the solid state since as it was described above self-organizing materials (e.g. by nano-phase separation)

are emerging systems with a wide number of applications,¹¹ such as nano-devices, polymer networks and conetworks,¹² nano-reactors,¹³ microelectronic, catalysis and biomedicine,¹⁴ including drug release and delivery systems¹⁵ and also antimicrobial ones.¹⁶ Very recently¹⁷ the synthesis of homopolymethacrylates with *N*-alkyl 1,3-thiazolium and 1,2,3-triazolium pendant groups (PMTA) leading to a library of polycations with different amphiphilic balance PMTA-RI (see Scheme 1) have been described. These polyelectrolytes present potent antimicrobial activity and non hemotoxicity. Basically, their dual chemical nature (polar and nonpolar) and therefore, the amphiphilic balance of each structure, became key factors on enhancing both the antimicrobial and non-hemolytic activities. Having all these in mind, in the present article, the solid state behavior of PMTAs and *N*-alkyl PMTAs-RI polymers have been study by small and wide-angle X-ray scattering (SAXS, WAXS) as well as differential scanning calorimetry (DSC) The morphology of these systems have been analyzed by using a quantitative analysis of the scattering SAXS curves, making possible to understand the nano-structuration of these systems. Furthermore, a prediction model of lattices further than the dependence on the alkyl phase volume fraction, taking into account the possible conformation and arrangement of the alkyl side-chains in each case, has been proposed. **Scheme 1.** Synthesis of amphiphilic polymethacrylates (PMTAs-RI) with various alkyl iodides.

2. EXPERIMENTAL SECTION

2.1. Materials

PMTAs were prepared by radical conventional polymerization of methacrylic 1,3-thiazoles and 1,2,3-triazoles, **MTAs**, as recently reported.¹⁷ Subsequently, the polymers were quaternized with five alkyl iodides (methyl, butyl, octyl, dodecyl and hexadecyl) and purified against distilled water and freeze-dried to yield polyelectrolytes **PMTAs-RI**. The Degree of Quaternization (DQ) of azole heterocycles was determined by ¹H-NMR spectroscopy (DQth for 1,3-thiazole and DQtr for 1,2,3-triazole groups).¹⁷ All the polyelectrolytes were quantitatively modified except **PMTA3** with long alkyl iodides (octyl, dodecyl and hexadecyl) as it is detailed in the Electronic Supporting Informaton (SI).

2.2. Thermal Analysis: Differential Scanning Calorimetry Measurements

A Differential Scanning Calorimeter (DSC) TA Instrument Q2000 was used. All samples were previously dried under vacuum. Measurements were performed under N₂ atmosphere flow in a temperature range from -150 °C to 150 °C. The treatment was always as follow: (i) Equilibration at -150 °C; (ii) First heating up to 150 °C; (iii) Cooling down to -150 °C; (iv) Second heating up to 150 °C. In all cases the rate imposed was 10 °C/min.

2.3. Small and Wide Angle X-Ray Scattering Measurements

Wide Angle X-Ray Scattering (WAXS) measurements to decipher the short-range order were performed on a Bruker D8 Advance diffractometer working in parallel beam geometry. By using a Göbel mirror, the originally divergent incident X-ray beam from a line focus X-ray tube (Cu, operating at 40 kV and 40 mA) is transformed into an intense and parallel beam that is free of K_β radiation. The parallel beam optic required in the secondary beam path is achieved by an equatorial axial Soller slit of 0.2°. The linear detector LYNXEYE used presents an active area of 14.4 mm × 16 mm. Measurements were performed in reflection (θ-2θ configuration) varying the scattering angle 2θ from 4 to 30° with a step of 0.05°. The measuring time employed was 10 s/point.

Small Angle X-Ray Scattering (SAXS) was used to probe the large-scale structure. Experiments were conducted on a Rigaku 3-pinhole PSAXS-L equipment operating at 45 kV and 0.88 mA. The MicroMax-002+ X-Ray Generator System is composed by a microfocus sealed tube source module and an integrated X-Ray generator unit which produces CuK_α transition photons of wavelength $\lambda = 1.54 \text{ \AA}$. The flight path and the

sample chamber in this equipment are under vacuum. The scattered X-Rays are detected on a two-dimensional multiwire X-Ray Detector (Gabriel design, 2D-200X). This gas-filled proportional type detector offers a 200 mm diameter active area with ca. 200 micron resolution. The azimuthally averaged scattered intensities were obtained as a function of wavevector q , $q = 4\pi\lambda^{-1} \times \sin(\theta)$. Reciprocal space calibration was done using silver behenate as standard. Samples were sandwiched between mica windows and placed in transmission geometry; with a sample to detector distance of 0.5 m. Measuring times of about 20 min were employed. In both SAXS and WAXS experiments, samples were investigated after synthesis process, without any prior thermal treatment.

Scattering Curves of Ordered Particle Systems

The intensity scattered at low angles by an isotropic system of polydisperse particles (phase 'A') dispersed according to a lattice in a matrix (phase 'B') is proportional to the product of the particle form factor $P(q)$ and the lattice factor $S(q)$. The functional form of $P(q)$ is determined by the shape of the particle, and contains information about its size through a suitable parameter: e. g. the radius R_{sph} in the case of a sphere, the radius R_{cy} and the length L_{cy} in the case of a cylinder, or the thickness d and the radius R_{D} in the case of a disk or lamella. Conversely, the structure factor $S(q)$ consists of peaks at q -positions q^* determined by the type of crystal lattice (lamellar, hexagonal, cubic, etc.) and the unit cell dimension a . For example, $q_h^* = 2\pi h/a$ for 1D-packing in a lamellar lattice, $q_{hk}^* = 4\pi(h^2 + hk + k^2)^{1/2}/(3^{1/2}a)$ for 2D-hexagonal packing, and $q_{hkl}^* = 2\pi(h^2 + k^2 + l^2)^{1/2}/a$ for a cubic lattice. Here, h , (h,k) and (h,k,l) are the Miller indices for a given crystal lattice plane corresponding respectively to the 1D, 2D and 3D system. Static disorder of the first kind (statistically independent displacements from the ideal lattice parameters) may be introduced through a Gaussian lattice point distribution which, together with the usually expected particle size distribution, leads to an effective damping of the higher order Bragg reflections. In addition, the finite domain size is reflected in a broadening of the peaks: the peak width δ can be related with the domain size D of the ordered domain via the Debye-Scherrer equation $D = 2\pi/\delta$.

All the above described parameters are considered in the fitting program 'Scatter'.^{18, 19} This very flexible program allows a quantitative analysis of small angle scattering data, providing different models for both, the form factor and the lattice factor.

3. RESULTS

3.1 Thermal Characterization. DSC Results.

The DSC thermograms obtained for all polymers investigated can be found in the Supporting Information (SI). The second heating scan of all polymers displayed a clear glass transition located in a temperature range, which depends on the particular chemical nature of the polymer considered. The glass-transition temperature **T_g** values obtained from the midpoint of the curves are compiled in **Table 1** and represented in **Figure 1A** as function the parameter **n_c** (number of carbons along the alkyl group of the quaternizing agent). A general trend is observed for the six families of polymers with different alkylating agents (**Figure 1A**). Upon methyl iodide quaternization (**PMTAs-Mel**), the **T_g** value sensibly increases with respect to that observed in the **PMTAs** counterpart. Increasing the length of the quaternizing agent, the **T_g** value gradually decreases from **n_c = 1** to **n_c = 8** (**PMTAs-Mel**, **PMTAs-Bul** and **PMTAs-Ocl**) indicating the plasticization of the system. A further increase of the alkyl length (**n_c = 12**, **PMTAs-Dol** and **n_c = 16**, **PMTAs-Hel**) produces however an increase of the value of the glass-transition temperature.

Table 1. Glass Transition Temperatures (**T_g**) of **PMTAs** and *N*-alkyl **PMTAs-RI**.

n_c^a	T_g (°C)					
	PMTA1-RI	PMTA2-RI	PMTA3-RI	PMTA4-RI	PMTA5-RI	PMTA6-RI
0	47	6	69	24	-8	29
1	144	57	126	108	71	82
4	111	36	90	74	39	48
8	87	27	77	67	28	36
12	92	23	83	68	30	41
16	108	30	85	78	29	49

^aNumber of carbon atoms of the alkylating agent [R = methyl (Mel), **n_c = 1**; R = butyl (Bul), **n_c = 4**; R = octyl (Ocl), **n_c = 8**; R = dodecyl (Dol), **n_c = 12**; R = hexadecyl (Hel), **n_c = 16**].

Additional features indicative for an intricate thermal behavior were found in the DSC traces for some members in the six families. On the one hand, in the dodecyl iodide quaternized systems (**PMTAs-Dol**, **Figure 1B**) a weak second transition could be resolved at low temperatures, in the range between -78 and -74 °C. On the other hand, a broad melting peak was found for all hexadecyl iodide quaternized systems (**PMTAs-Hel**), as can be seen in **Figure 1C**. For these samples, no hint for a second glass transition was evident in the experimental conditions used.

Figure 1. DSC thermograms. A) Influence of the Length of the Alkylating Agent on the Glass Transition Temperatures (T_g 's) of **PMTAs-RI**. B) Second heatingruns at 10 $^{\circ}\text{C}/\text{min}$ of dodecyl quaternized **PMTAs** (**PMTAs-Dol**). C) Second heatingruns at 10 $^{\circ}\text{C}/\text{min}$ of hexadecyl quaternized **PMTAs** (**PMTAs-Hel**).

3.2 Structural Characterization

3.2.1 Short-range order. WAXS Results.

The panels on the right of **Figure 2** compile the WAXS profiles of all the polymers investigated. The patterns of the **PMTAs** (prior to quaternization) display the typical features of amorphous polymers. General trends can be found for the polyelectrolytes of the six families: in the q-region investigated, the polymers quaternized with methyl iodide show two broad peaks centered in the ranges 1.2-1.4 $\text{\AA}^{-1}$ (**peak I**) and 1.8-2.0 $\text{\AA}^{-1}$ (**peak II**); with increasing n_c , the intensity of peak II gradually decreases and both peaks tend to merge in a single peak centered at about 1.5 $\text{\AA}^{-1}$. In addition, the results

corresponding to polymers with hexadecyl iodide quaternization (**PMTAs-Hel**) of families 2, 3, 4 and 6 show a weak crystalline peak around $1.53 \text{ \AA}^{-1}$.

Figure 2. SAXS (left) and WAXS (right) patterns of PMTAs-RI in bulk at room temperature. A) **PMTA1-RI**; B) **PMTA2-RI**; C) **PMTA3-RI**; D) **PMTA4-RI**; E) **PMTA5-RI** and F) **PMTA6-RI**.

3.2.2. Nanoscopic Length Scales. SAXS Results

SAXS results are represented in the left panels of **Figure 2**. At least for some of their members, the data of all families show more or less pronounced peaks in the region accessed by the experiments, revealing some degree of ordering in the nano-scale. With exception of the homopolymer **PMTA5**, which pattern shows a rather broad peak at around $0.5 \text{ \AA}^{-1}$, peaks are only clearly developed in the polyelectrolytes. Methyl- and butyl iodide quaternized systems do not show well-resolved peaks, except in the cases of families 5 and 6 quaternized with methyl iodide (**PMTA5-MeI** and **PMTA6-MeI**). Clear maxima are found in the quaternized systems with the longest alkylating agents ($n_c = 8, 12$ and 16). In particular, some systems display very well-defined and intense peaks, like e. g. **PMTA2-Hel** (**Figure 2B**).

4. STRATEGY TO DECIPHER THE NANO-STRUCTURES

A large fraction of the samples investigated showed clear signatures of nano-structuration. We tried to obtain the details of the underlying morphologies revealed by the SAXS patterns applying the following strategy.

In a first step, a simple phenomenological analysis of the SAXS data was performed consisting of the determination of the peak positions from direct inspection of the patterns. From the sequence of these positions, the type of lattice can in principle be elucidated; for example, peak positions at $q^*, 2q^*, 3q^*, 4q^*, \dots$ -- q^* to the first-order reflection position-- would correspond to a lamellar lattice (LAM); peak positions at $q^*, \sqrt{3}q^*, 2q^*, \sqrt{7}q^*, \dots$ to a hexagonal packing lattice (HEX). Also, the unit cell dimension can immediately be deduced as

$$a = 2\pi/q^* \quad (\text{Eq. 1})$$

The positions of the maxima identified are indicated in the left panels of **Figure 2**. Three situations could be distinguished:

(I) well defined peaks are observed, revealing one periodicity. Here we can distinguish two groups of polymers: **PMTA1-DoI**, **PMTA3-DoI**, **PMTA4-DoI**, **PMTA1-Hel**, **PMTA2-Hel**, **PMTA3-Hel**, **PMTA5-MeI** and **PMTA6-MeI**, which show a lamellar phase, and **PMTA4-Hel** and **PMTA2-DoI**, which present a hexagonal lattice. These systems can be categorized as displaying two-phase (AB) morphologies;

(II) two simultaneous periodicities have to be involved for a single sample. This is the case of **PMTA5-DoI** and **PMTA5-Hel**. The periodicities correspond to lamellae and

hexagonal packing. Moreover, a ratio between the principal scattering vectors q_1^* (corresponding to the lamellar structure) and q_2^* (corresponding to the hexagonal structure) of about $\sqrt{2}$ ($q_2^* \approx \sqrt{2}q_1^*$) is found, suggesting a more complex structure factor consisting of cylinders regularly located within lamellae. We thus infer a three-phase (ABC) morphology for these polyelectrolytes. Although less visibly, **PMTA6-DoI** and **PMTA6-Hel** belong to this group;

(III) only very broad peaks are seen (all octyl iodide quaternized polymers).

In a further step, the quantitative analysis of the SAXS patterns was performed by using the 'scatter' program. At this stage, fits were realized only for the results corresponding to the polymers included in the above-defined group (I), for which AB morphologies had been clearly identified. For the lamellar lattices a disc form factor is assumed, while for the hexagonal packing lattices a cylindrical form factor is considered. The 'scatter' fits delivered the main parameters defining the size of the dispersed phases, namely the thickness d of the lamella or the radius R_{cy} of the cylinder, and allowed a more accurate estimation of the lattice parameter a . With this information, the volume fractions of each phase could be deduced. These are given by

$$f_A = d/a \quad (\text{Eq. 2})$$

for an AB lamellar system (A-discs in a B-matrix)

$$f_A = (\pi R_{cy}^2 L_{cy})/a^2 L_{cy} = (\pi R_{cy}^2)/a^2 \quad (\text{Eq. 3})$$

for A-cylinders hexagonally packed in a B-matrix.

The resulting values of these parameters are listed in **Table 2**. There, the superscript 'fit' means that the given values were obtained from the 'scatter' fit of the experimental SAXS data.

The driving force for the observed nano-structuration or nano-phase separation will seek on the amphiphilic chemical nature of the polyelectrolytes, which naturally induces by self-assembly a segregation of moieties with different polarity. Therefore, a next step was to built the phase diagram based on the morphological phases found from the analysis of the experimental results (A, B, and later also C) onto chemically defined phases composed by moieties with well-differentiated polarity (we will refer them with Greek letters). **Scheme 2** shows a hierarchical classification of the molecular groups in the samples, according to their polarity. The α -group refers to the main-chain atoms and includes the α_H -moiety (heterocycles: thiazolium and triazolium iodides) and the

α_{MS} -group (composed by the methacrylate main-chain moiety and the particular spacer); in the β -group the alkyl side-group atoms in the quaternizing agent are considered.

Scheme 2. Chemical Groups of PMTAs-RI involved in nano-structuration by self-assembly.

Despite their complexity – these systems include mono-cationic and di-cationic groups, linear and branched quaternizing moieties, relatively broad molecular weight distributions ($\text{PDI} = 2.0\text{-}2.5$) of polymers with number-average molecular weight ranging from 53 to 150 kDa,^{20, 21} –, the chemical structure of these systems has perfectly been characterized by means of de ^1H -, ^{13}C -NMR, IR and Elemental Analysis techniques.¹⁷ In particular, the degree of quaternization of each polymer has been determined with high accuracy. Therefore, for a given polymer the volume fractions corresponding to the different molecular groups involved can be estimated. This was performed on the basis of theoretical calculations of the van der Waals (VvdW) volumes of these groups²². Such estimations were made for the 20 systems showing some degree of nano-structuration (those above included in situations (I), (II) and (III)). The details are given in the SI. In these calculations the counterions (iodides included in the polar part) as well as the degree of quaternization were taken into account (see **Tables S4-S10**).

The obtained values for the volume fractions of the different molecular groups in the nano-structured polymers are also compiled in **Table 2**. For the systems included in situation (I), where an unbiased fit of the SAXS results had been performed, we could now check the suitability of the hypothesis of self-assembly driven by differences in polarity of the molecular groups and the correct selection of the involved moieties. Thereby, for the polymers containing alkyl side-groups in the quaternizing agent (β -groups) we would expect that these β -groups would conform one of the two morphological phases. The good agreement between the volume fractions calculated for these chemical species f_{β}^{CALC} and one of the morphological phases in these

polyelectrolytes f^{fit} obtained from the fit of the SAXS patterns (namely the disks in the lamellae in **PMTA1-DoI**, **PMTA3-DoI**, **PMTA4-DoI**, **PMTA1-Hel**, **PMTA2-Hel** and **PMTA3-Hel**, the cylinders in **PMTA2-DoI** and the matrix embedding the cylinders in **PMTA4-Hel**) strongly support our hypothesis. In the case of **PMTA5-Mel** and **PMTA6-Mel**, which lack non-polar alkyl β -groups, the two chemical groups with polarity contrast are the α_{H} and the α_{MS} moieties. For these systems, we also find that the values of $f^{\text{fit}}_{\text{A}}$ nearly perfectly coincide with $f\alpha_{\text{H}}^{\text{CALC}}$, providing additional support to our assignment of chemical phases with different polarity to the morphological phases resolved by SAXS experiments.

Once the nano-structure of the systems belonging to situation (I) was deciphered and rationalized, we faced the more complex case of situation (II) (**PMTA5-DoI** and **PMTA5-Hel** and, less clearly, **PMTA6-DoI** and **PMTA6-Hel**), where an ABC morphology is suggested by the phenomenological SAXS analysis. As we have already mentioned, from the peak positions and their ratio, an underlying lattice of cylinders regularly located within lamellae can be inferred. A hint to identify the origin of these three phases is given by the above described observation of a nano-phase separation between the highly polar heterocycles (plus iodide cations) and the less polar α_{MS} -groups in the polyelectrolytes quaternized by methyl iodide (**PMTA5-Mel** and **PMTA6-Mel**). Now, the non-polar and long alkyl side-groups would conform a third phase. The shift of the first maximum q^*_1 —corresponding to the lamellar structure—toward lower values with increasing n_{c} (from 12 to 16) indicates that one of the lamellar phases has to be attributed to these alkyl (β) groups. Based on these considerations, we assumed lamellae with discs of β -groups alternating a polar phase where cylinders of heterocycles would be surrounded by the less polar α_{MS} -groups (based on the observation that $f\alpha_{\text{H}} < f\alpha_{\text{MS}}$). These cylinders themselves would be located in a hexagonal array. Notice that a large number of parameters are contained in this model. However, from the calculated volume fractions of the three molecular groups involved $f\beta$, $f\alpha_{\text{H}}$ and $f\alpha_{\text{MS}}$, we determined the expected values of $\mathbf{d}$ and $\mathbf{R}_{\text{cy}}$ with the assumed geometry ($\mathbf{d}^{\text{CALC}}$ and $\mathbf{R}_{\text{cy}}^{\text{CALC}}$ given in **Table 2**) and those values are introduced in the fitting procedure. We first considered the **PMTA5-Hel** SAXS patterns, which were those with more pronounced ordering features. A rather good agreement was found between the theoretical curves and the experimental results. In a further step, a refinement of the values of $\mathbf{d}$ and $\mathbf{R}_{\text{cy}}$ was performed, delivering the final values $\mathbf{d}^{\text{fit}}$ and $\mathbf{R}_{\text{cy}}^{\text{fit}}$ shown in **Table 2**. Given the success with this polymer, we applied the same procedure to confirm the suitability of the model with the patterns of **PMTA5-DoI** and to obtain an estimation of the unit cell size parameters from the fit. Finally, we considered the

relatively featureless results on **PMTA6-Dol** and **PMTA6-Hel**. In these cases, the compatibility with the proposed morphology was checked. The parameters obtained from all these fits are compiled in **Table 2**.

The much more featureless patterns of the polyelectrolytes with $n_c = 8$ (situation (III)), could not be univocally analyzed in an unbiased way. The data corresponding to **PMTA1-Ocl**, **PMTA2-Ocl**, **PMTA3-Ocl**, **PMTA4-Ocl** and **PMTA5-Ocl** could be best described assuming cylinders in a hexagonal array based on a rough estimation of the lattice suggested by the positions of the broad SAXS peaks. From comparison with the calculated chemical volume fractions, these cylinders should be attributed to the β -groups in all cases except for **PMTA5-Ocl**. In this polyelectrolyte, taking into account the alkyl nature of the spacer group –of similar length as that in the quaternizing chain in this system-, we found a more plausible scenario in cylinders of heterocycles (α_H) surrounded by a less polar environment provided by both, β - and α_{MS} -groups. Finally, **PMTA6-Ocl** is better described involving a more complex ABC morphology, in analogy to the other members of this family (**PMTA6-Dol** and **PMTA6-Hel**). We note that for all patterns of situation (III) (octyl iodide quaternization) the obtained values for the domain size are very reduced ($D/a \approx 1...3$), pointing to an actual frustration of the long-range order. This can be directly deduced from the extremely broad features of the peaks. Thus, the main information provided by the quantitative analysis is actually the hint for cylindrical domains, i.e., the presence of elongated regions rich either in non-polar (**PMTA1-Ocl**, **PMTA2-Ocl**, **PMTA3-Ocl**, and **PMTA4-Ocl**) or in polar (**PMTA5-Ocl** and **PMTA6-Ocl**) moieties.

The detailed analysis of each structure and the fits of the SAXS results of all the 20 polymers considered can be found in **Tables S4-S22** and **Schemes S2-S21**.

Table 2. Summary of Parameters involved in Nano-structuration

AB type Polymers with Hexagonally Packed Nonpolar Cylinders (HEX) (P6/mm)										
--> $A = \alpha_H + \alpha_{MS}; B = \beta$										
Sample	Polar Phase A Volume Fraction $f_A = f_{\alpha}^{CALC} = f_{\alpha_H}^{CALC} + f_{\alpha_{MS}}^{CALC}$				Nonpolar Phase B Volume Fraction $f_B = f_{\beta}^{CALC}$		Cell Dimension (Å)		Cell unit Parameter (Å)	
	$f_{\alpha_H}^{CALC}$	$f_{\alpha_{MS}}^{CALC}$	f_{α}^{CALC}	f_A^{fit}	f_{β}^{CALC}	f_B^{fit}	$a^{SAXS} = \frac{2\pi}{q^{*SAXS}}$	a^{fit}	R_{cy}^{CALC}	R_{cy}^{fit}
PMTA1-Ocl AB	0.31	0.31	0.62	0.58	0.38	0.42	24.07	22.51	8.37	8.21
PMTA2-Ocl AB	0.23	0.49	0.72	0.69	0.28	0.31	23.44	25.83	6.99	8.11
PMTA3-Ocl AB	0.38	0.20	0.58	0.57	0.42	0.43	26.94	24.91	9.85	9.23
PMTA4-Ocl AB	0.33	0.24	0.57	0.55	0.43	0.45	25.03	25.01	9.26	9.43
PMTA2-DoI AB	0.20	0.43	0.63	0.65	0.37	0.35	42.74	41.28	14.67	13.73

AB type Polymers with Lamellar Lattice (LAM) and Disks Particle --> $A = \alpha_H + \alpha_{MS}; B = \beta$										
Sample	Polar Phase A Volume Fraction $f_A = f_{\alpha}^{CALC} = f_{\alpha_H}^{CALC} + f_{\alpha_{MS}}^{CALC}$				Nonpolar Phase B Volume Fraction $f_B = f_{\beta}^{CALC}$		Cell Dimension (Å)		Cell unit Parameter (Å)	
	$f_{\alpha_H}^{CALC}$	$f_{\alpha_{MS}}^{CALC}$	f_{α}^{CALC}	f_A^{fit}	f_{β}^{CALC}	f_B^{fit}	$a^{SAXS} = \frac{2\pi}{q^{*SAXS}}$	a^{fit}	d^{CALC}	d^{fit}
PMTA1-DoI AB	0.26	0.26	0.52	0.50	0.48	0.50	33.78	32.53	16.21	16.24
PMTA3-DoI AB	0.33	0.17	0.50	0.49	0.50	0.51	34.52	35.44	17.26	18.08
PMTA4-DoI AB	0.27	0.20	0.47	0.49	0.53	0.51	34.33	32.93	18.19	16.66
PMTA1-Hel AB	0.225	0.225	0.45	0.44	0.55	0.56	40.54	38.94	22.30	21.68
PMTA2-Hel AB	0.18	0.38	0.56	0.58	0.44	0.42	49.09	48.44	21.60	20.28
PMTA3-Hel AB	0.30	0.16	0.46	0.43	0.54	0.57	36.53	35.74	19.73	20.28

AB type Polymers with Lamellar Lattice (LAM) and Disks Particle $\rightarrow A = \alpha_H; B = \alpha_{MS}$								
Sample	Polar Phase A Volume Fraction $f_A = f_{\alpha_H}$		Nonpolar Phase B Volume Fraction $f_B = f_{\alpha_{MS}}$		Cell Dimension (Å)		Cell unit Parameter (Å)	
	$f_{\alpha_H}^{CALC}$	f_A^{fit}	$f_{\alpha_{MS}}^{CALC}$	f_B^{fit}	$a^{SAXS} = 2\pi/q^{*SAXS}$	a^{fit}	d^{CALC}	d^{fit}
PMTA5-Mel AB	0.52	0.54	0.48	0.46	32.90	31.33	15.79	14.54
PMTA6-Mel AB	0.52	0.53	0.47	0.48	27.68	29.32	13.02	14.14

AB type Polymers with Hexagonally Packed Polar Cylinders (HEX) (P6/mm) $\rightarrow$ A = $\alpha_H + \alpha_{MS}$; B = β										
Sample	Polar Phase A Volume Fraction $f_A = f_{\alpha} = f_{\alpha_H} + f_{\alpha_{MS}}$				Nonpolar Phase B Volume Fraction $f_B = f_{\beta}$		Cell Dimension (Å)		Cell unit Parameter (Å)	
	$f_{\alpha_H}^{CALC}$	$f_{\alpha_{MS}}^{CALC}$	f_{α}^{CALC}	f_A^{fit}	f_{β}^{CALC}	f_B^{fit}	$a^{SAXS} = 2\pi/q^*$	a^{fit}	R_{cy}^{CALC}	R_{cy}^{fit}
PMTA4-Hel AB	0.23	0.17	0.40	0.42	0.60	0.58	37.18	41.93	13.27	15.32

AB type Polymers with Hexagonally Packed Polar Cylinders (P6/mm) --> A = α_H ; B = $\alpha_{MS} + \beta$										
Sample	Polar Phase A Volume Fraction $f_A = f_{\alpha_H}$		Nonpolar Phase B Volume Fraction $f_B = f_{\alpha_{MS}} + f_{\beta}$				Cell Dimension (Å)		Cell unit Parameter (Å)	
	$f_{\alpha_H}^{CALC}$	f_A^{fit}	$f_{\alpha_{MS}}^{CALC}$	f_{β}^{CALC}	$f_{\alpha_{MS}}^{CALC} + f_{\beta}^{CALC}$	f_B^{fit}	$a^{SAXS} = 2\pi/q^*$	a^{fit}	R_{cy}^{CALC}	R_{cy}^{fit}
PMTA5-Ocl AB	0.29	0.26	0.33	0.38	0.71	0.74	33.98	34.21	10.32	9.84

ABC type Polymers with Hexagonally Packed Polar Cylinders (HEX) (P6/mm) at Lamellae (LAM) --> A = α_H ; B = β ; C = α_{MS}																
Sample	Polar Phase A Volume Fraction $f_A = f_{\alpha_H}^{CALC}$		Nonpolar Phase B Volume Fraction $f_B = f_{\beta}^{CALC}$		Phase C Volume Fraction $f_C = f_{\alpha_{MS}}$		SYSTEM 1 Cell Dimension: (HEX) (Å)		SYSTEM 1 Cell unit Parameter: Rcy (Å)		SYSTEM 2 Cell Dimension: (LAM) (Å)		SYSTEM 2 Cell unit Parameter: d (Å)		Parameter of B Layer Distance $d_B = a_2 \cdot d$	
	$f_{\alpha_H}^{CALC}$	f_A^{fit}	f_{β}^{CALC}	f_B^{fit}	$f_{\alpha_{MS}}^{CALC}$	f_C^{fit}	$a_1^{SAXS} = 2\pi/q_1^*$	a_1^{fit}	R_{cy}^{CALC}	R_{cy}^{fit}	$a_2^{SAXS} = 2\pi/q_2^*$	a_2^{fit}	d^{CALC}	d^{fit}	d_B^{CALC}	d_B^{fit}
PMTA6-Ocl ABC	0.29	0.32	0.39	0.35	0.32	0.30	32.90	31.52	9.99	10.03	22.93	21.63	7.34	7.12	15.59	14.51
PMTA5-Dol ABC	0.25	0.22	0.48	0.46	0.27	0.32	40.02	39.52	11.29	10.54	28.43	28.52	7.68	9.06	20.75	19.46
PMTA6-Dol ABC	0.25	0.24	0.48	0.48	0.27	0.28	40.02	40.12	11.29	11.13	28.43	27.23	7.68	7.50	20.75	19.73
PMTA5-Hel ABC	0.21	0.20	0.55	0.54	0.24	0.26	45.53	46.54	11.77	11.63	32.39	32.31	7.77	8.26	24.62	24.05
PMTA6-Hel ABC	0.22	0.21	0.56	0.54	0.22	0.25	42.74	43.72	11.31	11.31	30.35	29.07	6.68	7.24	23.67	21.83

5. DISCUSSION

5.1. Thermal Properties

All polymers investigated present a clear glass transition (**Figure 1A**), which should be associated to the segmental dynamics of the main chains. In the parent homopolymers T_g values decrease with increasing length and flexibility of the side group. **PMTA1** and **PMTA3** are the polymers with highest T_g -values (47 and 69 °C, respectively). They both present relatively short side groups, but the more rigid triazole moiety in **PMTA3** hinders more efficiently the main-chain motions. **PMTA6** with a much longer side-group displays a T_g -value of 29 °C. This is rather close to the T_g -value of **PMTA4**, (24 °C), which side-group is rather shorter than that in **PMTA6**, but contains a butyl group conferring more flexibility to the motions. **PMTA5** is the system with longest (similar length as **PMTA6**) and most flexible side groups, and accordingly displays the lowest T_g (-8 °C). Longer side groups hamper the packing of the main chains and thereby facilitate their mobility.

Quaternization induces a dramatic effect on the main-chain mobility of all the polymers. In all cases the T_g -values of the polyelectrolytes are higher than that of the corresponding homopolymers. The inclusion of ionic charges introduces additional interactions between the polymer segments, which impede to a large extent the relaxation of the chains. The impact is particularly striking in the polymers quaternized with methyl iodide (**PMTAs-Mel**). The increment of the glass transition temperature values is about 50 °C when modifying from **PMTA2**, **PMTA6** and **PMTA3** to **PMTA2-Mel**, **PMTA6-Mel** and **PMTA3-Mel** respectively. This effect is even more pronounced for the other three families (**PMTA1**, **PMTA4** and **PMTA5**), where a difference of about 90 °C in the T_g -values is observed upon quaternization with methyl iodide. One possible explanation for this difference between the two groups of families is that in the latter (**PMTA1**, **PMTA4** and **PMTA5**) the spacer groups have a less polar character than in the former (**PMTA2**, **PMTA6** and **PMTA3**).

For all six families of polyelectrolytes investigated, the influence of the alkyl side-chain length on the glass-transition is qualitatively –and even semiquantitatively– the same (see **Figures 1A and S2**). When increasing n_c from 1 to 4 and 8, i.e., using butyl iodide and octyl iodide as quaternizing agents, the T_g -values gradually decrease (around 40 °C from $n_c = 1$ to 8). This plasticization can be attributed to the ability of alkylic branches to hinder the efficient packing of the main chains and thereby conferring them a higher mobility. However, a further increase of the alkyl side-chain length, i.e.,

considering dodecyl iodide and hexadecyl iodide as quaternizing agents, induces an increase of the value of the glass transition temperature with respect to that found for the octyl iodide counterpart. This observation is probably related to two other peculiarities revealed for the systems containing long alkyl side groups ($n_c \geq 12$), namely: (i) the weak second transition found in the dodecyl iodide quaternized systems (**PMTAs-Dol**, **Figure 1B**) and (ii) the broad melting peak observed for all hexadecyl iodide quaternized systems (**PMTAs-Hel**) (**Figure 1C**). The latter two thermal transitions could tentatively be assigned to a glass transition associated to the dodecyl tails and to a partial crystallization of the hexadecyl side-groups, as will be corroborated by the WAXS results, respectively. All these three features could be a consequence of the formation of well-defined nano-domains of non-polar alkylic chains (forming the discs in the AB or ABC morphologies previously identified) in the polyelectrolytes. The existence of regions exclusively containing alkylic side chains would imply an important enhancement of the hydrophobic interactions between side chains, possibly leading to their interdigitation. Such effect could impose constraints to the main-chain motions leading to an increase of the **T_g**-value. In addition, in large enough domains, an independent glass-transition of the alkyl side-groups could be developed, as it has already been proposed for poly(n-alkyl acrylates) (PnAAs) and poly(n-alkyl methacrylates) (PnMAs).²³⁻²⁵ In this context, it is worth mentioning the peculiarities reported for the structural relaxation within the alkyl nano-domains (so-called polyethylene (PE)-like nano-domains) in the latter systems, which arise as a consequence of the confinement effects imposed by the slower main chains.^{26, 27}

5.2. Short-Range Order

Deciphering the short-range order in amorphous polymers is by no means trivial. With exception of chemically extremely simple main-chain polymers like PE or polybutadiene, the proper interpretation of WAXS patterns in terms of the underlying atomic pair correlation functions is usually impossible without the help of fully atomistic molecular dynamics (MD) simulations. This is of course beyond the scope of this work. Instead, we will try to extract some information about the origin of the observed WAXS peaks on the basis of a qualitative comparison of our data with patterns of polymers like poly(methyl methacrylate) (PMMA), PE and poly(hexyl methacrylate) (PHMA) (**Figure 3**), which are well understood by now and which could be considered as simplified limiting cases of our polymers (or parts of them), or could capture some of their features.

Figure 3. WAXS patterns of **Poly(methyl methacrylate) (PMMA)**, **poly(n-hexyl methacrylate) (PHMA)**, **Molten High Density Polyethylene (PE)** and **PMTAs**. The results of PMTAs have been sorted such that the length of the spacer group is increased from top to bottom.

The main peak of PMMA WAXS pattern is centered at about $0.95 \text{ \AA}^{-1}$. MD-simulation results²⁸ demonstrated that this peak is in fact the result of a complex combination of different correlation functions, in particular of main-chain/main-chain (MC/MC) atomic pairs leading to a peak at about $0.8 \text{ \AA}^{-1}$ of mainly inter-molecular origin, and a more intense peak at around $1.2 \text{ \AA}^{-1}$ arising from side-group/side-group (SG/SG) correlations of both, inter and intra-molecular character. The second peak in the pattern –as usually found for peaks in the range $q \geq 2 \text{ \AA}^{-1}$ in the structure factor of polymers—arises from intramolecular correlations.²⁹ With increasing side-group length, the relative importance of SG/SG correlations in the patterns naturally increases. If the lateral groups tend to segregate from the main chains –as it seems to be the general case in comb-like polymers, even invoking merely entropic effects³⁰—the short-range order is finally dominated by the features of the ensemble of side groups, as it was demonstrated for PnMAs --in particular for PHMA²⁶—and also for poly(alkylene oxides)³¹. Thus, despite the bigger size of its monomeric unit, the interpretation of the main WAXS-peak ($q \sim 1.3 \text{ \AA}^{-1}$) of PHMA is rather simple: it results from correlations between pairs of atoms located in different neighboring alkyl side-groups (within the alkyl nano-domains developed in this polymer previously commented). Its similarity with the main peak of

molten PE (**Figure 3**) supports this interpretation. Conversely, the presence of the longer lateral groups induces a larger separation of the polymer backbones and therefore the peak corresponding to MC/MC intermolecular correlations is gradually shifted to lower q -values with increasing side-group length. In PHMA it is located in a q -range below that shown in the figure²⁶.

These arguments can be translated to the polymers here investigated. Let us first consider the case of the homopolymers. **Figure 3** shows their WAXS patterns, sorted by increasing side-group length. Given the bulky size of the side groups in all these polymers, we could infer that the inter-molecular MC/MC correlations would lead to peaks located at q -values smaller than that of PMMA ($0.8 \text{ \AA}^{-1}$)²⁸, i.e., in the range covered already by our SAXS measurements. We could note indeed hints for the presence of a peak in some of the homopolymers (**Figure 2**, left), in particular in **PMTA5**. On the other hand, according to the above discussion, the main WAXS **peak I** should be interpreted as mainly due to interplay between different correlations involving side-group atoms, in principle of both, intra- and inter-chain character. We observe a tendency of the peak position to increase with increasing side-group size. This could reflect a better packing of the side-groups if they are longer. We would expect some resemblance of this peak to that of molten PE (and PHMA) for **PMTA5**, which side-chains contain long alkylic groups. This is found indeed. The closer proximity achievable by alkyl side-groups as compared to succinate groups leads to a larger q -value of **peak I** for this polymer with respect to those for **PMTA2** and **PMTA6**. Now moving to the polyelectrolytes, we may apply again the same arguments and end to similar conclusions. For a given family, the relative contribution of the correlations involving now the atoms in the alkyl side groups of the quaternizing agents is obviously enhanced with increasing length of these groups. This effect is particularly important in the families **PMTA5-RI** and **PMTA6-RI** –where two long alkylic side-chains per monomer are introduced with quaternization. As can be seen in **Figure 2** (right), **peak I** gradually evolves toward a PE-like halo. In the extreme cases of the polymers quaternized with hexadecyl iodide, the environment surrounding a given alkylic side-group is so similar to that in PE that even partial crystallization is observed, leading to the sharp peaks in the patterns at the same value as that in high-density PE (see **Figure 4A**). This peak corresponds to an extended planar zig-zag³² conformation.

Figure 4. DSC Thermograms of **PMTAs-Hel** A) First Heating and B) First Cooling. C) WAXS patterns of **PMTAs-Hel** and **HD Polyethylene**.

As it has been suggested above, this PE-like crystalline feature would be associated to the melting process detected by DSC for **PMTAs-Hel**. This could be confirmed by the results on the first-heating scan (**Figure 4B**). Those polymers showing a melting above room temperature (RT) (**PMTA2-Hel**, **PMTA3-Hel**, **PMTA4-Hel** and **PMTA6-Hel**) display the crystalline peak in their WAXS patterns. Those polymers where the melting occurs below or close to RT (**PMTA1-Hel** and **PMTA5-Hel**) present purely amorphous halos instead. We note that in the cooling run after the first heating all polymers show a broad crystallization peak in the range from -15 to 7 °C (**Figure 4C**), which leads to the melting process displayed by all **PMTAs-Hel** in the second heating run above

commented (**Figure 1A**). A thorough investigation of these features will be subject of future work.

Finally, **peak II** in the WAXS patterns of the polyelectrolytes could tentatively be attributed to a peculiar preferential correlation involving the iodide ions. This hypothesis is based on the observation that this peak is absent in the homopolymers and it is particularly prominent in the polymers quaternized with methyl iodide, becoming weaker when the length of the side-group increases. This happens for all families, and suggests a 'dilution' effect of the correlation involving the ion with increasing size of the quaternizing side-group.

5.3. Nano-scale structure

With the above described strategy we are able to identify different morphologies formed by self-assembly in all families of polyelectrolytes and to assign a chemical nature to the phases involved (see **Figure 5** as a summary).

PMTAs-RI Self-Assembly of Amphiphilic Polyelectrolytes

Figure 5. Classification of **PMTAs-RI** polyelectrolytes according to their self-assembled nano-structures and identification of the chemical moieties involved in the different phases.

The ratio between the characteristic volumes of the well-differentiated chemical species in terms of polarity would be the key ingredient determining the particular morphology of the self-assembled system, in an analogous way as in the case of block-copolymers with incompatible blocks widely investigated in the literature³³. In particular, the relevant parameter seems to be the volume fraction of the alkyl side group f_β , which primarily defines the type of lattice. In this way, alkyl volume fractions in the range $f_\beta \approx 0.25$ -0.4 would give rise to non-polar cylinders surrounded by a polar environment; the opposite case $f_\beta \approx 0.6$ -0.75, to the inverse situation of polar cylinders in a non-polar matrix. If the volume fractions of the polar and alkyl groups are very similar (around 0.5), lamellar systems would be found. Within this situation, more complex structures could be formed, when this first nano-segregation between a non-polar (alkyl) phase and a polar phase would be followed by the assembly within the latter of the highly polar moieties of the heterocycles (plus iodide cations) in cylinders embedded in a α_{MS} -group-rich environment.

Figure 6. Examples of the different morphologies found illustrated by a particular polymer. SAXS patterns with the corresponding fits, as well as the values of the main parameters involved in each case, are also included.

In an illustrative way, **Figure 6** shows an example of each of the four different kinds of lattices identified in the **PMTAs-RI** polyelectrolytes. This figure also includes the fit of the SAXS results with the ‘scatter’ program and the proposed microscopic underlying scenario to reproduce the obtained unit cell and lattice parameters. A detailed analysis for all the systems investigated is described in the SI. We have tried to provide additional support to the proposed structures and further insight into the molecular conformations by comparison with the expected dimensions of the moieties involved in the nano-domains. These were estimated as follows: Both, the analysis of the SAXS data and the previously discussed features of the WAXS results point to the alkyl side groups to conform one of the nano-segregated phases (except, of course, in the case of the polyelectrolytes quaternized with methyl iodide). A priori, it is not possible to know what is the conformation –and, consequently, the effective length—of these alkyl groups and their arrangement within the phase. An alkyl group is chemically linked to a moiety belonging to another (polar) phase and the alkane segments close to this link would be expected to be more stretched than conforming a random walk. However, they are coiled to some extent, since –with exception of the weak crystalline peak displayed by some of the WAXS data—the structure factor reveals amorphous features. Thus, two limiting situations could be defined for an alkyl side-group composed by n_c carbons: (i) a zig-zag planar conformation (all-trans), for which the length R_z can be calculated taking into account the C-C bond length ($l = 1.54$ Å) and angle ($\theta = 68^\circ$) in PE

$$R_z = n_c l \cos(\theta/2) \text{ (Eq. 4)}$$

and (ii) a coiled conformation. For this state, the average length (square root of the average end-to-end distance) of the group R_c can be estimated on the basis of the characteristic ratio C_{n_c} ³⁴

$$R_c^2 = n l^2 C_{n_c} \text{ (Eq. 5)}$$

The obtained dimensions in both kind of conformations of the different alkyl groups involved in the samples are given in **Table 3**. In addition, using the software Chem 3D the repeating units of all families were simulated. After an energy minimization, the lengths of all the relevant moieties identified in the SAXS analysis were estimated. These values are collected in **Table 3**. In the following, we describe in general terms the main features found for each of the lattices identified. We compare the dimensions obtained for the particles with those of the associated moieties to check the assignment proposed. In addition, this comparison also allows us to infer the most probable conformation and relative arrangement of the alkyl groups within the nano-domains.

Table 3. Estimated lengths (Å) of Side-Chains and Spacer Groups in PMTAs-RI

N-Alkane Side-Chains	n_c	C_{n_c}	Rc: Random Coil Conformation (Å)	Rz: Extended Planar Zig-Zag Conformation ^a (Å)
Methyl	1	1	1.54	-
Butyl	4	2.12	4.48
Octyl	8	3.19	7.79
Dodecyl	12	4.38	11.16
Hexadecyl	16	4.70	13.35
2 × Dodecyl (between Main Chains) ^b	24	5.34	17.43
2 × Hexadecyl (between Main Chains) ^b	32	5.56	20.54
Spacer Groups				
MTA1
MTA2
MTA3
MTA4
MTA5
MTA6
N-Methyl Thiazolium and Triazolium
Thiazole and Triazole
Nonyl Methacrylate
Methacryloyloxy Ethyl Succinate

^a Calculated Spacing for an extended chains including carbon-hydrogen bonds in Chem 3D Pro. ^b Considered as a single alkyl chain.

Hexagonally Packed NonPolar Cylinders (Figure 6_I): The polar phase presents values of the volume fraction around 0.6. The SAXS patterns show peaks at q^* , $\sqrt{3}q^*$, $2q^*$. This phase is clearly formed by **PMTA2-DoI**. The value found for R_{cy} in **PMTA2-DoI** is about 14 Å, i.e., in the range between the average length of a dodecyl group in random coil and in extended conformation. Thus, the alkyl groups within the cylinders would be most probably in a slightly coiled conformation facing each other. PMTAs quaternized with octyl iodide (**PMTA1-OcI**, **PMTA2-OcI**, **PMTA3-OcI**, **PMTA4-OcI**) – with a very poor long-range order—could also present this morphology. As can be seen in **Table 2**, all **PMTAs-OcI** present similar values (between 7 and 10 Å) for the radius of the cylinder, compatible with octyl chains dimensions. They would also be facing each other within this phase and surrounded by the polar part. The latter would be consistent with the main chains, spacer groups and thiazolium iodide and triazole.

Lamellae (Figure 6_II): The volume fractions are around 0.5. SAXS peaks are located at q^* , $2q^*$, $3q^*$, etc.... This morphology is found for **PMTA1-DoI**, **PMTA1-HeI**, **PMTA2-HeI**, **PMTA3-DoI**, **PMTA3-HeI**, and **PMTA4-DoI** (where the non-polar fraction has increased with respect to the previously described case). The values of the thickness of the disks in the lamellae are too small to correspond to facing side-groups and thereby demand some degree of interdigitation. In some of the systems, namely **PMTA2-HeI** and **PMTA3-HeI**, the results would be compatible with planar extended (zig-zag) conformations of completely interdigitated side-groups. This kind of situation would give rise to highly crystalline regions. In view of the WAXS and DSC results, we could expect a certain fraction of such an arrangement, but it would coexist with other regions of coiled side groups interdigitated to some extent. On the other hand, the members of families 5 and 6 quaternized with methyl iodide (**PMTA5-MeI** and **PMTA6-MeI**) also self-assemble in lamellar phases. This could be explained considering now the long and hydrophobic spacer group (nonyl methacrylate in **PMTA5-MeI** and methacryloyloxyethyl succinate in **PMTA6-MeI**) as one of the phases, and the bisheterocyclic part (methyl-thiazolium and triazolium iodides) as the other one (more polar), as we have discussed above. This is corroborated by the good agreement between the sizes of the lamellae deduced from the SAXS analysis and the dimensions deduced from the Chem 3D software for α_H (8 – 12 Å) and α_{MS} (8 – 15 Å), if we assume interdigitation of the moieties. Such nano-structuration seems not to be developed by **PMTAs-MeI** in the other families (see **Figure 2, left**). The spacer-group length might be a key factor in this assembly process. Also, the presence of two heterocycles in the polymer seems to be necessary (**PMTA2-MeI** does not show this feature either).

Hexagonally Packed Polar Cylinders (Figure 6-III): This is the symmetric case with respect to that illustrated in **Figure 6-I**. In the SAXS diffractograms, peaks at q^* , $\sqrt{3}q^*$, $2q^*$... also appear, but now the polar phase is the minority component (volume fraction of around 0.4). This is clearly appreciated in the system **PMTA4-Hel**. There, cylinders would be composed by cations and anions, spacer groups and main chains, and would be embedded within a non-polar matrix of hexadecyl groups.

Polar Cylinders at Lamellae (Figure 6-IV): These multiphase nano-structures appear in the systems **PMTA5-Dol**, **PMTA5-Hel**, **PMTA6-Dol** and **PMTA6-Hel**. SAXS results reveal two periodicities (more evident in the family of **PMTA5**) with an approximate ratio of $\sqrt{2}$ between the scattering vectors ($q_2^* \approx \sqrt{2}q_1^*$, and therefore $a_1 \approx \sqrt{2}a_2$). In these systems, the volume fractions of the polar phases of thiazolium and triazolium iodides f_{α_H} are around 0.25. They are similar to those of the nonyl or ethyl succinate methacrylic main chains ($f_{\alpha_{MS}}$) and about half of those of the flexible non-polar phases (f_{β} of the alkyl side chains). The proposed nano-structure would consist of a lattice of polar cylinders embedded in the lamellar lattice of main chains and separated from the alkyl-side group phase. In this scenario, all the samples should present a similar value of the radius of the cylinder, independent of the quaternizing agent. As can be read from **Table 2**, this is indeed the case, with R_{cy} around 10-11 Å. These cylinders would exclusively be formed by thiazolium/triazolium cations and iodide anions. The lamellar phase containing these cylinders would be composed by main chains and spacer groups and would be of about 8 Å thickness –in agreement with the expected value of the length of these molecular groups-. The phase, which size varies from one system to another has thus to be assigned to the alkyl side groups: the associated thickness d_B ($d_B = a_2 - d$) increases from dodecyl ($d_B \approx 19$ Å) to hexadecyl iodide ($d_B \approx 23$ Å). The finding that these values of L_B are very similar to the thicknesses of the disks in the β -phases of the corresponding ‘simple’ lamellae (AB-type) polyelectrolytes strongly supports this picture. As in the AB-lamellae, the alkyl side groups in these more complex morphologies would show some interdigitation within the non-polar phase. Finally, we note that, as we found for the methyl iodide counterparts, this kind of self-assembly is only developed for polymers with two heterocycles per monomeric unit and long and flexible spacer groups.

As previously mentioned, the polyelectrolyte **PMTA6-Ocl** could probably be included in the group of polar cylinders at lamellae. In the case of **PMTA5-Ocl** the results rather suggest a lattice where cylinders of cations and anions would be surrounded by octyl groups or main-chains with nonyl spacer groups indistinctly (hexagonally packed polar cylinders, like in **Figure 6-III**). For **PMTA5-Ocl**, the value of R_{cy} is smaller than that

deduced for **PMTA4-Hel**, in accord with the given interpretation, and in both cases the value of this parameter is in agreement with the estimated length of the here suggested involved groups.

Finally, we propose a scheme to predict the kind of lattice and position of the first peak in the SAXS curves of **PMTAs-RI** systems (those developing AB-morphologies) on the basis of the scenario deduced from this investigation. Our study strongly suggests that the morphologies and dimensions of the unit cells obtained through self-assembly of the **PMTAs-RI** polyelectrolytes would in general be determined by the interactions between the alkyl side groups and their conformation within the nano-domains, which seems to be the same independently of the family considered. As explained above, the kind of lattice would be defined by the volume fraction of the alkyl side group f_β . This can be calculated following the procedure given in the SI, if the chemical composition and DQ of the system are known. If the value of f_β is smaller than 0.40...0.43, non-polar cylinders are formed (note that for very small values of f_β , spherical nano-domains in some cubic cell arrangement would be expected, but this condition is not fulfilled by any of the samples here investigated). When cylindrical alkyl nano-domains are formed, the alkyl side-groups seem to be coiled and facing each other within this phase.

Table 4. Guidelines to estimate wavevector q^* values and Lattice Prediction

f_β	Expected Lattice	q^{*CALC}	Fixed Parameters (Å)				Arrangement of β -Group: Alkyl Side-Chains
			n_c	8	12	16	
< 0.44	AB: HEX ^a	$(2\pi/R_{cy}) \times (f_\beta/\pi)^{1/2}$	$R_{cy_{coil}}$	7.79	11.16	13.35	Facing each other
			$R_{cy_{zig-zag}}$	10.75	15.84	20.94	
0.44-0.56	LAM	$2\pi f_\beta/d$	$d_{zig-zag}^c$	10.75	15.84	20.94	Interdigitating each other
			d_{coil}^d	13.35	17.43	20.54	
> 0.56	HEX ^b	$(2\pi/R_{cy}) \times (f_\alpha/\pi)^{1/2}$	Polar Group	α (PMTA4-Hel)	α_H ABC Systems		Arrangement of α -Group: Thiazolium/Triazoleium Iodides
			$R_{cy_{coil}}$	15	12		Facing each other

^a Nonpolar cylinders of alkyl side-chains (B) dispersed in a Polar matrix (A) of main chains, spacer and Thiazolium/Triazoleium iodides. ^b Polar cylinders (A) dispersed in a nonpolar matrix (B) of alkyl side-chains. ^c Considering alkyl side-chains totally interdigitated each other. ^d Considering two alkyl-side chains as a single coil of a total n_c atoms.

Then, we can predict that $R_{cy} \approx R_c(n_c)$. In the lamellae –obtained for values of f_β in the range $0.40...0.43 \leq f_\beta \leq 0.57...0.60$, the alkyl groups seem to adopt more or less coiled conformations with some degree of interdigitation. With the information at hand, it is not possible to unambiguously determine their exact arrangement. However, we have found that the thickness of the lamellae can be well approximated in all cases by the average end-to-end distance corresponding to an ‘effective’ alkyl segment composed

by $2n_c$ backbone atoms (compare values in **Table 2** and **3**). Therefore, we propose the ‘phenomenological’ rule $d \approx R_c(2n_c)$ for the thickness of the alkyl disk in the lamellae.

Based on these hypotheses, for each system the value of the corresponding lattice parameter a can be calculated by using **Eqs. 1-3**, and from this, we could predict the value of the scattering vector q^{*CALC} where the structure factor peak would present its first maximum. In an illustrative mode, **Figure 7** shows the results of these calculations for families 1-4 (showing AB-morphologies) and compares them with those experimentally observed in the SAXS curves. The agreement between both sets of data is very satisfactory, providing additional support to the scenario here proposed.

Figure 7. Predicted Lattice and wavevector q^* values in AB type self-assembled polymers. SAXS Peak Positions experimentally observed (q^{*SAXS}) and Calculated (q^{*CALC}) from theoretical alkyl phase volume fractions f_β^{CALC} and fixed lattice parameters (shown in **Table 4**) of A) PMTA1-RI, B) PMTA2-RI, C) PMTA3-RI and D) PMTA4-RI.

These results confirm thus that, knowing the chemical structure of a given system, the calculation of the volume fractions of the chemical groups with differentiated polarity allows predicting the morphology of the self-assembled structure. Taking into account the expected conformation of the alkyl groups within the non-polar phases, we can assume the positions and even the relative intensities of the peaks in the SAXS patterns (they are determined by the form factor of the dispersed phases). However, other parameters like the extension of the domains or the size distribution would be more difficult to predict since additional parameters like e.g. the molecular weight, tacticity, quaternization degree, etc. could have also an impact in their determination. Another conclusion from this work is that nano-structuring can only be well developed if the involved moieties are enough long and flexible. For example, butyl-quaternized polyelectrolytes seem to be unable to give rise to well-defined nano-structures, and those formed in the case of the octyl side groups are far from leading to a real long-range order.

6. CONCLUSIONS

We have investigated the thermal and structural properties of six families of heterocyclic polymethacrylates quaternized with five alkylating agents of different length. The calorimetric study reveals that quaternization induces a dramatic effect on the main-chain mobility of all the polymers. The presence of ionic charges strongly hinders the segmental relaxation. Increasing the length of the alkyl side-groups in the quaternizing agent, first a plasticization effect is observed, which can be attributed to a less efficient packing of the main chains. For the longest side-groups considered though, namely dodecyl and hexadecyl iodide quaternization, a further increase of the glass-transition temperature is found. This effect, together with evidences of a second glass transition and crystallization in these polymers, could be associated to the presence of well-developed alkyl nano-domains as evidenced by the structural investigation.

WAXS and SAXS results have been consistently interpreted by assuming the development of nano-structuration driven by the amphiphilicity in the polyelectrolytes. The degree of ordering is elevated in samples with 12 or more carbons along the alkyl quaternizing group, but a tendency to form well-defined nano-domains can already be found for the polymers quaternized with octyl iodide. In **PMTAs-RI**, the precursor effect of self-assembly previously invoked for poly(methyl methacrylates)^{23, 26} is thus fully developed for long enough side groups, suggesting 8 as the minimum number of carbons along them to achieve well-defined morphologies. We have been able to identify the different morphologies present in all families and to assign a chemical nature to the phases involved. The non-polar fraction can be considered as the control parameter defining the main features of the achieved morphology. The investigated samples present a variety of nano-structuration, ranging from hexagonally packed non-polar cylinders in a polar matrix to the inverse situation, passing through lamellar phases. Within the polar phase of these lamellae, a third phase can even be resolved for polymers with two heterocycles per monomeric unit, if the volume fraction of the main chain (methacrylate plus spacer group) is high (**PMTA5** and **PMTA6**). Then, cylinders of heterocycles can be formed within the polar lamellae. We have validated of the scenario proposed by comparing the sizes deduced from the analysis of the SAXS profiles with the expected characteristic lengths of the associated moieties. This comparison has also allowed inferring the how alkyl side groups are arranged within the nano-domains. Within non-polar cylinders, they seem to be coiled and facing each other, while within the lamellae they appear to have some degree of interdigitation.

The complete picture achieved in this investigation allows to elucidate the type of nano-structures formed by this class of polymers, if the chemical composition including the quaternization degree is known. The study of the effect of this parameter and temperature on the long- and short-range order of these polymers is currently under progress.

ASSOCIATED CONTENT

Supporting Information

DSC Thermograms of **PMTAs-RI** and a detailed analysis and curve-fitting of SAXS patterns of each polymer with the aid of Scatter Software. This material is available free or charge via the Internet at <http://pubs.acs.org>.

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Notes

The authours declare no competing financial interest.

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